Co-ordinaton Stoicheiometry and Edge-width in X-Ray Absorption Spectra—a Correlation

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Summary The X-ray absorption edge-width of the central metal in a complex is found to be quantitatively related to co-ordination stoicheiometry expressed in terms of the overall metal–donor electronegativity difference.

X-RAY absorption spectroscopy has been used for investigating many problems of structural-chemical importance,[1] particularly in the field of co-ordination chemistry. However, a very important feature of these spectra, *viz.* the width of the absorption edge, has not been sufficiently exploited. Keeling[2] has defined edge-width as the difference in energy between the inflection point and the main absorption maximum of the edge. Figure 1 shows a typical
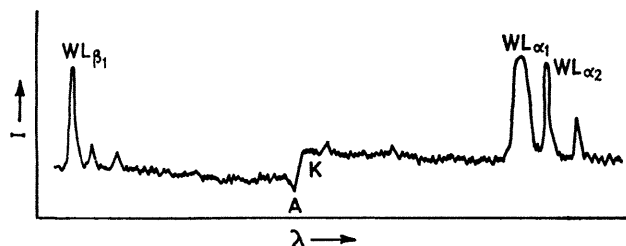

FIGURE 1. K-*Absorption edge of copper in* Cu–tpa.

microphotometer trace of the K-absorption edge of copper in Cu–thiopropionic acid complex and the difference in energy between A and K, as marked in the Figure, defines the edge-width. He has shown that the edge-width of Co²⁺ is significantly greater for compounds containing cobalt in tetrahedral sites than for those having the metal in octahedral sites. The vexed question of the co-ordination symmetry of Co²⁺ in Co[Al₂]O₄ spinel has been decided on this basis.

We have attempted (perhaps for the first time) to seek at least a semiquantitative correlation between the edge-width of the metal and the number and nature of the surrounding atoms in terms of the overall electronegativity difference between them. The latter in turn has been evaluated from 'co-ordination stoicheiometry', defined as the ratio of the central metal atom to the number of nearest neighbours. The observations relate to a series of copper complexes involving sulphur ligands. L_{III} edge-widths of lead in similar complexes have also been included. The nature of the metal–sulphur bond in these complexes has been extensively studied using a number of physico-chemical methods, as well as X-ray absorption spectroscopy.[3,4]

The X-ray absorption spectra were recorded photographically, employing a 40 cm radius curved crystal spectrograph using (201) reflection planes of mica as analyser. The system, standardized by resolving the $Mo_{\beta1,3}$ doublet ($\Delta\lambda = 0.57$ x.u.) gave a dispersion of about 12·5 x.u. per mm in the first order. A Machlett sealed X-ray tube with a tungsten target was used as the source of radiation. Microphotometer recordings were taken on a Kipp and Zonen

Moll microphotometer with magnification 8X which gave dispersions of *ca.* 10 eV and 21 eV per mm in the Cu-K and Pb-L_{III} regions, respectively. The energy separation between the inflection point and the absorption maximum was measured to give the edge-width. Other experimental details may be found elsewhere.[3,4]

The Table shows the co-ordination stoicheiometries of the complexes, together with the K and L_{III} edge-widths, respectively, of copper and lead in them. As the stoicheiometry varies as a result of the gradual replacement of metal–oxygen bonds by metal–sulphur ones (Nos. 1—4, Table) the edge-width shows a marked increase in its value. A variation in the proportion of sulphur and oxygen atoms
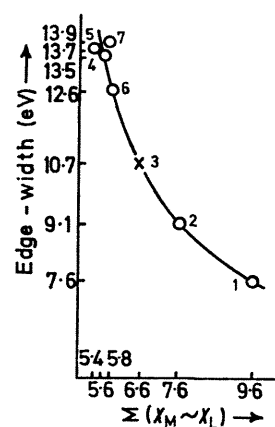

FIGURE 2

(which differ appreciably in their electronegativities) around copper is expected to effect a marked variation in the value of $(X_M \sim X_L)$. This quantity has been defined here as the sum of the individual metal–nearest neighbour electronegativity differences $(X_M \sim X_L)$ for all the atoms in the co-ordination sphere $(X_L$, *i.e.*, the electronegativity of the surrounding atoms, taken as usual from Pauling's scale,[5] is, as a first approximation, uncorrected for intra-ligand bonding). Figure 2 shows a plot of edge-widths and $\Sigma(X_M \sim X_L)$ for all the complexes listed in the Table. All points including those corresponding to lead complexes, lie close to a smooth curve, suggesting the existence of a close correlation between the edge-widths, as determined from the spectra, and the co-ordination stoicheiometry involved in the complex. The curve, resembling a rectangular hyperbola, leads us to suggest an empirical relationship:

$[\Sigma(X_M \sim X_L)\cdot$edge-width$]^{\frac{1}{2}}$ = constant for a given metal which, we find, can be verified using data in the literature.[2,6] The average values of the constants for cobalt and copper, both of first transition series, are respectively 7·7 and 8·5, while those for zirconium and niobium, both of the second transition series, are respectively 16·4 and 19·1.

As an illustration, we may consider the copper–thiovanol complex (experimental edge-width = 10·7 eV, *vide* Table).

copper has an effective co-ordination number of 3 by virtue of a spiral polymeric structure.

TABLE

No. on the curve (Fig. 2)	Complex	Co-ordination stoicheio-metry[a] M:S:O	$\Sigma(X_M \sim X_L)$	λ_k (x.u.) ±0·05	λ_A (x.u.) ±0·05	Edge-width $\lambda_k - \lambda_A$ (x.u.)	Edge-width Δ eV ±0·6 eV
1.	CuSO$_4$,5H$_2$O	1:–:6	9·6	1376·33	1375·19	1·14	7·6
2.	Cu–thiopropionic acid Cu(tpa)$_2$,2H$_2$O	1:2:4	7·6	1376·40	1374·87	1·53	9·1
3.	Cu–thiovanol (Cu–tv)$_n$	1:3:3[b]	6·6	1377·21	1375·57	1·64	10·7
4.	Cu–thiosalicylic acid Cu(tsa)$_4$,2H$_2$O	1:4:2	5·6	1376·54	1374·50	2·04	13·5
5.	Cu–carboxymethylmercapto-succinic acid Cu(ea3cs),H$_2$O ..	1:1:3	5·4	1376·47	1374·38	2·09	13·7
6.	Pb–thiopropionic acid Pb(tpa),2H$_2$O	1:1:3	5·8	948·75	947·83	0·92	12·6
7.	Pb–thiosalicylic acid Pb(tsa),2H$_2$O	1:1:3	5·8	948·56	947·46	1·1	13·9

[a] M = Cu, Pb; [b] Interpolated.

On the graph this would have an abscissa value of 6·6. A stoicheiometry of Cu:S:O::1:3:3 would give the same value theoretically. This complex has been shown earlier by Nigam and Pandeya[7] to be polymeric, consisting of linear chains of $(-O-Cu^L-S-R-O-Cu^L-)_n$, giving a sulphur–oxygen ratio of 1:1. This may be explained by considering the possibility that in the solid state the complex may possess a spiral polymeric structure, by virtue of which the copper atom in it may become surrounded by one sulphur and one oxygen along each of the three-dimensional axes, thus making the co-ordination stoicheiometry agree with that interpolated from edge-width. Such a modification in the solid state is well known for $K[Cu(CN)_2]$[8] in which

It may be noted that the edge-width is least for CuSO$_4$,-5H$_2$O (Table) which is expected to be more ionic than all the other copper complexes studied herein. In the case of Cu–tpa and Cu–tsa, the edge-width for the latter, in which the metal–ligand bond may be expected to be more covalent, is found to be greater than that due to former. Similarly, the edge width for Pb–tsa is greater than that for Pb–tpa. On the basis of studies on the L_{III} absorption edges of lead in these complexes, we have earlier arrived at a similar conclusion.[3]

[1] R. L. Barinskii, *Zhur. strukt. Khim.*, 1967, **8**, 897.

[2] R. O. Keeling, jun., "Developments in Applied Spectroscopy", Plenum Press, New York, 1963, vol. 2, p. 263.

[3] U. C. Srivastava, H. L. Nigam, and A. N. Vishnoi, *Indian J. Pure Appl. Phys.*, 1971, **9**, 63.

[4] U. C. Srivastava, H. L. Nigam, and A. N. Vishnoi, *Indian J. Pure Appl. Phys.*, in the press; H. L. Nigam and U. C. Srivastava *Inorg. Chim. Acta*, in the press.

[5] L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960.

[6] H. L. Nigam and U. C. Srivastava, *Z. Naturforsch.*, submitted for publication; M. Obashi, Scientific Report No. 10, College of General Education, Osaka University, 1961; G. B. Deodhar, "Röntgenspektren und Chemische Bindung", Vortrage des Internationalem Symposium (Leipzig: Physikalich-Chemisches Institut der Karl-Marx Universitat) 1966, p. 65; A. N. Nigam, personal communication.

[7] H. L. Nigam and K. B. Pandeya, *Indian J. Chem.*, 1970, **8**, 454.

[8] F. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley, New York, 1966, p. 896.