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# Hormone Anchored Metal Complexes 1: Synthesis, Structure, Spectroscopy and *in vitro* Antitumor Activity of Testosterone Acetate: Thiosemicarbazone and its Metal Complexes

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## Soft X-ray photochemistry at the $L_{2,3}$ -edges in $K_3[Fe(CN)_6]$ , $[Co(acac)_3]$ and $[Cp_2Fe][BF_4]^+$

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Soft X-ray photoreduction has been observed in  $K_3[Fe(CN)_6]$ ,  $[Co(acac)_3]$  and  $[Cp_2Fe][BF_4]$ .

**Keywords:** L-edge; photoreduction; soft X-ray;  $K_3[Fe(CN)_6]$ ;  $[Co(acac)_3]$ ;  $[Cp_2Fe][BF_4]$ .

### 1. Introduction

3d L-edge X-ray absorption spectroscopy is potentially a very powerful tool for the investigation of electronic structure in first row transition metal compounds. The well resolved spectra are very sensitive to *oxidation state*, *spin state*, *ligand field* and *local environment*, because there is a strong interaction between the 2p core-hole and the valence 3d orbitals. However, as part of a detailed investigation of the applicability of 3d L-edge XAFS to the study of 3d transition metal complexes we have recently observed spectral changes occurring whilst recording  $L_{2,3}$ -edge X-ray absorption spectra. In particular, we have observed soft X-ray induced photoreduction in some vanadium complexes (Collison *et al.* (1998a)), photoreduction and photoisomerisation in nickel dithiocarbamate and xanthate complexes (Collison *et al.* (1998b)), and soft X-ray induced spin transitions at low temperatures (< 50 K), and photochemistry at all temperatures (50 - 300 K) in  $[Fe(phen)_2(NCX)_2]$  complexes (phen = 1,10-phenanthroline, and X = S, Se) (Collison *et al.* (1997)). In this paper we report further examples of soft X-ray induced photochemistry in a number of iron and cobalt compounds.

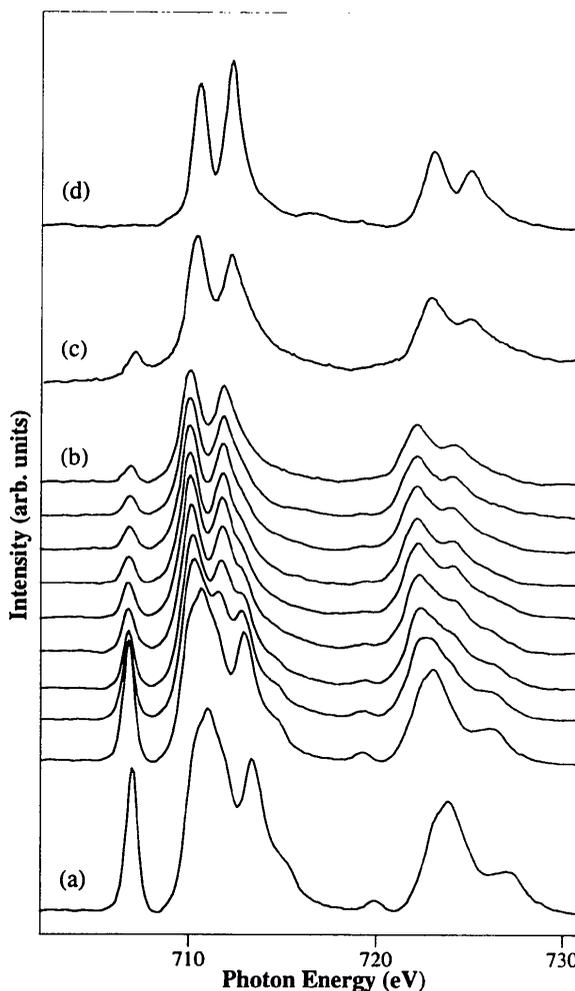
### 2. Experimental

The 3d L-edge data were collected using TEY (both channeltron and drain current) at station 5U.1 on the undulator beamline at the Daresbury SRS, and the details of the experimental facility have been described in detail previously, including the capability

of recording *in-situ* calibration spectra simultaneously (Collison *et al.* (1997)). The Fe L-edge data were calibrated against the  $L_{3-}$  edge features of  $K_4[Fe(CN)_6]$  at 710.35 and 712.05 eV (Peng *et al.* (1995)) and the Co L-edge spectra were calibrated using values of the  $L_{3-}$  edge peaks in  $K_3[Co(CN)_6]$  at 782.7 and 785.5 eV. The sampling depth is related to the electron escape depth and is of the order of 30 - 100 Å. All of the compounds were obtained from commercial sources (Aldrich, BDH, M&B) and used as supplied.

### 3. Results and Discussion

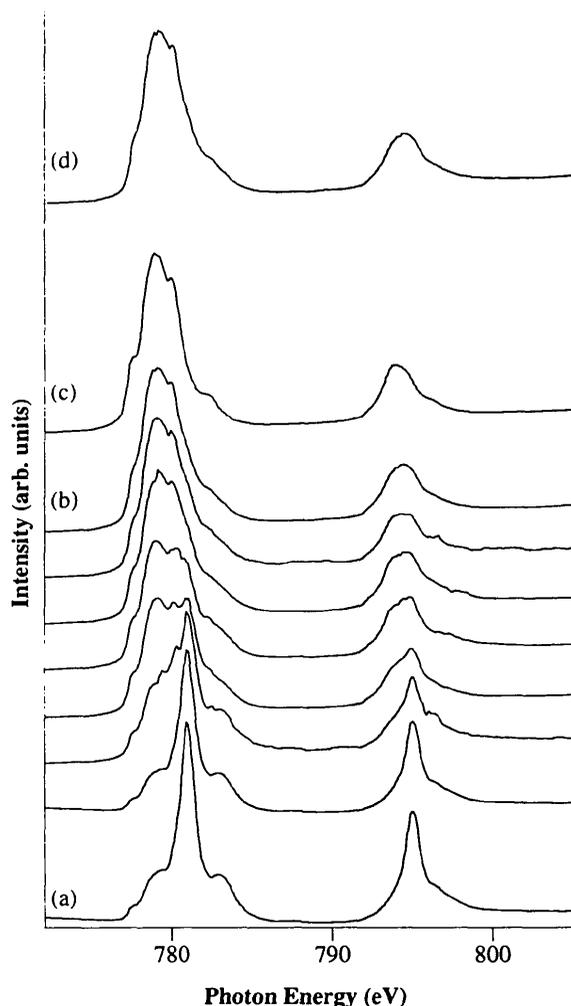
Fig.1 shows the Fe L-edge spectra observed for  $K_3[Fe(CN)_6]$  at room temperature. Fig.1(a) shows the initial spectrum, which is in good agreement with that previously published, (Cartier dit Moulin *et al.*, (1992)) with the sharp feature at 707.1 eV being assigned to a transition from the core 2p orbitals into the hole in the  $t_{2g}$  orbital in  $d^5$  low spin Fe(III). The spectra immediately above it (Fig. 1(b)) are successive spectra recorded for 23 min each at the same sample position. It is immediately obvious that significant changes are occurring, with the loss of intensity of the sharp feature at 707.1 eV, the gradual shift to lower energy of the



**Figure 1**  
Fe L-edge spectra of  $K_3[Fe(CN)_6]$  (a) initial spectrum, (b) successive 23 min spectra, (c) final spectrum, (d) Fe L-edge spectrum of  $K_4[Fe(CN)_6]$ .

\* Soft X-ray photochemistry at the  $L_{2,3}$  edges of 3d transition metal complexes, Part 3. For Part 2 see Collison *et al.*, 1998b.

other  $L_3$  and  $L_2$  features, and a reduction in the overall intensity of both the  $L_3$  and  $L_2$  peaks. The final spectrum is shown in Fig. 1(c), and there is a very considerable difference between this and Fig. 1(a). These changes and the similarity between the final spectrum (Fig. 1(c)) and that of  $K_4[Fe(CN)_6]$  (Fig. 1(d)) are indicative of a reduction in oxidation state as the 2p binding energy is reduced with lower oxidation states, and the intensity of the transitions is directly related to the number of electron holes in the 3d manifold (Wang *et al.* (1998)). Significantly, there were no observable changes during multiple scans at the Fe L-edge for  $K_4[Fe(CN)_6]$ . Whilst the final spectra of the photoreduction of  $K_3[Fe(CN)_6]$  and  $K_4[Fe(CN)_6]$  are not identical, the similarities are strong enough to confirm that in this case when  $K_3[Fe(CN)_6]$  is exposed to soft X-rays it is photoreduced to a species that appears to be very similar to  $[Fe(CN)_6]^{4-}$ . In order to understand more fully the causes of soft X-ray photochemistry we carried out a series of further, detailed experiments on  $K_3[Fe(CN)_6]$ . These have shown that if the sample is exposed to visible light (400 - 700 nm, 200 W Hg-Xe lamp) there is no appreciable change in the Fe L-edge spectra. However, the rate of photoreduction is dependent on the photon flux and the photon energy of the soft X-rays as well as the sample temperature. There appears to be a reasonably linear relationship between photon flux and rate of



**Figure 2**

Co L-edge spectra of  $[Co(acac)_3]$  (a) initial spectrum, (b) successive 20 min spectra, (c) final spectrum, (d) Co L-edge spectrum of  $[Co(acac)_2]$ .

photoreduction with 2 scans at *ca.* 230 mA beam current displaying the same extent of change as 3 scans with a *ca.* 175 mA beam current. If instead of scanning through the spectral energy range, the photon energy is tuned to a particular value and the sample left for a length of time equivalent to one scan, then it is possible to assess how much of a resonance effect there is in the photoreduction. When this was carried out using a photon energy of 697.5 eV, less photoreduction was observed than when 707.0 or 710.9 eV photon energies were used. The rate of change observed for the latter two photon energies was comparable to that observed after scanning through the whole spectrum. Therefore, the photoreduction is greater if one of the L-edge absorption bands is illuminated. To check the temperature dependence a fresh sample was cooled to *ca.* 50 K, and the observed rate of photoreduction was much reduced, with 3 scans at 50 K showing about half the change observed after 2 scans at 298 K. Whilst we have previously observed both photon flux and photon energy dependence in the detailed study of  $[Ni^{IV}(S_2CNET_2)_3][BF_4]$ , temperature dependence was not observed (Collison *et al.* (1998(b))). Whilst the Fe L-edge spectrum of  $K_3[Fe(CN)_6]$  has been reported previously, (Cartier dit Moulin *et al.* (1992)) there was no report of any photochemistry. The observation of soft X-ray induced photoreduction in  $K_3[Fe(CN)_6]$  is no surprise, as there have been several reports of detailed studies into the kinetics of photoreduction during XPS experiments, (Oku (1993), Oku (1994)).

Prolonged exposure to soft X-rays during sequential scanning of  $K_3[Co(CN)_6]$  (Fig. 3(c)) did not result in any spectral changes. However, we have observed significant changes occurring in the spectra of  $[Co(acac)_3]$  on prolonged exposure to soft X-rays. Fig. 2(a) shows the initial spectrum recorded for  $[Co(acac)_3]$ , with the successive spectra shown in Fig. 2(b) and the final spectrum in Fig. 2(c). As in the case of  $K_3[Fe(CN)_6]$  there are very significant changes occurring when  $[Co(acac)_3]$  is left exposed to soft X-rays. The changes observed are consistent with a reduction from a Co(III) centre to a Co(II) centre, and this is confirmed by the striking comparison of the final spectrum (Fig. 2(c)) with that of  $[Co(acac)_2]$  shown in Fig. 2(d), which itself showed no changes on subsequent exposure to soft X-rays. When the experiments were carried out at *ca.* 50 K, there was still appreciable photoreduction, of the order of half of that observed at room temperature. Therefore, whilst reducing the temperature at which the experiment is carried out, may reduce the likelihood of photochemistry, this is not necessarily always going to be the case. As for  $K_3[Fe(CN)_6]$ , photoreduction of  $[Co(acac)_3]$  in organic solvents by near-ultraviolet irradiation to give  $[Co(acac)_2]$  has been previously reported (Filipescu and Way (1969)).

To assess the relationship between the ease of photoreduction and known oxidising properties, the metal L-edge spectra of  $[Cp_2Fe][BF_4]$  and  $[Cp_2Co][PF_6]$  were recorded (Fig. 3). The initial (lower) spectrum of  $[Cp_2Fe][BF_4]$  has a low energy feature similar to that in the spectrum of  $K_3[Fe(CN)_6]$ , consistent with an  $a_{1g}^2 e_{2g}^3$  electronic configuration. (Deeming (1982)) On further exposure to soft X-rays the spectra change, with the most marked differences being the change in relative intensities of the low energy feature and the main  $L_3$  peak, the change in branching ratio and the shift of *ca.* 0.2 eV of the main  $L_3$  peak to lower energy. Whilst it would have been attractive to measure the spectra of  $[Cp_2Fe]$  this is too volatile for use in the UHV chamber. Therefore, the spectrum of  $[Cp_2Co][PF_6]$  (Fig. 3(b))

was collected as this is expected to have a similar L-edge spectrum as both will be low spin  $d^6$  complexes, and this was confirmed by comparison with the ISEELS spectrum of  $[\text{Cp}_2\text{Fe}]$  (Hitchcock *et al.* (1990)). Whilst it is not completely clear whether the photoproduct of  $[\text{Cp}_2\text{Fe}][\text{BF}_4]$  leads to a formal Fe(II) product, there is evidence that  $[\text{Cp}_2\text{Fe}][\text{BF}_4]$  is photochemically altered on exposure to soft X-rays. In contrast, we could detect no difference in the successive spectra of  $[\text{Cp}_2\text{Co}][\text{PF}_6]$ , and this correlates well with the known oxidising and reducing powers of  $[\text{Cp}_2\text{Fe}][\text{BF}_4]$  and  $[\text{Cp}_2\text{Co}][\text{PF}_6]$ , respectively.

#### 4. Conclusions

It is clear from this work that soft X-ray photochemistry is probably more prevalent and pernicious than previously recognised. Therefore, we recommend that steps such as multiple scans at the same sample position using a simultaneous *in-situ* calibration device be taken either to confirm or to rule out its presence in spectra. One possible explanation for the lack of previously reported photochemistry in 3d L-edge experiments is that the experiments described herein were carried out on an

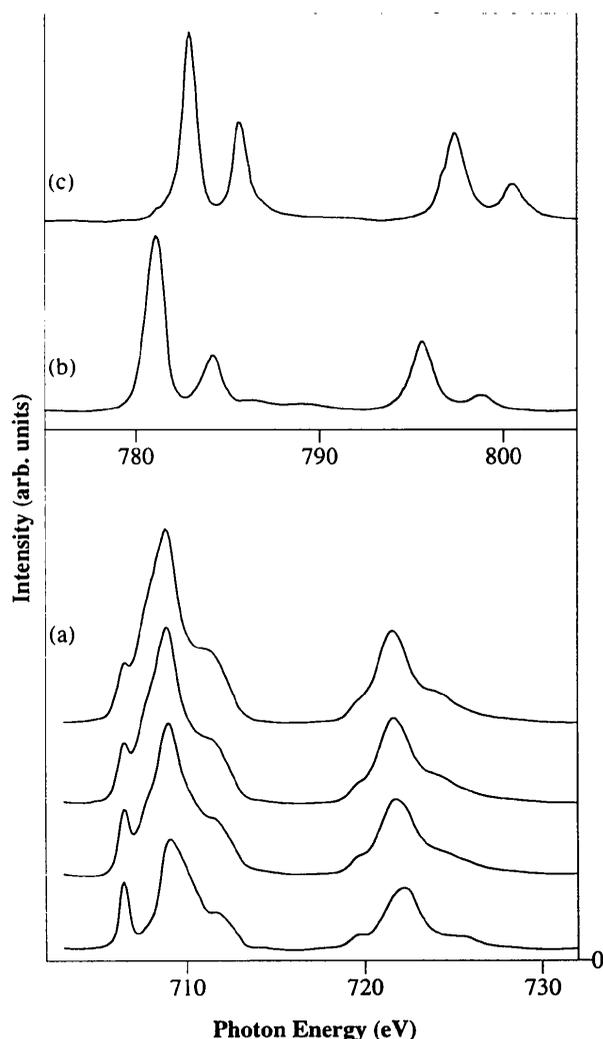
undulator beamline with focusing optics, which will deliver a higher photon flux to the sample compared to a bending magnet beamline. Therefore, there might be severe implications for the use of 3<sup>rd</sup> generation synchrotron sources for carrying out 3d L-edge experiments, and in particular those that use micro-focusing techniques.

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**Figure 3**

(a) Successive Fe L-edge spectra of  $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ , (b) Co L-edge spectrum of  $[\text{Cp}_2\text{Co}][\text{PF}_6]$  and (c) Co L-edge spectrum of  $\text{K}_3[\text{Co}(\text{CN})_6]$ .