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Some metal complexes of dihydroxycyclobutenedione

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SOME METAL COMPLEXES OF DIHYDROXYCYCLOBUTENEDIONE

by

STEWART MICHAEL CONDREN, 1942-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

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ABSTRACT

This study involves an investigation of some of the physical and chemical properties of the trivalent metal squarate complexes of iron, vanadium, and indium in order to determine their structure In this investigation studies were made of the infrared spectra, electronic spectra, x-ray diffraction powder photographs and diffractometer patterns, magnetic susceptibilities, and thermogravimetric patterns for the trihydrate, dihydrate, and anhydrous squarate complexes of vanadium(III) and iron(III) and the dihydrate squarate complex of indium(III).

These studies suggest that the structures of the vanadium(III) and iron(III) squarate complexes are dimeric with hydroxyl bridges between the metal atoms. This is supported by the presence of a band between 980 and 1050 cm^{-1} in the infrared spectrum associated with metal-hydroxyl bridging. Crystal field calculations made from data obtained from the electronic spectra of the vanadium(III) squarate trihydrate and vanadium(III) squarate dihydrate suggest that the vanadium atoms are in an approximately cubic crystal field, Racah parameter B = 611 and 655 cm^{-1} respectively and crystal field splitting 10Dq = 18,900 and 19,650 cm^{-1} respectively. The x-ray diffraction studies indicate that the vanadium(III) squarate trihydrate and iron(III) squarate trihydrate are isostructural. The magnetic moments of approximately 2.80 B.M. for the trihydrate and dihydrate vanadium(III) squarate complexes are normal for a paramagnetic d^2 metal complex. However, the magnetic moment of 2.60 B.M. for the anhydrous vanadium(III) squarate complex suggest some spin coupling between metal atoms. The

reduced magnetic moment of 5.08 B.M. at room temperature for iron(III) squarate dihydrate, 5.9 B.M. is normal for a d^5 metal complex, and the temperature dependence study of the magnetic susceptibility indicate that the complex is a binuclear antiferromagnetic system with $S = 5/2$ and $J = -6.8$. The reduced moment of 4.6 B.M. and the temperature dependence study of the magnetic susceptibility of anhydrous iron (III) squarate suggest that it is an antiferromagnetic system with the spin-spin exchange taking place between more than two metal atoms.

The data collected for indium(III) squarate dihydrate were inconclusive in determining its structure.

ACKNOWLEDGMENTS

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TABLE OF CONTENTS

APPENDICES

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

Since Cohen, Lacher, and Park (1) first illustrated the chelating properties of dihydroxycyclobutenedione* (1,2-dihydroxy-3,4-diketocyclobutene), several studies of its metal complexes have been made (2-7). Most of these metal complexes studied to date have been polymeric in nature. West and Niu reported powder x-ray diffraction data, infrared spectra, and magnetic moments for their squarate complexes of copper(II), iron(II), iron(III), nickel(II), etc. (2). Macintyre and Werkema in 1964 performed a single crystal x-ray structure analysis on potassium squarate monohydrate (8). Ligand field parameters have been reported for the nickel and cobalt(II) squarate complexes by Ludi and Schindler (4).

It was the purpose of this work to continue the study into the chelating properties of squaric acid. Specifically, the object of this study was to prepare some new squarate metal complexes and then to make a concentrated study of the properties of some of them. It was decided that the three vanadium complexes offered the most interesting challenge. In the study of these complexes, this work involved the investigation of:

1. The infrared spectra of these compounds.
2. Their x-ray powder diffraction patterns.
3. Their thermogravimetric patterns and related data.
4. Their magnetic susceptibilities.
5. Their electronic spectra.

It was hoped that this data would provide some insight into the structures of these compounds.

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*Hereafter, dihydroxycyclobutenedione will be referred to by its accepted common name, squaric acid, and the dianion, dihydroxycyclobutenedionate will be referred to as the squarate anion.

II. REVIEW OF LITERATURE

Squaric acid, Figure I, was first synthesized in 1959 by Cohen, Lacher, and Park by the aqueous hydrolysis of 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene and by the aqueous and acid hydrolysis of 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene (1). They reported it to be a solid, white dibasic acid which decomposed without melting at about 293°C. They further reported infrared absorption bands at 4.3μ, 5.5μ, and 6.1μ with the band at 4.3μ attributed to strong hydrogen bonding. The 5.5μ band and the 6.1μ band were attributed to the carbonyl absorption and the conjugated C=C absorption respectively (1).

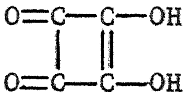


Figure I. Squaric Acid

Squaric acid is a strong acid, $pK_1 = 1.2 \pm 0.2$ and $pK_2 = 3.48 \pm 0.02$ at 25°C (9). Cohen and coworkers suggested that the dianion, Figure II, would have much resonance stabilization with four equivalent oxygen atoms. Their theory was substantiated by the infrared spectrum which they obtained for the dipotassium salt. The 5.5μ carbonyl absorption band along with the 6.1μ conjugated C=C absorption band had vanished and had been replaced by a very intense, broad band from 6.5μ to

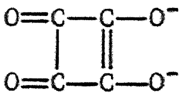


Figure II. Squarate Dianion

6.75µ (1). This structure can best be represented by Figure III (1).

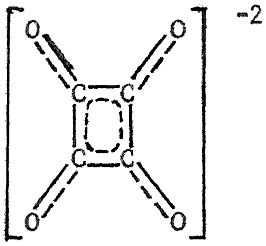
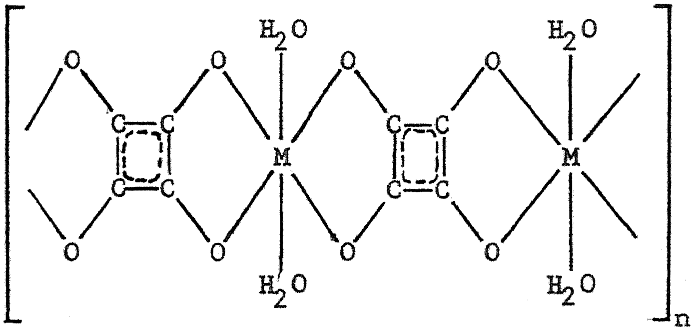


Figure III. Resonance Structure of Squarate Dianion

Squaric acid reacts with bromine water, ceric nitrate, and permanganate solutions as evidenced by their decolorizing action (1). With HNO_3 at room temperature, it undergoes oxidative ring cleavage to oxalic acid and carbon dioxide. With milder conditions, such as HNO_3 or bromine water at 0^oC, the four membered ring remains intact, and the product obtained is cyclobutaneoctol (10). An aqueous solution of squaric acid reacts with ferric chloride to give an intensely purple color (1). In 1963 West and Niu reported squarate complexes with the following metal ions: divalent Cu, Fe, Zn, Ni, Mn, Co, Ca, and Mg and trivalent Al, Fe, and Cr (2). The bivalent complexes corresponded to the empirical formula $M(II)C_4O_4 \cdot 2H_2O$ while the trivalent complexes were given by the empirical formula $M(III)(OH)C_4O_4 \cdot 3H_2O$. They proposed that the bivalent complexes would have a polymeric structure such as



M=bivalent metal

Figure IV. Bivalent Metal Squarates

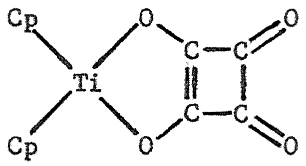
that which is shown in Figure IV. They did not propose a structure for the trivalent complexes but did state that the complexes were isostructural as shown by the identical, within the limits of experimental error, x-ray powder diffraction patterns (2). However, in his dissertation Niu proposed a hydroxyl bridged, dimeric structure for the trivalent metal squarate trihydrates (16).

In 1964 Macintyre and Werkema reported their x-ray crystal analysis of the monohydrate potassium salt of squaric acid (8). They found in their study that the anions stack almost parallel and very close together. They were able to obtain the stacking distance along with the cell dimensions and the space group of the system (8).

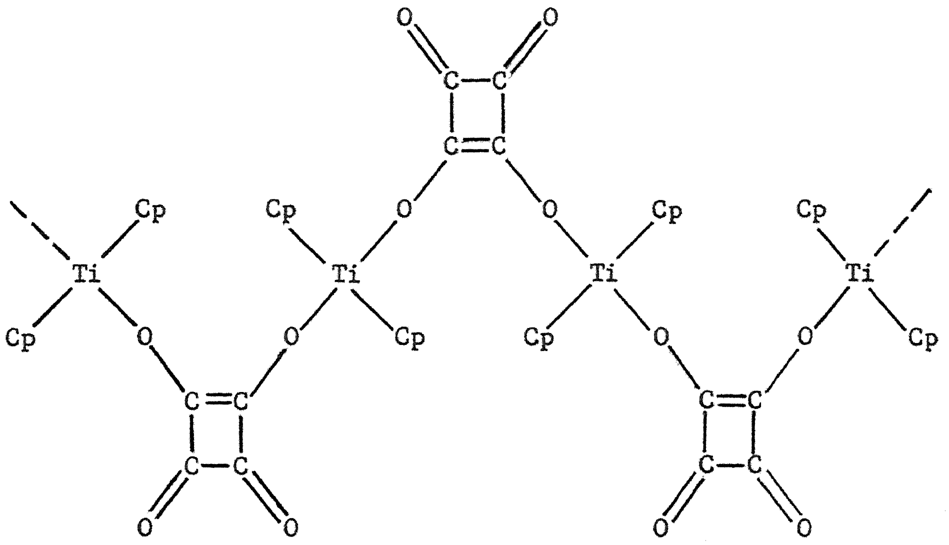
In 1967 Ireland and Walton reported log Ksp values for the copper (II) complex and the iron(II) complex at various pH values (3). For the iron(III) complex at pH = 1.61, they obtained a value of log Ksp = -20.35. They found that the Ksp value increased with increasing pH to a value of log Ksp = -19.28 at pH = 2.33. They reported a Ksp value of the order of 10^{-9} for the copper(II) complex at pH values near 2 (3).

As partial fulfillment of the requirements for the degree Master of Science, this author began a study of the squarate complexes of some of the less common metals. In connection with this study, a thesis was submitted in 1967 to the Graduate Faculty of the University of Missouri at Rolla in which the author discussed the preparation of complexes of squaric acid with Ti(III), ZrO(IV), and In(III) (7). Also discussed were the attempted preparation of complexes with several other metals.

In 1968 Doyle and Tobias reported the preparation of a bis(cyclopentadienyl)titanium(IV) complex with the squarate anion (5). This new complex had an empirical formula of $(\mu - C_5H_5)_2\ TiC_4O_4$. From the infrared spectrum, 16 bands between 300 and 1800 cm^{-1} were assigned to the squarate ligand as compared to the four bands normally associated with the squarate ligand in the bivalent metal complexes. Because of the complicated nature of the vibrational spectrum, they suggested that the complex is much less symmetrical than the bivalent complexes and that the squarate ligand is probably bidentate in this complex. However, due to the low solubility of the complex (10^{-4} M in $C_6H_5NO_2$ and even much less in less polar solvents), they were unable to decide between the structures in Figure V (5).



1.



Cp = (π - C_5H_5)

2.

Figure V. Possible Structures for 1,2-Dihydroxycyclobutenedionatobis (cyclopentadienyl)titanium(IV)

In 1969 Tedesco and Walton published formation constants for several metal squarate complexes (6). They also reported the preparation of titanium(III) and (IV) and uranium(VI) complexes. These new complexes appeared to form in 1:1 ratios between metal ion and squarate ion (6).

III. EXPERIMENTAL METHODS

A. PREPARATIONS

This work is a continuation of the study begun as partial fulfillment of requirements for the author's Master of Science Degree (7). Several new complexes were studied in this work in addition to those previously reported by this author (7). The complexes were all prepared by reacting either squaric acid or its potassium salt with the corresponding metal halide.

1. Preparation of Squaric Acid

The squaric acid was prepared using the procedure outlined in the author's M.S. thesis (7) or was purchased from Aldrich Chemical Company. In either case, it was recrystallized at least twice in water. The potassium salt of the acid was also prepared using the procedure outlined in the author's M.S. thesis (7).

2. Preparation of Vanadium(III) Squarate Trihydrate

Previous attempts at preparing vanadium(III) squarate have not been totally successful because the product was mixed with some unreacted vanadium oxychloride (7). Attempts at purification proved unsuccessful. Because the material which was purchased as vanadium trichloride was yellow in color instead of the violet color normally associated with vanadium trichloride, the author undertook to prepare a sample of vanadium trichloride from vanadium pentoxide.

Six grams of vanadium pentoxide were added to a flask containing 60 ml. of hexachloropropene. The flask was then attached to a condenser which had a drying tube connected to the other end. The mixture was refluxed for about five hours, during which time the solution turned dark brown in color with the bottom of the flask covered with a dark violet precipitate, vanadium trichloride. The flask was stoppered and transferred to a glove box containing a dry nitrogen atmosphere to prevent hydration of the product. The mixture was then filtered, and the precipitate was washed with reagent grade carbon tetrachloride which had been dried over calcium chloride. The precipitate was then transferred to a clean, dry flask and stoppered tightly. The flask was then removed from the glove box and was attached to a vacuum line containing a dry ice-acetone slurry cold trap between the product flask and the vacuum pump. After pumping on the flask for an hour, the flask was removed from the vacuum line and again was stoppered tightly to prevent hydrolysis (11).

Because water was to be used as the solvent in the preparation of the vanadium(III) squarate trihydrate, a small portion of the anhydrous vanadium trichloride was placed in a beaker and left exposed to the air overnight so that it would hydrolyze to vanadium trichloride hexahydrate, leaf green in color (11).

A solution containing 0.76 g. (2.9 mmol) of vanadium trichloride hexahydrate was mixed with a solution containing 0.50 g.(4.5 mmol) of squaric acid. The dark brown color of the vanadium trichloride solution was almost immediately replaced by an olive green precipitate. The solution was stirred for about 24 hours before the precipitate was filtered, washed with acetone and ether, and dried in a vacuum desiccator over calcium chloride.

Analytical: Calculated for $V(III)(OH)C_4O_4 \cdot 3H_2O$: V, 21.8; C, 20.5; H, 2.99. Found: V, 20.2; C, 20.7; H, 3.17.

3. Preparation of Anhydrous Vanadium(III) Squarate

Anhydrous vanadium(III) squarate was prepared by placing a small, preweighed bulb containing vanadium(III) squarate trihydrate in a vacuum desiccator which in turn was placed in a drying oven preset at 80°C. Before weighing the bulb after the dehydration process, the desiccator was removed from the oven, and the vacuum was released through a calcium chloride drying tube as the desiccator cooled to room temperature. The bulb came to a constant weight after two days. The experimental weight loss amounted to 23.0% which corresponded to a molecular weight loss of 53.8 for the molecular formula of $V(III)(OH)C_4O_4 \cdot 3H_2O$. The molecular weight of $3H_2O$ is 54.0.

Analytical: Calculated for $V(III)(OH)C_4O_4$: C, 26.7; H, 0.55. Found: C, 23.7, 24.7; H, 2.00, 1.64.

4. Preparation of Vanadium(III) Squarate Dihydrate

The vanadium(III) squarate dihydrate was prepared by placing a small, preweighed bulb containing a sample of anhydrous vanadium(III) squarate in a metal Desicooler (Fisher Scientific) which was partially filled with water. The bulb was suspended over the water from a small hook attached to the lid. The Desicooler was then placed on top of a drying oven which heated the water to approximately 45°C. Visible water on the outside of the bulb was removed by blotting with tissue paper, and the bulb was then placed in a desiccator over calcium chloride for several hours before weighing. The sample came to constant weight after two days with a weight gain of 19.9% which corresponded to a molecular weight gain on the basis of the molecular weight of $V(III)(OH)C_4O_4$ of 35.8 as compared to a calculated molecular weight of $2H_2O$ of 36.0.

Analytical: Calculated for V(III)(OH)$C_4O_4 \cdot 2H_2O$: C, 22.2; H, 2.31. Found: C, 21.35, 21.66; H, 2.95, 2.78.

5. Preparation of Indium(III) Hydroxysquarate Dihydrate

The indium(III) hydroxysquarate was prepared using the procedure outlined in the author's M.S. thesis (7).

Analytical: Calculated for In(III)(OH)$C_4O_4 \cdot 2H_2O$: In, 41.07; C, 17.14; H, 1.79. Found: In, 41.07; C, 17.07; H, 1.87.

6. Preparation of Iron(II) Squarate and Iron(III) Squarate Trihydrate

The iron(II) squarate and the iron(III) squarate were prepared by the method outlined by West and Niu (2).

Analytical: Calculated for Fe(II)$C_4O_4 \cdot 2H_2O$: C, 23.56; H, 1.98. Found: C, 23.45; H, 2.02. Calculated for Fe(III)(OH)$C_4O_4 \cdot 3H_2O$: C, 20.10; H, 2.95. Found: C, 20.71; H, 3.16.

7. Preparation of Anhydrous Iron(III) Squarate

The anhydrous iron(III) squarate was prepared by placing a preweighed weighing bottle containing iron(III) squarate trihydrate in a vacuum desiccator which in turn was placed in a drying oven at 80°C. After continuously evacuating for 12 days, the desiccator was removed from the oven, and the vacuum was released through a drying tube containing calcium chloride as the desiccator cooled to room temperature. After 12 days the sample had incurred a weight loss of 21.4 % which corresponded to a molecular weight loss of 51.1 for the molecular formula of Fe(III)(OH)$(C_4O_4) \cdot 3H_2O$. The molecular weight of $3H_2O$ is 54.0.

Analytical: Calculated for Fe(III)(OH)(C_4O_4): C, 25.26; H, 0.54. Found: C, 24.70; H, 0.90.

8. Preparation of Iron(III) Squarate Dihydrate

A thermogravimetric study of a sample of iron(III) squarate trihydrate, discussed in detail elsewhere in this work, indicated that it lost water upon heating. The thermogravimetric pattern indicated that first one water molecule was lost followed by two water molecules to form anhydrous iron(III) squarate. Therefore, the first attempt at preparing iron(III) squarate dihydrate involved the dehydration under vacuum at 80°C. Because this resulted in the complete dehydration of the iron(III) squarate trihydrate, another attempt was made under vacuum at a lower temperature of 50°C. Even at this lower temperature and much slower dehydration, three weeks to achieve a weight loss equivalent to the loss of one water, the iron(III) squarate trihydrate continued to lose weight. The temperature of the oven was then lowered to 34°C, and a preweighed sample of iron(III) squarate trihydrate was placed in the desiccator with the partially dehydrated sample. At this lower temperature and under continuous evacuation, some of the water which was lost by the iron(III) squarate trihydrate was apparently absorbed by the partially dehydrated sample as illustrated by its increase in weight. However, the process was very slow and was discontinued after two weeks because only a 1.2% weight loss had occurred compared to a 7.4% weight loss expected for the loss of one water molecule.

The iron(III) squarate dihydrate was prepared by hydrating a preweighed sample of the anhydrous iron(III) squarate in a desiccator containing the water for one day and then placing the sample in a vacuum desiccator over calcium sulfate. The sample was then alternately weighed and desiccated until the weight became constant. After three weeks the sample had gained 16.3% in weight which corresponded to a molecular weight gain of 36.0 for the molecular formula of $Fe(III)(OH)(C_4O_4)$. The molecular weight of $2H_2O$ is 36.0.

Analytical: Calculated for $Fe(III)(OH)(C_4O_4)\cdot 2H_2O$: C, 19.83; H, 2.07. Found: C, 20.73; H, 2.43.

9. Preparation of Deuterated Iron(III) Squarate Trideuterate

The deuterated sample of iron(III) squarate trideuterate was prepared by dissolving the squaric acid in 99.8% deuterium oxide (International Chemical and Nuclear Corporation). To this solution was added a deuterium oxide solution containing a stoichiometric amount of anhydrous ferric chloride. The resulting solution was stirred for one day and vacuum filtered.

This compound was prepared so that a study could be made of the isomeric shifts in the infrared spectra. Because the infrared spectra indicated the presence of both deuterated and ordinary water in the compound, elemental analyses were not made.

B. ELEMENTAL ANALYSES

The elemental analyses of the complexes in this study can be divided into two groups with regard to who performed the analyses: metal analyses by the author and carbon-hydrogen analyses by commercial laboratories.

1. Metal Analyses

The indium(III) hydroxysquarate dihydrate was analyzed for indium by igniting the complex to the sesquioxide, In_2O_3, and weighing. Because of the similarity of squaric acid and oxalic acid, it was concluded that the indium squarate complex would ignite cleanly. The indium complex was weighed directly into porcelain crucibles. The crucibles were then placed in a muffle furnace which had been cooled to room temperature after the empty crucibles had come to constant weight. The furnace was cooled to room temperature so that the complex would be warmed gently to 400^{o} to allow slow combustion of the complex without splattering. After ignition, the indium sesquioxide, In_2O_3, was fired to constant weight. Higher temperatures resulted in some loss of the oxide by sublimation.

Attempts at analyzing vanadium(III) hydroxysquarate trihydrate for vanadium gravimetrically initially proved unsuccessful due to the apparent reaction of the ignition product, vanadium pentoxide, with the porcelain crucibles. An attempt was then made to analyze the complex volumetrically for the vanadium (12).

The volumetric analysis which was used was the ammonium persulfate method (12) which employs ammonium persulfate as the reducing agent to insure that all the vanadium is in the plus two oxidation state. The plus two vanadium then was oxidized to the vanadyl ion by a standardized solution of potassium permanganate. This technique gave inconsistent results so modifications were made to the gravimetric method. These modifications involved the use of platinum crucibles instead of porcelain ones and the use of a lower temperature of 650^{o}C instead of 700^{o}C for the muffle furnace. With these changes the gravimetric technique gave reproducible results.

2. Carbon-Hydrogen Analyses

The carbon-hydrogen analyses were made by Huffman Laboratories, Wheatridge, Colorado or by Galbraith Laboratories, Knoxville, Tenn.

C. INFRARED SPECTRAL STUDIES

The infrared spectra were measured with a Perkin-Elmer 337 and a Beckman IR12A. Spectrophotometric grade potassium bromide pellets were used in obtaining the spectra of the solids. These pellets were made using a 300:1 weight ratio of potassium bromide to metal squarate complex.

D. ELECTRONIC SPECTRA STUDIES

The electronic spectra were measured with a Cary Model 14 spectrophotometer using Kel-F 90 grease (Minnesota Mining and Manufacturing, Chemical Division) mulls of the solid between silica plates or using methanol solutions of the compounds.

E. POWDER X-RAY DIFFRACTION STUDIES

The powder diffraction photographs were made using a 57.7 mm diameter Debye-Scherrer camera, Straumanis type. The sample, mounted on a glass fiber, was exposed to Fe-filtered Co Kα radiation for 15 to 20 hours. To offset the darkening of the film by fluorescence, several Ni and Al screens were used alternatively and simultaneously, and the exposure time was greatly increased without improving the resolution. Since even after a 22 hour exposure no back diffraction lines were evident, the film was consequently mounted in the regular manner so that the center of the film was at zero degrees.

Diffraction patterns were also obtained using a Siemens Crystalloflex IV Diffractometer, Type U-13. Ni-filtered Cu Kα radiation was used for the patterns in the region of $2\theta = 7^{\circ}$ to 100° using a scanning speed of 1° per minute.

F. MAGNETIC MEASUREMENTS

The magnetic susceptibility measurements were made using a Guoy balance. A single pan Mettler Model H20GD balance modified for under the pan weighing was used to measure the apparent weight changes as the magnetic field was varied. A Varian Associates Model V-4005 four inch electromagnet was used to provide field strengths up to 10,000 G. The electromagnet was powered by a Varian Associates Model V-2900 two kilowatt current regulated power supply with a 1 to 65 ampere rating. The magnetic field was calibrated using the standard, $Hg[Co(SCN)_4]$.

G. THERMOGRAVIMETRIC STUDIES

The thermogravimetric studies were made with a Mettler Recording Vacuum Thermoanalyzer. This instrument is capable of simultaneously graphing the thermogravimetric analysis, TGA; the expanded thermogravimetric analysis, ETGA; the differential thermal analysis, DTA; and the differential thermogravimetric analysis, DTG, as it graphs the reaction temperature. The samples were prepared for analysis by loading the sample material into platinum crucibles 8 mm in height with a vibrating spatula. A similar crucible was loaded with Al_2O_3 as a reference material for the differential thermal analysis. The weights of all materials were measured on a Mettler Model H18 analytical balance. Several of the thermal decomposition reactions appeared to be stepwise as evidenced by their TGA patterns. Where possible the steps were separated by heating to a temperature near the end of a step and holding that temperature until the weight was constant. The runs were all made using a heating rate of $2^{o}C$ per minute with a lid on the sample crucible to prevent the sample from splattering during heating. The residue from each run was spectrally analyzed by infrared and powder x-ray methods as outlined elsewhere in this work.

IV. RESULTS AND DISCUSSION

In this section the experimental results will be discussed with regard to the information they provide in determining the structures of the compounds.

A. INFRARED SPECTRAL STUDIES

The results of the infrared spectral studies of several of the metal squarate complexes investigated are given in Tables I and II. The spectrum of $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ (13) and the spectrum of $V(III)(OH)(C_4O_4)\cdot 3H_2O$ (Figure VI) as given in Table I, are almost identical. The spectra of $V(III)(OH)(C_4O_4)\cdot 2H_2O$ and $V(III)(OH)(C_4O_4)$ (Figure VII) as given in Table I, and the spectra of $Fe(III)(OH)(C_4O_4)\cdot 2H_2O$ and $Fe(III)(OH)(C_4O_4)$, as given in Table II, are quite similar to those of the other trivalent metal squarates. Also, the spectrum of $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ and the spectrum of $Fe(III)(OD)(C_4O_4)\cdot 3D_2O$, as given in Table II, are identical with the exception of those bands resulting from the presence of the deuterium isotope in $Fe(III)(OD)(C_4O_4)\cdot 3D_2O$. However, the spectra of the trivalent metal squarates are very different from the spectrum of $Fe(II)(C_4O_4)\cdot 2H_2O$ (13) as shown in Table I. Another exception is the spectrum of $In(III)(OH)(C_4O_4)\cdot 2H_2O$, as given in Table II, which differs from the spectra of the other trivalent metal squarates.

The spectra of the three iron(III) complexes and of the three vanadium(III) complexes each contain a band at approximately 450 cm^{-1}. This band can be assigned to the metal-oxygen, single bond stretch (14). Niu in his dissertation proposed a dimeric structure for the trivalent metal squarates with the metal atoms connected by two hydroxyl bridges

TABLE I

INFRARED SPECTRAL DATA

$K_2C_4O_4 \cdot H_2O$	$Fe(II)(C_4O_4) \cdot 2H_2O$	$Fe(III)(OH)(C_4O_4) \cdot 3H_2O$	$V(III)(OH)(C_4O_4) \cdot 3H_2O$	$V(III)(OH)(C_4O_4) \cdot 2H_2O$	$V(III)(OH)(C_4O_4)$
	425 cm^{-1} m	430 cm^{-1} s	450 cm^{-1} s	445 cm^{-1} s	445 cm^{-1} m
		495 w	520 w,sh	505 w,sh	510 vw,sh
590 s,b	550 m,b	545 m	535 m		
				615 w,sh	
			645 w	635 w	635 vw,sh
680 m		700 w,sh	720 w,sh	720 w-m	685 w,sh
750 m	740 m,b	750 m,sp	750 m	750 w-m	760 w,sh
880 m		860 m,b	875 m	870 m	885 w
		980 m,b		985 w	990 vw,sh
			1048 w	1020 w	
1090 m,sp	1102 s,sp	1085 m,sp	1090 m,sp	1085 m,sp	1055 w,sh
1100 m,sp		1105 m,sp	1108 m,sp	1105 m-s,sp	1100 m,sp
		1140 w	1145 vw	1140 w	1150 vw,sh
1450 s,b	1520 vs,vb	1490 vs,vb	1515 vs,b	1490 vs,vb	1510 vs,vb
1530 s,b					
		1620 s,sp	1615 s	1610 s,b	1625 s,b
1720 w		1800 w,sp	1801 w	1800 w	1805 w
		2480 w,sh	2500 w,sh	2480 w,sh	
3320 s,vb	3280 s,vb	3180 s,vb	3280 s,vb	3150 s,vb	3410 s,b

All values are in wavenumbers: m, medium; s, strong; w, weak; b, broad; sh, shoulder; sp, sharp; v, adverb very.

TABLE II

INFRARED SPECTRAL DATA

$Fe(III)(OH)(C_4O_4)\cdot 3H_2O$	$Fe(III)(OD)(C_4O_4)\cdot 3D_2O$	$Fe(III)(OH)(C_4O_4)\cdot 2H_2O$	$Fe(III)(OH)(C_4O_4)$	$In(III)(OH)(C_4O_4)\cdot 2H_2O$
420 cm^{-1},s	425 cm^{-1},s	435 cm^{-1},s	435 cm^{-1},s	436 cm^{-1},s
495 w	495 w	495 w	495 w	
				581 m,sp
645 m	645 m	635 w	635 w	666 m,b
	710 w			
750 m	755 m	755 m	745 m	
855 m	850 m	860 m		846 m
980 w	980 w	980 w	1015 wsh	1036 wsh
1085 m,sp	1085 m,sp	1095 m,sp	1090 s,sp	1091 s,sp
1105 msp	1105 s,sp	1105 m,sp		1108 s,sp
				1116 m,sp
1140 w	1140 w	1160 w	1130 vs	1134 m,sp
	1215 w			1416 s,sh
1500 vs,b	1500 vs,b	1500 vs,b	1490 vs,b	1510 vs,sp
				1540 vs,sh
1800 m,sp	1800 m,sp	1800 m,sp	1800 m,sp	1740 w,sh
	2270 s,sh			
	2370 s			
3150 s,vb	3170 s,b	3280 s,vb	3280 s,vb	3520 m,sp

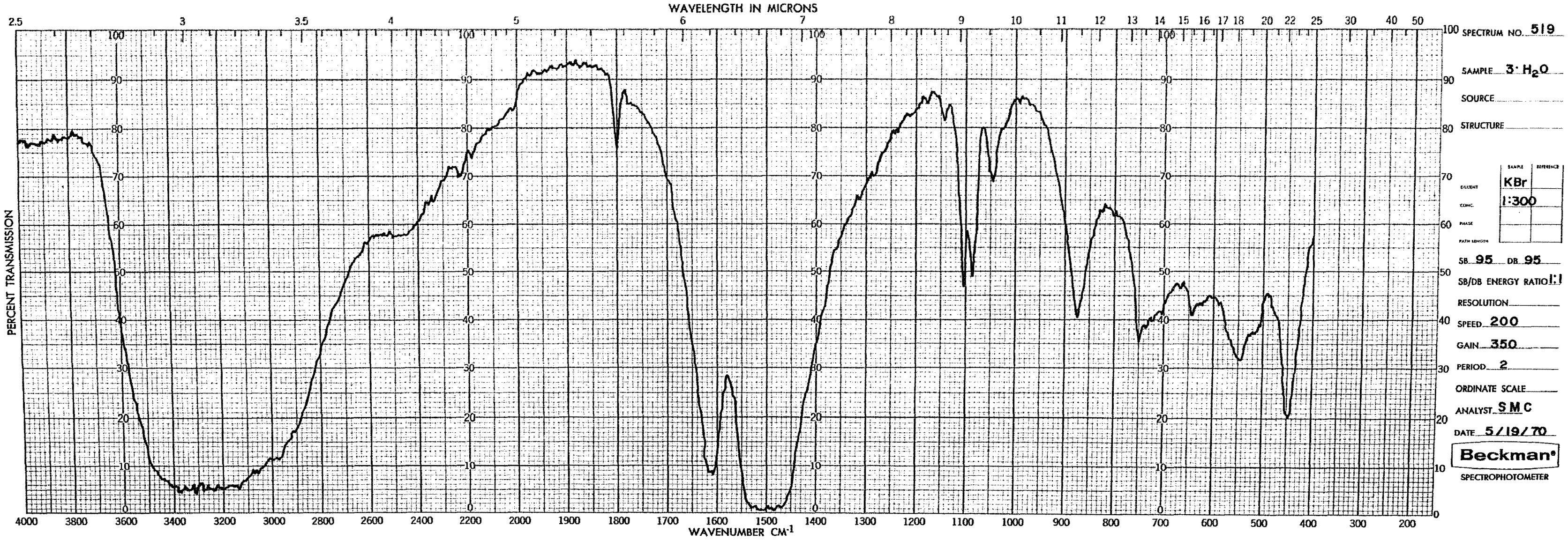


Figure VI. Infrared Spectrum of $V(III)(OH)(C_4O_4)\cdot 3H_2O$

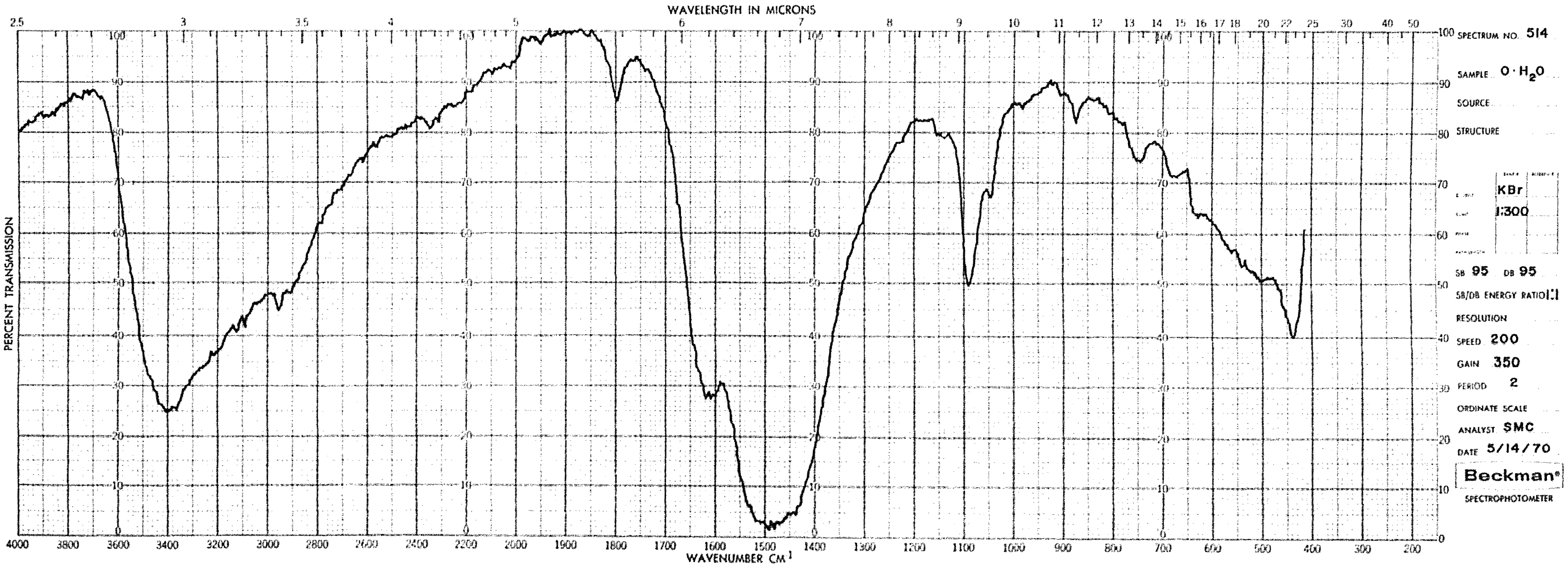


Figure VII. Infrared Spectrum of V(III)(OH)(C_4O_4)

(16). Ferraro reported that the band resulting from the stretch of the metal oxygen bond in the hydroxyl bridge of several iron(III) complexes appeared at approximately 500 cm^{-1} (15). The band at approximately 495 cm^{-1} in the iron(III) squarates and at approximately 510 cm^{-1} in the vandaium(III) squarates was assigned to this metal-oxygen stretch of the squarate anion (1,2,16). There is a strong band at 1615 cm^{-1} which can be assigned to a C = C conjugated system (1,2,16). The presence of these bands suggests that all the oxygen atoms are not coordinated because these bands are absent in the divalent metal squarates which contain only coordinated oxygen atoms and a resonating ring in the squarate ligand (2,5,16). The very strong, very broad band at approximately 1500 cm^{-1} can be assigned as a mixture of the C - C and C - O stretch vibrations (1,2,16). This is also the approximate region of the bending vibration of H_2O in liquid water (17).

The bending O - H vibration in the hydroxyl bridge appear between 980 and 1035 cm^{-1} in the iron complexes and between 1020 and 1055 cm^{-1} in the vanadium complexes. The decrease in frequency of this vibration as one goes from trivalent vanadium to trivalent iron is the behavior expected for these transition metals (15). This band appears at 980 cm^{-1} in $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ and shifts to about 710 cm^{-1} in the deuterated complex. The deuterated complex also shows a shift of the O - H stretching vibration from 3170 cm^{-1} to a doublet at 2270 and 2370 cm^{-1}. These shifts compare favorably with those observed by Ferraro and Walker for deuterated complexes (18). The H_2O bending vibration, normally at approximately 1500 cm^{-1}, shifts to 1214 cm^{-1} in the deuterated complex. The D_2O bending vibration is found at 1215 cm^{-1} in liquid D_2O (17).

The $Fe(III)(OH)(C_4O_4)\cdot3H_2O$ and the $V(III)(OH)(C_4O_4)\cdot3H_2O$ spectra both have sharp bands of equal strength at approximately 1085 and 1105 cm^{-1}. These bands can be assigned to C - C stretch vibrations (19). The $V(III)(OH)(C_4O_4)$ spectrum also has two bands in this region. However, the band which appears at 1100 cm^{-1} is much stronger than the one at 1055 cm^{-1}. In fact, the band at 1055 cm^{-1} appears as a weak shoulder on the 1100 cm^{-1} band and is assigned to the bending O - H vibration in the hydroxyl bridge. The $Fe(III)(OH)(C_4O_4)$ has only one band at 1090 cm^{-1} because the O - H bridge vibration in this complex is at 1015 cm^{-1}. The spectra of the $V(III)(OH)(C_4O_4)\cdot2H_2O$ and $Fe(III)(OH)(C_4O_4)\cdot2H_2O$ also contain the two bands in this region. These two sharp bands are of almost equal strength with the band at 1105 cm^{-1} being somewhat stronger than the 1085 cm^{-1} band.

The spectra of the complexes studied all contain a strong band at approximately 3200 cm^{-1}. In the spectra of $Fe(III)(OH)(C_4O_4)\cdot3H_2O$, $Fe(III)(OH)(C_4O_4)\cdot2H_2O$, $V(III)(OH)(C_4O_4)\cdot3H_2O$, and $V(III)(OH)(C_4O_4)\cdot2H_2O$ this band is very broad. However, in the spectrum of $V(III)(OH)(C_4O_4)$ and $Fe(III)(OH)(C_4O_4)$, the width of this band has greatly decreased but is still broad. This band is normally assigned to the O - H stretch in water and the hydroxyl radical where there is considerable hydrogen bonding. This band in the spectra of $V(III)(OH)(C_4O_4)$ and $Fe(III)(OH)(C_4O_4)$ is not as broad as the band in the other spectra because this complex contains only a hydroxyl group whereas the other complexes contain both hydroxyl groups and water molecules. The presence of both hydroxyl groups and water molecules along with possible hydrogen bonding broaden the O - H stretch frequency (1).

B. ELECTRONIC SPECTRAL STUDIES

The electronic spectra discussed in this section were made using techniques outlined earlier in this work. The electronic spectra for the three vanadium complexes, the three iron(III) complexes, the potassium and indium salts, and the iron(III) squarate trihydrate and potassium squarate solutions are given in Tables III, IV, V, and VI respectively.

The vanadium(III) ion is a d^2 configuration with a $^3T_{1g}(F)$ ground state in an octahedral crystal field. The band in the electronic spectra of $V(III)(OH)(C_4O_4)\cdot 3H_2O$ at 17,900 cm^{-1} and $V(III)(OH)(C_4O_4)\cdot 2H_2O$ at 17,800 cm^{-1} can be assigned to the d - d transition of $^3T_{2g}(F) \longleftarrow {}^3T_{1g}(F)$. The $^3T_{2g}(F) \longleftarrow {}^3T_{1g}(F)$ transition in a $V(H_2O)_6^{+3}$ solution appears at 17,200 cm^{-1} (20). The band in the electronic spectra of $V(III)(OH)(C_4O_4)\cdot 3H_2O$ at 26,000 cm^{-1} and $V(III)(OH)(C_4O_4)\cdot 2H_2O$ at 26,700 cm^{-1} can be assigned to the d - d transition of $^3T_{1g}(P) \longleftarrow {}^3T_{1g}(F)$. This band in a $V(H_2O)_6^{+3}$ solution appears at 25,600 cm^{-1} (20).

Using these assignments for d - d transitions, it is possible to estimate the crystal field splitting parameter 10Dq and the Racah parameter B using the method outlined by Figgis (20,21).

From these data and the energy of transition, the Racah parameter was found to be

$$B = 611 \text{ cm}^{-1}$$

for $V(III)(OH)(C_4O_4)\cdot 3H_2O$ and

$$B = 655 \text{ cm}^{-1}$$

for $V(III)(OH)(C_4O_4)\cdot 2H_2O$. Hence, the crystal field splitting was found to be

$$10Dq = 18{,}900 \text{ cm}^{-1}$$

TABLE III

ELECTRONIC SPECTRA OF VANADIUM(III) SQUARATE MULLS

$V(III)(OH)(C_4O_4)\cdot 3H_2O$ frequency, cm^{-1}	$V(III)(OH)(C_4O_4)\cdot 2H_2O$ frequency cm^{-1}	$V(III)(OH)(C_4O_4)$ frequency, cm^{-1}
4080	5000	
5000	5270	5210
5560	5710	
6670	6670	6900
9800	12500	
12500	17800	
17900	26700	40100
26000	42600	40100
33900	47200	43900
40000		

TABLE IV

ELECTRONIC SPECTRA OF IRON(III) SQUARATE MULLS

$Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ frequency, cm^{-1}	$Fe(III)(OH)(C_4O_4)\cdot 2H_2O$ frequency, cm^{-1}	$Fe(III)(OH)(C_4O_4)$ frequency, cm^{-1}
5000	4330	4130
5700	4980	4410
6550	5710	5180
20000	6670	17700
38450	18200	32400
40000	40000	41000

TABLE V

ELECTRONIC SPECTRA OF SOME OTHER SQUARATE MULLS

$K_2C_4O_4 \cdot H_2O$ frequency, cm^{-1}	$In(III)(OH)(C_4O_4) \cdot 2H_2O$ frequency, cm^{-1}
5010	4220
5210	4480
5650	4570
6670	5130
	5560
	6890
	34200
	40800

TABLE VI

ELECTRONIC SPECTRA OF METHANOL SOLUTIONS

$Fe(III)(OH)(C_4O_4) \cdot 3H_2O$ frequency, cm^{-1}	ϵ	$K_2C_4O_4 \cdot H_2O$ frequency, cm^{-1}	ϵ
20000	2400	36800	12000
38450	29000	39200	9800
40300	30000	$6.6x10^{-5}M$	
$2.3x10^{-5}M$			

for $V(III)(OH)(C_4O_4)\cdot 3H_2O$ and

$$10Dq = 19{,}650\ cm^{-1}$$

for $V(III)(OH)(C_4O_4)\cdot 2H_2O$. These values compare favorably to the values of $B = 665\ cm^{-1}$ and $10Dq = 18{,}600\ cm^{-1}$ for $V(H_2O)_6^{+3}$ (15) and suggest that the vanadium ion could be in a slightly distorted octahedral field.

The band at approximately 5,000 cm^{-1} is an overtone combination of the bending and asymmetrical stretching vibrational modes of water (22). The spectrum of most of these complexes contains this band even though two of these complexes are supposedly anhydrous. This can be explained by the fact that these spectra are made from mulls of the complexes of unknown concentration, and therefore the extinction coefficents for these bands can not be determined. Without knowing the extinction coefficients for the bands, it is not possible to compare the strength of the bands. A small amount of moisture wetting the surface of the anhydrous complex could give a band as intense as a similar band for the hydrated complex provided that the mull of the anhydrous complex were more concentrated than the mull of the hydrated complex. A weak water band in the $Fe(III)(OH)(C_4O_4)$ spectrum could also result from the small amount of water not removed during dehydration as indicated by the weight loss data.

Crystal field calculations were not made on the iron complexes because the electronic spectrum of high spin iron(III) complexes, d^5 case, contain no allowed crystal field d - d transitions in an octahedral field.

The bands in the ultraviolet region of the electronic spectra of these complexes in both solutions and mulls, those bands above 33,000

cm^{-1}, are probably due to charge transfer transitions between metal and ligand.

Solubility studies were made on the vanadium(III) and iron(III) squarate trihydrate complexes in an attempt to find a solvent for solution electronic spectral studies. No solvent was found for vanadium(III) squarate trihydrate among the approximately 25 investigated. However, it was found that iron(III) squarate trihydrate and potassium squarate monohydrate were slightly soluble in methanol, solubilities were 4.6×10^{-3}M and 1.15×10^{-3}M respectively. The results of the electronic spectral studies of these solutions are given in Table VI. Methanol proved to be a suitable solvent only in the visible and ultraviolet regions of the spectra because it contained strong bands in the near infrared region.

C. POWDER X-RAY DIFFRACTION STUDIES

The powder x-ray diffraction data was obtained using the methods outlined previously in this work. The lattice spacings which were calculated from this data along with the data for trivalent metal squarates reported by West and Niu (2) are given in Table VII.

The lattice spacings of the $V(III)(OH)(C_4O_4)\cdot 3H_2O$ complex at 6.61, 6.37, and 6.18 Å were calculated from the diffractometer pattern which contained three corresponding peaks because the powder photograph contained only one strong line in this region. This one line corresponded to a lattice spacing of 6.34 Å. West and Niu (2) report that the powder photograph of their trivalent metal squarates contained only one line corresponding to a lattice spacing of 2.48 Å whereas the author

TABLE VII

LATTICE SPACINGS OF METAL SQUARATES IN Å

$M(III)(OH)(C_4O_4)\cdot 3H_2O$ (2)	$V(III)(OH)(C_4O_4)\cdot 3H_2O$	$V(III)(OH)(C_4O_4)\cdot 2H_2O$	$V(III)(OH)(C_4O_4)$
7.72	7.72	7.57	
6.76	6.61		6.65
6.40	6.37	6.28	
6.16	6.18		
5.75	5.72	5.70	5.51
5.19	5.17	5.17	5.04
4.56	(4.53)		
4.25	4.24	4.23	
3.95	3.96	3.95	3.93
3.70	3.70	3.66	
3.43	3.44	3.41	3.28
3.25	3.23	3.22	
3.13	3.14	3.12	
3.04	3.03	3.03	
2.84	2.84	2.82	
2.74	2.76	2.73	
2.68	2.66	2.66	
2.58	2.58	2.57	2.54
2.48	(2.49) (2.46)	2.48	2.45
2.41	2.39	2.40	
2.29	2.29	2.29	
2.16	2.15	2.15	

TABLE VII (cond.)

LATTICE SPACINGS OF METAL SQUARATES IN Å

M(III)(OH)(C_4O_4) $\cdot 3H_2O$	V(III)(OH)(C_4O_4) $\cdot 3H_2O$	V(III)(OH)(C_4O_4) $\cdot 2H_2O$	V(III)(OH)(C_4O_4)
2.11	2.10		
2.06	2.05	2.05	
2.02			
1.980	1.980		
1.930			
1.851	1.852	1.84	
	1.8264		
1.797			
1.763			
1.738			
	1.712		
1.704			
1.675			
1.649			

The values inside parentheses are values which were obtained from the defractometer spectra because these lines on the film were too weak to measure.

observes two peaks in the diffractometer pattern which correspond to lattice spacings of 2.46 and 2.49 Å. With these minor exceptions the lattice spacings for $M(III)(OH)(C_4O_4)\cdot 3H_2O$ (2) and $V(III)(OH)(C_4O_4)\cdot 3H_2O$ agree very well at low angle. However, at relatively high angles the agreement is not quite as good. This lack of agreement could be due to the increasing difficulty in decerning lines on the fluorescent darkened film at these higher angles. However, the overall agreement is such that the powder x-ray diffraction data supports the proposal that the complex $V(III)(OH)(C_4O_4)\cdot 3H_2O$ is isostructural with the trivalent metal squarates reported by West and Niu (2).

The lattice spacings of the $V(III)(OH)(C_4O_4)\cdot 2H_2O$ complex, which were calculated from the diffractometer pattern, are almost identical to the lattice spacings for the trihydrate complex. The greatest differences appear at low angles where the lattice spacing is the greatest. Because the lattice spacings compare so well, the structures of the dihydrate and the trihydrate must be closely related.

The lattice spacings of the $V(III)(OH)(C_4O_4)$ complex were also calculated from the diffractometer pattern. The data is not as complete as for the other complexes because the peaks could not be completely resolved from the background. However, there is a noticeable decrease in comparing these lattice spacings to those for the other trivalent squarate complexes. The only exception is the lattice spacing of 3.93 Å as compared to 3.95 Å for the corresponding lattice spacing for $M(III)(OH)(C_4O_4)\cdot 3H_2O$ (2). The lattice spacing of 3.28 Å is such that it could correspond to either the value of 3.43 or 3.25 Å for $M(III)(OH)(C_4O_4)\cdot 3H_2O$ (2). Considering the trend elsewhere of decreasing lattice spacings, it must be assumed this value corresponds to the value of 3.43 Å. This data, although incomplete as compared to the data for the other complexes, suggests that there is a decrease in the lattice spacings as the three water molecules are removed in its preparation.

The lattice spacings which were calculated from the diffractometer patterns for the $In(III)(OH)(C_4O_4)\cdot 2H_2O$ are given in Table VIII.

TABLE VIII

LATTICE SPACINGS OF INDIUM SQUARATE IN Å

d	d	d
6.65	2.69	1.94
5.64	2.61	1.90
4.05	2.48	1.83
3.69	2.29	1.79
3.41	2.24	1.77
3.29	2.17	1.71
3.26	2.12	1.69
3.07	2.09	1.67
2.91	2.01	1.62
2.83	1.99	1.58
2.76		

The powder photographs of the indium complex differs from the photographs of the iron(III) and vanadium(III) squarate complexes in that the indium photograph shows back angle reflections which the other photographs do not show. This suggests that the indium(III) squarate complex has a structure much different from the structures of the iron(III) and vanadium(III) squarate complexes.

The relative intensities of the front and back angle reflections is a function of the number of atoms in the diffracting species. A diffraction pattern with the front angle reflections much stronger than the back angle reflections suggests a system with a large particle causing the diffraction of the x-rays. This suggests that the iron(III) and vanadium(III) squarate complexes are either dimeric or polymeric in nature. In turn, this suggests that the indium(III) squarate complex is either a monomer or lower order polymer than the other trivalent metal squarates.

D. MAGNETIC STUDIES

The magnetic data was obtained using the procedures outlined previously in this work. Before magnetic moments could be calculated on the materials under consideration in this thesis, the field strength constant, β, needed to be determined for the Guoy tube to be used. This constant was calculated using Equation 1 and the magnetic data obtained for a known compound, in this case $HgCo(SCN)_4$.

$$\beta = \frac{\chi_g M}{\Delta F - \delta} \qquad \underline{1}$$

where χ_g = gram susceptibility of known = $16.44 \frac{303}{T+10} \times 10^{-6}$ for $HgCo(SCN)_4$

M = weight of known in grams

ΔF = change in weight of loaded tube with and without field

δ = change in weight of empty tube with and without field.

Using this constant the molar susceptibility, χ_M, of the material under consideration could be calculated using Equation 2.

$$\chi_M = \frac{\beta(\Delta F-\delta)\ MW}{M} \qquad \underline{2}$$

where β = field strength constant previously determined

ΔF = change of weight of loaded tube with and without field

δ = change of weight of empty tube with and without field

MW = molecular weight of the material under consideration

M = weight of the material in grams.

Using the molar susceptibility from Equation 2 the effective magnetic moment, μeff, could be calculated using Equation 3 (24).

$$\mu eff = 2.828(\chi_M T)^{1/2} \qquad \underline{3}$$

where χ_M = molar susceptibility from Equation 2

T = absolute temperature in °K.

Tabulated in Table IX are the magnetic moments which were calculated using Equation 3 for the three vanadium complexes. The trivalent vanadium, being a d^2 case, should have an effective magnetic moment of 2.83 B.M. for the free metal ion. A d^2 metal ion in an octahedral field has a $^3T_{1g}$ ground state and should have a temperature dependent magnetic moment (25).

TABLE IX

EFFECTIVE MAGNETIC MOMENTS OF VANADIUM COMPLEXES

Complex	χ'_m, 10^{-6}cgs	Temperature	μeff
$V(III)(OH)(C_4O_4)\cdot 3H_2O$	3340	295.0 °K	2.81 B.M.
	9830	103.0	2.84
$V(III)(OH)(C_4O_4)$	2990	294.6	2.66
	8320	101.8	2.61
$V(III)(OH)(C_4O_4)\cdot 2H_2O$	3320	294.9	2.80
	9910	101.9	2.83

TABLE X

TEMPERATURE DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITIES OF Fe(III)(OH)(C_4O_4)·XH_2O

$3H_2O$		$2H_2O$		$0H_2O$	
T, °K	χ_M', 10^{-6}cgs	T, °K	χ_M', 10^{-6}cgs	T, °K	χ_M', 10^{-6}cgs
				297.0	8110
295.0	11880	297.0	10900	286.6	8340
247.5	13490	256.0	12500	247.0	9410
221.5	14640				
202.0	15320	198.1	14700	200.9	10300
178.5	16500				
157.5	17660				
143.0	18730	125.1	18400	129.6	12500
109.5	20970	106.7	19340	106.0	13700
88.2	22100				
63.5	22890				
50.5	22900				
38.6	22560				
23.8	21570				
20.2	21150				

χ_M' refers to the corrected molar magnetic susceptibility.

TABLE XI

TEMPERATURE DEPENDENCE OF THE MAGNETIC MOMENTS OF Fe(III)(OH)(C_4O_4)· H_2O

$3H_2O$		$2H_2O$		OH_2O	
T, °K	μeff	T, °K	μeff	T, °K	μeff
295.0	5.29	297.1	5.08	297.0	4.39
				286.6	4.37
247.5	5.17	256.0	5.06	247.0	4.30
221.5	5.09				
202.0	4.97	198.1	4.84	200.9	4.09
178.5	4.86				
157.5	4.72				
143.0	4.63	125.1	4.29	129.6	3.63
109.5	4.28	106.7	4.05	106.0	3.42
88.2	3.95				
63.5	3.41				
50.5	3.04				
38.6	2.64				
23.8	2.03				
20.2	1.85				

Figgis reported effective magnetic moments for $(NH_4)V(SO_4)_2 \cdot 12H_2O$ of 2.80 and 2.78 B.M. at 300 and 80°K respectively. He suggested that the magnetic moment was not more temperature dependent because the low symmetry component was large as compared to the spin-orbit coupling component (25). The slight increase in the magnetic moment of the complex $V(III)(OH)(C_4O_4) \cdot 3H_2O$ as the temperature decreases could be the result of a similar situation. However, without further study, it is impossible to determine if this increase is real or is merely experimental error.

The magnetic moment of the complex $V(III)(OH)(C_4O_4)$ shows more of a temperature dependence. However, more important than the slight decrease in the magnetic moment with decreasing temperature, is the marked decrease in the magnetic moment in going from the complex $V(III)(OH)(C_4O_4) \cdot 3H_2O$ to the complex $V(III)(OH)(C_4O_4)$. This decrease suggests that there is some coupling between metal atoms in the complex $V(III)(OH)(C_4O_4)$. This in turn suggests that the metal atoms in this complex are closer together than those in the trihydrate complex.

The magnetic moment increases as two water molecules are added to the complex $V(III)(OH)(C_4O_4)$ to form the complex $V(III)(OH)(C_4O_4) \cdot 2H_2O$. This increase in magnetic moment suggests that the metal to metal atom distance increases as the two water molecules are added. However, the temperature dependence of this complex is such that it can not be distinguished from experimental error.

Niu reported the magnetic moment of $(Fe(III)(OH)(C_4O_4) \cdot 3H_2O$ as 5.26 Bohr magnetons (2,16). A spin-free iron(III) complex should have five unpaired electrons and should have a magnetic moment of about 5.9 Bohr magnetons. He explained that the significantly lower value of the magnetic moment was probably the result of some exchange spin-pairing or metal-metal bonding between the iron atoms. He suggested that the material was probably antiferromagnetic and, thus, should have a temperature dependent magnetic moment (16). Long, Condren, and McDonald made a study of the temperature dependence of the magnetic susceptibilities of $Fe(III)(OH)(C_4O_4) \cdot 3H_2O$ (13). Their data is given in Table X along with similar data which this investigator obtained for $Fe(III)(OH)(C_4O_4)$ and $Fe(III)(OH)(C_4O_4) \cdot 2H_2O$. The magnetic moments as a function of temperature for these three complexes are given in Table XI as a comparison to the values reported by West and Niu (2). However, experimentally determined magnetic moments only have significance for a paramagnetic system. Therefore, the data will be discussed in terms of magnetic susceptibilities.

The magnetic susceptibilities as a function of temperature for $Fe(III)(OH)(C_4O_4) \cdot 3H_2O$, as given in Table X, show a Curie temperature of about 55°K (13). This data appears to fit a binuclear exchange model for an antiferromagnetic system proposed by Earnshaw and Lewis (26) having an S value of 5/2, g value of 1.97, and J value of -6.8. A comparison of the experimentally determined value of $1/\chi_M$ versus temperature with the binuclear exchange model is shown in Figure VIII. The fit of this data to a binuclear exchange model suggests that there is short range spin-spin coupling between adjacent metal atoms (13).

Although the magnetic susceptibilities as a function of temperature for $Fe(III)(OH)(C_4O_4) \cdot 2H_2O$, as given in Table X, do not exhibit a Curie temperature in the temperature range investigated, these data

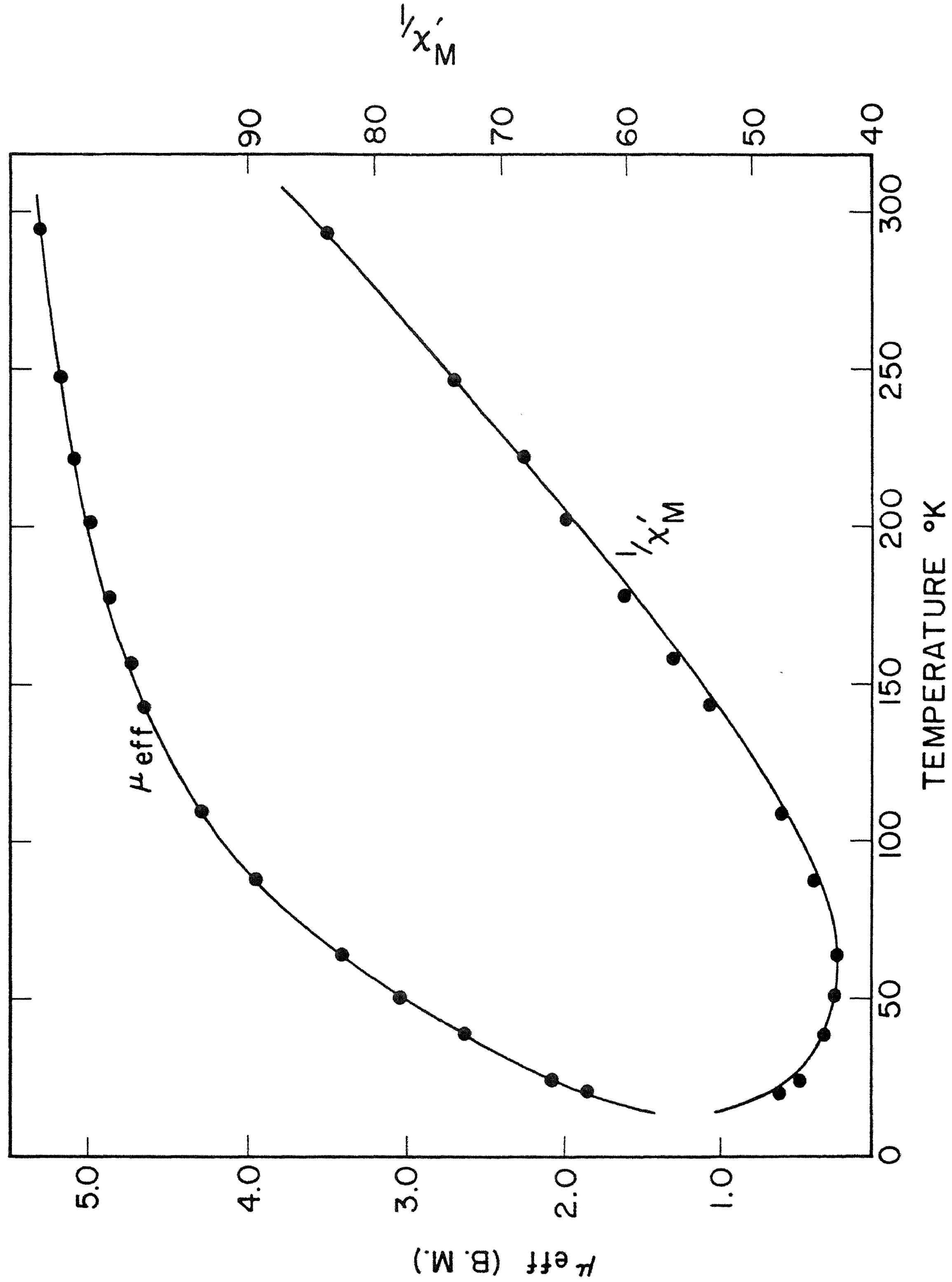


Figure VIII. Temperature Dependence of the Magnetic Susceptibility of Fe(III)(OH)$(C_4O_4)\cdot 3H_2O$

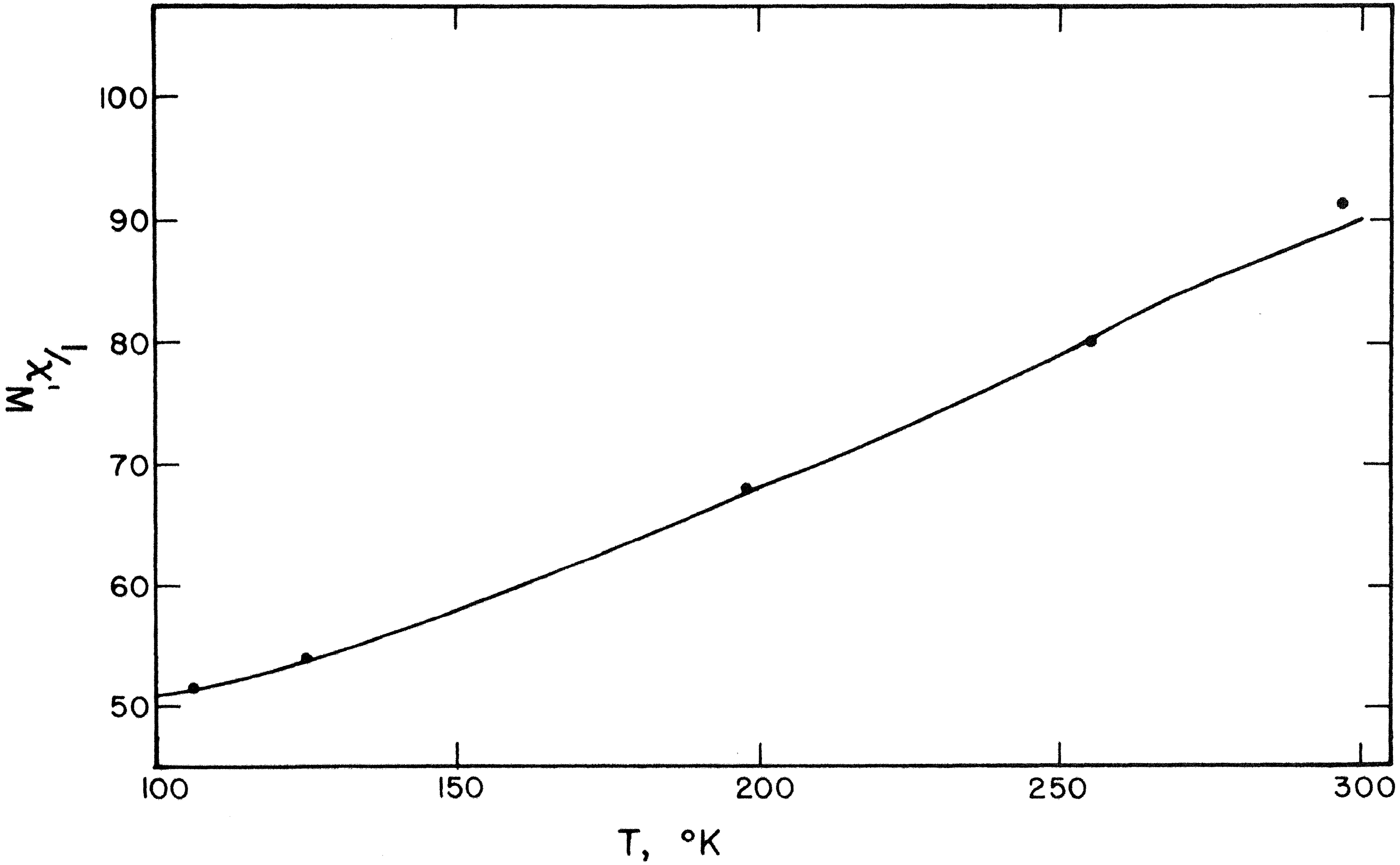


Figure IX. Temperature Dependence of the Magnetic Susceptibility of Fe(III)(OH)$(C_4O_4) \cdot 2H_2O$

appear to fit a similar binuclear exchange model with an S value of 5/2, g value of 1.97, and J value of -7.6 as shown in Figure IX. This suggests that this material also exhibits short range spin-spin coupling between adjacent metal atoms.

The magnetic susceptibilities as a function of temperature for Fe(III)(OH)(C_4O_4) as given in Table X could not be fitted to a binuclear exchange model for an antiferromagnetic material. However, this does not mean that this material is not antiferromagnetic, for the large value of the magnetic susceptibilities does suggest this type of magnetism (27). The greater degree of temperature dependence of the magnetic susceptibility suggests an antiferromagnetic system resulting from the exchange of more than two metal atoms. This type of spin exchange coupling between several metal atoms would become important as the metal-metal distance decreases during dehydration. However, without a study of the magnetic susceptibility of this material to lower temperatures, it is impossible to state that this material is truly antiferromagnetic.

E. THERMOGRAVIMETRIC STUDIES

The thermogravimetric studies involved not only the study of the thermal decomposition of the three vanadium complexes but also the identification of the residue of the decomposition reactions. The thermal decomposition of the vanadium complexes was studied in both an air and an argon atmosphere. The thermogravimetric data for the vanadium complexes V(III)(OH)(C_4O_4)$\cdot$3H_2O, V(III)(OH)(C_4O_4), and V(III)(OH)(C_4O_4)$\cdot$2H_2O are given in Tables XII, XIII, and XIV respectively. A typical thermogravimetric pattern is shown in Figure X.

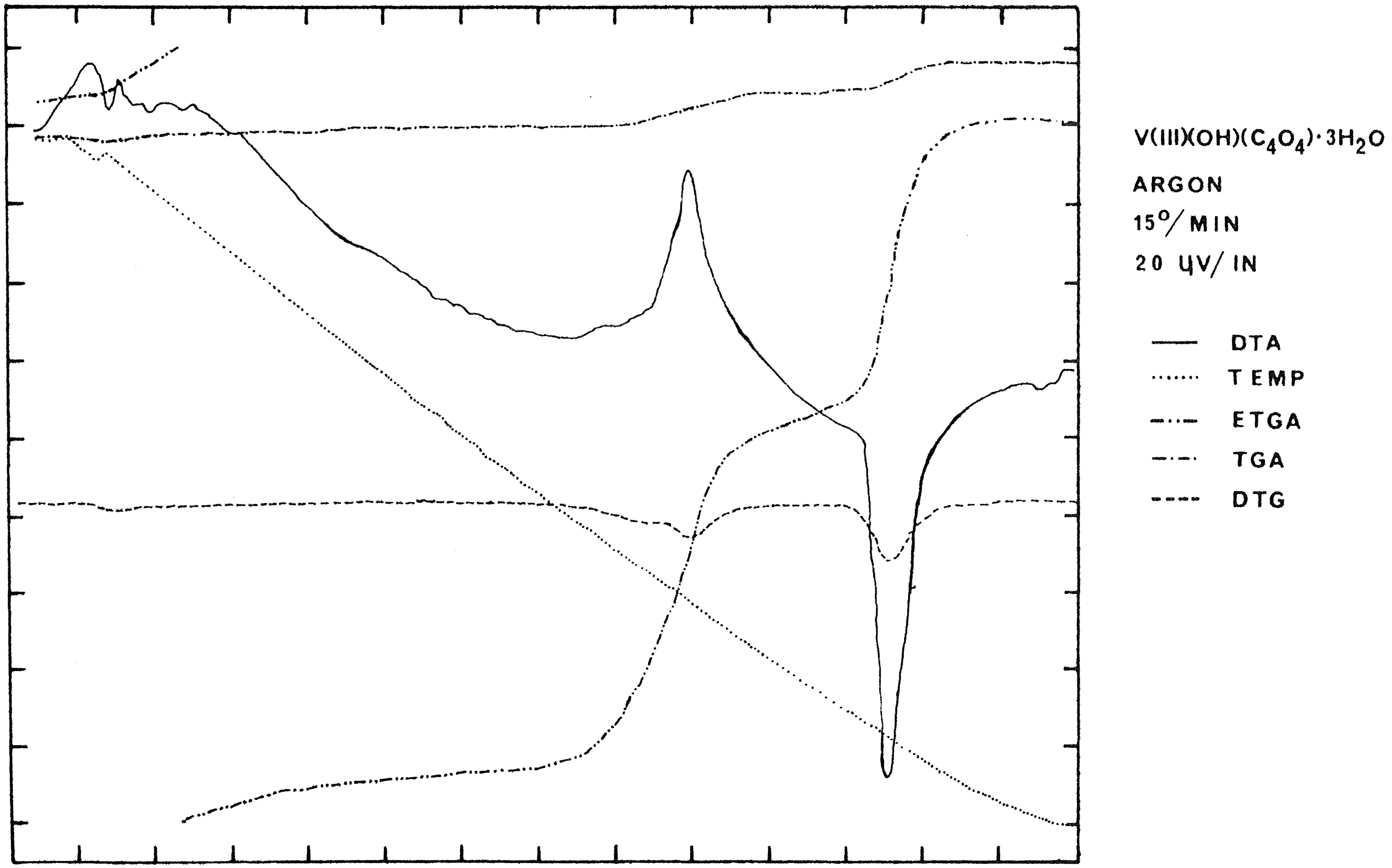


Figure X. Thermogravimetric Pattern of Vanadium(III) Squarate Trihydrate

TABLE XII

THERMOGRAVIMETRIC DATA FOR $V(III)(OH)(C_4O_4)\cdot 3H_2O$

Atmosphere	Maximum Temperature	DTA Peaks	Weight Loss Steps	Weight Loss Percent	Residue
Air	1020°C	endo 230°C exo 330°C	2	85.4%	V_2O_5
Air	300°C	endo 200°C exo 240°C	1	62.5%	V_2O_5
Air	140°C	endo 140°C	1	20.5%	$V(III)(OH)(C_4O_4)$
Argon	710°C	endo 200°C exo 340°C	2	88.1%	V_2O_3
Argon	360°C	endo 200°C exo 340°C	2	52.4%	unidentifiable
Argon	160°C	endo 160°C	1	21.2%	$V(III)(OH)(C_4O_4)$

endo - refers to endotherm

exo - refers to exotherm

When a sample of $V(III)(OH)(C_4O_4)\cdot 3H_2O$ was heated to 1020°C under an air atmosphere, it decomposed by two distinct steps as evidenced by the weight loss. The break between the two weight loss steps appeared at approximately 250°C.

The first step resulted from the endothermic loss of three water molecules. The peak of the endotherm was located at approximately 230°C. The second step involved the oxidative decomposition of the complex to water, carbon dioxide, and a metal oxide residue. This residue was identified as V_2O_5 by x-ray diffraction analysis by comparing the d spacings with those reported on A.S.T.M. (American Society for Testing Materials) card #3-0206 for V_2O_5. This exothermic step had a peak located at approximately 330°C. The weight then became constant above 400°C with a total weight loss of 85.4%. This large weight loss was the result of the splattering and consequent loss of some of the sample during the heating due to too high a heating rate. For the remainder of the analyses, the heating rate was reduced from six to two degrees per minute.

A second air oxidation of the complex $V(III)(OH)(C_4O_4)\cdot 3H_2O$, this time to 300°C, resulted in a thermogravimetric pattern with the weight loss steps better defined. Prior to a shoulder at 240°C, the weight loss was endothermic as before. Following the shoulder the weight loss was exothermic with a total weight loss of 62.5%. The residue of this oxidation was identified as V_2O_5 by x-ray diffraction analysis as before. With V_2O_5 as the end product, the calculated weight loss for this complex is 61.1%. This rather good agreement for this analysis confirms the postulate that some of the sample was lost in the first analysis.

In an effort to study the first step of the decomposition, a third thermogravimetric analysis was run in air on the vanadium trihydrate complex at a temperature considerably below the shoulder. The maximum temperature chosen for this run was 140°C. This thermogravimetric analysis resulted in a total weight loss of 20.5% which compares well to the calculated value of 23.1% weight loss for three water molecules. In addition the residue from this analysis was identified by infrared analysis to be the complex $V(III)(OH)(C_4O_4)$ which differs from the trihydrate complex by three water molecules.

The three thermal analyses on the trihydrate complex were then repeated using an inert argon atmosphere in an attempt to slow down the rapid oxidation of the complex. It was hoped that if the oxidation was slower the reaction could be separated into more distinct steps. However, the results of the analyses in argon did not differ greatly from those in air. In fact, the main difference was in the metal oxide product. In the oxygen deficient argon atmosphere, the metal was not oxidized to V_2O_5. In the run to 710°C, the metal was only oxidized to V_2O_3. When this residue was then heated in air to 710°C, it was oxidized to V_2O_5. These two oxides of vanadium were identified by x-ray diffraction analysis by comparing the d spacings with those reported on A.S.T.M. card #3-0206 for V_2O_5 and #1-1293 for V_2O_3. The residue for the 360°C run did not appear to be V_2O_5, and it could not be positively identified by either x-ray diffraction or infrared analysis as any other oxide of vanadium because of the amorphous nature of the residue.

The run made to a temperature of 160°C resulted in a weight loss of 21.2% and a residue which was identified by infrared analysis to be $V(III)(OH)(C_4O_4)$.

The thermogravimetric data for $V(III)(OH)(C_4O_4)$ is given in Table XIII. The thermal decomposition of this complex appears to be almost independent of the atmosphere used. The atmosphere used in these thermal decompositions does affect the final product of the oxidation. In air the final product is V_2O_5 as identified by x-ray diffraction analysis as before. The final product for the argon run was unidentifiable by either x-ray diffraction or infrared analysis.

TABLE XIII

THERMOGRAVIMETRIC DATA FOR $V(III)(OH)(C_4O_4)$

Atmosphere	Maximum Temperature	DTA Peaks	Weight Loss		Residue
			Steps	Percent	
Air	710°C	exo 380°C	1	57.7%	V_2O_5
Argon	710°C	exo 380°C	1	53.9%	unidentifiable

exo - refers to exotherm

The complex $V(III)(OH)(C_4O_4)$ in both air and argon decomposed in a single step weight loss. The weight loss of 57.7% in air and 53.9% in argon was larger than the value of 50.4% calculated for the decomposition of the complex to V_2O_5. This again could be the result of some splattering of the complex during heating. The thermogravimetric analysis patterns for this complex appear to be identical to the patterns for the $V(III)(OH)(C_4O_4)\cdot 3H_2O$ complex above the dehydration temperature for the hydrated complex. This is to be expected since the complex $V(III)(OH)(C_4O_4)$ is prepared by dehydrating the complex $V(III)(OH)(C_4O_4)\cdot 3H_2O$.

The thermogravimetric patterns for the complex $V(III)(OH)(C_4O_4)\cdot 2H_2O$ are by far the most complicated as evidenced by the data given in Table XIV. The weight was lost in one distinct step with a shoulder located at 240°C. Attempts at separating the two steps proved futile. The endothermic dehydration was not complete before the exothermic oxidation process began. Even with the heating rate of two degrees per minute, these processes could not be separated in either air or argon decomposition. The total weight loss was 63.8% in air and 58.2%

TABLE XIV

THERMOGRAVIMETRIC DATA FOR $V(III)(OH)(C_4O_4)\cdot 2H_2O$

Atmosphere	Maximum Temperature	DTA Peaks	Weight Loss Steps	Weight Loss Percent	Residue
Air	695°C	endo 240°C exo 260°C exo 280°C endo 430°C endo 670°C	2	63.8%	V_2O_5
Argon	710°C	endo 195°C exo 330°C	2	58.2%	unidentifiable

endo - refers to endotherm

exo - refers to exotherm

in argon. The final product of the air run was found to be V_2O_5 by x-ray analysis as before. The final product of the argon run could not be identified. The calculated weight loss for this complex decomposing to V_2O_5 is 57.9%. The disagreement between calculated and experimental weight loss could again be due to splattering of the sample during heating.

The mechanism for the decomposition of $V(III)(OH)(C_4O_4)\cdot 2H_2O$ must differ somewhat from the mechanism for the decomposition of the other two vanadium complexes as shown by the differences in their thermogravimetric data given in Tables XII, XIII, and XIV. However, since the steps of the mechanism could not be separated, the thermogravimetric data can not suggest any clues as to the nature of the mechanisms.

Thermogravimetric studies in air were made on the complexes $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ and $In(III)(OH)(C_4O_4)\cdot 2H_2O$ to ascertain if they lost their water molecules in a manner similar to the vanadium(III) squarate complexes. The thermogravimetric data for these studies is given in Table XV.

TABLE XV

THERMOGRAVIMETRIC DATA FOR
$Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ and $In(III)(OH)(C_4O_4)\cdot 2H_2O$

Complex	Maximum Temperature	DTA Peaks	Weight Loss Steps	Residue
$Fe(III)(OH)(C_4O_4)\cdot 3H_2O$	600°	120° endo 185° endo 230° exo	3	Fe_2O_3
$In(III)(OH)(C_4O_4)\cdot 2H_2O$	400°	220° exo	1	In_2O_3

The thermogravimetric pattern of $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ illustrates a two step endothermic weight loss followed by a one step exothermic weight loss. The endotherms occur at 120° and 185°C, and the exotherm occurs at about 230°C. The endotherms are the result of stepwise loss of water, one water molecule loss in the first step followed by two water molecules in the second step. This is followed by the exothermic decomposition of the complex to the metal oxide, in this case Fe_2O_3.

The first step of the weight loss began at about 110°C. At the time that the second weight loss step began at about 140°C, the sample had lost approximately 3% of its weight. The second step had accounted for an additional 20% weight loss when the third step began. The second and third steps were separated by a shoulder in the thermogravimetric curve at approximately 200°C. The total weight loss for the decomposition process was 66.9% as compared to a calculated weight loss of 66.6% for the sample decomposing to Fe_2O_3. This thermogravimetric study indicated that $Fe(III)(OH)(C_4O_4)\cdot 2H_2O$ could be prepared by heating $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ and removing one water molecule per molecule of complex. In turn, the fact that the second and third steps were separated only by a shoulder in the thermogravimetric curve would indicate that, in air at approximately one atmosphere and 200°C, $Fe(III)(OH)(C_4O_4)$ could not be prepared. It was hoped that under vacuum conditions and lower temperatures that both $Fe(III)(OH)(C_4O_4)\cdot 2H_2O$ and $Fe(III)(OH)(C_4O_4)$ could be prepared. This investigator found that the vacuum dehydration techniques developed for the vanadium(III) squarate trihydrate even at 50°C resulted in the complete dehydration of the $Fe(III)(OH)(C_4O_4)\cdot 3H_2O$ to form $Fe(III)(OH)(C_4O_4)$. This investigator was able to prepare a stable $Fe(III)(OH)(C_4O_4)\cdot 2H_2O$ by hydrating a sample of $Fe(III)(OH)(C_4O_4)$ using the techniques developed for the vanadium(III) squarate complexes.

The thermogravimetric pattern for $In(III)(OH)(C_4O_4)\cdot 2H_2O$ contained a single step exothermic weight loss. There was no evidence in the thermogravimetric pattern that the $In(III)(OH)(C_4O_4)\cdot 2H_2O$ dehydrated prior to its complete decomposition. Therefore, further attempts of preparing $In(III)(OH)(C_4O_4)$ or other hydrates of indium(III) squarate were discontinued.

V. CONCLUSIONS

The elemental analyses of the product of the reaction of metal chloride and squaric acid in aqueous solution suggests a compound with an empirical formula such as $M(III)(OH)(C_4O_4)\cdot 3H_2O$. The one exception to this is the indium trichloride squaric acid reaction which gives a product which agrees with the empirical formula $In(III)(OH)(C_4O_4)\cdot 2H_2O$. A pseudo-octahedral structure which agrees with the empirical formula for the trivalent metal squarate trihydrate is given in Figure XI.

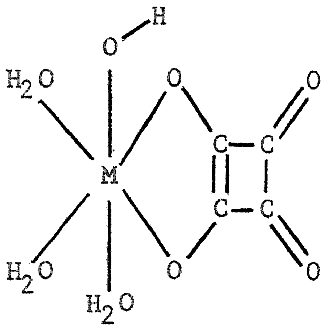


Figure XI. Proposed Pseudo-octahedral Structure of Trivalent Metal Squarate Trihydrate

This structure agrees with the infrared spectra of these complexes except for the appearance of the hydroxyl bridge bands in said spectra. The data derived from the electronic spectra can agree with this structure as well as any other in which the central metal atom is in an approximately cubic crystal field. However, the magnetic study does not agree with this structure for it suggests that the system is binuclear. The x-ray diffraction data would also be better explained by a system with a larger molecular unit. In addition, the thermogravimetric pattern for the iron(III) squarate trihydrate suggests the existence of two different types of water molecules in the system. This is contrary to the structure given in Figure XI because it predicts that all the water molecules would be equivalent.

A dimeric structure which agrees better with all the available data is given in Figure XII. This structure was first proposed by Niu (16). He stated that the structure shown in Figure XII best fit his data. He predicted two types of water molecules, one type of four water molecules per dimer in the coordination sphere of the metal and the other type of two water molecules per dimer hydrogen bonded somehow to the dimer.

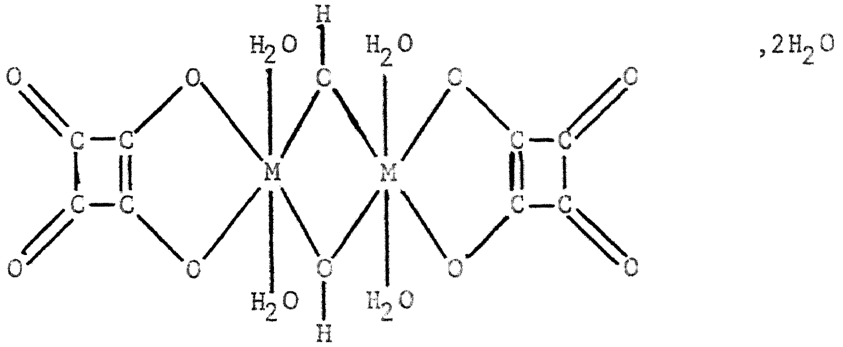


Figure XII. Proposed Dimeric Structure of Trivalent Metal Squarate Trihydrates

This type of structure agrees well with the various data this author obtained. It contains the hydroxyl bridge which is seen in the infrared spectra. It has the central metal atom in an approximately cubic crystal field as predicted by the electronic spectra. The absence of the back angle reflections in the x-ray diffraction powder photograph of these compounds could be the result of a dimer material. The magnetic data for the iron(III) squarate trihydrate can best be fitted to a binuclear antiferromagnetic exchange model. This model gives a value of J = -6.8 cm^{-1} which compares well with the value of J = -8 cm^{-1} which Schugar, Rossman, and Gray obtained for antiferromagnetic $[Fe(pic)_2OH]_2$ with a dihydroxy bridge between the iron atoms (28). They suggested that the spin coupling between metal atoms occurred through the hydroxyl bridges and assigned the band at 950 cm^{-1} in their infrared spectrum to the vibrational mode associated with the $Fe_2(OH)_2^{+4}$ structural unit which compares with the band of 980 cm^{-1} in the iron(III) squarate trihydrate. The band at 950 cm^{-1} in $[Fe(pic)_2OH]_2$ disappeared in the spectrum of $[Fe(pic)_2OD]_2$ in agreement with their assignment (28). They stated that they did not observe a shift upon deuteration because the shift would be to a region of the spectrum where the ligand picarate contains bands (28). G. J. Long states that the results of his Mössbauer study of iron(III) squarate trihydrate are consistent with the dimeric structure because they suggest that the metal ions are in a high spin, octahedral crystal field (29).

The elemental carbon and hydrogen analyses of the anhydrous and dihydrate complexes disagree with the empirical formulas previously proposed for these complexes. These analyses for anhydrous iron(III) squarate, iron(III) squarate dihydrate, anhydrous vanadium(III) squarate, and vanadium(III) squarate dihydrate can best be fitted to the empirical formulas $Fe(III)(OH)(C_4O_4)\cdot 0.5H_2O$, $Fe(III)(OH)(C_4O_4)\cdot 2.5H_2O$, respectively, as shown in Table XVI. However, these analyses disagree with the dehydration studies using weight loss techniques, with the

TABLE XVI

ELEMENTAL CARBON-HYDROGEN ANALYSIS

	Found		Calculated			
$Fe(III)(OH)(C_4O_4)$			$0H_2O$		$0.5H_2O$	
	C%	H%	C%	H%	C%	H%
	24.70	0.90	25.26	0.54	24.61	1.02
$Fe(III)(OH)(C_4O_4)\cdot 2H_2O$			$2H_2O$		$2.5H_2O$	
	C%	H%	C%	H%	C%	H%
	20.73	2.43	19.83	2.07	20.78	2.60
$V(III)(OH)(C_4O_4)$			$0H_2O$		$0.8H_2O$	
	C%	H%	C%	H%	C%	H%
	24.70 ± 0.02*	1.82 ± 0.18*	26.67	0.56	24.74	1.55
$V(III)(OH)(C_4O_4)\cdot 2H_2O$			$2H_2O$		$2.5H_2O$	
	C%	H%	C%	H%	C%	H%
	21.50 ± 0.16*	2.86 ± 0.08*	22.22	2.31	21.33	2.67

*The error limits refer to the variations in duplicate analyses.

hydration studies using weight gain techniques, and with the thermogravimetric studies. The dehydration studies along with the thermogravimetric studies began with a complex which fit the empirical formula $M(III)(OH)(C_4O_4)\cdot 3H_2O$ as shown by elemental analysis. The dehydration studies and the thermogravimetric studies show that 2.9 ± 0.1 water molecules are lost from the complex with empirical formula $M(III)(OH)(C_4O_4)\cdot 3H_2O$. In turn, the hydration studies show that 1.9 ± 0.1 water molecules are added to the dehydrated complex. The author is unable to explain this discrepancy. However, assuming that the dehydration, hydration, and thermogravimetric studies are more informative than elemental analyses in determining the amount of hydration of complexes, the product of the dehydration will be assumed to be anhydrous, and the product of the hydration will be assumed to be dihydrates.

The infrared spectra of the anhydrous complexes show the bands of a squarate ligand with uncoordinated oxygens. They also contain the bands typical of a hydroxyl bridged complex. Therefore, the infrared spectra agree with a dimeric structure similar to the one for the trihydrates with the waters of hydration removed. Such a dimeric structure is shown in Figure XIII. The electronic spectra of these complexes neither prove nor disprove this structure. The absence of back angle reflections in the x-ray diffraction powder photographs of these complexes could be the results of a dimeric species. The apparent shrinkage of the lattice spacings upon dehydration could be the result of the dimeric molecules moving closer together. The magnetic data support this idea because they suggest that the antiferromagnetic exchange occurs between more than two metal atoms which are very close in the crystal lattice. The thermogravimetric pattern for the anhydrous

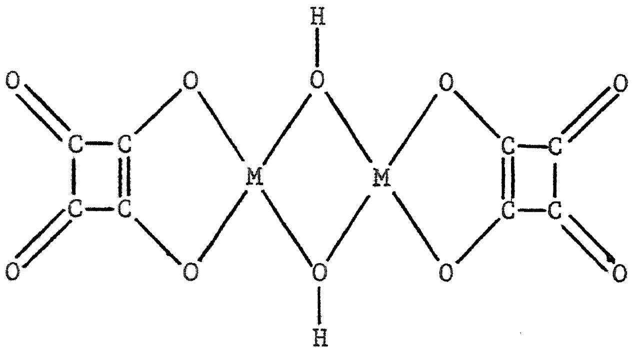


Figure XIII. Proposed Dimeric Structure of Anhydrous Trivalent Metal Squarates vanadium(III) squarate complex suggests that it contains very little if any water of hydration.

The similarities between the infrared spectra of the dihydrates and trihydrates suggest that their structures are quite similar. Therefore, a dimeric structure is proposed for the dihydrates as shown in Figure XIV which differs from the structure of the trihydrate complexes by the absence of the hydrogen bonded water molecules. The electronic spectra of the vanadium(III) squarate dihydrate suggest that the central metal atoms are in a near cubic crystal field. The lattice spacings calculated from the x-ray diffraction data agree with such a structure. The magnetic data of the iron(III) squarate dihydrate have been shown to agree with a binuclear antiferromagnetic exchange model similar to the one for the trihydrate iron(III) squarate. The single endothermic step weight loss in the thermogravimetric pattern for $V(III)(OH)(C_4O_4)\cdot 2H_2O$ implies the presence of only one type of water in this complex. This agrees well with the structure shown in Figure XIV which contains only equivalent water molecules.

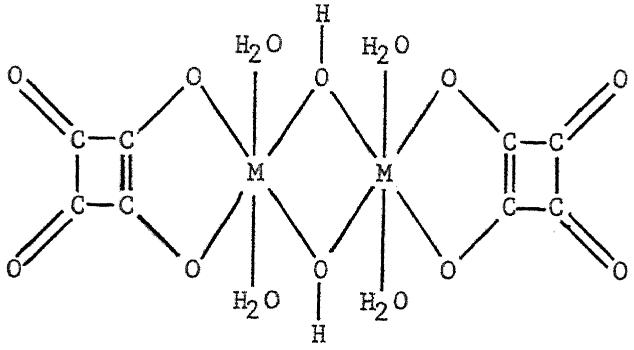


Figure XIV. Proposed Dimeric Structure of Trivalent Metal Squarate Dihydrates

The apparent stability of both the trihydrate and dihydrate complexes at ambient temperature and pressure appears to be impossible. A possible explanation for this apparent impossibility could be differences in crystal structure. The magnetic data imply that during the dehydration the metal atoms in the dimeric molecules move closer together. If the trihydrate complexes were arranged with the dimeric molecules stacked exactly on top of each other allowing the hydrogen bonded water to lie between layers, as the water molecules were removed, the anhydrous dimeric molecules would stack one on top of the other.

If during the hydration, the dimers shift from their vertical stacking to allow the water molecules to move into the coordination sphere there would not be sufficient room between the layers for the hydrogen bonded water molecules. This would result in the layers being closer together than in the trihydrate complexes which is suggested by the x-ray diffraction data.

Therefore, the structures shown in Figures XII, XIII, and XIV agree with the data obtained for the trihydrate, anhydrous, and dihydrate vanadium(III) and iron(III) squarate complexes respectively.

The structure of indium(III) squarate dihydrate appears to be quite different because the infrared spectra and x-ray diffraction powder photographs are quite different from similar data for any other squarate complex. The indium(III) ion has no unpaired electrons and a completed d shell, so that the magnetic moment and electronic spectra would not give any information as to the environment of the metal atom in the molecule. Therefore, a monomeric structure similar to Figure XI can be proposed for indium(III) squarate dihydrate.

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VITA

Stewart Michael Condren was born on September 13, 1942 in Fort Smith, Arkansas. His parents are Stewart and Margaret Condren of Fort Smith, Arkansas.

He received his primary and secondary education in the public schools of Van Buren, Arkansas. He attended the University of Arkansas from September 1960 until June 1965 from which he received his Bachelor of Science Degree in June 1965.

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APPENDIX I

SUCCESSFUL PREPARATIONS

APPENDIX I

In this study the author investigated several reactions between metal salts and squaric acid which did not provide completely satisfactory results. These reactions require future investigation before an empirical formula or a structure can be assigned. Among this group of reactions is the one which involved the preparation of zirconium(IV) oxysquarate.

The preparation of zirconium(IV) oxysquarate was first reported in this author's M.S. thesis (7). However, since that work, a different procedure has been developed for the preparation of this complex. In this procedure, zirconium(IV) oxychloride (Alfa Inorganics, Beverly, Mass.) was added directly to the squaric acid solution instead of preparing the oxychloride from zirconium(IV) nitrate. Otherwise the preparations were the same. The elemental metal analyses on eleven different preparations of the complex ranged from 31-35% Zr.

If the zirconium(IV) oxysquarate corresponded to the empirical formula $Zr(IV)\ O\ (C_4O_4)\cdot 2H_2O$, the percentage composition would be 35.8% zirconium, 1.56% hydrogen, and 18.8% carbon. The percentage composition which was determined for one preparation was 33.8% zirconium, 2.55% hydrogen, and 17.12% carbon. The complex was analyzed for the metal content by igniting it to ZrO_2 and then firing it to constant weight in a muffle furnace at 600°C. The carbon-hydrogen analysis was performed by Huffman Laboratories, Wheatridge, Colorado. The discrepancies between calculated and determined percentages and the lack of reproducibility between preparations could be due to unattached water wetting the sample. The use of phosphorous pentoxide instead of calcium chloride as the drying agent for the metal squarate complex could result in reproducible preparations.

Because some difficulty was experienced by this author in previous attempts at preparing titanium(III) hydroxysquarate (7), it was decided that all future work should be performed in a glove bag (Instruments for Industry and Research, Philadelphia, Pa.) under a nitrogen atmosphere. Otherwise the preparation followed the procedure outlined in this author's M.S. thesis (7).

After mixing the titanium trichloride with the squaric acid solution, a greenish color developed. The solution was stirred for several hours to allow the reaction to go to completion. However, before the solution was filtered, it was noted that some orange particles were floating on the surface of the solution. It was concluded that these orange particles were lumps of titanium(III) hydroxysquarate which had been partially oxidized by oxygen which had leaked into the bag or had not been flushed from the bag initially. It was also possible that the oxygen could have been dissolved in the water used to make the solutions. Therefore, the distilled water was hereafter refluxed under a stream of nitrogen gas before each preparation.

However, even these precautions did not eliminate all of the oxidation of the titanium as evidenced by the formation of orange particles on the surface of the solution. It was then decided to switch from the glove bags previously used to a glove box (Labconco, Kansas City, Mo.) in the hope that it would hold a better atmosphere. Even this did not prevent some oxidation.

Since the titanium(III) hydroxysquarate could not be isolated as a pure product, it was decided that the titanium should be oxidized to the plus four oxidation state, and the corresponding complex prepared. To accomplish this oxidation, air was bubbled slowly through the solution of titanium trichloride before the squaric acid solution was added. After the purple solution had turned yellow, the squaric acid solution was added. The resulting orange precipitate was filtered, washed with acetone and then ether, and then dried in a vacuum desiccator, the material was analyzed and was found to contain 30.4% titanium, 19.7% carbon, and 2.10% hydrogen. The material was analyzed for the metal gravimetrically by igniting it to TiO_2 and then firing it to constant weight in a muffle furnace at 700°C. The carbon-hydrogen analyses were performed by Huffman Laboratories, Wheatridge, Colorado.

Concurrently, yet independently, Tedesco and Walton (6) were conducting research on titanium(IV) oxysquarate. In April, 1969 they reported the preparation of orange titanium(IV) oxysquarate using titanium tetrachloride as their source of metal ion. Although their metal analyses were what they expected, they could not explain the large deviations in the carbon-hydrogen analyses (Calculated for $Ti(IV)OC_4O_4$: Ti, 27.3; C, 27.3. Found: Ti, 27.2; C, 19.0; H, 0.92). Since it appeared from the color and elemental analyses that the product that they reported was the same product we had prepared, this author attempted to reproduce their results. However, difficulty was encountered in reproducing their results as evidenced by the lack of reproducibility of the titanium elemental analyses of consecutive preparations. For this reason, this portion of the project was discontinued.

This author believes that additional work on the titanium(III) and (IV) squarate complexes can provide reproducible products. The main problem in the preparation of titanium(III) hydroxysquarate is the oxidation of the metal. This author believes this problem could be eliminated by the use of an enclosed glass system such as Schlenk tubes, which could be effectively purged with nitrogen before the reaction was begun. If the solution could be filtered, and the precipitate dried before being removed from this apparatus, the author believes the oxidation could be eliminated.

The author believes that the titanium(IV) oxysquarate can be prepared by using a 1:1 stoichiometric ratio of titanium tetrachloride and squaric acid and then drying the filtered precipitate in vacuo over phosphorous pentoxide at room temperature. Tedesco and Walton (6) dried their precipitate at 155°C. From thermogravimetric studies on other metal squarate complexes, this author has found that those complexes began to loose chemically bonded water at a much lower temperature than Tedesco and Walton's drying temperature. The partial dehydration of their complex could explain the difference between their hydrogen analysis as compared to the author's. Therefore, this author has suggested the somewhat more moderate drying conditions so that the hydrated complex might be isolated.

Several attempts were made before success was achieved in the preparation of lanthanum(III) hydroxysquarate. The first attempt involved dissolving lanthanum oxide in hydrochloric acid. Hydrogen chloride gas, generated in a separate flask by the addition of phosphorous pentachloride to water, was bubbled through the solution to maintain a saturated solution under an HCl atmosphere. To this solution was added, with stirring, a solution of squaric acid. After several days there was no reaction as evidenced by the lack of a precipitate. A second attempt was then made which differed from the first in that the squaric acid solution was added before the hydrogen chloride gas was bubbled through the reaction mixture. This also showed no evidence of reaction after several days.

A precipitate was finally formed by dissolving lanthanum nitrate in water and adding to this a solution containing a 1:1 stoichiometric amount of squaric acid which had previously been partially neutralized to a pH of 5 using a 0.1N solution of NaOH. The white precipitate which formed overnight was filtered, washed with acetone and ether, and dried under vacuum over calcium chloride. The precipitate was analyzed for its lanthanum content by igniting it to La_2O_3 and then firing it to constant weight in a muffle furnace at 700°C.

Analytical: Calculated for $La(III)(OH)C_4O_4 \cdot 3H_2O$: La, 43.2. Found: La, 41.6.

Having shown that lanthanum(III) ions react with squaric acid under proper conditions, a comprehensive study can now be made on this system. Included in that study should be some refinements in the preparation to insure a purer product.

The cerium(III) hydroxysquarate was prepared by dissolving 2.27 g, (9.19 mmol) of cerium trichloride in about 50 ml. of water. To this solution was added a solution containing 1.05 g. (9.37 mmol) of squaric acid. The resulting solution was stirred for approximately 24 hours, after which the cream colored precipitate was filtered, washed with acetone and ether, and dried in a vacuum desiccator over calcium chloride for 2 days. The complex was shown by elemental metal analysis to still contain some unattached water so it was redried under vacuum over phosphorous pentoxide.

The elemental metal analysis was made by igniting the cerium(III) hydroxysquarate to Ce_2O_3 and then firing it in a muffle furnace at 700°C.

Analytical: Calculated for $Ce(III)(OH)C_4O_4 \cdot 3H_2O$: Ce, 43.6. Found: Ce, 42.1.

Additional work needs to be done on the preparation of cerium(III) hydroxysquarate to insure a purer product. When this has been accomplished, a comprehensive study of this compound can be begun.

Gadolinium(III) hydroxysquarate was prepared by dissolving 3.38 g. (9.21 mmol) of gadolinium oxide in a minimum amount of hydrochloric acid. To this solution was added a solution containing 1.0 g. (8.93 mmol) of squaric acid. The white precipitate was filtered, washed with acetone and ether, and vacuum dried over calcium chloride. A small sample of the precipitate charred upon heating indicating that it contained carbon.

Before any other work is begun on the gadolinium(III) hydroxysquarate, a check must be made as to the purity of the compound. This can best be done by elemental analysis. After the purity is established, a comprehensive study including infrared and x-ray analysis can be begun.

In preparation of neodymium(III) hydroxysquarate, 3.14 g. (1.92 mmol) of neodymium oxide were dissolved in a minimum amount of nitric acid. This solution was then neutralized with 1N NaOH to prevent the oxidation of the squaric acid by the nitric acid. The solution containing 1.0 g. (8.9 mmol) of squaric acid was likewise neutralized by 1N NaOH. The two solutions were then mixed, and the resulting, light violet colored precipitate was filtered, washed with acetone and ether, and dried in a vacuum desiccator over calcium chloride. A small sample of the product charred upon heating indicating the presence of carbon.

Again the purity of the product needs to be checked by elemental analysis before beginning a comprehensive study of the compound.

APPENDIX II

UNSUCCESSFUL PREPARATIONS

APPENDIX II

Included in this appendix are those preparations which the author attempted but which proved unsuccessful in producing a metal squarate complex.

Previous attempts at preparing tantalum(V) squarate in non-aqueous solvents (7), necessary because of the reactivity of tantalum pentachloride, have been unsuccessful because of the insolubility of the squaric acid in the non-aqueous solvent. In an attempt to eliminate this problem, a search was made of the literature to find a derivative of squaric acid which was soluble in a suitable non-aqueous solvent.

In 1966 Cohen and Cohen (30) reported the preparation of a new derivative of squaric acid, dimethoxycyclobutenedione, which was soluble in several organic solvents including benzene. This derivative was chosen as our chelating agent in our attempt to prepare tantalum(V) squarate.

To prepare the dimethoxycyclobutenedione, a solution containing 5.46 g. (48.8 mmol) of squaric acid in about 250 ml. of water was neutralized with a 0.1N solution of potassium hydroxide. To this solution was then added a solution containing 16.3 g. (87.6 mmol) of silver nitrate in about 100 ml of water. The light yellow precipitate of disilver squarate was filtered and washed with water, acetone and ether. After the silver salt had been dried in a vacuum desiccator over calcium chloride, it was added to 25 ml. of methyl iodide and 50 ml. of ether, boiled for two hours, and then shaken for two days. The mixture was filtered, and the residue was washed with ether. The washed ether was concentrated and filtered, and the residue was added to the earlier residue. The resulting white crystals were then set aside to be later reacted with tantalum pentachloride.

Because of the extreme reactivity of tantalum pentachloride, the tantalum pentachloride was freshly prepared from the metal by the following procedure developed by McDonald (31).

McDonald found that the best way of preparing tantalum pentachloride was by the reaction of the metal with a gaseous mixture of chlorine and carbon tetrachloride. The chlorine gas was first bubbled through concentrated sulfuric acid to remove any moisture. The gas was then bubbled into a flask of boiling carbon tetrachloride. This flask was connected to the high end of the reaction tube by a 75° angle, Pyrex connecting tube fitted with ground glass jounts. The tantalum metal (Alfa Inorganics, Beverly, Mass.) in a porcelain boat was placed inside a tube furnace operating at approximately 500°C. The lower end of the reaction tube was connected to a flask in such a manner that the carbon tetrachloride vapor and the chlorine gas were passed through a drying tube of calcium chloride. With the exception of the chlorine gas cylinder, the whole apparatus was located inside a fume hood. As the tantalum pentachloride was formed, it was carried down the sloping reaction tube by the carbon tetrachloride to the lower flask (31).

The carbon tetrachloride solution containing the tantalum pentachloride was mixed in a dry box under a nitrogen atmosphere with a benzene solution containing the previously prepared dimethoxycyclobutenedione. This solution was sealed in a flask with a ground glass joint and set aside to allow time for reaction. After several weeks the solution was filtered in a glove box under a dry nitrogen atmosphere and the residue was fired to determine if it contained carbon.

The residue did not char indicating that it did not contain carbon, thus it was not tantalum(V) squarate.

After previously experiencing difficulty at preparing palladous squarate (7), an attempt was made using a slightly different preparation. In this preparation, 2.5 g. (14 mmol) of palladous chloride were placed in about 250 ml. of water to which a few milliliters of HCl were added to aid in dissolving the palladous chloride. To this solution was added a solution containing 2.0 g (18 mmol) of squaric acid. The squaric acid precipitated almost immediately due to the high hydrogen ion concentration. The solution was set aside to allow time for reaction. After several months the solution was filtered. The precipitate dissolved in water giving an acidic solution. Therefore, it was concluded that the precipitate was unreacted squaric acid, so the wash solution was mixed with the original solution. The solution was then refluxed at 100°C for about an hour at which time the solution had changed from a brown to a colorless solution with a dark gray precipitate. The solution was filtered, and the precipitate was washed with acetone and ether and dried in a vacuum desiccator over calcium chloride. Because the precipitate dissolved in HNO_3 without the visible evolution of carbon dioxide and did not char when it was fired in a porcelaine crucible over a Fisher burner, it was concluded that the precipitate could possibly be palladous oxide which is reported to be a black powder.

Previous attempts at preparing iridium(III) squarate have been unsuccessful (7). Therefore, a new procedure was attempted in which 1.0 g. (3.3 mmol) of iridium trichloride was added to an aqueous solution containing 0.5 g. (4.5 mmol) of squaric acid. This solution was then refluxed for several days. The resulting olive green precipitate was filtered, washed with acetone and ether, and dried in a vacuum desiccator over calcium chloride. A small sample was fired in a porcelain crucible, but it did not char indicating the lack of carbon in the product. Thus, the precipitate was not iridium(III) squarate. The product could possibly be iridium oxide which is olive green in color.