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Selected first row transition metal coordination compounds of 2-(N-Aminomethyl)-3-Quinuclidinone chelates

Richard Cecil Dickinson

Department: Chemistry

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SELECTED FIRST ROW TRANSITION METAL COORDINATION COMPOUNDS OF 2-(N-AMINOMETHYL)-3-QUINUCLIDINONE CHELATES

by

RICHARD CECIL DICKINSON, 1943-

A DISSERTATION

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Gary J. Long
Advisor

W. P. Tappmeyer

Wm. H. Webb

Raymond L. Venable

K. G. Mayhan

ABSTRACT

As part of a project directed towards elucidating the characteristics of ligands which coordinate to give complexes having tetrahedral structures, a study of chelates containing the bulky quinuclidine group has been made. With 2-(N-morpholinylmethyl)-3-quinuclidinone (MQN), complexes having the general formula $M(MQN)X_2$ were prepared where the metal ion was Co(II), Ni(II), Fe(II), Cu(II), and Mn(II). The ligands 2-(N-piperidinylmethyl)-3-quinuclidinone (PQN) and 2-(N-dimethylaminomethyl)-3-quinuclidinone (DQN) were prepared along with the analogous cobalt(II) chloride complexes.

The series of complexes $Co(MQN)X_2$ where X = Cl, Br, or I were prepared, and magnetic susceptibilities and spectral data obtained. They have room temperature magnetic moments in the range 4.66-4.85 with slight decreases at lower temperatures. Spectral parameters derived from their electronic absorption spectra are typical of tetrahedrally coordinated Co(II) ions with Dq varying between 390-430 cm^{-1} in the solid phase. Band assignments corresponding to spin-allowed d-d transitions were made. Properties of $Co(MQN)Cl_2$, $Co(PQN)Cl_2$, and $Co(DQN)Cl_2$ show distortion from tetrahedral symmetry in the order MQN < PQN < DQN in the solid phase and PQN < MQN $\sim$ DQN in solution. Infrared spectra are essentially identical for the MQN series and tentative Co-X stretching frequencies are given.

The complex $Co(MQN)(NCS)_2 \cdot C_2H_5OH$ is octahedrally coordinated by virtue of bridging thiocyanate groups. A value of μ_{eff} of 4.38 was found for this compound and band assignments yield 970 cm^{-1} for Dq in pure O_h symmetry.

A series of nickel complexes, viz., $Ni(MQN)X_2$ where X = Cl, Br, or I were obtained by the addition of the appropriate metal salt to MQN. Two forms of a complex of general formula $Ni(MQN)Cl_2$ were prepared and characterized. The purple $Ni(MQN)Cl_2$ analog along with the corresponding purple bromide and green iodide were found to have pseudotetrahedral symmetries. Magnetic susceptibility data at 300° K give μ_{eff} values between 3.35 and 3.58 for these compounds. Further data were obtained from room temperature to 18° K for the three halide complexes and these show a slight decrease in μ_{eff} for $Ni(MQN)Br_2$, a slight increase in μ_{eff} for purple $Ni(MQN)Cl_2$, and a sharp increase in μ_{eff} for $Ni(MQN)I_2$ below 50° K. Some of the low temperature moments were found to be dependent upon the strength of the magnetic field. Band assignments were made and calculation of spectral parameters yield Dq values in the solid phase ranging from 525 to 550 cm^{-1}. The electronic absorption spectrum of $Ni(MQN)Br_2$ at 25° and 300° K is reported and tentative Ni-X stretching frequencies are given.

In contrast to the purple, pseudotetrahedral $Ni(MQN)Cl_2$, an off-white compound of the same formula was prepared and characterized. This off-white analog contains octahedrally coordinated nickel atoms by virtue of halogen bridging. μ_{eff} is 3.40 at room temperature and Dq is found to be 1000 cm^{-1}. Low temperature electronic absorption spectra and infrared data in the range 600-200 cm^{-1} are given.

Compounds having the formulas $Ni(MQN)(NCS)_2 \cdot CH_3OH$ and $Ni(MQN)(NO_3)_2$ were found to have octahedral symmetries about the central metal atom. The thiocyanate complex is believed to contain bridging and terminal thiocyanate groups and a structure similar to that of $Co(MQN)(NCS)_2 \cdot C_2H_5OH$ is proposed. The nitrate complex contains bridging or chelating nitrate groups. Room temperature μ_{eff} is 3.23 and Dq is 970 cm^{-1} for $Ni(MQN)(NCS)_2 \cdot CH_3OH$. These parameters are, respectively, 3.33 and 950 cm^{-1} for $Ni(MQN)(NO_3)_2$.

The only iron(II) complex obtained was $Fe(MQN)Cl_2$ and this has a pseudotetrahedral structure. The electronic absorption spectrum shows a broad, asymmetric band at about 6700 cm^{-1} assigned to the $^5E \rightarrow {}^5T_2$ transition in pure T_d symmetry. μ_{eff} is 5.27 at 294° and is essentially independent of temperature, as expected. The Mössbauer parameters ΔE_Q and δ are 2.74 mm/sec and 0.91 mm/sec, respectively, at 300° K.

Two manganese(II) complexes are reported, viz., $Mn(MQN)Cl_2$ and $Mn(MQN)Br_2$. Electronic absorption spectral bands could not be observed and values of μ_{eff} were not helpful in deducing the structures of these compounds. A comparison of d-spacings obtained for the Mn(II) complexes with the corresponding Ni(II) and Co(II) complexes was not useful.

The series of complexes $Cu(MQN)X_2$ where X = Cl, Br, or NO_3 have been prepared and each was found to exhibit a broad band in the electronic absorption spectrum as is usually found in Cu(II) complexes. Values of μ_{eff} were found in the range 1.83-1.89 and showed essentially no dependence upon temperature. Comparison of X-ray diffraction data with analogous Co(II) and Ni(II) compounds and examination of Cu-X stretching frequencies suggested pseudotetrahedral structures for the chloride and bromide complexes. The nitrate complex is most likely octahedrally coordinated through bridging or chelating nitrate groups. Confirmation of these structures must await an X-ray crystallographic study.

Perchlorate complexes of several metal(II) compounds were prepared. The cobalt, nickel, and copper complexes were found to contain two MQN ligands in the coordination spheres. Some of the complexes were hydrates.

μ_{eff} was found to be 4.36 for $Co(MQN)_2(ClO_4)_2$; 4.02 for $Ni(MQN)_2(ClO_4)_2 \cdot 4H_2O$; 1.98 for $Cu(MQN)_2(ClO_4)_2$. All of the perchlorate complexes appeared to be tetrahedrally coordinated with two nitrogen-coordinated ligands.

ACKNOWLEDGEMENT

The author wishes to thank Dr. G. J. Long for acting as his research advisor during his doctoral work. Dr. Long provided the idea for the project and offered many helpful suggestions in the course of the laboratory work and through the completion of this dissertation.

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The author appreciates the consultations concerning organic synthesis and the NMR spectra used in this work, all provided by Dr. B. W. Peace and R. S. McDaniel. Dr. J. D. Bucci is thanked for his aid in X-ray diffraction studies.

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Introduction

As a consequence of the rapid development of methods of obtaining structural data, and with the accumulation of a vast body of chemical knowledge, it is now possible to summarize stereochemical trends associated with various coordination numbers. Reviews of these trends for coordination number five[1] and seven through twelve[2] have appeared. Compounds of coordination number eight have also been reviewed extensively.[2,3]

Compounds having coordination numbers four and six attracted little attention until recently, since their structural behavior had not been particularly unusual. Before 1950, work with compounds of coordination number four dealt mainly with synthetic methods; few X-ray crystallographic structures were reported.[4] Around 1950, emphasis shifted to structural studies and theoretical interpretations of experiments in magnetochemistry and absorption spectroscopy.

Many early studies with first row transition metals yielded an abundance of compounds having planar configurations and only a few tetrahedral complexes were identified.[5] The synthesis of tetrahedral complexes

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(1) E. L. Muetterties and R. A. Schunn, Quart. Rev., 20, 245 (1966).

(2) E. L. Muetterties and C. M. Wright, Quart. Rev., 21, 109 (1967).

(3) S. J. Lippard, Prog. Inorg. Chem., 8, 109 (1967).

(4) A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1952.

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966.

of the general formula $Ni[(C_2H_5)_3P]_2X_2$ (where X = Cl, Br, I, NO_3, NCS)[6] and the isolation of tetrahedral complexes of the type MX_4^{2-} (where M = Mn, Fe, Co, Ni, Cu, and Zn, and X = Cl, Br, and I)[7] hastened the search for, and the characterization of, tetrahedral complexes which were hitherto unknown.

To date, examples of tetrahedral complexes of most all divalent first row transition metal ions are known,[5,8] and their electronic absorption spectra are well understood in several cases.[9]

Magnetic susceptibility affords the chemist an excellent means of gathering structural and bonding information about transition metal complexes. This technique is now widely used and a number of books and review articles on the subject have appeared.[10-15]

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(6) L. M. Venanzi, J. Chem. Soc., 719 (1958).

(7) N. S. Gill and R. S. Nyholm, J. Chem. Soc., 3997 (1959).

(8) R. Colton and J. H. Canterford, "Halides of the First Row Transition Metals," Wiley-Interscience, London, 1969.

(9) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Company, 1968.

(10) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1956.

(11) R. S. Nyholm, J. Inorg. Nucl. Chem., 8, 401 (1958).

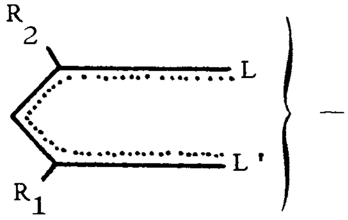
(12) J. Lewis and R. G. Wilkins, ed, "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y. 1960.

(13) B. N. Figgis and J. Lewis, Prog. Inorg. Chem., 6, 37 (1964).

(14) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966.

(15) A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, London, 1968.

After the discovery that certain nickel(II) complexes exhibit a planar $\rightleftharpoons$ tetrahedral equilibrium,[16] a large number of other complexes have been found which also undergo this interconversion. Equilibria of this type afford experimentalists an opportunity to study factors causing certain stereochemical configurations to be most favorable. Holm and O' Conner[17] have published a comprehensive summary of experimental data and stereochemical trends found in bis(chelate)metal(II) complexes containing chelating agents of the general types 1 and 2. Here, R_1 and R_2 are hydrogen, alkyl, and aryl substituents, and L and L' represent



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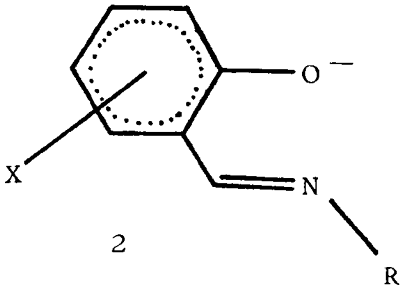

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N-R, O, Se, or S. The substituent X may be varied but this action causes only secondary effects upon stereochemistry as compared to the effects

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(16) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciamplini, Proc. Chem. Soc., 255 (1962); R. H. Holm and K. Swaminathan, Inorg. Chem., 2, 181 (1963); L. Sacconi, P. Paoletti, and G. Del Re, J. Amer. Chem. Soc., 85, 411 (1963).

(17) R. H. Holm and M. J. O' Conner, Prog. Inorg. Chem., 14, 241 (1971).

caused by varying R. Type 1 chelates were found effective in investigating stereochemistry as a function of central metal ion, and chelates of type 1 and 2 were both found useful in observing changes in stereochemistry associated with graded changes in ligand structure. Holm and O' Conner outlined[17] stereochemical trends seen in these complexes, and the following points seem to be most important:

(1) Complexes of iron(II) containing sterically active donor groups are tetrahedral in structure.

(2) Cobalt(II) complexes have stereochemistries which are variable between planar and tetrahedral with most compounds containing sterically active donor groups being tetrahedral.

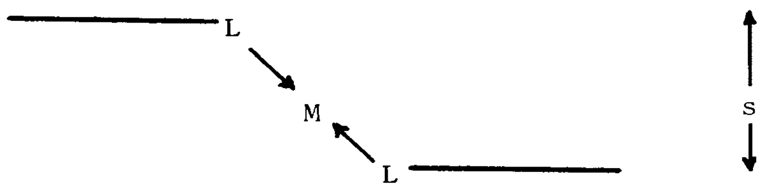
(3) Nickel(II) complexes have stereochemistries which are also variable between planar and tetrahedral with most complexes which contain sterically active donor sets being tetrahedral.

(4) In general, the tetrahedral isomer in a series of complexes gains stability in the sequence R = H $<$ CH_3 $<$ n-alkyl $\sim$ aryl $<$ α-branched alkyl $<$ t-butyl.

(5) Those ligands which do not form tetrahedral nickel(II) complexes to any extent may form planar or tetrahedral cobalt(II) complexes or an equilibrium mixture.

(6) Those ligands which do stabilize tetrahedral Ni(II) to any measureable extent will form only tetrahedral Co(II) complexes.

(7) Copper(II) complexes which contain sterically inactive donor groups were found to have planar structures. If sterically active donor groups are present, the complexes are either pseudotetrahedral or stepped planar. Stepped planarity is depicted as



where the ligand rings are planar, but not coplanar and are separated by a small step s. Fox example, s = 0.29 Å in the transition metal complex bis(salicylaldimato)copper(II).[18]

Holm and O' Conner[17] have not reviewed complexes of types MX_4^{2-}, MLX_3^-, ML_2X_2 (where L = pyridine or other heterocyclic amines, phosphines, arsines, *etc*.) and bis(chelate) species like ML_2^{2+} and ML_2X_2 (where L = ethylenediamine, diphosphines, *etc*.) since complexes of this sort are often sparingly soluble in non-coordinating solvents and/or dissociate to give species of different coordination number. Katzin[19] has reviewed the structural equilibria for many compounds of this type.

Eaton, Phillips, and Caldwell[20] have made a study of the configuration and magnetic properties of Ni(II) aminotroponeimineates of general formula 3. R_1 and R_2 represent aryl groups which are substituted with functional groups of various electronegativity. Complexes in this series range from diamagnetic planar to paramagnetic tetrahedral in configuration as the bulkiness of the R groups progresses through the order $R_1 = R_2 = H$, CH_3, aryl, C_2H_5 and higher alkyls. The authors concluded that the magnetic properties of these compounds were dependent upon steric

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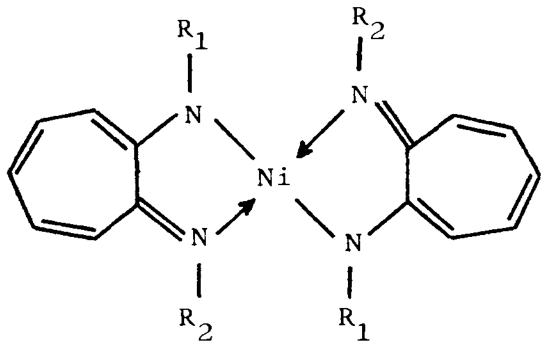
(18) E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 680, (1966).

(19) L. I. Katzin, *Transition Metal Chemistry*, *3*, 56 (1966).

(20) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, *85*,397 (1963).



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properties of the ligand. Based on studies with models, they proposed that a planar configuration could be accommodated if the N-substituted aryl groups were twisted 90° out of plane with the tropone ring. On the other hand, C_2H_5 and higher alkyl groups hinder the formation of a planar configuration and the tetrahedral or distorted tetrahedral configuration becomes more stable. In addition to steric factors, they found a good correlation between the Taft inductive parameter σ_I[21] and energy differences, ΔE, between the diamagnetic and paramagnetic isomers of a given chelate complex. The value of ΔE increases with an increase in σ_I and this may be interpreted to mean that the population of the tetrahedral isomer is favored by an increase in ligand basicity and presumably ligand field strength.[22]

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(21) R. W. Taft, J. Amer. Chem. Soc., 79, 1045 (1957).

(22) The parameter σ_I is a measure of the ability of a substituent to supply electron density to a conjugated system. Thus, electron density in the position para to the substituent is intensified as the substituent is changed in the order $CH_3 \rightarrow H \rightarrow Br \rightarrow Cl \rightarrow F$. For a discussion of Taft's induction parameter, the reader is referred to E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, pages 227 to 230.

Steric interactions within bis(tertiary phosphine)nickel dihalides have been surveyed,[23a] and the trend toward population of the tetrahedral state is enhanced as one chooses ligands of increasingly weak ligand field strength. In general, the pattern of ligand strength was found to be $\Phi_3P > R\Phi_2P > R_2\Phi P > R_3P$. This observation seems to conflict with results for complexes of aminotroponeimines.[20]

Dahlhoff, *et al.*, have described[23b] the structures of a group of transition metal complexes containing phosphinopyridine ligands. Each ligand molecule contains three possible coordination sites. The authors concluded that the stereochemical structure obtained in the complexes was dependent largely upon the rigidity and size of the chelate ring.

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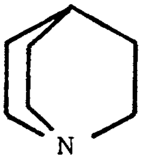
(23) (a) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); C. R. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961); F. A. Cotton and R. Francis, *J. Inorg. Nucl. Chem.*, *17*, 62 (1961); F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, *83*, 344 (1961); M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962); R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, *4*, 1701 (1965); (b) W. V. Dahlhoff, T. R. Dick, G. H. Ford, W. S. J. Kelly, and S. M. Nelson, *J. Chem. Soc. A*, 3495 (1971).

In the course of an investigation of the characteristics of ligands which coordinate with first row transition metal salts to give compounds having regular or slightly distorted tetrahedral structures, we have begun a study of chelating ligands containing quinuclidine (4). Of particular interest to us are those of type 5. Many examples of this type of compound have been described[24] where R may be nitrogen-substituted dimethylamine, morpholine, piperidine, *etc*.



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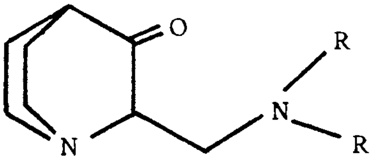

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Fisher-Hirschfelder models of 5 indicate a bulky and rigid structure with considerable steric hindrance at the nitrogen coordination sites. It was our feeling that these chelates could be expected to coordinate *via* both nitrogen atoms to form complexes of type MLX_2 (where L is the bidentate ligand, and X is a halide, pseudohalide, *etc*.). In view of the rigid five-membered ring which could be formed with the central metal ion, and in view of the steric factors present in these ligands, we further anticipated that the metal ion would be tetrahedrally coordinated. Indeed, this has been shown to be the case, and the purpose of this dissertation is to report our findings on complexes of 2-(N-morpholinylmethyl)-3-quinuclidinone (6). In addition, we report cobalt(II) chloride complexes of 2-(N-dimethylaminomethyl)-3-quinuclidinone (7) and 2-(N-piperidinylmethyl)-3-quinuclidinone (8).

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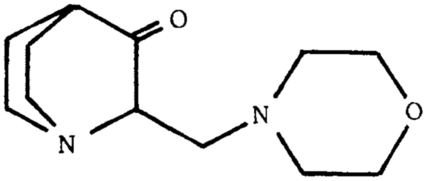
(24) A. R. Hansen and H. Bader, *J. Het. Chem.*, *3*, 109 (1966); J. H. Biel, H. B. Hopps, and H. Bader, *U. S. Patent* 3,384,641; J. H. Biel and H. B. Hopps, *U. S. Patent* 3,462,442.



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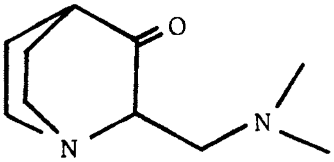

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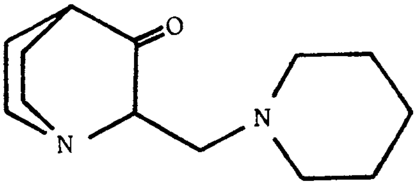

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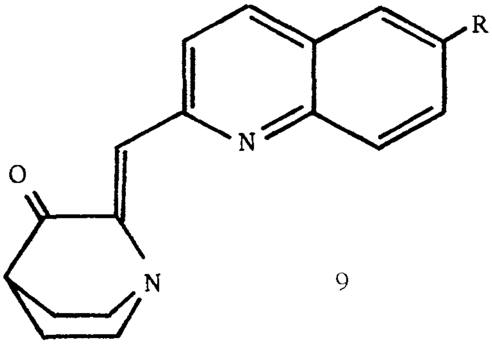
We shall denote compounds 6, 7, and 8 as MQN, DQN, and PQN, respectively.

The only complexes reported involving ligands of type 5 appear to be those of Coffen and McEntee[25] who report several cobalt(II), nickel(II), and copper(II) complexes of trans-2-(2'-quinolyl)-methylene-3-quinuclidinones (9). Their examination of the complexes was cursory and since the appearance of the initial work, a more detailed investigation of some of these complexes has been undertaken.[26]



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(25) D. L. Coffen and T. E. McEntee, Jr., *J. Org. Chem.*, *35*, 503 (1970).

(26) G. J. Long and D. L. Coffen, personal communication.

The use of the bicyclic amine quinuclidine (4) as a ligand is also limited. In a study of the steric configuration of triethylamine, Brown and Sujishi[27] have demonstrated that quinuclidine forms one-to-one mole ratio complexes with trimethylboron which are much more stable than complexes with triethylamine. This difference was attributed to the peculiar steric arrangement of the ethyl groups in the latter compound. The same trend in relative stability was found in complexes of lithium alkyls.[28]

Yoke and his coworkers have reported a few complexes involving quinuclidine and $AgNO_3$,[29] $CuCl_2$,[30] $CoCl_2$[30] and $Cu(C_2H_3O_2)_2$.[31] The first and second formation constants for the complex $AgNO_3 \cdot 2$ QUIN (where QUIN represents quinuclidine) were determined and the complex isolated under vacuum. The complex $CuCl_2 \cdot$QUIN was reported stable and magnetically normal. Likewise, $CoCl_2 \cdot 2$ QUIN was found to be stable and to have a magnetic moment and visible spectrum typical of pseudotetrahedral coordination. Quinuclidine was found to have sufficient coordinating ability to form the complex $Cu(C_2H_3O_2)_2 \cdot$QUIN in dimethylformamide solution whereas triethylamine was unable to replace the dimethylformamide from the coordination sphere. This acetate complex shows the antiferromagnetic

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(27) H. C. Brown and S. Sujishi, *J. Amer. Chem. Soc.*, *70*, 2878 (1948).

(28) C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, *87*, 3276 (1965).

(29) H. M. Hilliard and J. T. Yoke, *Inorg. Chem.*, *5*, 57 (1966).

(30) H. M. Hilliard, D. D. Axtell, M. M. Gilbert, and J. T. Yoke, *J. Inorg. Nucl. Chem.*, *31*, 2117 (1969).

(31) E. D. Stevens and J. T. Yoke, *Inorg. Chim. Acta*, *4*, 244 (1970).

behavior typically found in dimeric copper(II) acetate systems.

Clark and Natile[32] have prepared five- and six-coordinate complexes of vanadium(III) and chromium(III) halides with quinuclidine. Complexes of the type $VX_3 \cdot 2$ QUIN (where X = Cl or Br) were found to have *trans*-trigonal bipyramidal structures both in the solid phase and in solutions of non-polar solvents. Both the complexes $CrCl_3 \cdot 3$ QUIN and $CrCl_3 \cdot 2$ QUIN could be formed, the former having an octahedral structure and the latter having the *trans*-bipyramidal structure seen in the analogous vanadium(III) compound. The five-coordinate compound $CrBr_3 \cdot 2$ QUIN was the only isolable adduct found for chromium(III) bromide.

The nitrogen-14 hyperfine splitting in the electron spin resonance spectra of one-to-one ratio adducts of copper(II) bisacetylacetonate and copper(II) bishexafluoroacetylacetonate with pyridine and quinuclidine has been examined.[33] The resulting complexes are five-coordinate.

Crystal structures of two quinuclidine organometallic compounds have been reported recently. Both dimethylbis(quinuclidine)beryllium[34a] and trimethyl(quinuclidine)aluminum[34b] form crystals containing four monomers per monoclinic cell. A distorted tetrahedral field surrounds the central metal atom.

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(32) R. J. H. Clark and G. Natile, *Inorg. Chim. Acta*, *4*, 533 (1970).

(33) B. B. Wayland and M. D. Wisniewski, *Chem. Commun.*, 1025 (1971).

(34) (a) C. D. Whitt and J. L. Atwood, *J. Organometal. Chem.*, *32*, 17 (1971); (b) C. D. Whitt, L. M. Parker, and J. L. Atwood, *J. Organometal. Chem.*, *32*, 291 (1971).

Quagliano, *et al.*,[35] have investigated a series of four- and five-coordinate transition metal complexes containing the 1,4-diazabicyclo[2.2.2]octonium cation.

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(35) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, *8*, 2331 (1969); J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, *92*, 482 (1970).

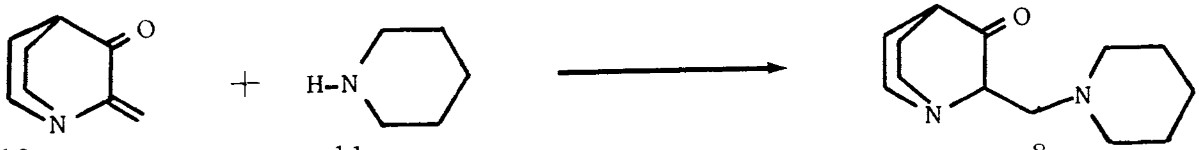
Experimental Section

Preparation of Ligands.—The ligand 2-(N-morpholinylmethyl)-3-quinuclidinone (6; MQN) has been briefly described in the chemical literature.[24] Rather than purify the product by distillation as previously suggested,[24] we have found that the oily reaction product may be purified by recrystallization from boiling acetone.

Twenty grams of 3-quinuclidinone hydrochloride dissolved in 32 ml of ethanol and 20 ml of distilled water was mixed with a solution of 5.2 g of NaOH in 25 ml of distilled water and refluxed momentarily to free the bicyclic amine. After cooling the mixture, 12.6 g of morpholine and 11.7 g of 37 % aqueous formaldehyde were added and the mixture refluxed gently for one hour and then heated with stirring at 70° for 17 additional hours. An amber-colored oil resulted when the solvents were removed by evaporation at reduced pressure. The oil was dissolved in methanol and dried several days over anhydrous Na_2SO_4. After removing the methanol, dry diethyl ether was mixed with the oil to precipitate the unused portion of the bicyclic amine along with some tar-like by-products. The ether was removed leaving a yellowish solid or yellowish oil which was recrystallized from boiling acetone. The pure ligand was a white, crystalline solid that melted at 101.5-102.7° (uncorr.) and the yield was about 70 % of the theoretical value. Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.98; N, 12.48. Found: C, 64.17; H, 8.93; N, 12.25.

The ν(C=O) vibrational mode was found at 1710 cm^{-1} in KBr matrix, and the n $\rightarrow \pi^*$ transition associated with the ketone group was observed at 31,200 cm^{-1} in a mull and at 31,000 cm^{-1} in acetonitrile solution (ϵ_M = 62). The C-O-C asymmetric stretching mode is generally found as a strong band occuring between 1140-1085 cm^{-1}.[36] The infrared spectrum of MQN showed bands at 1112 cm^{-1} and 1150 cm^{-1}. We observed that the band at 1150 cm^{-1} decreases in intensity upon complexation and presumed the strong band at 1112 cm^{-1} to be associated with the C-O-C group. The proton magnetic resonance spectra of 3-quinuclidinone and morpholine showed chemical shifts for CH_2 groups falling in the same general ranges. As a result, the spectrum of MQN was complicated in that chemical shifts could not be clearly resolved. Infrared and NMR data for MQN are tabulated in Appendices 1 and 2.

2-(N-Piperidinylmethyl)-3-quinuclidinone (8; PQN) was prepared using methods already described in the literature[24] and elsewhere.[37] The procedure involved the following reaction scheme:



10 11 8

2-(N-Dimethylaminomethyl)-3-quinuclidinone was prepared[24] and distilled under vacuum to yield the starting material 2-methylene-3-quinuclidinone (10). Compound 10 was dissolved in anhydrous methanol and mixed with an equimolar quantity of piperidine (11) which had been distilled and stored over solid NaOH in a refrigerator. The reaction mixture was stirred for eight days at which time the solvents were removed by evaporation at reduced pressure leaving an amber-colored oil. The oil was dissolved in diethyl ether and dried over anhydrous K_2CO_3 for 24 hours. The ether was removed and the resulting oil (8) was subjected to a vacuum for two

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(36) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

(37) H. B. Hopps, personal communications.

days to remove traces of solvent. *Anal*. Calcd for $C_{13}H_{22}N_2O_2$: C, 70.23; H, 9.98; N, 12.60. Found:[38] C, 66.52; H, 9.65; N, 8.79.

2-(N-Dimethylaminomethyl)-3-quinuclidinone (7; DQN) was prepared using the methods already described[24,37] and involved the following reaction scheme:

10 12 7

The reactant 10 was obtained as in the preparation of PQN and was dissolved in methanol and an excess of 40 % by weight aqueous dimethylamine was added. The mixture was stirred for eight days and the product purified in the same manner as PQN. *Anal*. calcd for $C_{10}H_{18}N_2O$: C, 65.90; H, 9.96; N, 15.37. Found:[38] C, 64.02; H, 9.61; N, 14.28.

Preparation of Metal(II) Complexes of 2-(N-Morpholinylmethyl)-3-quinuclidinone (MQN).—Co(MQN)Cl_2.—A mixture of 25 ml of ethanol and 25 ml of diethyl ether containing 0.70 g (0.003 mole) of $CoCl_2 \cdot 6H_2O$ was added dropwise with stirring to a mixture of 2.00 g (0.009 mole) of MQN dissolved in the same solvent. The precipitate, which formed at once, was washed with ethanol and ether and air dried. The product was a bright

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(38) It was our feeling that the deviation in the actual elemental analyses from the calculated values was primarily the result of solvent impurities which were not removed from the oily reaction products of PQN and DQN. Small quantities of compound 10 did seem to be present as judged by the presence of a weak band at 1645 cm^{-1} which may be associated with a $C=CH_2$ vibration. This vibration is reported to occur at 1640 cm^{-1} by Hanson and Bader.[24] Corresponding $CoCl_2$ complexes did analyze well which suggested that the reaction products of PQN and DQN were essentially pure.

blue polycrystalline solid. Anal. Calcd for $CoC_{12}H_{20}N_2O_2Cl_2$: C, 40.70; H, 5.60; N, 7.91. Found: C, 40.80; H, 5.74; N, 7.73.

$Co(MQN)Br_2$.—This complex was prepared using the same procedure as for the corresponding $CoCl_2$ complex. The product was a dark blue, polycrystalline solid. Anal. Calcd for $CoC_{12}H_{20}N_2O_2Br_2$: C, 32.53; H, 4.55; N, 6.32. Found: C, 32.79; H, 4.61; N, 6.31.

$Co(MQN)I_2$.—A 2.30-gram sample of $CoI_2 \cdot 2H_2O$ (0.007 mole) was dissolved in a mixture of 25 ml of anhydrous methanol and 25 ml of anhydrous diethyl ether, and this solution was added dropwise with stirring to 1.50 g of MQN (0.007 mole) dissolved in the same solvent mixture. The green product which crystallized was collected by filtration and washed with fresh solvent. Anal. Calcd for $CoC_{12}H_{20}N_2O_2I_2$: C, 26.84; H, 3.75; N, 5.22. Found: C, 26.32; H, 3.90; N, 4.81.

$Co(MQN)(NCS)_2 \cdot CH_3OH$.—A 1.51-gram sample of $Co(NCS)_2 \cdot 3H_2O$ (0.007 mole) was dissolved in a mixture of 25 ml of anhydrous methanol and 25 ml of anhydrous diethyl ether. This solution was added dropwise with stirring to a solution of 1.50 g of MQN (0.007 mole) in 50 ml of the same solvent. To promote crystallization, several hundred milliliters of pentane were added until the solution became cloudy. Upon standing, a deep purple crystalline product formed, was collected by filtration, and washed with ethanol and diethyl ether. The product was dried *in vacuo* for several days. Anal. Calcd for $CoC_{15}H_{24}N_4O_3S_2$: C, 41.76; H, 5.61; N, 12.99. Found: C, 41.69; H, 5.66; N, 13.43.

$Co(MQN)(NCS)_2 \cdot C_2H_5OH$.—A mixture of 1.16 g of $Co(NCS)_2$ (0.007 mole) in 50 ml of ethanol was heated to boiling and filtered. To this hot filtrate was added a hot solution of 1.50 g of MQN (0.007 mole) in 25 ml of ethanol. The solution was cooled to room temperature and filtered to remove a flocculent precipitate which had formed. About 100 ml of cyclohexane was added to the filtrate to promote crystallization. The walls of the container were scratched, and a purple solid formed upon standing. The product was collected by vacuum filtration and was washed using ethanol and ether. After drying <u>in vacuo</u> over P_4O_{10} for several days, the product was a light purple, crystalline powder. <u>Anal</u>. Calcd for $CoC_{16}H_{26}N_4O_3S_2$: C, 43.14; H, 5.88; N, 12.58. Found: C, 43.09; H, 6.06; N, 12.61.

$Ni(MQN)Cl_2$.——In the course of preparation of complexes of nickel(II) chloride, we found that, by varying the experimental conditions, we were able to prepare two complexes which had the formula $Ni(MQN)Cl_2$ and which had dissimilar properties. The most efficacious means of obtaining the off-white and the purple forms of this complex are described. The purple $Ni(MQN)Cl_2$ complex.——A sample of $NiCl_2 \cdot 6H_2O$ (0.005 mole) was dissolved in a mixture of 50 ml of n-butanol and 25 ml of 2,2-dimethoxypropane[39] and the solution heated to boiling. A boiling solution composed of 1.00 g of MQN (0.005 mole) in 25 ml of n-butanol was added in one portion to the nickel(II) chloride solution with rapid stirring. The mixture was allowed to boil for several minutes until a purple, crystalline solid had formed and was filtered quickly. The product was a purple solid and was dried <u>in vacuo</u> at 65° for several hours. <u>Anal</u>. Calcd for $NiC_{12}H_{20}N_2O_2Cl_2$: Ni, 16.58; C, 40.72; H, 5.70; N, 7.91. Found: Ni, 16.52; C, 40.45; H, 5.90; N, 7.71.

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(39) The use of 2,2-dimethoxypropane as a dehydrating agent in the preparation of anhydrous metal complexes has been described by K. Starke, <u>J</u>. <u>Inorg</u>. <u>Nucl</u>. <u>Chem</u>., <u>11</u>, 77 (1959).

The off-white Ni(MQN)Cl_2 complex.—A 1.56-gram sample of $NiCl_2 \cdot 6H_2O$ (0.007 mole) was dissolved in 350 ml of boiling ethanol and 50 ml of 2,2-dimethoxypropane added. After boiling for several minutes, the hot solution was filtered. To the boiling filtrate was added (in one portion) a hot solution of 1.50 g of MQN (0.007 mole) in 50 ml ethanol. Upon mixing, the solution turned deep violet in color. The mixture was heated briefly and then quenched in an ice-water bath. An off-white solid formed immediately. The sample was collected by filtration, washed with ethanol, diethyl ether, and dried *in vacuo* over P_4O_{10} for several days. The product was off-white in appearance, very finely powdered, and very hygroscopic. *Anal*. Calcd for $NiC_{12}H_{20}N_2O_2Cl_2$: C, 40.72; H, 5.70; N, 7.91. Found: C, 40.52; H, 5.74; N, 7.86.

When this off-white compound was left exposed to the air for a short time, it quickly absorbed one quarter mole of water and turned pale green in color. *Anal*. Calcd for $NiC_{12}H_{20.5}N_2O_{2.25}Cl_2$: C, 40.21; H, 5.77; N, 7.82. Found: C, 40.02; H, 5.69; N, 7.75. This pale green complex was also prepared in a number of other solvents (for example, methanol, ethanol, and methyl benzoate) by mixing together solutions of MQN and nickel(II) chloride at ambient temperature. If no special precautions were taken to remove moisture from the solvents and reactants, the resulting complexes contained random quantities of absorbed water. Several pale green $NiCl_2$ complexes were prepared in this work using several solvents. Ni(MQN)$Cl_2 \cdot \frac{1}{2} H_2O$ was prepared in ethanol. *Anal*. Calcd for $NiC_{12}H_{21}N_2O_{2.5}Cl_2$: C, 39.71; H, 5.83; N, 7.91. Found: C, 39.61; H, 6.02; N, 7.84. The complex Ni(MQN)$Cl_2 \cdot H_2O$ was prepared in one-to-one anhydrous methanol-anhydrous diethyl ether. *Anal*. Calcd for $NiC_{12}H_{22}N_2O_3Cl_2$: C, 38.75; H, 5.96; N, 7.53. Found: C, 38.82; H, 6.17;

N, 7.30. The complex Ni(MQN)$Cl_2 \cdot \frac{1}{4} H_2O$ was prepared in a four-to-one volume ratio n-butanol-2,2-dimethoxypropane solution. Anal. Calcd for $NiC_{12}H_{20.5}N_2O_{2.25}Cl_2$: C, 40.21; H, 5.77; N, 7.82. Found: C, 40.51; H, 5.92; N, 7.74.

Ni(MQN)Br_2.——A sample of anhydrous $NiBr_2$ weighing 1.44g (0.007 mole) was dissolved in a mixture of 25 ml of ethanol and 25 ml of 2,2-dimethoxypropane and the mixture refluxed for several hours. A solution composed of 1.50 g of MQN (0.007 mole) in 25 ml of one-to-one ethanol-2,2-dimethoxypropane was also refluxed and added dropwise with stirring to the hot solution of nickel(II) bromide. Crystallization began almost immediately. The product was collected by filtration and was washed with anhydrous diethyl ether and dried *in vacuo*. The sample was a deep purple, polycrystalline solid. Anal. Calcd for $NiC_{12}H_{20}N_2O_2Br_2$: Ni, 13.26; C, 32.54; H, 4.55; N, 6.32. Found: Ni, 13.27; C, 32.51; H, 4.63; N, 6.21.

Ni(MQN)I_2.——A sample of $NiI_2 \cdot 6H_2O$ weighing 2.78 g (.007 mole) was dissolved in 30 ml of n-butanol, heated to boiling, and filtered. To the hot filtrate was added a hot solution of 1.50 g of MQN (0.007 mole) in 20 ml of n-butanol. Crystallization occured immediately. The mixture was cooled, filtered, and the pasty solid added to boiling ethanol. This mixture was cooled, filtered, and washed with ethanol and diethyl ether. The product, a dark green crystalline solid, was dried for several days over P_4O_{10} *in vacuo*. Anal. Calcd for $NiC_{12}H_{20}N_2O_2I_2$: C, 26.84; H, 3.76; N, 5.22. Found: C, 26.74; H, 3.74; N, 5.16.

Ni(MQN)$(NCS)_2 \cdot CH_3OH$.——A sample of $Ni(NCS)_2$ weighing 1.15 g (0.007 mole) was dissolved in 50 ml of hot anhydrous methanol and the mixture cooled and filtered. A mixture of 1.50 g of MQN (0.007 mole) in 25 ml of anhydrous methanol was added dropwise with stirring to the metal salt solution and 50 ml of anhydrous diethyl ether added to promote crystallization. After stirring overnight, 100 ml of ether was added and the mixture refrigerated and filtered. The product was a light green powder and was dried over P_4O_{10} *in vacuo* for several days. *Anal.* Calcd for $NiC_{15}H_{24}N_4O_3S_2$: Ni, 13.62; C, 41.78; H, 5.61; N, 12.99. Found: Ni, 13.78; C, 41.62; H, 5.78; N, 12.76.

$Ni(MQN)(NO_3)_2$.—A sample of $Ni(NO_3)_2 \cdot 6\,H_2O$ weighing 1.95 g (0.007 mole) was dissolved in 30 ml of hot n-butanol and the hot solution filtered. A solution of 1.50 g of MQN (0.007 mole) in 20 ml of hot n-butanol was added dropwise with stirring to the boiling solution of nickel(II) nitrate. Crystallization occured almost at once. The mixture was cooled and filtered, and the product washed with ethanol and diethyl ether. The product was dried several days over P_4O_{10} *in vacuo*. The sample was a fine crystalline solid, light green in color. *Anal.* Calcd for $NiC_{12}H_{20}N_4O_8$: C, 35.41; H, 4.95; N, 13.76. Found: C, 35.32; H, 4.86; N, 13.61.

$Mn(MQN)Cl_2$.—A sample of $MnCl_2 \cdot 4\,H_2O$ weighing 1.31 g (0.007 mole) was dissolved in a solution of 30 ml of ethanol and 30 ml of 2,2-dimethoxypropane and refluxed gently for six hours under an atmosphere of dry, high purity nitrogen. A 1.50-gram sample of MQN (0.007 mole) was dissolved in 20 ml of one-to-one ethanol-2,2-dimethoxypropane solution which had been refluxed for three hours. Both solutions were cooled to room temperature and the ligand solution added dropwise with stirring to the manganese(II) chloride solution under nitrogen atmosphere. The mixture was stirred overnight under nitrogen. A white solid product precipitated overnight and was collected by filtration and washed with anhydrous diethyl ether. The product was dried at 76° _in vacuo_ for five hours; it was a white powder. _Anal_. Calcd for $MnC_{12}H_{20}N_2O_2Cl_2$: C, 41.16; H, 5.76; N, 8.00. Found: C, 41.24; H, 5.89; N, 7.96.

$Mn(MQN)Br_2$.——This complex was prepared using the same procedure used in preparing the corresponding manganese(II) chloride complex. The product was dried at 76° _in vacuo_ for 18 hours and was a cream-colored powder. _Anal_. Calcd for $MnC_{12}H_{20}N_2O_2Br_2$: C, 32.82; H, 4.59; N, 6.38. Found: C, 32.62; H, 4.75; N, 6.28.

$Mn(MQN)I_2$.——After a number of unsuccesful attempts to prepare this complex, its synthesis was abandoned.

$Fe(MQN)Cl_2$.——A sample of $FeCl_2 \cdot 4H_2O$ weighing 4.32 g (0.022 mole) was dissolved in a deoxygenated mixture of 50 ml of anhydrous methanol and 50 ml of 2,2-dimethoxypropane. The mixture was refluxed under a nitrogen atmosphere for 12 hours. After refluxing, the solution was diluted to 100 ml with the same solvent to replenish that which was carried off in the stream of nitrogen. A 50-milliliter aliquot of this solution was used. To this solution was added a solution composed of 2.40 g of MQN (0.011 mole) in 50 ml of one-to-one methanol-2,2-dimethoxypropane solution. The solid product was collected by filtration in an atmosphere of nitrogen and was washed with anhydrous methanol and with anhydrous diethyl ether. The complex was a cream-white powder. _Anal_. Calcd for $FeC_{12}H_{20}N_2O_2Cl_2$: C, 41.06; H, 5.74; N, 7.98. Found: C, 41.36; H, 5.56; N, 7.71.

$Fe(MQN)Br_2$ and $Fe(MQN)I_2$.——Several attempts to prepare these compounds failed to give products of sufficient purity to warrant study.

$Cu(MQN)Cl_2$.——A 0.50-gram sample of $CuCl_2$ (0.004 mole) was dissolved in a mixture of 50 ml of anhydrous diethyl ether and 50 ml of anhydrous methanol. To this solution was added a solution of 1.00 g (0.004 mole) of MQN in the same solvent. Crystallization began at once. The product was collected by filtration and was washed with anhydrous methanol and anhydrous diethyl ether and then dried *in vacuo*. The complex was a gold crystalline solid. *Anal*. Calcd for $CuC_{12}H_{20}N_2O_2Cl_2$: C, 40.18; H, 5.62; N, 7.81. Found: C, 40.39; H, 5.63; N, 7.69.

$Cu(MQN)Br_2$.—This complex was prepared using the same procedure as was used for the corresponding chloride complex. The product was a dark orange crystalline solid. *Anal*. Calcd for $CuC_{12}H_{20}N_2O_2Br_2$: C, 32.20; H, 4.50; N, 6.26. Found: C, 32.41; H, 4.48; N, 6.15.

$Cu(MQN)(NO_3)_2$.—A sample of $Cu(NO_3)_2$ weighing 1.60 g (0.007 mole) was dissolved in 50 ml of boiling n-butanol and filtered while hot. To this boiling solution was added a hot solution composed of 1.50 g of MQN (0.007 mole) in 20 ml of n-butanol. The addition was dropwise with stirring, with crystallization at once. The pasty product was stirred into boiling ethanol and the mixture cooled to room temperature and the product collected by filtration, washed with ethanol and diethyl ether, and dried *in vacuo* over P_4O_{10} for several days. The complex was light blue. *Anal*. Calcd for $CuC_{12}H_{20}N_4O_8$: C, 35.00; H, 4.90; N, 13.60. Found: C, 34.85; H, 4.93; N, 13.53.

Preparation of Cobalt(II) Chloride Complex of 2-(N-Piperidinylmethyl)-3-quinuclidinone (PQN).—$Co(PQN)Cl_2$.—About one gram of PQN was dissolved in 35 ml of ethanol and added to a solution of cobalt(II) chloride prepared as follows: A 1.13-gram sample of $CoCl_2 \cdot H_2O$ (0.048 mole) was dissolved in a mixture of 20 ml of ethanol and 10 ml of 2,2-dimethoxypropane and the solution heated at the boiling point for about 10 minutes and then cooled to room temperature. Upon addition of the PQN solution, a blue solid crystallized almost at once. After stirring for about one-half hour, the solid was collected by filtration and washed with diethyl ether. The product was blue in color and crystalline in nature and was dried several days *in vacuo* over P_4O_{10} at room temperature. *Anal.* Calcd for $CoC_{13}H_{22}N_2OCl_2$: C, 44.34; H, 6.30; N, 7.95. Found: C, 44.13; H, 6.32; N, 7.78.

Preparation of Cobalt(II) Chloride Complex of 2-(N-Dimethylaminomethyl)-3-quinuclidinone (DQN).——$Co(DQN)Cl_2$.——The procedure used in preparing this complex was the same as that used to prepare $Co(PQN)Cl_2$. The product was a blue, crystalline solid. *Anal.* Calcd for $CoC_{10}H_{18}N_2OCl_2$: C, 38.49; H, 5.81; N, 8.98. Found: C, 38.67; H, 6.00; N, 8.74.

Preparation of Metal(II) Perchlorates of 2-(N-Morpholinylmethyl)-3-quinuclidinone (MQN).——The general procedure involved dropwise addition of a solution of the metal(II) perchlorate to a solution of MQN. The solutions were made up of 0.007 mole of MQN dissolved in 50 ml of one-to-one volume ratio ethanol-diethyl ether solution and 0.003 mole of the particular metal perchlorate dissolved in 30 ml of the same solvent. Upon mixing, a solid formed which was collected by filtration, washed with ethanol and anhydrous ether, and air dried.

$Co(MQN)_2(ClO_4)_2$ was obtained as a purple powder. *Anal.* Calcd for $CoC_{24}H_{40}N_4O_{12}Cl_2$: C, 40.85; H, 5.72; N, 7.93. Found: C, 41.00; H, 5.90; N, 7.88.

$Ni(MQN)_2(ClO_4)_2 \cdot 4H_2O$ was a dull-white solid and was very powdery. *Anal.* Calcd for $NiC_{24}H_{48}N_4O_{16}Cl_2$: C, 37.04; H, 6.22; N, 7.20. Found: C, 37.19; H, 5.94; N, 7.01.

$Cu(MQN)_2(ClO_4)_2 \cdot H_2O$ was a dull-blue powder. *Anal.* Calcd for

$CuC_{24}H_{42}N_4O_{13}Cl_2$: C, 39.50; H, 5.80; N, 7.67. Found: C, 39.12; H, 5.71; N, 7.37.

Spectroscopic Studies.——Electronic absorption spectra were recorded in the range 33,300-3850 cm^{-1} using a Cary 14 Spectrophotometer. Spectra of the complexes in the solid phase were obtained by mulling the powder with Kel-F #90 fluorocarbon grease[40] and spreading the emulsion between two thin quartz discs. Solution electronic absorption spectra were obtained using Spectral Grade solvents and matched quartz cells of various path lengths. A Cryo-Tip refrigerator[41] with temperature continuously variable from ambient temperature to 24° K was used to record spectra in the range 33,300-3850 cm^{-1} using solid emulsions. Infrared spectra in the range 4000-400 cm^{-1} were recorded using a Perkin-Elmer 337 grating spectrophotometer and spectra in the range 800-200 cm^{-1} were obtained with a Beckman IR-12 grating spectrophotometer. In the lower range, samples were ground with freshly-dried cesium iodide and pressed into thin discs. Potassium bromide was used as the matrix in the upper infrared range.

Magnetic Susceptibility Studies.——Susceptibility measurements were made at various temperatures using the Gouy method.[42] The system was

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(40) Kel-F is a trademark of 3 M Company.

(41) Manufactured by Air Products & Chemicals, Inc.

(42) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," ed J. Lewis and R. G. Wilkins, Interscience, New York, N. Y., 1960, chapter 6; R. Nyholm, "Chemistry of the Coordinate Compounds," Pergammon Press, 1958, pages 401-429.

calibrated using $HgCo(NCS)_4$ prepared in this laboratory[43] and diamagnetic corrections to the total susceptibilities were made using Pascal's constants.[42] Sample temperatures were obtained using a copper-constantan thermocouple in conjunction with an ice bath reference thermocouple.

Mössbauer Effect Studies.—Mössbauer spectral results were obtained using an Austin Science Associates constant acceleration spectrometer calibrated with natural iron foil. Low temperature data were obtained using a liquid nitrogen cryostat. The γ-ray source was maintained at room temperature in all measurements.

X-Ray Diffraction Studies.—A Siemanns recording X-ray unit fitted with a copper tube and nickel filter was used. Samples were mounted on the face of a glass plate using a thin film of silicone vacuum grease.

Elemental Analyses.—Metal analyses of the nickel complexes were done in this laboratory using EDTA titrations. Analyses for carbon, hydrogen, and nitrogen content were done at Galbraith Laboratories, Knoxville, Tennessee.

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(43) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958). We have used 16.44×10^{-6} cgs as the gram susceptibility for $HgCo(NCS)_4$.

Results and Discussion

Cobalt(II) Halide Complexes.—The complexes Co(MQN)X_2 (X = Cl, Br, or I), Co(PQN)Cl_2, and Co(DQN)Cl_2 are air-stable and are soluble in most common organic solvents but are decomposed in aqueous solutions. The X-ray powder diffraction patterns have been recorded for each of these compounds and all are dissimilar. We have recorded the electronic absorption spectra of these compounds and find their appearances similar to one another. Band positions found in mull and solution spectra are presented in Table I, and the spectrum of Co(MQN)Cl_2 in chloroform solution is depicted in Figure 1.

The relationships between electronic properties and stereochemistry of cobalt(II) complexes are well-established,[44] and the spectra reported here have characteristics typical of approximately tetrahedrally-coordinated cobalt(II) ions. On this basis, the ligand field splitting parameter Dq and the Racah interelectronic repulsion parameter B were calculated[45] using the ligand field equations derived for a d^7 ion in a tetrahedral field. The group of bands at lower energy is assigned to components of the ν_2, ${}^4A_2(F) \rightarrow {}^4T_1(F)$ transition and the bands at higher energy are assigned to components of the ν_3, ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition. Using methods of group theory, it can be shown that the orbital triplet in pure T_d symmetry is split in the presence of crystal fields of lower than tetrahedral symmetry. Hence, the ${}^4T_1(F)$ level splits into the components

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(44) R. L. Carlin, Transition Metal Chemistry, 1, 1 (1965).

(45) For a discussion of these spectral parameters, see references 9 and 14.

Table I

Electronic Absorption Spectral Data for Cobalt(II) Halide Complexes[a]

Compound	Solvent	$^4A_2(F) \longrightarrow {}^4T_1(F)$ ν_2, cm^{-1}	$^4A_2(F) \longrightarrow {}^4T_1(P)$ ν_3, cm^{-1}
Co(MQN)Cl_2	Mull	5830; 7220; 9660	15,150; 15,565 sh; 17,240; 18,050 sh; 19,050 sh,w
	$CHCl_3$	5715 (25); 7145 (42); 10,000 (13)	14,705 (470); 15,015 sh; 15,750 (400); 17,390 (305); 18,050 sh; 19,050 sh,w
Co(MQN)Br_2	Mull[b]	5715; 6895; 9435	14,925; 16,395; 17,545 sh; 18,520 sh
	Mull[c]	5680; 6950; 9430	10,400 sh; 15,000; 15,600 sh; 16,400; 16,700; 17,540; 18400; 18,700
	$CHCl_3$	5620 (22); 6850 (51); 9525 (21)	14,815 (590); 16,100 sh; 16,665 (295); 17,545 sh; 18,180 sh,w
Co(MQN)I_2	Mull	5550 sh; 6710; 9090	14,085; 14,700; 15,750; 16,000 sh; 17,700 sh
	$CHCl_3$	5400 (15); 6495 (66); 8930 (42)	14,165 (630); 14,620 (640); 15,530 (375); 16,395 sh; 17,420 sh,w

Table I (Continued)

Compound	Solvent	ν_2, cm^{-1}	ν_3, cm^{-1}
Co(PQN)Cl_2	Mull	5830; 7245; 9800	15,150; 15,530 sh; 17,170; 18,020 sh; 18,890 sh,w
	$CHCl_3$	5750 (24); 7190 (43); 9900 (18)	15,150 (380); 15,625 (345); 17,270 (235); 18,020 sh; 18,725 sh,w
Co(DQN)Cl_2	Mull	5970; 7245; 10,200	15,385; 17,125; 18,020; 18,780 sh
	$CHCl_3$	5815 (20); 7220 (41); 10,100 (15)	15,130 (350); 15,550 sh; 17,390 (185); 18,020 sh; 18,725 sh,w

[a] Abbreviations: w, weak; sh, shoulder. Molar extinction coefficients are given in parentheses.

[b] Spectral data obtained at 280° K. [c] Spectral data obtained at 25° K.

Figure 1.——Electronic absorption spectrum of Co(MQN)Cl_2 in chloroform solution.

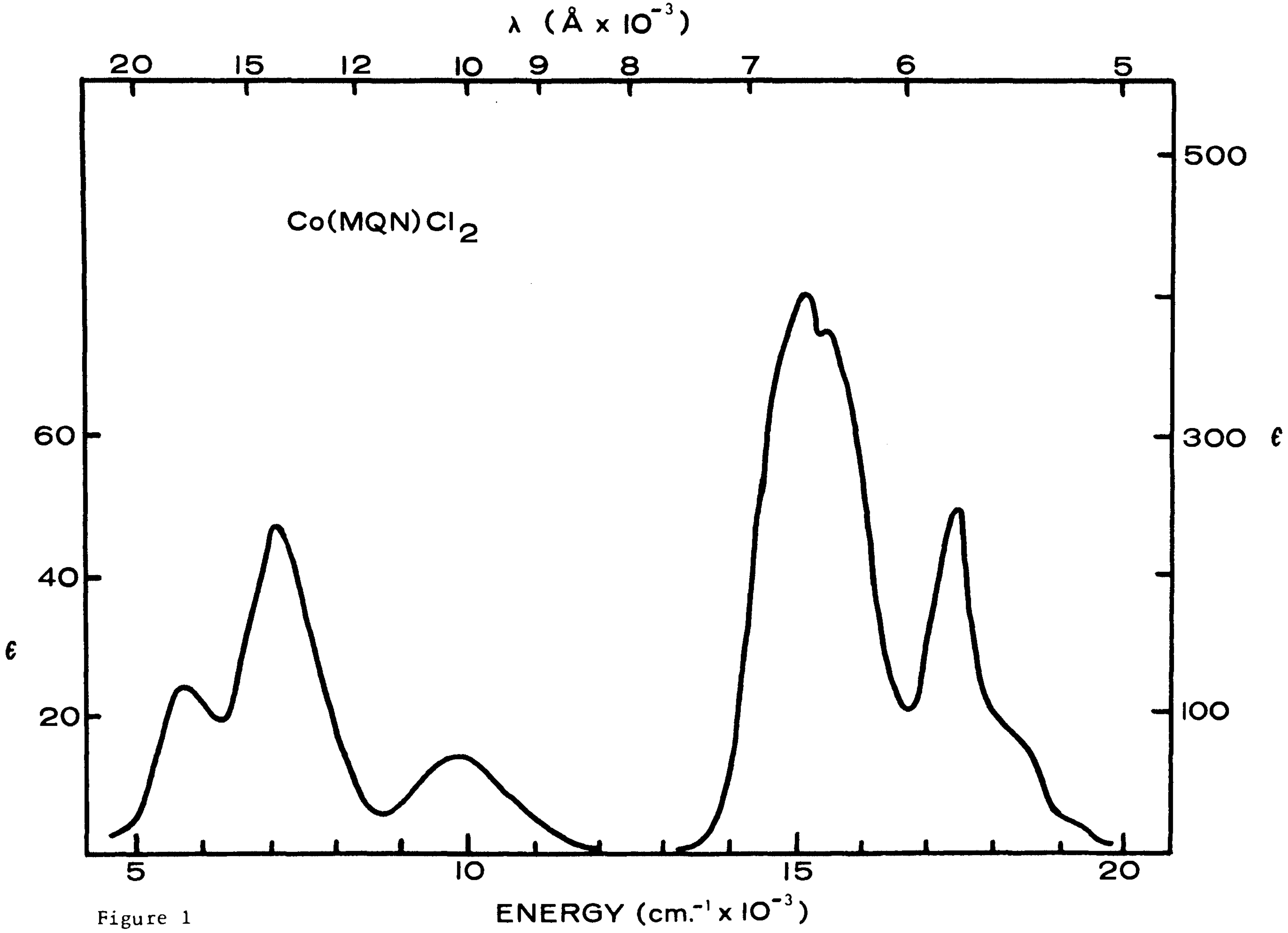
λ (Å x 10⁻³)
20
15
12
10
9
8
7
6
5
Co(MQN)Cl₂
60
40
20
ε
500
300 ε
100
5
10
15
20
ENERGY (cm.⁻¹ x 10⁻³)

Figure 1

$^4A_2(F)$, $^4B_1(F)$, and $^4B_2(F)$; likewise, $^4T_1(P)$ becomes $^4A_1(P)$, $^4B_1(P)$, and $^4B_2(P)$ in C_{2v} symmetry.[46] The more intense components in each band are presumably transitions to these energy levels. Those bands and shoulders of low intensity may be due to spin-forbidden transitions which become partially allowed by spin-orbit mixing of energy levels. The electronic absorption spectrum of $Co(MQN)Br_2$ in a Kel-F #90 mull has been observed at several temperatures, and its spectra at 280° K and 25° K are shown in Figure 2. We do not know the exact origins of the shoulders and peaks which become well-resolved at low temperature.

As is often the case in tetrahedrally-coordinated cobalt(II) ions,[47] the ν_1, $^4A_2(F) \longrightarrow {}^4T_2(F)$ transition was not identified. It is usually predicted to be around 3000-3500 cm^{-1} and this is unfortunately the region where one often observes ligand vibrations and the absorption band of water.[48]

Where broad, structured bands are involved, it is difficult to make unambiguous assignments of band positions. In this case, we have chosen to estimate band positions by drawing the best smooth curve and taking the band position to be the center of the curve at half maximum. Values of the spectral parameters Dq, B, and $\beta = B/B_o$ are listed in Table II along with the values of ν_2 and ν_3 used in making the calculations. The magnitudes of Dq and B are typical for cobalt(II) ions in pseudotetrahedral ligand fields[44] and follow the same order generally

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(46) M. Orchin and H. H. Jaffe, "Symmetry, Orbitals and Spectra," Wiley-Interscience, New York, N. Y., 1966; references 9 and 14.

(47) Reference 9, page 328.

(48) A recent study has dealt with this problem: M. B. Quinn and D. W. Smith, J. Chem. Soc. A, 2496 (1971).

Figure 2.—Electronic absorption spectrum of $Co(MQN)Br_2$ in mull at 280° and 25° K.

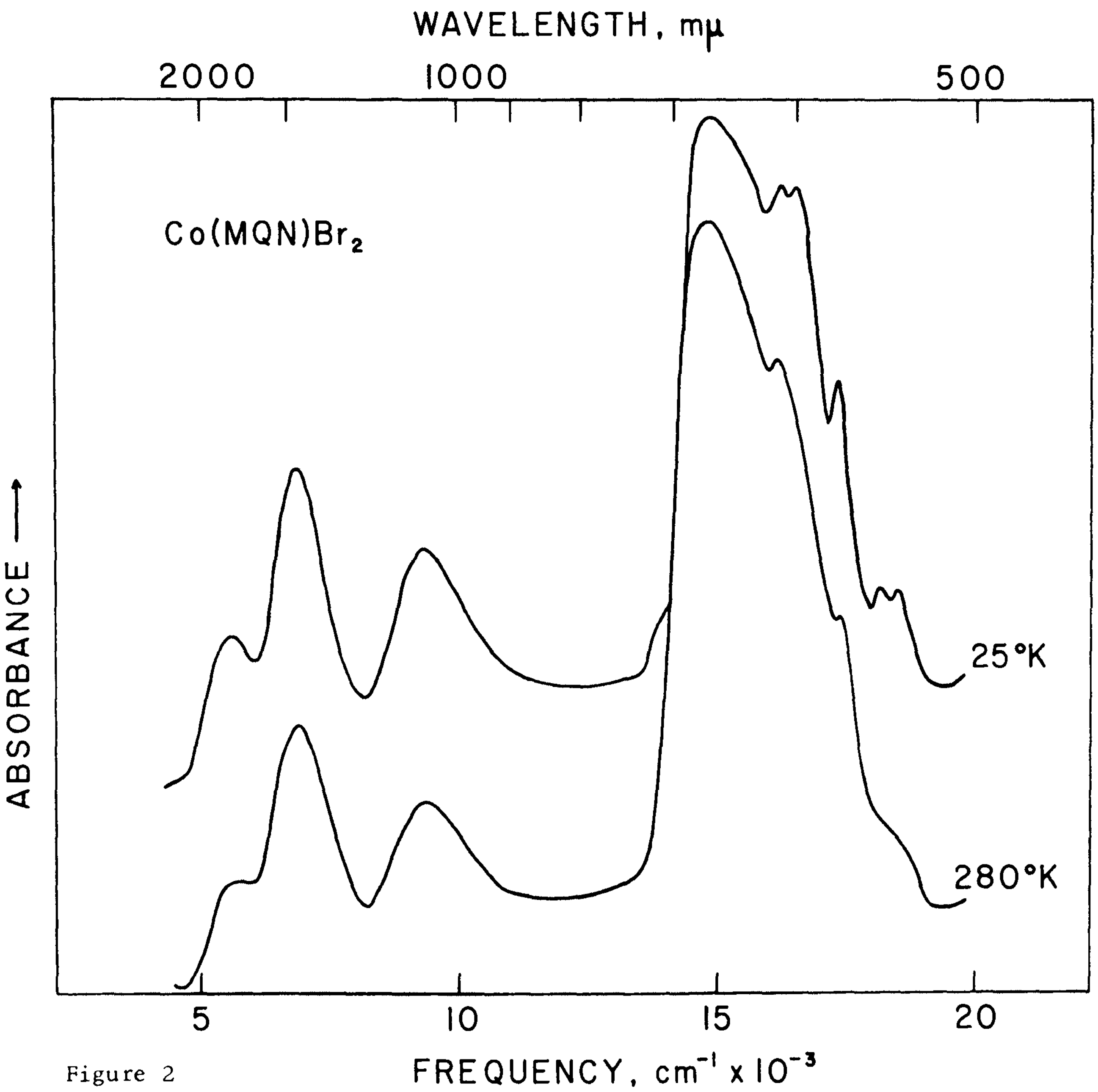
WAVELENGTH, mμ
2000
1000
500
Co(MQN)Br$_2$
ABSORBANCE →
25°K
280°K
5
10
15
20
FREQUENCY, cm^{-1} x 10^{-3}

Figure 2

Table II

Spectral Parameters for Cobalt(II) Halide Complexes

Compound	Solvent	ν_2, cm^{-1}	ν_3, cm^{-1}	Dq, cm^{-1}	B, cm^{-1}	β^*
$Co(MQN)Cl_2$	Mull	7335	15,890	428	694	0.72
	Acetone	7230	15,820	420	695	0.72
$Co(MQN)Br_2$	Mull	7045	15,530	410	685	0.71
	Acetone	6980	15,445	405	684	0.71
$Co(MQN)I_2$	Mull	6740	15,045	392	669	0.69
	Acetone	6675	14,910	387	664	0.69
$Co(PQN)Cl_2$	Mull	7275	15,850	423	694	0.72
	$CHCl_3$	7275	15,750	426	687	0.71
$Co(DQN)Cl_2$	Mull	7650	16,000	446	681	0.71
	$CHCl_3$	7150	15,800	415	697	0.72

* $\beta = B/B_0$ where the free ion value B_0 is taken to be 967 cm^{-1}.

found in the spectrochemical series and the nephelauxetic series, *i. e.*, I < Br < Cl. Assuming the average ligand field approximation[49] is valid, Dq for the MQN ligand was calculated and used to predict Dq values for the corresponding cobalt(II) bromide, iodide, and thiocyanate complexes. The approximation is as good as indicated by the results presented in Table III. In view of this internal consistency, values of Dq for the ligands PQN and DQN were calculated and listed in Table III. It is apparent that the ligand field strengths of MQN and PQN are almost identical and both are somewhat lower in field strength than DQN.

After an investigation of the near infrared spectra of some pseudo-tetrahedral cobalt(II) and nickel(II) complexes of the type ML_2X_2 and MLX_3^- (L = ligand containing N, P, or As donor atoms; X = Cl, Br, I or NCS), Goodgame and Goodgame[50] have reaffirmed a general conclusion made earlier[51] that the electronic absorption spectrum, especially in the case of the ν_2 transition, is very sensitive to the environment of the central metal ion. They concluded that the degree of splitting of the ν_2 band and the intensity of the ν_1 band in cobalt(II) complexes may be used as a guide to distortion from pure T_d symmetry. For a given ligand, they found that the extent of the distortion decreased in the order I < Br < Cl.

In every case, more extensive splitting of the ν_2 band is seen in

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(49) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, *83*, 4690 (1961).

(50) D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, *4*, 139 (1964).

(51) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Amer. Chem. Soc.*, *83*, 4161 (1961).

Table III

Comparison of Experimental and Calculated Dq Values

Species	Experimental Dq, cm^{-1}	Calculated Dq, cm^{-1}
$CoCl_4^{2-}$ [a]	298.5	75/Cl ligand
$CoBr_4^{2-}$ [a]	279.0	70/Br ligand
CoI_4^{2-} [a]	259.0	65/I ligand
$Co(NCS)_4^{2-}$ [b]	455.0	114/NCS ligand
$Co(MQN)Cl_2$	428.0	-
MQN	-	278/MQN ligand
$Co(MQN)Br_2$	410.0	418.0
$Co(MQN)I_2$	392.0	408.0
$Co(MQN)(NCS)_2$	470.0[c]	505.0
PQN	-	273.0
DQN	-	296.0

[a] Reported as $\left[n\text{-}Bu_4N\right]_2\left[CoX_4\right]$ by F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, J. Amer. Chem. Soc., 83, 4690 (1961). [b] Reported as $\left[(CH_3)_4N\right]_2\left[Co(NCS)_4\right]$ by F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, J. Amer. Chem. Soc., 83, 4157 (1961). [c] This value is calculated from the solution spectrum of $Co(MQN)(NCS)_2 \cdot C_2H_5OH$ in acetone. See discussion of this complex in text.

the components reported here than are found in the spectra of tetrahedral CoX_4^{2-} ions[49] (X = Cl, Br, or I). We find splitting in the order of 4000 cm^{-1} for the cobalt(II) chloride complexes as opposed to ca. 1500 cm^{-1} found in $CoCl_4^{2-}$. This extensive splitting is not observed in the ν_3 bands, and the fact that components of the ν_3 transition are not similarly affected has been discussed by Ferguson.[52]

Splittings between the lowest and highest energy components of the ν_2 band for each complex are listed in Table IV. Examination of the values in mulls and chloroform solutions reveals the following trends. (1) Distortion in the coordination geometry of the MQN complexes occurs in the order I < Br < Cl, both in the solid phase and in solution. (2) Distortion apparently increases upon solution of the MQN complexes, except in the iodide which remains essentially unchanged. (3) Cobalt(II) chloride complexes of MQN, PQN, and DQN are distorted in the order MQN < PQN < DQN in the solid phase and PQN < MQN ~ DQN in solution.

Magnetic susceptibility data for the cobalt(II) complexes are given in Table V. Values of χ_M' are corrected for diamagnetism but not for temperature independent paramagnetism. The ground state term for a cobalt(II) ion in a regular tetrahedral field is $^4A_2$ and the moment is theoretically independent of temperature. The values of μ_{eff} at room temperature are consistent with those normally found in tetrahedral and pseudotetrahedral compounds containing this ion.[13,44,48] The slight temperature dependence seen in the magnetic moments of these compounds may be ascribed to the second order Zeeman effect and to a small amount of electron delocalization. The small increase in μ_{eff} for $Co(MQN)Br_2$ at low temperature may be the result of the presence of ferromagnetic

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(52) J. Ferguson, *J. Chem. Phys.*, *32*, 528 (1960).

Table IV

Splittings of the ν_2 Band in Spectra of Cobalt(II) Halide Complexes

Compound	Solvent	ν_2 Splitting, cm^{-1}
$Co(MQN)Cl_2$	Mull	3830
	$CHCl_3$	4285
$Co(MQN)Br_2$	Mull	3720
	$CHCl_3$	3905
$Co(MQN)I_2$	Mull	3540
	$CHCl_3$	3530
$Co(PQN)Cl_2$	Mull	3970
	$CHCl_3$	4150
$Co(DQN)Cl_2$	Mull	4230
	$CHCl_3$	4285

Table V

Magnetic Susceptibilities of Cobalt(II) Halide Complexes

Compound	T, $^{\circ}$K	$\chi'_M \times 10^6$ cgs	μ_{eff}
$Co(MQN)Cl_2$	293.0	9425	4.66
	285.0	9425	4.64
M W = 354.1	247.0	11,055	4.67
	215.0	12,350	4.61
$\chi_c = -206 \times 10^{-6}$ cgs	187.5	14,095	4.60
	134.5	19,430	4.57
	103.0	24,980	4.54
	66.5	38,270	4.51
	39.5	67,560	4.61
	29.7	94,550	4.74
	26.8	109,000	4.83
$Co(MQN)Br_2$	294.5	8900	4.58
	258.0	10,110	4.57
M W = 443.0	232.0	11,120	4.54
	193.0	13,230	4.52
$\chi_c = -228 \times 10^{-6}$ cgs	158.0	15,980	4.49
	122.5	20,390	4.47
	94.5	25,680	4.41
	65.5	37,450	4.42
	48.5	50,400	4.44
	28.5	90,480	4.56
	25.0	100,500	4.48
$Co(MQN)I_2$	296.5	9935	4.85
	110.5	24,785	4.68
M W = 537.0			
$\chi_c = -258 \times 10^{-6}$ cgs			

impurities.

The infrared spectra of the complexes are essentially the same except in the low energy region where fundamental vibrational modes occur. The ν(C=O) vibrational band seen in the ligand infrared spectrum does not shift upon complexation. Energies of metal-halide stretching frequencies are useful in distinguishing tetrahedral complexes from octahedral complexes,[53] and values of ν(Co-X) reported in Table VI are in the ranges found for pseudotetrahedral structures.

For complexes of the same metal, the ratio ν(M-Br)/ν(M-Cl) generally falls in the range 0.74-0.77, and the ratio ν(M-I)/ν(M-Cl) is 0.65.[54] Here, ν(Co-Br)/ν(Co-Cl) is found to be 0.80, and examination of this ratio for the other metal(II) complexes reported in this dissertation shows the same value. This consistency indicates reasonable assignments of stretching frequencies. The ratio ν(Co-I)/ν(Co-Cl) is 0.67 and, though it is somewhat greater than expected, indicates a logical ν(Co-I) assignment.

In view of the results for the complexes of MQN, it seems reasonable to assign ν(Co-Cl) in $Co(PQN)Cl_2$ to bands at 352 and 317 cm^{-1}. In $Co(DQN)Cl_2$ this vibration is represented by bands at 355 and 320 cm^{-1}.

Nickel(II) Halide Complexes.—As were the cobalt(II) halide complexes, the nickel(II) halide complexes are air-stable, soluble in most organic

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(53) R. J. H. Clark, "Review of Metal-Halogen Vibrational Frequencies" in Halogen Chemistry, Vol. 3, Academic Press, New York, N. Y., 1968.

(54) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, 2nd ed, 1970, page 214.

Table VI

Tentative ν(M-X) Vibrational Assignments for Complexes of MQN*

ν(M-X)	Assignment, cm^{-1}	ν(M-Br)/ν(M-Cl)	ν(M-I)/ν(M-Cl)
Co-Cl	355 sh; 343 s; 319 s	0.80	0.67
Co-Br	274 m; 257 m		
Co-I	245 sh; 230 s		
Ni-Cl	342 s	0.81	0.65
Ni-Br	277 s		
Ni-I	223 s		
Cu-Cl	310 sh; 292 s	0.81	
Cu-Br	250 sh; 235 m		
Mn-Cl	340 sh; 316 br,s; 268 s	0.81	
Mn-Br	275 sh; 254 br,s; 224 s		

* Abbreviations: sh, shoulder; s, strong; m, medium; br, broad; w, weak.

Table VI (Continued)*

Vibrational Bands Observed in the Purple $\mathrm{Ni(MQN)Cl_2}$ Complex (cm^{-1}):

714 m;670 w; 650 m; 628 m; 612 sh; 606 m; 565 w,br; 522 m; 515 m; 460 m; 450 m; 398m; 376 sh; 370 m; 342 s; 302 m; 265 sh; 246 m; 227 m

Vibrational Bands Observed in the Off-white $\mathrm{Ni(MQN)Cl_2}$ Complex (cm^{-1}):

710 m; 668 sh; 653 m; 634 m; 608 m; 520 w,br; 465 w,br; 403 m,br; 245 m,br

* Abbreviations: sh, shoulder; s, strong; m, medium; br, broad; w, weak.

solvents, and decompose in aqueous solution. The X-ray powder diffraction patterns have been recorded for each of these compounds and all are dissimilar. Evidence presented below indicates that they are pseudotetrahedral in structure, and unlike most tetrahedral nickel(II) complexes which are intense blue in color,[5] these are purple or dark green. This variance in coloration is due to charge transfer bands which extend into the visible region and is usually seen in compounds containing coordinated bromide or iodide ions.[5] In addition to this "blue band" in the absorption spectrum, tetrahedrally-coordinated nickel compounds usually exhibit a second band around 8000 cm^{-1}. Another identifying feature of tetrahedral nickel(II) compounds is the high intensity of each of these bands. The typical value of the molar extinction coefficient for the "blue band" is ca. 200.

Two complexes corresponding to the formula $Ni(MQN)Cl_2$ have been prepared and characterized. One of these, the purple form, is tetrahedral, and the other, an off-white form, is octahedral by virtue of bridging chloride ligands.

The purple chloride, the bromide, and the iodide complexes are discussed first. All of the compounds in this group have the spectral properties characteristic of pseudotetrahedral nickel(II) complexes. On this basis we have calculated the spectral parameters Dq and B, and have verified their tetrahedral coordination by comparing these parameters with those of compounds of known geometry.[9] The electronic absorption spectral data in mulls and solutions are listed in Table VII; spectral parameters are given in Table VIII. The appearance of the spectrum of $Ni(MQN)Br_2$ in acetonitrile solution presented in Figure 3 is very similar to that of the purple $Ni(MQN)Cl_2$ and $Ni(MQN)I_2$. The most

Table VII

Electronic Absorption Spectral Data for Nickel(II) Halide Complexes[a]

Compound	Solvent	$^3T_1(F) \longrightarrow {}^3T_2(F)$ ν_1, cm^{-1}	$^3T_1(F) \longrightarrow {}^3A_2(F)$ ν_2, cm^{-1}	^1D cm^{-1}
$Ni(MQN)Cl_2$	Mull	-	10,115	11,325; 11,765
Purple form	CH_3CN	~7200 sh	10,000 (43)	11,390 (18); 11,810 (14)
	CH_3NO_2	~7200 sh	10,000 (45)	11,385 (18); 11,800 (14)
$Ni(MQN)Br_2$	Mull[b]	~7200 sh	9885	10,915; 11,353
	Mull[c]	~6670 sh; 8630	10,000; 10,150 sh	10,460; 11,200
	CH_3CN	~7200 sh	9780 (53)	10,990 (26); 11,395 (19)
$Ni(MQN)I_2$	Mull	~7200 sh	9660	-
	CH_3NO_2	~7200 sh	9400 (53)	10,280 sh; 10,540 sh
	ϕNO_2	~7200 sh	9350 (80)	10,255 sh

[a] Abbreviations: sh, shoulder; ϕ, phenyl. Molar extinction coefficients are given in parentheses.

[b] Spectral data obtained at 300° K. [c] Spectral data obtained at 25° K.

Table VII (Continued)[a]

Compound	Solvent	${}^3T_1(F) \longrightarrow {}^3T_1(P)$ ν_3, cm^{-1}
Ni(MQN)Cl_2	Mull	19,050
Purple form	CH_3CN	16,000 sh; 18,180 sh; 19,370 (90); 22,200 sh
	CH_3NO_2	16,000 sh; 18,180 sh; 19,415 (97)
Ni(MQN)Br_2	Mull[b]	17,390 sh; 18,470
	Mull[c]	14,900 sh; 15,600 sh; 17,900 sh; 18,400; 21,300 sh
	CH_3CN	15,385 sh; 17,475 sh; 18,570 (122)
Ni(MQN)I_2	Mull	14,290 sh; 17,000
	CH_3NO_2	14,290 sh; 17,115 (218)
	ϕNO_2	14,290 sh; 16,950 (337)

[a] Abbreviations: sh, shoulder; ϕ, phenyl. Molar extinction coefficients are given in parentheses.

[b] Spectral data obtained at 300° K. [c] Spectral data obtained at 25° K.

Table VIII

Spectral Parameters for Nickel(II) Halide Complexes*

Compound	Solvent	ν_2, cm^{-1}	ν_3, cm^{-1}	Dq, cm^{-1}	B, cm^{-1}	β
Ni(MQN)Cl_2	Mull	10,115	19,050	550	1010	0.94
Purple form	CH_3NO_2	10,000 (45)	18,965 (97)			
Ni(MQN)Br_2	Mull	9830	17,850	530	940	0.87
	CH_3CN	9780 (53)	18,230 (122)			
Ni(MQN)I_2	Mull	9730	17,000	525	885	0.82
	CH_3NO_2	9400 (53)	17,040 (218)			

* Values of spectral parameters were calculated from band centers. Free ion value B_o = 1080 cm^{-1}.

Figure 3.——Electronic absorption spectrum of Ni(MQN)Br_2 in acetonitrile solution.

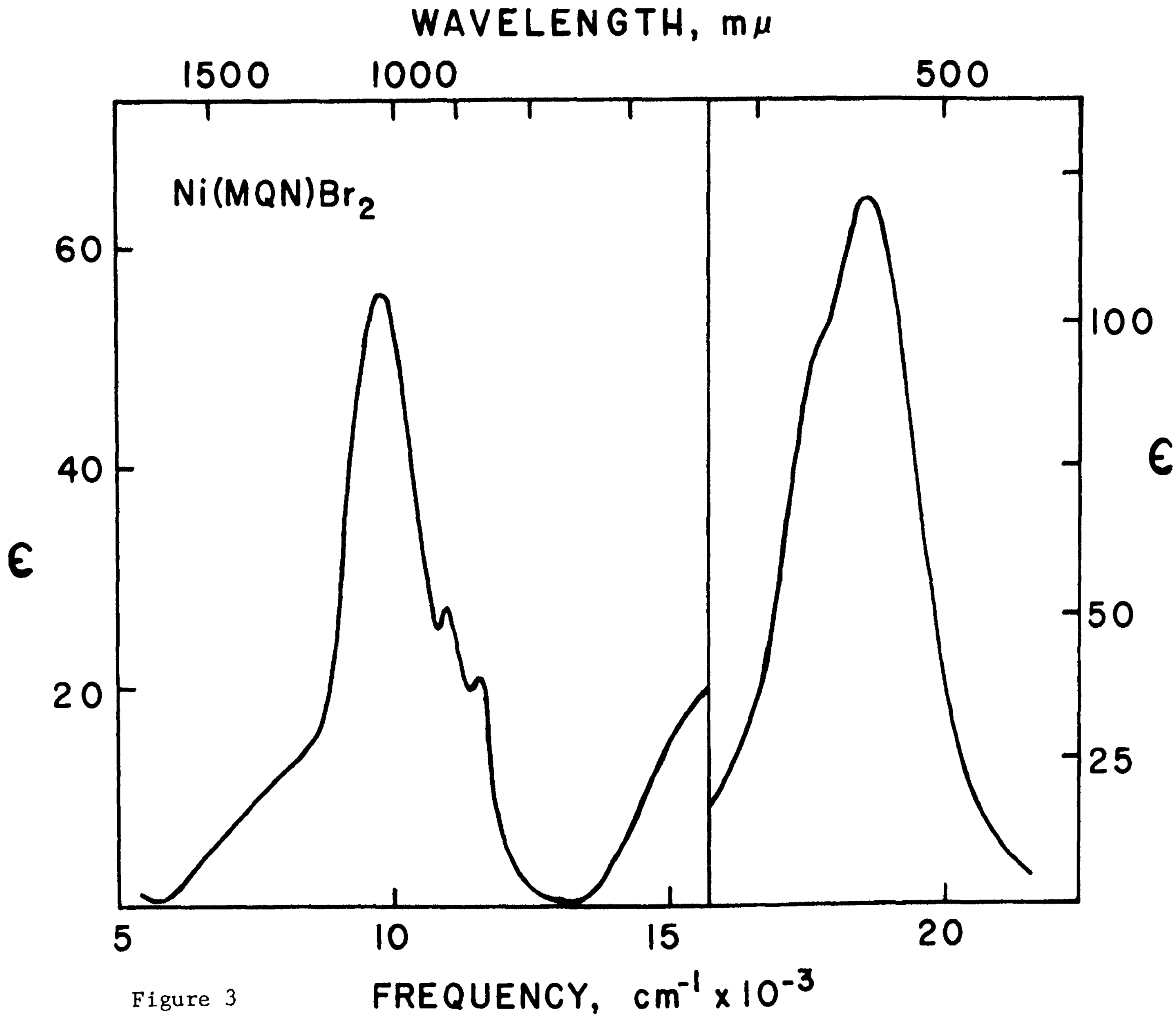
WAVELENGTH, mμ
1500
1000
500
Ni(MQN)Br$_2$
60
40
20
ε
100
50
25
ε
5
10
15
20
FREQUENCY, cm^{-1} x 10^{-3}

Figure 3

noticeable difference is in the iodide where the two small peaks seen in the chloride and bromide at _ca_. 11,200 cm^{-1} are present only as shoulders.

Three spin-allowed d-d transitions are theoretically predicted for a nickel(II) ion in a regular tetrahedral field.[55] These are ν_1, $^3T_1(F) \longrightarrow {}^3T_2(F)$; ν_2, $^3T_1(F) \longrightarrow {}^3A_2(F)$; ν_3, $^3T_1(F) \longrightarrow {}^3T_1(P)$. The ν_1 transition corresponds to the broad shoulder found at about 7200 cm^{-1}. The more intense band at _ca_. 10,000 cm^{-1} is assigned to ν_2, and the intense band at highest energy is assigned to ν_3. The two peaks on the high energy side of ν_2 have been tentatively assigned[51,56] to spin-forbidden transitions arising from the ^1D free ion state.

A study of the effect of low temperature on the intensity of these two peaks was made in an attempt to verify their nature. Supposedly, a band associated with a spin-allowed transition will become sharper at low temperature, but the oscillator strength will remain constant. Likewise, a spin-forbidden transition should decrease in intensity.[57] Figure 4 illustrates the mull spectrum of $Ni(MQN)Br_2$ at room temperature and 25° K. It is somewhat surprising that these two peaks become well-resolved at low temperature, and the exact interpretation of this result remains to be unraveled.

The magnitudes of Dq and B found in these complexes are typical and

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(55) Reference 9 and references therein.

(56) F. A. Cotton and D. M. L. Goodgame, _J. Amer. Chem. Soc._, _82_, 5771 (1960); L. Sacconi, I. Bertini, and F. Mani, _Inorg. Chem._, _6_, 262 (1967).

(57) A. J. McCaffery, J. R. Dickinson, and P. N. Schatz, _Inorg. Chem._, _9_, 1563 (1970).

Figure 4.—Electronic absorption spectrum of Ni(MQN)Br_2 in mull at 300° and 25° K.

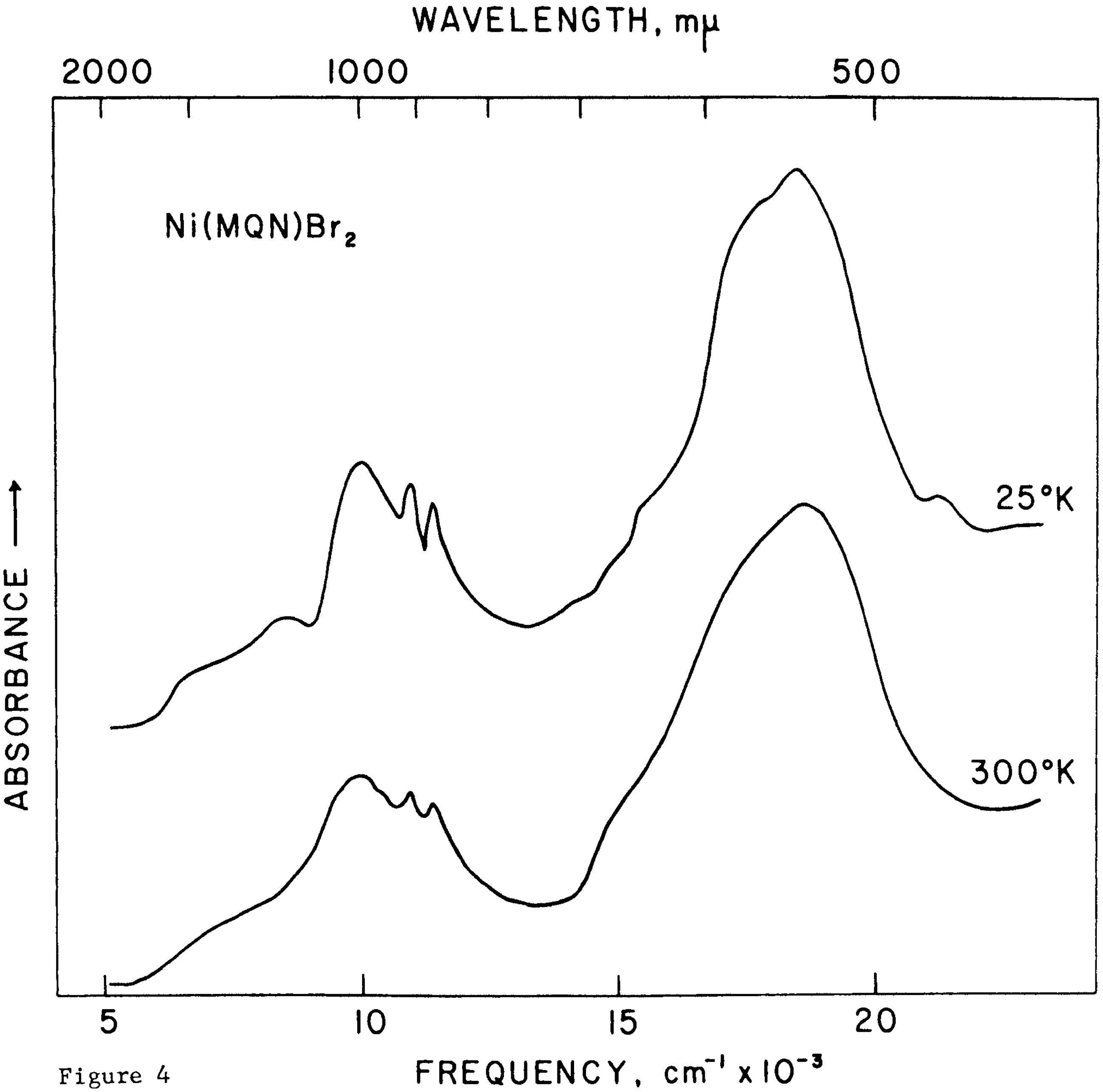
WAVELENGTH, mμ
2000
1000
500
Ni(MQN)Br$_2$
ABSORBANCE ⟶
25°K
300°K
5
10
15
20
FREQUENCY, cm^{-1} x 10^{-3}

Figure 4

follow the order of the spectrochemical series and the nephelauxetic series, *i. e.*, I < Br < Cl. Table VII gives the results.

Magnetic susceptibility data are listed in Table IX. The values of μ_{eff} for the purple chloride, the bromide, and the iodide are a good deal greater than the spin-only value (2.83) indicating a considerable orbital contribution. Even though these values are lower than predicted for regular tetrahedral complexes, they are in keeping with those values found in pseudotetrahedral nickel(II) complexes.[5] This reduction may be explained by the fact that lower symmetry removes orbital degeneracy. The temperature dependence is expected for complexes containing approximately $^3T_1$ ground states. The increase in μ_{eff} values below *ca*. 90° K for the Ni(MQN)I_2 may be the result of a small amount of ferromagnetic impurity. The field dependence of the low temperature values tends to support this conclusion. This increase in μ_{eff} at low temperatures has also been observed in other similar pseudotetrahedral nickel(II) complexes.[58]

Perhaps the most interesting complex reported here is the off-white complex corresponding to the formula Ni(MQN)Cl_2. This material possesses properties very different from those seen in the purple, tetrahedrally-coordinated complex of the same empirical formula. The off-white isomer is best prepared in non-coordinating solvents which can pick up moisture from the reactants; hot solvents seem to work best. We have prepared this complex under a variety of conditions (hot solvents, cold solvents, solvents of various polarities, inert atmosphere) and have demonstrated its reproducibility. In fact, we believe the off-white product to be the

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(58) P. LaMarche and W. A. Baker, Jr., unpublished results.

Table IX

Magnetic Susceptibilities of Nickel(II) Halide Complexes

Compound	T, ^{o}K	χ_M' x 10^6 cgs	μ_{eff}
$Ni(MQN)Cl_2$ Purple form M W = 353.9 χ_c = -203 x 10^{-6} cgs	300.5	4660	3.35
	267.0	5350	3.38
	246.0	5820	3.39
	228.5	6060	3.34
	191.0	7650	3.41
	174.0	8390	3.41
	154.0	9480	3.41
	112.5	12,730	3.38
	95.5	14,950	3.39
	71.5	20,300	3.41
	55.0	26,800	3.43
	36.5	40,050	3.41
	19.0	76,900	3.44
$Ni(MQN)Cl_2$ Off-white form M W = 353.9 χ_c = -203 x 10^{-6} cgs	298.0	4885	3.40
$Ni(MQN)Cl_2 \cdot H_2O$ Pale green hydrate M W = 371.0 χ_c = -216 x 10^{-6} cgs	293.0	5180	3.49
	248.5	5990	3.45
	201.0	7630	3.50
	143.0	11,200	3.60
	102.5	16,525	3.68
$Ni(MQN)Br_2$ M W = 442.8 χ_c = -226 x 10^{-6} cgs	300.0	4720	3.37
	293.0	4790	3.35
	273.0	5200	3.37
	249.0	5680	3.36
	233.0	5980	3.34
	210.5	6530	3.31
	192.5	7160	3.32
	188.5	7350	3.33
	172.5	7960	3.32
	161.5	8390	3.30
	154.5	8750	3.28
	122.0	11,200	3.31
	121.0	11,350	3.30
	112.0	12,100	3.31
	94.5	14,500	3.31
	72.5	18,700	3.29

Table IX (Continued)

Compound	T, ^{o}K	$\chi_M' \times 10^6$ cgs	μ_{eff}
$Ni(MQN)Br_2$	53.0	25,000	3.26
	33.5	39,800	3.28
	19.0	68,000	3.20*
$Ni(MQN)I_2$	296.0	5420	3.58
	269.0	5960	3.59
M W = 536.8	253.0	6350	3.57
	230.0	6850	3.55
$\chi_c = -258 \times 10^{-6}$ cgs	210.0	7640	3.59
	190.5	8410	3.59
	171.0	9280	3.56
	130.5	12,100	3.55
	112.0	14,150	3.54
	92.5	17,200	3.55
	70.0	24,350	3.69
	52.0	33,650	3.74
	35.5	59,600	4.12*
	18.5	125,500	4.34*

* Value which is dependent upon strength of magnetic field; highest field value used to calculate μ_{eff}.

thermodynamically stable form for the reasons given below.

Samples of purple Ni(MQN)Cl_2 dissolved in boiling ethanol (a purple solution results) and quenched in an ice bath are converted to the off-white compound (pale green, if the solvent is wet). If some off-white or pale green Ni(MQN)Cl_2 is dissolved (it dissolves slowly) in hot ethanol, it likewise forms a purple solution, but we cannot isolate a purple product. The product isolated is always the initial reactant.

When samples of the off-white isomer and purple isomer are dissolved quantitatively in 0.1 N hydrochloric acid, the resulting electronic absorption spectra are essentially identical. Furthermore, the two spectra are the same as that obtained by dissolving nickel(II) chloride and MQN in 0.1 N hydrochloric acid indicating that the decomposition products are the same, apparently $Ni(H_2O)_6^{2+}$ and MQN·2 HCl.

In a sealed capillary tube, the off-white Ni(MQN)Cl_2 appears to change to dark purple and then brown at about 253°. Purple Ni(MQN)Cl_2 turns brown around 248° under the same conditions. These compounds have been examined in air by differential thermogravimetry (DTA-TG). Over the range 25-245° the patterns for weight loss for purple and off-white Ni(MQN)Cl_2 are similar and both show an exotherm in the DTA at 245°. Above 245° the weight loss and DTA for the purple and off-white Ni(MQN)Cl_2 complexes are not the same. The DTA-TG pattern of the ligand MQN shows a melting endotherm at 103° and another endotherm centered at 195° and accompanied by an 85 % weight loss.

The off-white material is practically insoluble in non-coordinating solvents (alcohols, chloroform, acetone) and is decomposed, *i. e.*, solvated, in "stronger" solvents (for example, CH_3NO_2 and DMF) as judged by a comparison of the solution absorption spectrum and mull spectrum.

In nitromethane or acetonitrile, off-white $Ni(MQN)Cl_2$ dissolves to give a pink-colored solution whose absorption spectrum has the same appearance and band positions as the purple, tetrahedral $Ni(MQN)Cl_2$ complex in the same solvents. Figure 5 shows the mull spectrum of off-white $Ni(MQN)Cl_2$ at room temperature and 25° K. Very concentrated mulls were required to obtain the spectrum indicating the intensities of the bands are low. The appearance of the spectrum is typical of octahedral coordination,[9] and spectral parameters calculated on this basis are consistent with this geometry. Three spin-allowed transitions are expected for a d^8 ion in an octahedral field, and these are ν_1, ${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$; ν_2, ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$; and ν_3, ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$. Band locations and calculated spectral parameters are given in Table X. The values of B given in Table X were calculated from the values of ν_1, ν_2, and ν_3 presented in the table using the approximate ligand field equation[9]

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15.$$

The value of Dq is $\nu_1/10$. The abnormally low value of B at 300° K reflects the difficulty in choosing band locations accurately when the absorption band is not well-resolved, as in the case of ν_1. It is worth noting that, if experimental values of ν_2 and ν_3 at 25° K are used to calculate Dq (hence, ν_1) using the equation[9]

$$1360\ Dq^2 - 72(\nu_2 + \nu_3)^2 - (\nu_3 - \nu_2)^2 = 0,$$

the calculated Dq is about 95 % of the value given in Table X. This internal consistency is in good agreement with an octahedral model.

The decrease in d-orbital splitting seen between the anhydrous off-white form and the partially hydrated pale green form may be explained as a swelling of the crystal lattice due to a random quantity

Figure 5.—Electronic absorption spectrum of off-white Ni(MQN)Cl_2 in mull at (a) 300° K and (b) 25° K.

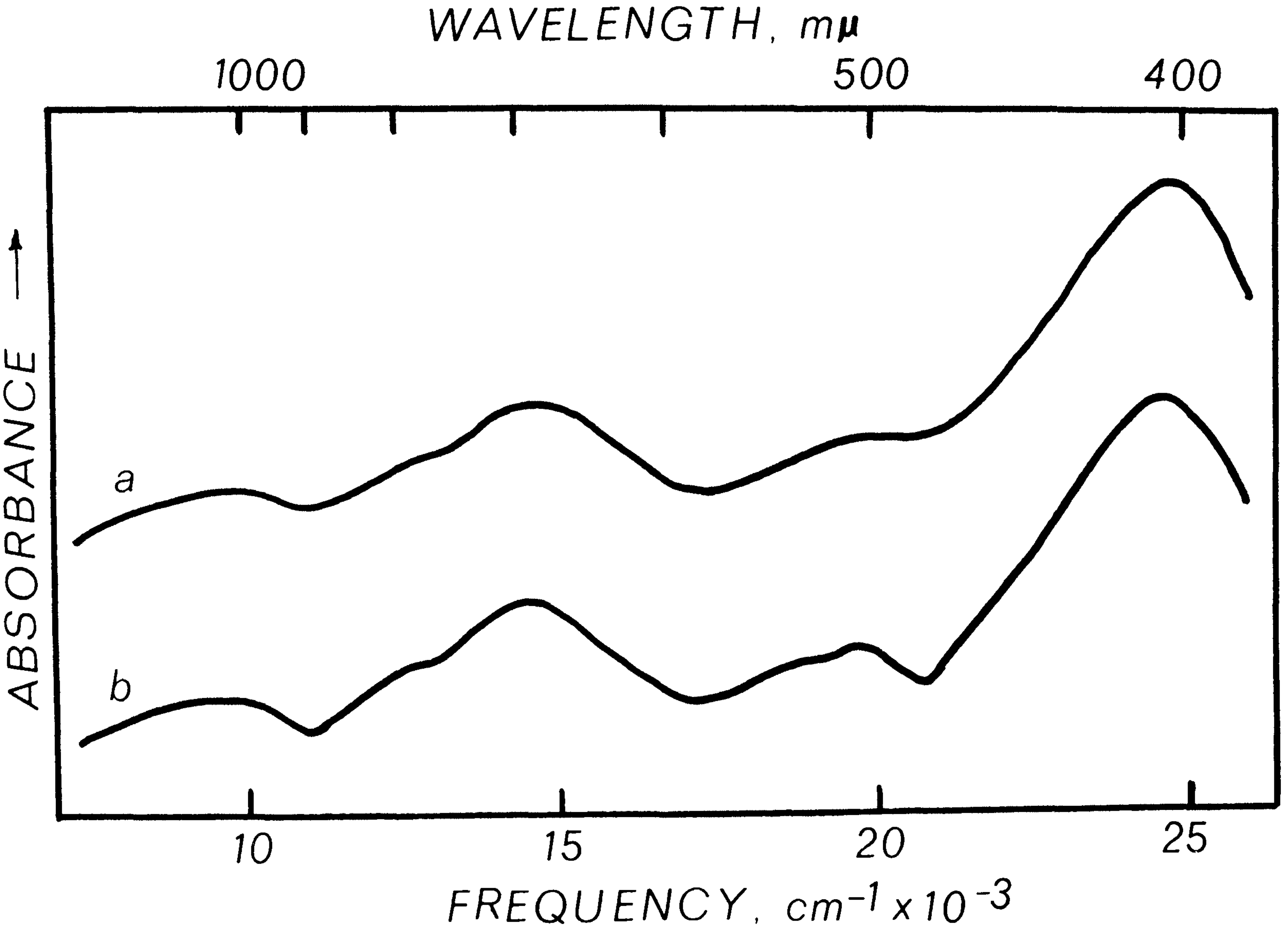
WAVELENGTH, mμ
1000
500
400
ABSORBANCE →
a
b
10
15
20
25
FREQUENCY, cm⁻¹ x 10⁻³

Figure 5

Table X

Band Positions and Spectral Parameters for Octahedral Ni(MQN)Cl_2 Complexes*

Compound	T, °K	Band Positions		
		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ν_1, cm^{-1}	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ν_2, cm^{-1}	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ν_3, cm^{-1}
Ni(MQN)Cl_2	300	10,000	12,270 sh; 14,285; 15,625 sh; 16,130 sh	18,520 sh; 19,800 sh; 24,240
	25	9660	12,500 sh; 14,985; 15,625 sh; 16,260 sh	18,520 sh; 19,600; 24,690
Ni(MQN)$Cl_2 \cdot \frac{1}{4} H_2O$	300	9400	12,120 sh; 14,185; 15,625 sh	20,000 sh; 24,270
	25	9350	12,500 sh; 14,250; 15,600 sh	18,200 sh; 19,900; 24,700

* Abbreviations: sh, shoulder. Free ion value of B_o taken to be 1080 cm^{-1}.

Table X (Continued)*

Spectral Parameters

Compound	T, ^{o}K	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	Dq, cm^{-1}	B, cm^{-1}	β
Ni(MQN)Cl_2	300	10,000	14,285	24,240	1000	568	0.53
	25	9660	14,295	24,690	966	713	0.66
Ni(MQN)$Cl_2 \cdot \frac{1}{4} H_2O$	300	9400	14,185	24,270	940	683	0.63
	25	9350	14,250	24,700	935	725	0.67

* Abbreviations: sh, shoulder. Free ion value of B_o taken to be 1080 cm^{-1}.

of water molecules. This swelling would result in a decrease in ligand-metal ion interaction. If these molecules of water replaced chloride ions in the nickel(II) coordination sphere, increased d orbital splitting would be expected. The observed opposite trend implies absorbed water in lieu of coordinated water.

Pseudooctahedral coordination in the off-white and pale green Ni(MQN)Cl_2 complexes is thought to be due to formation of halide bridges between metal atoms. It is known[59a] that the metal-halogen stretching frequencies in bridging structures are lower than in terminal metal-halogen structures. This frequency lowering is most pronounced where a change in coordination number is involved and has often been used as evidence for a bridging halide.[59b] Figure 6 shows the infrared spectra of purple tetrahedral Ni(MQN)Cl_2 and off-white octahedral Ni(MQN)Cl_2 in the region 700-200 cm^{-1}; band locations are given in Table VI. The bands at 302 and 342 cm^{-1} found in the spectrum of the tetrahedral Ni(MQN)Cl_2 complex have previously been assigned to Ni-Cl stretching frequencies (see Table VI). These bands are clearly absent from the spectrum of the off-white octahedral Ni(MQN)Cl_2 and their absence is further evidence for chloride bridging.

The proposed polymeric pseudooctahedral structure for the off-white compound is also supported by the X-ray powder diffraction patterns. These patterns are completely different from those of the tetrahedral Ni(MQN)X_2 complexes and in general show three broad lines at 2θ values of _ca_. 8.8°, 11.6°, and 16.1°. These angles would correspond to repeat units of _ca_. 5.5, 7.6, and 10.3 Å.

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(59) (a) Reference 54, page 216, and references therein; (b) R. J. H. Clark and C. S. Williams, _Inorg_. _Chem_., _4_, 350 (1965) and others therein.

Figure 6.—Infrared spectra of Ni(MQN)Cl_2 isomers: (A) purple tetrahedral isomer, (B) off-white, octahedral, halogen-bridged isomer.

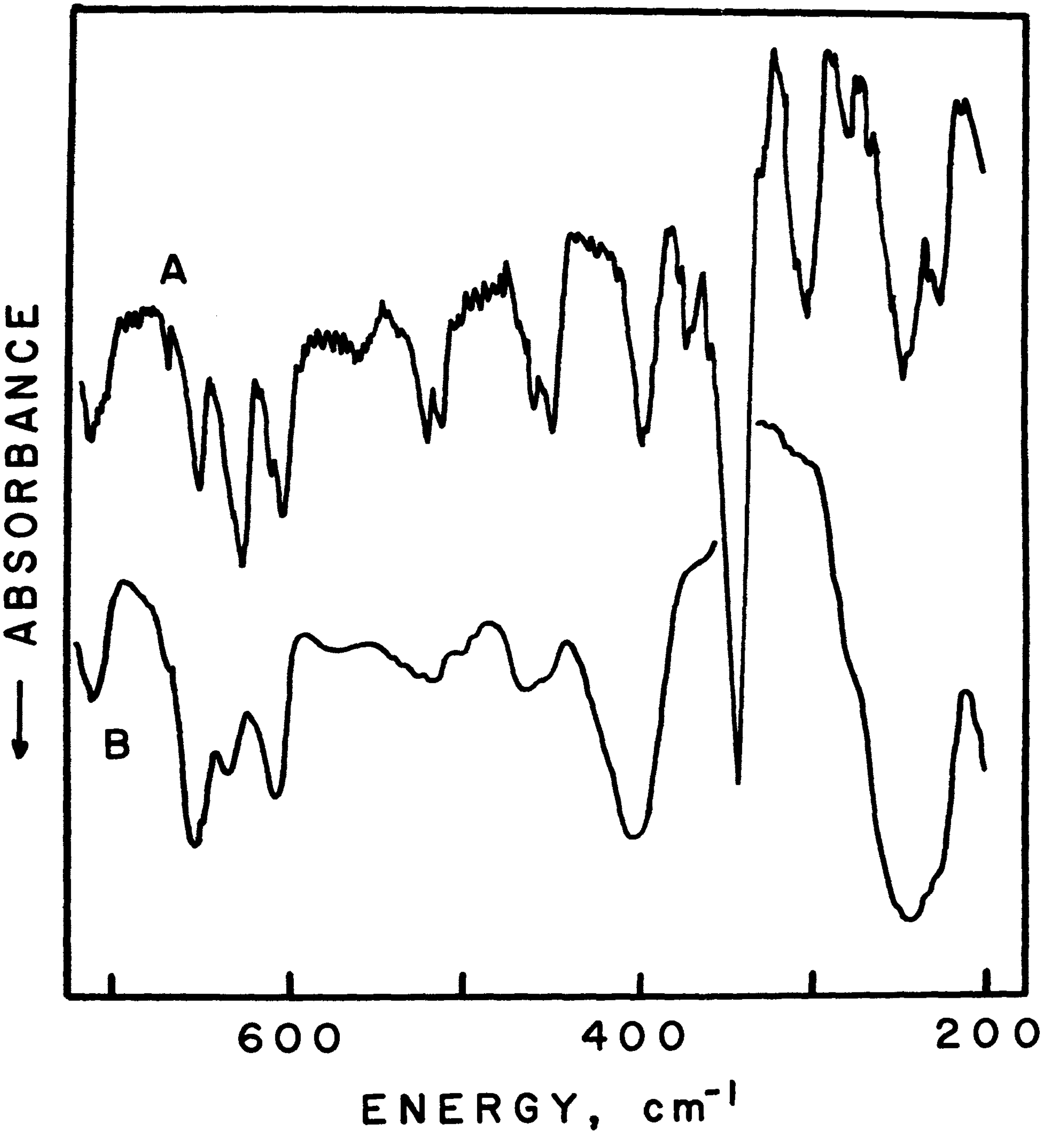

Figure 6

Magnetic susceptibilities listed in Table IX for off-white $Ni(MQN)Cl_2$ and pale green $Ni(MQN)Cl_2 \cdot H_2O$ are total susceptibilities uncorrected for TIP. Values of μ_{eff} were calculated from these susceptibilities using the expression $\mu_{eff} = 2.828(\chi_M' T)^{\frac{1}{2}}$. In detailed magnetic studies corrections for TIP must be made in systems of octahedrally-coordinated nickel(II). A plot of $1/\chi_M'$ versus T for the pale green compound gives a straight line over the temperature range studied. These values are consistent with an octahedral geometry.[5]

Octahedral nickel(II) complexes have a $^3A_{2g}$ ground state and their magnetic moments are expected to be independent of temperature and independent of slight distortions from regular octahedral symmetry.[13] The increase in μ_{eff} with decrease in temperature seen in the off-white complex is surprising and may indicate a magnetically non-dilute system with magnetic exchange.

Cobalt(II) and Nickel(II) Thiocyanate and Nitrate Complexes.—The thiocyanate ligand is known to coordinate in different modes,[60] and infrared spectroscopy has proved an effective method of distinguishing them.[54] Complexes containing N-bonded thiocyanate exhibit a C-N stretching frequency generally in the range 2040-2080 cm^{-1}, and the S-bonded ligand exhibits this vibration in the range 2080-2120 cm^{-1}. The C-S stretching frequency is found in the general regions 780-860 cm^{-1} and 690-720 cm^{-1} for terminal, N-bonded and S-bonded thiocyanate groups,

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(60) J. L. Burmeister, Coord. Chem. Rev., 3, 225 (1968); A. H. Norbury and A. I. P. Sinha, Quart. Rev., 24, 69 (1970); R. A. Bailey, S. L. Kozak, T. W. Michelson, and W. N. Mills, Coord. Chem. Rev., 6, 407 (1971).

respectively; similarly, the N-C-S bending mode occurs in the ranges 450-490 cm^{-1} and 400-440 cm^{-1}. A number of cobalt and nickel thiocyanate complexes have been reported[61] where the C-N stretching frequencies are 30-60 cm^{-1} higher than in the case of terminal thiocyanate groups, and the C-S stretch is usually found at intermediate frequencies.[62] This is supposedly due to the presence of M-NCS-M bridges.[61] Furthermore, it has been suggested[61g,61h] that extensive splitting of the band corresponding to the antisymmetric stretch occurs in complexes containing both terminal and bridging thiocyanates.

Examination of the infrared spectra of $Co(MQN)(NCS)_2 \cdot C_2H_5OH$ and $Ni(MQN)(NCS)_2 \cdot CH_3OH$ provides the information given in Table XI. The cobalt complex shows definite splitting of the C-N stretching mode into two bands of almost equal intensity, indicating bridging thiocyanate, and the bands at 2070, 780, and 490 cm^{-1} are indicative of terminal, N-bonded thiocyanate ligands. The cobalt coordination sphere is completed by a coordinated molecule of ethanol, the solvent in which the complex was prepared. The O-H stretching frequency for ethanol is observed[63] as a

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(61) (a) P. C. Mitchell and R. J. P. Williams, _J. Chem. Soc._, 1912 (1960); (b) M. M. Chamberlain and J. C. Bailar, Jr., _J. Amer. Chem. Soc._, _81_, 6412 (1959); (c) A. Turco and C. Pecile, _Nature_, _191_, 66 (1961); (d) J. Lewis, R. S. Nyholm, and P. W. Smith, _J. Chem. Soc._, 4590 (1961); (e) A. Sabatini and I. Bertini, _Inorg. Chem._, _4_, 959 (1965); (f) L. Sacconi, I. Bertini, and F. Mani, _Inorg. Chem._, _6_, 262 (1967); (g) J. Chatt and L. A. Duncanson, _Nature_, _178_, 997 (1956); (h) S. M. Nelson and J. Rodgers, _Inorg. Chem._, _6_, 1390 (1967).

(62) C. Puglisi and R. Levitus, _J. Inorg. Nucl. Chem._, _29_, 1069 (1967).

(63) G. M. Barrow, _J. Chem. Phys._, _20_, 1739 (1952).

Table XI

Infrared Spectral Data for

Cobalt(II) and Nickel(II) Thiocyanate Complexes*

Compound	$Co(MQN)(NCS)_2 \cdot C_2H_5OH$	$Ni(MQN)(NCS)_2 \cdot CH_3OH$
C-N Stretch	2110 s; 2070 s; 2025 sh	2130 s; 2090 s
C-S Stretch	780 w	-
N-C-S Bend	490 m	480 m
M-NCS Stretch	280 s,br	290 s
O-H Stretch	3225 br	3400 br

* Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad. Values of vibrational frequencies are expressed in cm^{-1}.

broad band at 3660 cm^{-1} and is found at lower frequencies in coordinated ethanol. The ν(O-H) mode in the cobalt complex corresponds to a broad band centered around 3225 cm^{-1}. A dimeric structure is proposed for this complex, but the exact structure awaits an X-ray crystallographic study. One of several possible dimeric structures is shown in Figure 7. This structure requires an octahedral ligand field and this is confirmed by analysis of electronic absorption spectra and magnetic properties. There are three spin-allowed d-d transitions predicted for a cobalt(II) ion in a regular octahedral field represented by ν_1, $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$; ν_2, $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$; ν_3, $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$. Band assignments have been made according to pure octahedral symmetry, and band positions are listed in Table XII. The coordination sphere of the cobalt(II) ion is a distorted one as judged by the band splitting seen in the mull spectrum presented in Figure 8 of $Co(MQN)(NCS)_2 \cdot C_2H_5OH$. The transition to the $^4T_{1g}$ term (ν_2) in regular octahedral symmetry is triply degenerate and this degeneracy is lost in lower symmetries.[46] On this basis, the bands at 19,230 and 20,875 cm^{-1} are assigned as components of ν_3, and the band at 9215 cm^{-1} with its shoulder at ca. 7550 cm^{-1} is assigned to components of ν_1. The ν_2 transition corresponds to the band located at 18,180 cm^{-1}. The calculated parameters Dq and B are given in Table XII and these values are typical for octahedrally coordinated cobalt(II) ions.[9]

The dimeric cobalt thiocyanate complex is decomposed in solution; in acetone, the product is distinctly tetrahedral and is most likely $Co(MQN)(NCS)_2$ monomers. The solution absorption spectrum is very similar to those of the cobalt(II) halide complexes. Bands located at 6370, 8200, and 10,700 cm^{-1} are associated with the ν_2 transition in pseudotetrahedral symmetry. The bands at 15,450, 16,020(sh), 17,860, and

Figure 7.——Proposed structure for $\mathrm{Co(MQN)(NCS)_2 \cdot C_2H_5OH}$ and $\mathrm{Ni(MQN)(NCS)_2 \cdot CH_3OH}$. Metal atoms represented by M, and methyl or ethyl group represented by R.

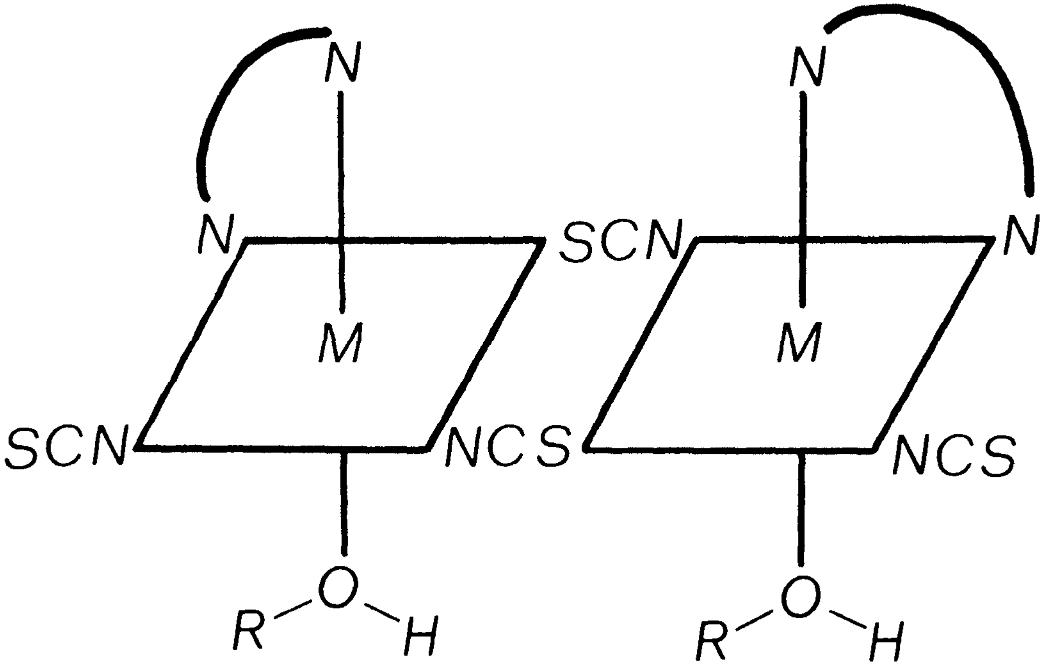

Figure 7

Table XII

Electronic Spectral Data for Cobalt(II) and Nickel(II) Thiocyanate and Nitrate Complexes[a]

Compound	Solvent	Symmetry	ν_1, cm^{-1}	ν_2, cm^{-1}
Co(MQN)$(NCS)_2 \cdot C_2H_5OH$	Mull	Octahedral	7550 sh; 9215	18,180
	Acetone	Tetrahedral	-	6370 (10); 8200 (35); 10,700 (20)
Ni(MQN)$(NCS)_2 \cdot CH_3OH$	Mull	Octahedral	9240	15,300; 12,230 sh
	DMF	Octahedral	9100 (10)	15,450 (13); 16,165 sh; 17,000 sh; 13,000 sh
Ni(MQN)$(NO_3)_2$	Mull	Octahedral	9100	15,400; 12,500 sh
	CH_3NO_2	Octahedral	9750 (15)	15,600 (30)

Table XII (Continued)[a]

Compound	Solvent	ν_3, cm^{-1}	Dq, cm^{-1}	B, cm^{-1}
$Co(MQN)(NCS)_2 \cdot C_2H_5OH$	Mull	19,230; 20,875	970[b]	844
	Acetone	15,450 (450); 16,025 sh; 17,860 (150); 18,520 sh	490[c]	628
$Ni(MQN)(NCS)_2 \cdot CH_3OH$	Mull	25,500 sh	970	835
	DMF	25,560 (25)	955	820
$Ni(MQN)(NO_3)_2$	Mull	25,650	950	838
	CH_3NO_2	25,975 (45)	965	850

[a] Abbreviations: sh, shoulder. Molar extinction coefficients given in parentheses. [b] Values of Dq were calculated from values of ν_2 and ν_3 where ν_3 was taken as the simple average of components assigned to ν_3. [c] Value of ν_3 taken as center of band at half maximum; ν_2 taken as 8200 cm^{-1}.

Figure 8.——Electronic absorption spectrum of Co(MQN)$(NCS)_2 \cdot C_2H_5OH$ in mull.

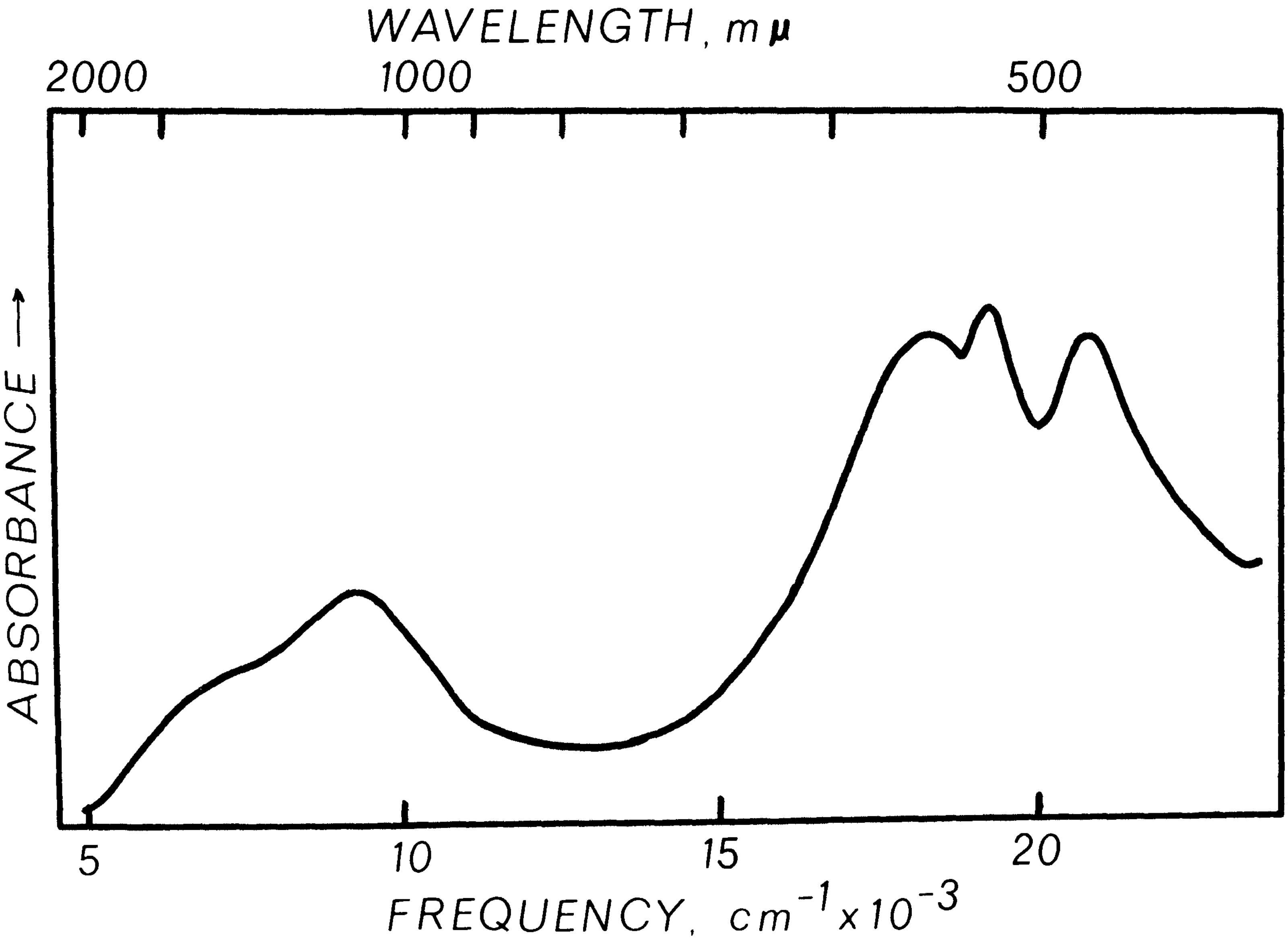
WAVELENGTH, mμ
2000
1000
500
ABSORBANCE →
5
10
15
20
FREQUENCY, cm^{-1} x 10^{-3}

Figure 8

18,520 (sh) cm^{-1} are components of the ν_3 transition in pseudotetrahedral symmetry. The calculated values of Dq and B are 490 and 628 cm^{-1}, respectively.

Magnetic properties are given in Table XIII. The magnetic moment of 4.38 B.M. is somewhat lower than expected[44] for cobalt(II) in an octahedral symmetry. However, the temperature dependence of the moment is anticipated for this symmetry.

The complex $\mathrm{Ni(MQN)(NCS)_2 \cdot CH_3OH}$ is distinctly octahedral as judged from the mull absorption spectrum presented in Figure 9, the calculated spectral parameters (Table XII), and the magnetic susceptibility data (Table XIII). As in the case of the analogous cobalt(II) complex, the octahedral ligand field is apparently generated by thiocyanate bridging forming a dimeric structure and coordinated solvent molecules. In the infrared spectrum, splitting of the C-N stretching mode into bands of almost equal intensity at 2090 and 2130 cm^{-1} indicates the presence of thiocyanate bridging ligands. The band at 2090 cm^{-1} is in the range found for S-bonded thiocyanate, however, a medium intensity band at 480 cm^{-1} suggests N-bonded terminal groups. Unfortunately, examination of the spectrum between 700-900 cm^{-1} reveals no band unique to the thiocyanate complex when compared to spectra of free MQN and the analogous halide complexes. A band of strong intensity at 290 cm^{-1} is, however, unique to this complex and is assigned to the Ni-NCS metal-ligand stretching frequency. This vibration is reported[64] at 295 cm^{-1} (strong intensity) in anhydrous nickel(II) thiocyanate. Evidently, the terminal thiocyanates are N-bonded. The molecules of methanol acquired from the solvent are coordinated to the central metal atom. We observe an O-H

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(64) C. D. Flint and M. Goodgame, J. Chem. Soc. A, 442 (1970).

Table XIII

Magnetic Susceptibilities of Cobalt(II) and Nickel(II) Thiocyanates and Nitrates

Compound	T, ^{o}K	χ_M' x 10^6 cgs	μ_{eff}
$Co(MQN)(NCS)_2 \cdot C_2H_5OH$	295.0	8120	4.38
	130.0	16,380	4.13
M W = 445.5			
$\chi_c = -253 \times 10^{-6}$ cgs			
$Ni(MQN)(NCS)_2 \cdot CH_3OH$	291.0	4480	3.23
	167.0	7650	3.20
M W = 431.2	122.0	10,130	3.14
$\chi_c = -241 \times 10^{-6}$ cgs			
$Ni(MQN)(NO_3)_2$	296.5	4690	3.33
	104.5	12,640	3.25
M W = 407.0			
$\chi_c = -194 \times 10^{-6}$ cgs			

Figure 9.——Electronic absorption spectrum of $Ni(MQN)(NCS)_2 \cdot CH_3OH$ in mull.

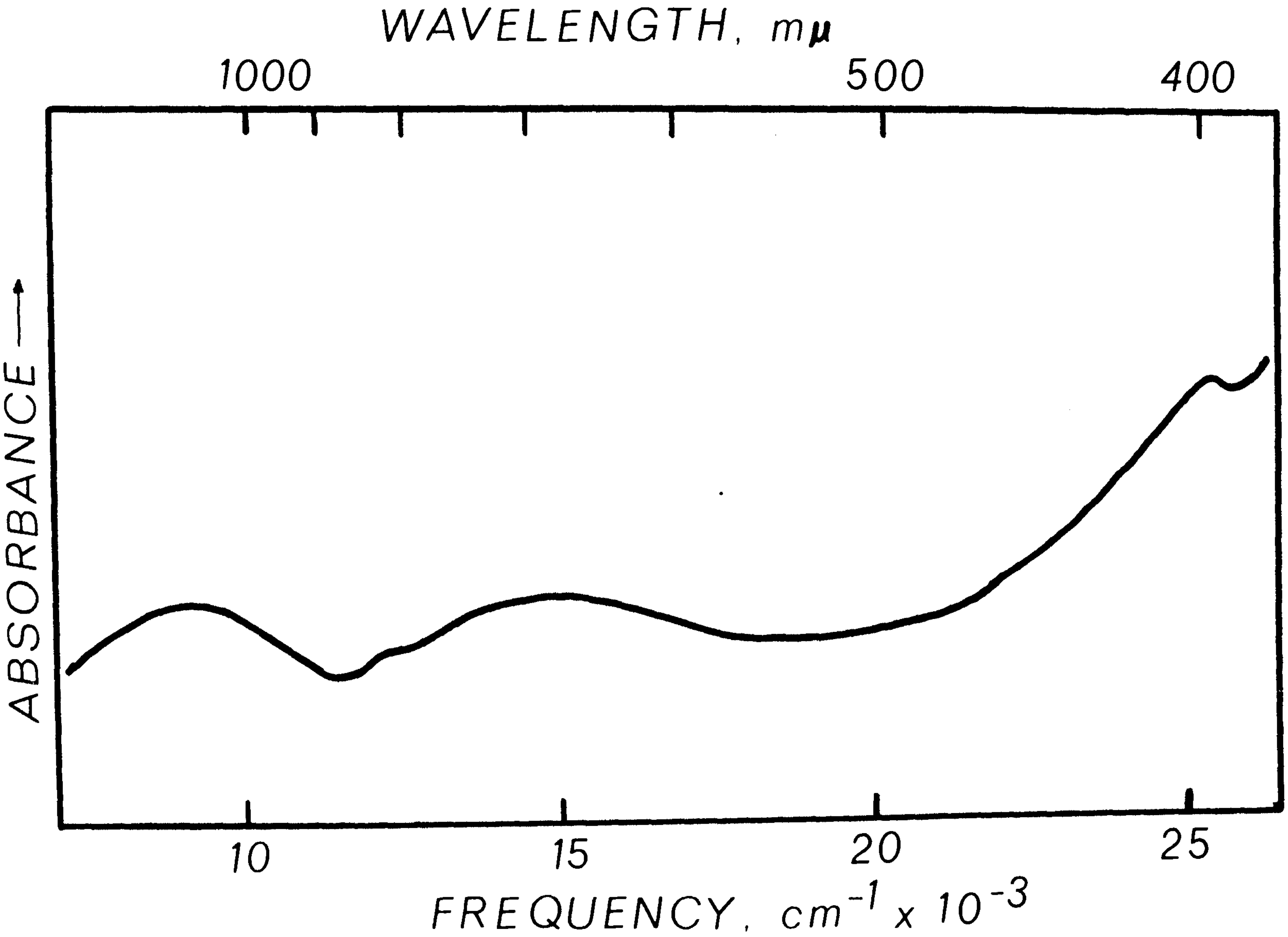
WAVELENGTH, mμ
1000
500
400
ABSORBANCE ⟶
10
15
20
25
FREQUENCY, $cm^{-1} \times 10^{-3}$

Figure 9

stretching frequency at 3400 cm^{-1} in the complex as opposed to the free methanol value[65] of 3683 cm^{-1}. Data pertaining to the infrared spectral properties of $Ni(MQN)(NCS)_2 \cdot CH_3OH$ are given in Table XI. In the absence of a crystallographic study, we suggest this complex has a structure similar to the cobalt(II) thiocyanate complex (Figure 7).

The nickel nitrate complex, $Ni(MQN)(NO_3)_2$, has spectral and magnetic properties which characterize it as having a pseudotetrahedral microsymmetry about the nickel atom. Its electronic absorption spectrum is very similar in appearance to that of the octahedral complex $Ni(MQN)(NCS)_2 \cdot CH_3OH$. The pertinent spectral and magnetic data are given in Tables XII and XIII. The nitrate ion is known[66] to act as a monodentate, chelating, and bridging ligand. Infrared spectroscopy has proved useful in distinguishing the particular mode, but the difficulties in doing so have been pointed out.[67] In the case at hand, the infrared spectrum is too complex to allow interpretation without recourse to other techniques (isotopic labeling, *etc*.) and no mode of nitrate coordination is proposed. In view of the octahedral structure and the stochiometry, the mode is, *a priori*, chelating or bridging.

The X-ray diffraction patterns of the cobalt(II) and nickel(II) thiocyanate complexes reported here were recorded and they show no

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(65) H. D. Noether, *J. Chem. Phys.*, *10*, 693 (1942).

(66) Reference 54, page 171, and references therein.

(67) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, *2*, 1162 (1963); F. A. Cotton and R. H. Soderburg, *J. Amer. Chem. Soc.*, *85*, 2402 (1963); A. B. P. Lever, *Inorg. Chem.*, *4*, 1042 (1965); J. I. Bullock and F. W. Parrett, *Chem. Commun.*, 157 (1969).

similarity to one another or to any of the other complexes reported here.

The preparation of the cobalt(II) nitrate complex resulted in a material of unknown stoichiometry. Although its magnetic and spectral properties are indicative of an octahedral geometry, no discussion or conclusion can be made at this time.

Iron(II) Chloride Complex of MQN.—The only complex of a divaltent iron halide which was prepared in high purity was Fe(MQN)Cl_2, and this was prepared and handled in a dry inert atmosphere. Results of the bromide, iodide, and perchlorate preparations were never reproducible and their preparation was abandoned.

The iron(II) ion has the free ion ground state term ^5D which, in the presence of a ligand field of T_d symmetry, is split into ^5E and $^5T_2$ terms. The ^5E term is the ground state in high-spin complexes involving ligands of weak field strengths, whereas, in sufficiently strong fields, a $^3T_2$ term becomes the ground state.[14] Thus, a single d-d electron transition corresponding to $^5E \rightarrow {}^5T_2$ is expected, and single bands are usually found aroung 4000 cm^{-1} [5] although split bands are not uncommon.[68]

The electronic absorption spectrum exhibited by Fe(MQN)Cl_2 is shown in Figure 10 and spectral and magnetic data for this complex are listed in Table XIV. The band asymmetry seen in the mull spectrum is also seen in nitromethane solution and is best attributed to loss of degeneracy of the $^5T_2$ state. This results from the actual symmetry being closer to C_{2v} than T_d.[69] The energy of the $^5E \rightarrow {}^5T_2$ transition

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(68) "Spectroscopic Properties of Inorganic and Organometallic Compounds," Vol. 1-3, Specialist Periodical Reports of The Chemical Society, London, 1968-71, and references therein.

(69) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 454 (1965).

Figure 10.—Electronic absorption spectrum of $Fe(MQN)Cl_2$ in mull.

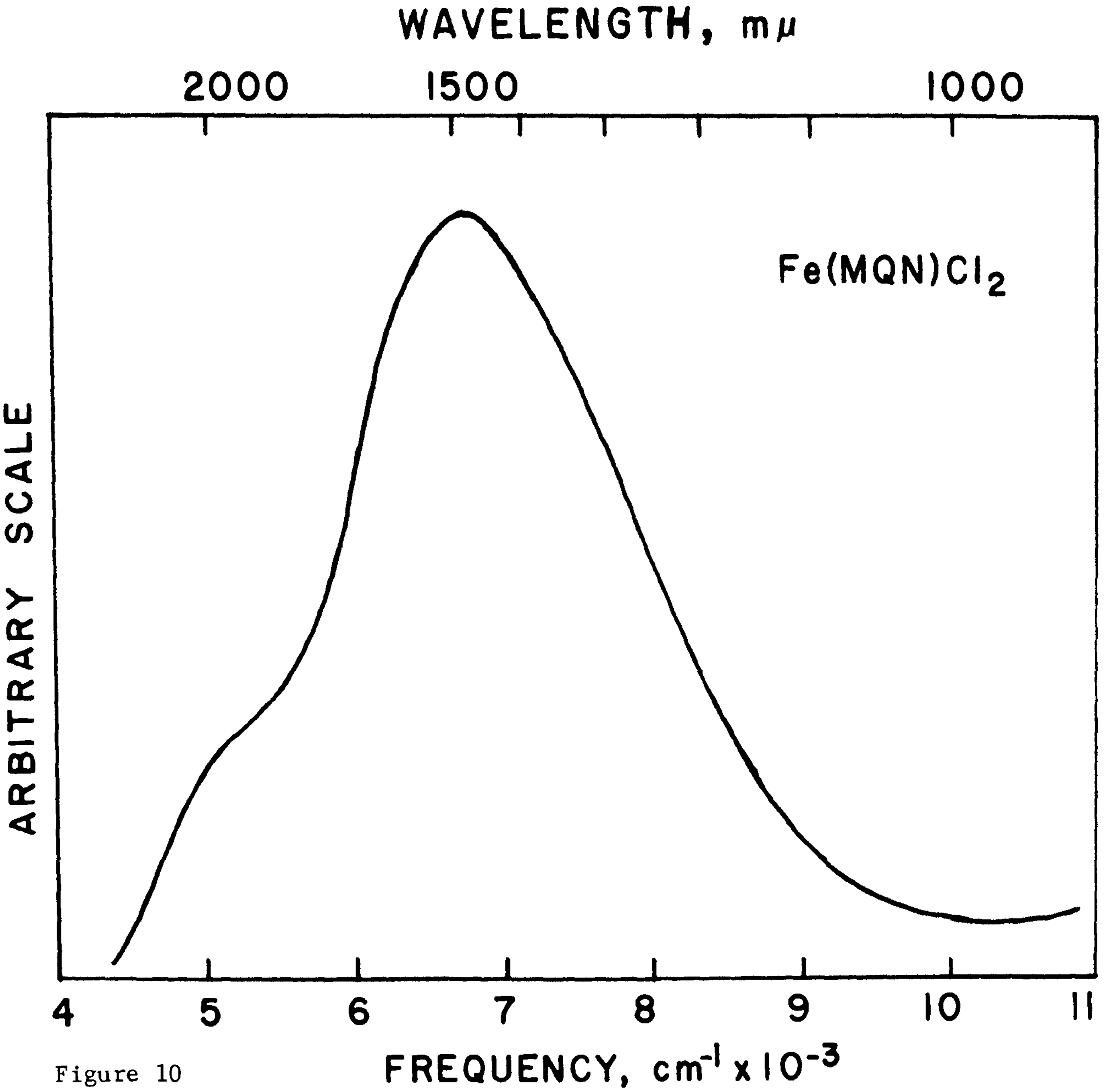
WAVELENGTH, mμ
2000
1500
1000
Fe(MQN)Cl$_2$
ARBITRARY SCALE
4
5
6
7
8
9
10
11
FREQUENCY, cm^{-1} x 10^{-3}

Figure 10

Table XIV

Spectral and Magnetic Properties of Fe(MQN)Cl_2*

Electronic Absorption Spectra

Solvent	$^5E \longrightarrow {}^5T_2$ (cm^{-1})
Mull	5300 sh; 6700
CH_3NO_2	5550 sh; 6500 (20)

Magnetic Susceptibilities

T, °K	$\chi_M' \times 10^6$ cgs	μ_{eff}
294.0	11,830	5.27
257.0	13,500	5.27
203.0	17,130	5.27
143.0	23,600	5.21
102.0	32,650	5.16

M W = 351.0 $\chi_c = -233 \times 10^{-6}$ cgs

Mössbauer Parameters

T, °K	Quadrupole Splitting ΔE_Q, mm/sec	Isomer Shift δ, mm/sec
300.0	2.74	0.91
195.0	2.67	0.86
78.0	2.57	0.79

* Abbreviations: sh, shoulder. Values in parentheses are molar extinction coefficients taken at the band maximum.

is rather typical of pseudotetrahedral iron(II) complexes although a molar extinction coeffient of 20 is less than expected. In compounds containing the tetrahedral $FeCl_4^{2-}$ ion[70] values of $\in_M$ are found in the range 60-80.

The magnetic behavior of this material is rather characteristic of pseudotetrahedral iron(II) compounds.[71] Observed magnetic moments are not expected to have orbital contributions which increase the moment above the spin-only value of 4.90 B.M. However, many compounds containing tetrahedrally-coordinated iron(II) have been reported[72] which have μ_{eff} in the range 5.3-5.4. These results have been explained by considering the effect of mixing of the first excited state with the ground state via spin-orbit coupling. The moment is given[14] by

$$\mu_{obs.} = \mu_{s.o.} \left[1 - 2\lambda/10Dq\right].$$

Thus, the value of 5.27 for μ_{eff} reported for $Fe(MQN)Cl_2$ is in keeping with a tetrahedral structure and its slight variation with temperature is in keeping with a ^5E ground state.

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(70) C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.*, **25**, 159 (1953).

(71) R. J. H. Clark, R. S. Nyholm, and F. B. Taylor, *J. Chem. Soc.*, 1802 (1967).

(72) N. S. Gill, *J. Chem. Soc.*, 3512 (1961); D. Forster and D. M. L. Goodgame, *ibid.*, 454 (1965); 268 (1965).

The Mössbauer effect[73] has become a most useful tool applied to the study of chemical properties of materials,[74] and much has been published concerning this technique.[68,75] Compounds containing the iron(II) nucleus have been extensively studied and interpretation of their properties has undergone critical review and discussion.[76] We have studied Fe(MQN)Cl_2 at several temperatures and have derived the Mössbauer parameters ΔE_Q and δ, the quadrupole splitting and isomer shift, respectively. The values confirm the pseudotetrahedral nature of the complex by comparison to compounds of known structure.[77]

Manganese(II) Halide Complexes.—The manganese(II) ion is a d^5 ion and, for high-spin complexes, a $^6A_1$ ground state is expected in both tetrahedral and octahedral ligand fields. The spin-only magnetic moment is 5.92 B.M. and is expected to be independent of temperature. Spin-orbit coupling should not cause a reduction in the moment.[14] Excellent agreement between theory and experiment results in magnetic susceptibility data being of little value in unraveling the nature of these compounds. Values of μ_{eff} listed in Table XV are somewhat lower than the spin-only

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(73) H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin, New York, N. Y., 1962.

(74) For example, see G. K. Wertheim, "Mössbauer Effect, Principles and Applications," Academic Press, New York, N. Y., 1964.

(75) V. I. Goldanskii and R. H. Herber, ed, "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

(76) C. E. Johnson, Symposia Faraday Soc., No. 1, 7 (1968).

(77) P. R. Edwards, C. E. Johnson, and R. J. P. Williams, J. Chem. Phys., 47, 2074 (1967); C. D. Burbridge and D. M. L. Goodgame, J. Chem. Soc. A, 1074 (1968).

Table XV

Magnetic Susceptibilities of Manganese(II) Halide Complexes

Compound	T, °K	$\chi_M' \times 10^6$ cgs	μ_{eff}
Mn(MQN)Cl_2	294.5	14,500	5.85
	284.0	15,200	5.85
M W = 350.1	105.5	40,125	5.82
$\chi_c = -203 \times 10^{-6}$ cgs			
Mn(MQN)Br_2	294.0	14,240	5.78
	105.0	39,000	5.72
M W = 439.0			
$\chi_c = -226 \times 10^{-6}$ cgs			

moment and are, within experimental error, independent of temperature. Although this reduction in moment may indicate a magnetically non-dilute system,[78] we have not investigated the magnetic interaction.

Numerous attempts were made to observe the electronic absorption spectra of $Mn(MQN)Cl_2$ and $Mn(MQN)Br_2$ in mulls and solution, but absorption bands were never found. All d-d transitions in manganese(II) complexes are spin-forbidden and are of very low intensity.[5] For example, $\epsilon_M = 0.01-0.04$ for octahedral $Mn(H_2O)_6^{2+}$ and $\epsilon_M = 1-4$ for tetrahdral $MnBr_4^{2-}$. The absence of spectral data makes difficult an attempt to determine stereochemistry.

Examination of infrared spectral data (Table VI) is no more helpful in this case. Vibrational frequencies of fundamental modes are known[54] to depend upon stereochemistry. Nuttall[79] has written of the use of metal-halogen vibrational frequencies in the characterization of unknown complexes formed from divalent metal halides, and Clark has done a similar study.[53] Ordinarily, Mn-Cl stretching frequencies in tetrahedral complexes fall in the range 272-311 cm^{-1}, while Mn-Br stretching modes fall in the range 230-248 cm^{-1}. In octahedral manganese(II) halide complexes, ν(Mn-Cl) falls below 240 cm^{-1} and ν(Mn-Br) below 200 cm^{-1}. Vibrational frequencies in Table VI for $Mn(MQN)Cl_2$ and $Mn(MQN)Br_2$ seem to rule out an octahedral structure and their positions only hint of tetrahdral structure.

Comparison of the X-ray diffraction patterns with patterns of the analogous nickel(II) and cobalt(II) halide complexes does not indicate

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(78) For example, see I. Collamati and C. Ercolani, *J. Chem. Soc. A*, 1541 (1969).

(79) R. H. Nuttall, *Talanta*, *15*, 157 (1968).

isomorphous compounds. A strong similarity exists between the X-ray patterns of $Mn(MQN)Br_2$ and $Ni(MQN)Br_2$, but the likenesses are insufficient to conclude they are isomorphous. Comparisons of this sort must be made cautiously, since small-angle scattering gives particle size and not necessarily crystal size.[80] The nature of the stereochemistry of $Mn(MQN)Cl_2$ and $Mn(MQN)Br_2$ remains unknown.

Copper(II) Halide and Nitrate Complexes.—Copper(II) complexes usually show routine colors: some are brown, but most all are blue or green.[5] In the present series, the complexes $Cu(MQN)X_2$ (X = Cl, Br, or NO_3) have been prepared and exhibit a variety of colors. The nitrate is light blue, the chloride is yellow, and the bromide is orange. The copper(II) ion can sometimes be stabilized in iodide complexes,[81] but we have yet to isolate the MQN iodide complex. The mull electronic absorption spectra of the halide complexes show a band at *ca*. 12,500 cm^{-1} with a very broad shoulder on the low energy side which is lost in solution. The mull spectrum of the nitrate shows a band at 14,280 cm^{-1} but does not show the same broad shoulder. Spectral data are summarized in Table XVI.

It has been suggested[82] that complexes containing copper(II) ion in square planar ligand fields exhibit d-d transitions in the range 14,000-18,000 cm^{-1}. As the planar structure is distorted toward a tetrahedral one, this transition is expected[83] to decrease in energy.

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(80) C. W. Bunn, "Chemical Crystallography," 2nd ed, Oxford at the Clarendon Press, 1961, page 444.

(81) Reference 8 and references therein.

(82) I. Bertini and F. Mani, *Inorg. Chem.*, *6*, 2032 (1967).

(83) C. Furlani and C. Morpurgo, *Theoret. Chim. Acta*, *1*, 102 (1963).

Table XVI

Electronic Absorption Spectral Data for Copper(II) Complexes*

Compound	Solvent	Band Positions (cm^{-1})
$Cu(MQN)Cl_2$	Mull	9100 br,sh; 12,500
	DMSO	12,850 (148)
	DMF	12,450 (128)
$Cu(MQN)Br_2$	Mull	7150 br,sh; 12,450
	DMSO	13,650 (179)
	DMF	12,580 (180)
	CH_3CN	11,900 (155)
$Cu(MQN)(NO_3)_2$	Mull	14,280
	DMF	14,650 (103)

* Abbreviations: sh, shoulder; br, broad. Values within parentheses are molar extinction coefficients taken at the band maximum.

Thus, band energies of *ca.* 12,500 cm^{-1} imply distorted tetrahedral configuration for the halide complexes of copper reported here. A comparison of the X-ray diffraction patterns (Table XVII) of these compounds with analogous cobalt(II) and nickel(II) complexes shows $Cu(MQN)Cl_2$ to be isomorphous with $Co(MQN)Cl_2$. This latter compound was shown earlier in this paper to be of pseudotetrahedral symmetry. Even though the copper(II) bromide complex is apparently not isomorphous with its cobalt(II) or nickel(II) analogs, it seems reasonable to expect it to also be pseudotetrahedral in view of the similar energies of the electronic transitions and especially in view of the trend in tetrahedral coordination seen in the cobalt(II), nickel(II), and iron(II) complexes of MQN.

Copper-halide stretching frequencies listed in Table VI do not fall in the range predicted for tetrahedral copper complexes,[53] but this is likely due to increased distortion of the tetraheral structure toward square planar.

Magnetic susceptibilities are given in Table XVIII and are typical of copper(II) complexes. In a regular tetrahedral field, the ground state term is $^2T_2$. Although the magnetic moment is expected to decrease with decrease in temperature,[84] moments for compounds containing the $CuCl_4^{2-}$ and $CuBr_4^{2-}$ ions fall in the range 1.93-2.00 B.M. and do not vary to any extent with temperature.[85] This can be explained by the fact that the coordination sphere is distorted in both cuprate anions.[86]

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(84) B. N. Figgis, *Nature*, *182*, 1568 (1958).

(85) L. Sacconi, M. Ciampolini, and U. Campigli, *Inorg. Chem.*, *4*, 407 (1965).

(86) Reference 8, page 485, and references therein.

Table XVII

Values of d Spacings From X-Ray Diffraction Patterns*

$Cu(MQN)Cl_2$	$Co(MQN)Cl_2$	$Ni(MQN)Cl_2$
9.15 w	9.11 w	9.21 m
8.18 s	8.10 s	6.67 s
6.65 sh,w	6.45 vs	6.46 m
6.41 vs	6.00 w	5.86 m
5.86 sh	5.70 m	5.69 s
5.82 m	5.57 w	5.32 s
5.43 w	5.47 w	5.15 m
5.06 w	5.05 w	5.00 m
4.55 sh,m	4.95 w	4.58 s
4.52 m	4.90 w	4.41 m
4.44 sh,m	4.55 m	4.08 s
4.13 s	4.39 m	4.00 w
4.04 m	4.15 m	3.95 m
3.97 w	4.06 m	3.78 m
3.81 m	3.86 m	3.46 s
3.62 w	3.70 m	3.31 s
3.36 w	3.63 m	3.21 w
3.29 m	3.39 m	3.11 m
3.12 m	3.26 m	3.03 m
3.00 w	3.22 m	2.97 m
2.94 w	3.21 m	2.87 w
	3.13 m	
	2.97 m	

* Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

Table XVIII

Magnetic Susceptibilities of Copper(II) Complexes

Compound	T, ^{o}K	χ_M' x 10^6 cgs	μ_{eff}
Cu(MQN)Cl_2	293.5	1520	1.89
	122.5	3390	1.82
M W = 359.7 χ_c = -203 x 10^{-6} cgs			
Cu(MQN)Br_2	292.5	1430	1.83
	123.5	2980	1.72
M W = 447.6 χ_c = -225 x 10^{-6} cgs			
Cu(MQN)$(NO_3)_2$	295.0	1500	1.88
	106.0	3960	1.83
M W = 411.8 χ_c = -194 x 10^{-6} cgs			

Variation of μ_{eff} with temperature for the complex Cu(MQN)Cl_2 is essentially negligible, but may indicate a temperature dependence which would be more pronounced at lower temperatures. Temperature dependence, although small, is seen in Cu(MQN)Br_2 and suggests a $^2T_2$ ground state. This implies pseudotetrahedral coordination as was proposed earlier.

Judging from the energy of the electronic absorption band seen in Cu(MQN)$(NO_3)_2$, tetrahedral coordination is apparently excluded. A square planar structure involving bidentate coordination is more likely. We do not have sufficient evidence to make an exact distinction.

Metal(II) Perchlorate Complexes.—Perchlorate complexes of cobalt, nickel, and copper were prepared. In each case, the coordination sphere involves two MQN chelates. Their X-ray diffraction patterns show diffuse lines and poor resolution of the less intense lines. Even with strong similarities in their patterns, conclusions suggesting an isomorphous nature would be risky.

Electronic absorption spectra of these compounds have been observed and spectral properties are given in Table XIX. The materials are not particularly soluble in non-coordinating solvents, and extensive solvation takes place in coordinating solvents. The cobalt(II) complex does not exhibit a useful absorption spectrum in the near infrared and visible regions. However, the magnetic susceptibilities given in Table XX are quite useful since the value of 4.36 for μ_{eff} indicates a tetrahedral ligand field about the cobalt(II) ion. In view of the complex's stoichiometry, it is proposed that the two MQN ligands make up the coordination sphere, and due to their bulkiness, the chelates must be "staggered" in such a way as to give a pseudotetrahedral microsymmetry about the central metal atom.

Table XIX

Electronic Absorption Spectra of Metal(II) Perchlorate Complexes*

Compound	Solvent	Band Positions (cm^{-1})
$Co(MQN)_2(ClO_4)_2$	Mull	8700 w,sh; 11,800 w,sh; 17,200 sh; 19,000 sh
$Ni(MQN)_2(ClO_4)_2 \cdot 4\,H_2O$	Mull	10,350 sh; 14,850; 19,800 sh; 26,000 sh
$Cu(MQN)_2(ClO_4)_2$	Mull	17,600
	Acetone	17,150 (100)
	DMF	14,770 (107)
	DMSO	14,290 (79)

* Abbreviations: sh, shoulder; w, weak. Values within parentheses are molar extinction coefficients taken at the band maximum.

Table XX

Magnetic Susceptibilities of Metal(II) Perchlorate Complexes

Compound	T, ^{o}K	$\chi'_M \times 10^6$ cgs	μ_{eff}
$Co(MQN)_2(ClO_4)_2$	299.5	7940	4.36
	105.0	20,800	4.18
M W = 706.4			
$\chi_c = -364 \times 10^{-6}$ cgs			
$Ni(MQN)_2(ClO_4)_2 \cdot 4\,H_2O$	297.0	6790	4.02
M W = 778.3			
$\chi_c = -\ 416 \times 10^{-6}$ cgs			
$Cu(MQN)_2(ClO_4)_2$	292.0	1670	1.98
	102.0	4800	1.98
M W = 713.0			
$\chi_c = -364 \times 10^{-6}$ cgs			

Much the same may be said of $Ni(MQN)_2(ClO_4)_2 \cdot 4H_2O$. Absorption bands are resolved and shifted to higher energies. The shoulder located at 10,350 cm^{-1} is assigned to the ν_2 transition and the band at 14,850 cm^{-1} is assigned to the ν_3 transition in tetrahedral symmetry. From these assignments, Dq is calculated to be 520 cm^{-1} and B is 720 cm^{-1}. Using these values of Dq and B, ν_1 is predicted to appear at 4800 cm^{-1}. Unfortunately, this band is not observed and, hence, the internal consistency of the above assignment cannot be checked. It is interesting to note that the average ligand field approximation[49] gives a Dq of 556 cm^{-1} using the Dq value per ligand given in Table III. The value of 4.02 for μ_{eff} is rather definite proof of tetrahedral coordination. The unusually high moment indicates a field generated by four identical atoms; the most reasonable structure is, again, two "staggered" MQN chelates and non-coordinated perchlorate groups.

The absorption band in $Cu(MQN)_2(ClO_4)_2$ is shifted to high energy indicating a ligand field of some strength. A comparison of the infrared spectra of this complex with the corresponding cobalt and nickel complexes shows them to be essentially identical in the range 4000-200 cm^{-1}. Thus, we presume the copper(II) ion to be surrounded by the two chelates to give a tetrahedral ligand field.

SUMMARY

The complexes Co(MQN)X_2, Ni(MQN)X_2 (where X = Cl, Br, or I), and Fe(MQN)Cl_2 were studied using the methods of electronic absorption spectroscopy, infrared spectroscopy, and magnetochemistry, and they were found to have pseudotetrahedral structures. Similarly, the ligands PQN and DQN gave pseudotetrahedral complexes of cobalt(II) chloride. This tetrahedral coordination is apparently the result of the steric crowding at the nitrogen atom coordination sites provided by the bulky ligand and the five-membered chelate ring. The variable side group R makes this series of ligands (5) useful in studying the effects of graded changes of steric properties, aromaticity, basicity, etc., on the resulting stereochemistry of transition metal complexes of the general type MLX_2 where L represents a bidentate ligand.

The group of 2-(N-aminomethyl)-3-quinuclidinone chelates discussed in this dissertation tend to favor the formation of tetrahedral coordination except in cases where the anionic group X is bridging or chelating. Ligands of this type are also useful in that they offer an opportunity to prepare pseudotetrahedral complexes of transition metals which have yielded few, if any, compounds of this geometry. For example, few tetrahedral chromium(II) halide complexes have been prepared, and isolation and characterization of complexes such as Cr(MQN)X_2 would provide a test of ligand field theory and magnetic theory for chromium in this oxidation state and in this configuration.

Although electronic absorption spectroscopy and magnetic susceptibility measurements have shown octahedral coordination for Ni(MQN)X_2 and Co(MQN)X_2 where X = NCS or NO_3, the exact mode of coordination of

the anionic groups is not known. Molecular weight detetminations of the thiocyanate complexes would be useful in supporting or refuting the proposed dimeric, thiocyanate-bridged structures (Figure 7). Similarly, the molecular weight of the complex $Ni(MQN)(NO_3)_2$ would be helpful in deciding if the octahedral microsymmetry is the result of chelating or bridging nitrate groups. The synthesis of the complex $Ni(MQN)(NO_3)(ClO_4)$ and the observation of shifts in the two N-O stretching frequencies may also be useful in distinguishing the mode of coordination.[87] If single crystals of the thiocyanate and nitrate complexes can be obtained, their exact structures can be found by X-ray crystallography, although this would be quite an endeavor in view of the many light atoms making up the ligand.

The complexes $Cu(MQN)Cl_2$ and $Cu(MQN)Br_2$ are most likely flattened pseutotetrahedral, but this proposal is open to question in view of the limited usefulness of the electronic absorption spectral data and the magnetic susceptibility data for a d^9 ion. X-Ray crystallographic analysis is perhaps the most effective method of determining their stereochemistries. Likewise, the structures of the $Mn(MQN)Cl_2$ and $Mn(MQN)Br_2$ complexes must be determined by X-ray methods, since limited spectral and magnetic data were obtainable.

Some suggestions for work supplementary to that described in this dissertation includes the following. Both of these problems are in keeping with the overall purpose of the project initiated in this work. (1) If a suitable solvent can be found, one may observe planar-tetrahedral equilibrium in the Co(II) and Ni(II) halide complexes. This

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(87) Reference 54, page 171, and references therein.

interconversion could be studied using the NMR method of Holm *et al.*[88] (2) The exact origin of the two peaks at *ca.* 11,200 cm^{-1} in the electronic absorption spectra (Figure 3) of purple $Ni(MQN)Cl_2$ and $Ni(MQN)Br_2$ is unknown and provides an interesting problem for study.

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(88) Reference 17 and references therein.

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VITA

Richard Cecil Dickinson was born on March 30, 1943, in Childersburg, Alabama. He received his elementary and secondary education in Oak Ridge, Tennessee and was graduated from Oak Ridge High School on June 3, 1961. His undergraduate and masters degree work was taken at Tennessee Technological University. The Bachelor of Science degree in Chemistry was received on June 4, 1966, and the Master of Science degree in Chemistry was received on August 24, 1968.

His enrollment in the Graduate School of the University of Missouri at Rolla began in September 1968.

Appendix 1

Infrared Spectral Data for 2-(N-Morpholinylmethyl)-3-quinuclidinone (MQN)*

2960	s,br
2900	s
2880	s
2863	s
2825	s
2770	sh
2752	sh
2700	m,br
2730	sh
1765	sh
1727	s
1718	s
1660	sh
1480	m
1465	s
1458	s
1440	s
1380	s
1362	s
1345	s
1335	sh
1327	s
1295	s
1264	m
1252	s
1227	m
1203	s
1192	m
1180	w
1160	sh
1152	s
1115	s,br
1075	s,br
1057	m
1040	m
1030	m
1010	s
1000	s
990	sh
963	w
925	s
900	s
875	sh
861	s
853	sh
820	m
778	s
760	s
682	m
656	s
628	w
584	s
552	m
525	m
497	w
477	m
440	s
398	m
378	w
327	s
295	w
288	w
270	sh
260	m
253	sh

* Data given in cm^{-1}. Abbreviations: sh, shoulder; s, strong; m, medium; w, weak; br, broad.

Appendix 2

Nuclear Magnetic Resonance Spectral Data for 2-(N-Morpholinylmethyl)-3-quinuclidinone (MQN)*

238.8	s
229.0	s
227.0	s
224.0	s
218.0	w
213.0	w
209.0	w
204.0	w
199.5	w
190.5	m
188.5	m
181.0	m
173.0	w
168.0	s
163.5	w
161.0	s
158.5	m
156.3	s
151.7	s
148.7	m
145.5	m
143.0	w
130.5	m
127.6	m
122.3	m
119.5	m
115.0	m
112.5	m
61.0	w

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* Data given in Hz. Abbreviations: s, strong; m, medium; w, weak.

PUBLICATION THESIS OPTION

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