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K-Absorption Spectral Correlations on some Copper Complexes Involving Sulphur Ligands

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K–absorption edges of copper in complexes formed with some organic sulphur ligands have been investigated. Correlation of the shape of absorption coefficiet curves vis-a-vis coordination symmetry has been attempted using essentially the crystal field approach. The relative positions of the absorption maxima in these complexes have been shown to be related to the covalent bond strength of the metal-sulphur bond (nephelauxetic effect). Suggestions with regard to the positions of these sulphur-ligands in the spectrochemical series have also been made.

Introduction

The role of X-ray absorption spectroscopy in providing concrete details about the optical levels and the coordination sphere of a particular metal ion in a complex, has, in recent years, shown considerable promise.[1-5] The structure of the absorption edge of the central metal has been of unique value in solving many stereochemical problems when many other physicochemical methods such as X-ray diffraction (when the sample is amorphous) and magnetic measurements fail to give unambiguous results.[3] However, exhaustive interpretative procedures directed to explain the absorption edge features completely, have yet not been satisfactorily developed.

The element sulphur offers an interesting case for observing the effect of chemical combination on X-ray spectra[6] and has been extensively studied from this stand point.[7-9] In regard to complexes involving some transition metals and ligands containing sulphydryl (–SH) group this element has been known to possess pronounced coordinating ability in comparison to other donors such as oxygen. This has been attributed to (i) its capacity to bring about *d*–orbitals into hybridization with *s* and *p* orbitals increasing its maximum coordination number to six, (ii) the feasibility of bond formation resulting from overlap with its *p* and *d* orbitals (low promotion energies make d–participation possible), and (iii) its low effective nuclear charge resulting in enhanced strength of σ and π types of bonds.[10,11] However, the position of sulphur ligands in the spectrochemical series[12] which is an increasing order arrangement of the spectroscopic splitting parameter, is not yet properly understood. While it is more appropriate to discuss the position of these sulphur ligands in the spectrochemical and nephelauxetic series[13,14] using data from electronic absorption spectra of the complexes, an attempt has been made in the present paper to examine if the X-ray absorption spectroscopic data can be used for such coorelations. This may also contribute to the study of the nature of the metal-sulphur bond in the complexes.

Experimental Section

Measurements have been made on copper complexes of (β) thiopropionic acid–$[Cu(C_3H_5O_2S)_2\text{-}(H_2O)_2]$. Thio Salicylic Acid$[H_2(Cu(C_7H_5O_2S)_4(H_2O)_2]$, Carboxy methyl mercapto succinic acid $[H_2(Cu(C_6H_5\text{-}O_6S)(H_2O))]$ and Thio Vanol $[–Cu–SCH_2CHOHCH_2–O–Cu–]_n$. The compounds $CuSO_4 . 5H_2O$ and Cu^{II}–pyridine $[Cu(py)_4]SO_4$ have also been included for the sake of comparison. The complexes have been prepared under specified conditions[15-18] starting from $CuSO_4 . 5H_2O$ which was of analytical reagent grade. The formulae and structures proposed for them were earlier arrived at by Nigam and coworkers[15-18] using a number of analytical and physico-chemical methods, the details of which may be found elsewhere.[15-18]

X-ray absorption studies were carried out on a Machlett sealed X-ray tube having a tungsten target which was operated at 16 KV and 12 mA. A 40 cm radius Cauchois type curved crystal spectrograph using $(-\bar{2}01)$ reflection planes of mica as analyser was employed to record the spectra on Ilford X-ray films. The set up was standardized by resolving the $MoK\beta_{1,3}$ doublet in the first order which gave a disper-

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sion of about 12 x.u. per mm. The reference lines used were $L\alpha_1$, $L\alpha_2$, $L\beta_1$, and $L\beta_4$ of tungsten. The absorption screens were prepared by evenly spreading the substances in fine powder form on Scotch tape. Suitable thin screens were preferred and were placed between the X-ray tube window and the analysing crystal. The exposure time varied from 15 to 20 hrs. Several spectrograms were taken for each sample. The microphotometer records were taken on a Kipp and Zonen Moll microphotometer with magnifications 50 X and 8 X, the latter having been used for measurements. The absorption coefficient versus energy curves have been shown in Figure 1 in which the energy is based on the inflection point of the K-edge in metal as zero. Table I contains the wavelength and energy (ν/R) positions of the K-absorption maxima of copper in the various complexes studied.

Table I.

Complex	λ abs. max. in x.u. ± 0.05	(ν/R)
1. $CuSO_4.5H_2O$	1375.19	662.65
2. Cu-pyridine	1374.72	662.88
3. Cu-TPA	1374.87	662.80
4. Cu-TSA	1374.50	662.98
5. Cu-EA3CS	1374.38	663.04
6. Cu-TV	1376.13	662.46

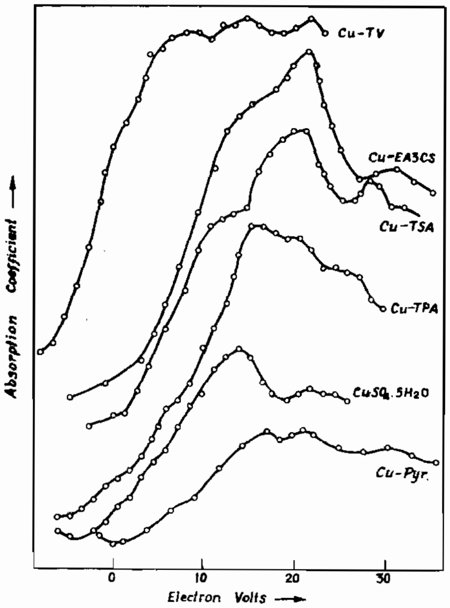

Figure 1.

Results and Discussion

It can be observed from the absorption coefficient curves as also from the data in Table I that the absorption maxima in the various complexes exhibit a gradual shift to the high energy side which is in the sequence $CuSO_4 . 5H_2O \rightarrow Cu–TPA \rightarrow Cu–TSA \underset{=}{\rightarrow} Cu–EA3CS$. The K-absorption peak in case of the compounds of first transition series metals has been assigned a transition $1s \rightarrow 4p^*$ (antibonding) by Cotton and Hanson[19] and others.[20] Glen and Dodd[20] have observed a similar high energy shift in the position of the main peak in the K absorption spectra of cobalt in the three complexes $Co(Et_4dien)X_2$ [$Et_4dien = HN\text{-}[CH_2CH_2N(C_2H_5)_2]_2$] where X=Br, NCS, N_3 in the order $N_3 > NCS > Br$ and have thereby suggested that the covalent bond strength of Co–X bond is in the same order. It seems plausible to explain the shifts of the peaks in our complexes in a similar manner. $CuSO_4 . 5H_2O$ may well be expected to be more ionic than any of these complexes. Similarly Cu–TSA is supposed to be more covalent than Cu–TPA. Such an enhanced covalent bond strength due to the ligand thio salicylic acid as compared to thio propionic acid has been shown earlier by the present authors from their L_{III}-edge-shift studies[21] of some lead complexes formed with these ligands as also from their infrared spectral investigations.[21] Including Cu-pyridine in the series, we find that the corresponding absorption maximum energetically lies, as expected, in between the oxy-coordinated $CuSO_4 . 5H_2O$ and the sulphur-donor complexes of Cu^{II}, excepting however, Cu–TPA. The sequence assignable to the various ligands involved here on the basis of the relative energies of the principal absorption maxima in the respetive complexes thus seems to agree, in general, with their tentatively assigned positions in the nephelauxetic series

$$\text{----}\, RS^- > \text{----} > C_5H_5N \approx NH_3 > H_2O$$

This is also supported by the results of our investigations[22] on the width of the K-absorption edges of copper in these complexes.

The complexes Cu–TSA and Cu–TPA have been shown earlier on the basis of their electronic absorption, infrared and EPR studies to possess a distorted octahedral symmetry (respectively D_{4h} and D_{2h}).[15,16] A broad band has been observed in the electronic spectra at 15600 cm^{-1} corresponding to the electronic transition $2E_g \rightarrow T_{2g}$ as is usually observed with octahedral Cu^{II} complexes.[23] Further, Lewis and Figgis[24] have described that the broad nature of the band corresponds to Jahn-Teller distortion.[23-24] For Cu^{II} EA3CS no conclusive evidence for the symmetry obtaining in the complex is available.[17] However a comparison of the values of the K-edge shifts of copper in these three complexes[25] favours a tetrahedral configuration for Cu–EA3CS, as suggested earlier.[17] The K-edge shifts for Cu^{II}TPA, Cu^{II}TSA, and Cu^{II}EA3CS have been found to be respectively 7.0 eV, 5.1 eV, and 5.4 eV. It may be noted that the bonding assignment dsp^2 for a square planar configuration for Cu^{II}EA3CS, as normally expected would require a relatively much smaller edge shift since the main edge in this hybridization would correspond to $1s \rightarrow$partially vacant $4p$

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where as in the other two complexes it would be 1s→ 4p* antibonding.[19,20] A somewhat broadened out peak indicates[20] a distorted tetrahedral symmetry.

The Cu–pyridine complex has four pyridine–nitrogens in a square plane with the octahedral coordination being completed by two oxygen atoms from sulphate ions as in the case of $Cu(NH_3)_4(NO_3)_2(D_{4h})$.[5] It may be noted that the absorption maximum in case of Cu–pyridine has been split up into two components as expected from the theory developed by Cotton and Ballhausen[26] with regard to the symmetry-dependent crystal field splittings of the metal *p*–orbital degeneracy. $Cu(NH_3)_4(NO_3)_2$ has also been shown to cause a similar splitting[5] (Figure 2a). It is well known that ammonia and pyridine occur close together in the spectrochemical series. In the rest of cupric complexes we observe that only in the case of Cu–TPA does the peak split up apparently into two rather broad maxima. Such a splitting has been observed by Cotton and Hanson[5] in case of Cu^{II} DL–prolinate dihydrate (Figure 2c) which according to X-ray studies,[27] appears to possess the same coordination symmetry as that of Cu–TPA, there being, in the latter, sulphur atoms in place of nitrogen. In Cu–TSA, which has a symmetry analogue in $Cu(NH_3)_4(NO_3)_2$ or $Cu(py)_4SO_4$ mentioned above, however, no splitting and only a general broadening can be observed.

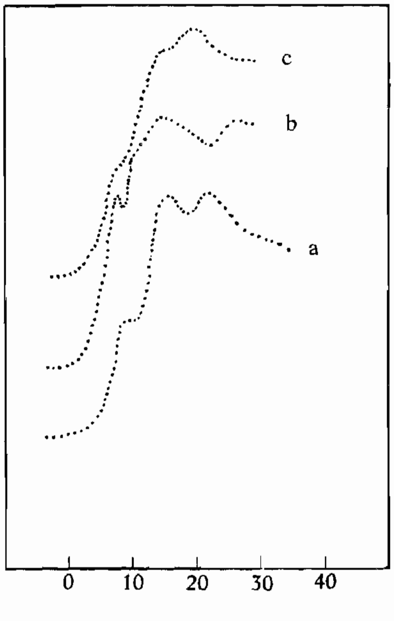

Figure 2.

This may be due to one or more of the following reasons and symmetry considerations alone may not always explain the present feature.[19]

(i) In the spectrochemical series, ammonia finds a place much higher than that tentatively assigned to sulphur donor groups which may therefore be unable to cause as large a splitting.

(ii) The splitting, which just shows up in case of Cu–TPA and which is altogether absent in Cu–TSA, may be due to the former having a lower symmetry of the coordination sphere and hence greater distortion of the crystal field, than the latter.

(iii) The theory due to Cotton and Ballhausen[26] is limited to systems involving largely ionic metal-ligand interactions whereas in Cu–TSA the bond is expected to be appreciably covalent.

Copper-Thio Vanol - the yellow Cu^I complex, as shown by Nigam and Pandeya,[18] is polymeric consisting of linear chains of [-R-O-Cu-S-R-]. Figure 1 shows that this complex exhibits an unusual peak structure involving extensive broadening (and probably some splitting). This may be explained by the metal being surrounded by one oxygen and one sulphur as nearest neighbours on all the three axes by virtue of possessing a spiral polymeric structure as pointed out earlier on the basis of our edge-width studies.[22] A greatly resembling peak-structure has been observed by Cotton and Hanson[5] in case of anhydrous cupric chloride (yellow brown) (Figure 2b) which has been found[28] to contain, in the solid state, infinite chains of copper ions connected by chloride bridges giving square coordination about each copper (Cu–Cl, 2.29 A) with chloride ions from other chains filling out the six-fold coordination shell at 2.98 A.

The shoulder appearing more or less on all the curves at ~10 eV lower energy with respect to the main peak may be assigned, as suggested by Glen and Dodd,[20] a normally disallowed transition 1*s*→4*s** (antibonding). It may be noted that in Zn^{2+} which provides a close approximation to the K-excited Cu^{2+} ion, the configurations $3d^94s$ and $3d^94p$ are about 10 eV apart.[29] In Cu^{2+}, therefore, the 1*s*→4*s** absorption may well be expected to occur ~10 eV below 1*s*→4*p** as observed. The transition may become allowed as a result of mixing with ligand p-orbitals which may thus result in some delocalization of the 4*s* orbitals. The effect appears to be more pronounced in the more covalent Cu–TSA and Cu–EA3CS for which this absorption appears to be considerably broadened.

The peaks subsequent to the maxima may be attributed either to 1*s*→*np* ($n \geq 5$) transitions as usual or to the interaction with the antibonding π levels of the ligand.[20] The π bonding system is known to be present in sulphur donors in general and in thio salicylic acid in particular in which case this peak is rather prominent. In one or two cases *e.g.* Cu–TPA a low energy absorption, presumably corresponding to 1*s*→(partially vacant) 3*d* apepars faintly.

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