K-Absorption Spectra and the Nature of Metal–Ligand Bond in Some Cobalt Complexes

V. KRISHNA, J. PRASAD and H. L. NIGAM

Chemistry Department, University of Allahabad, Allahabad-211002, India

Shifts and widths of the K-absorption edge of cobalt in a specifically chosen variety and number of complexes involving donor atoms like nitrogen, oxygen and sulphur have been measured using a bent crystal spectrograph. The expected change in ionic/ covalent character of the metal–ligand bond in these complexes on the basis of Pauling's electronegativities and also observed from the optical spectra (where known) appears to be reflected in their X-ray edge-shifts and widths.

Introduction

Several correlations [1–5] between X-ray absorption spectral measurements and the various stereochemical parameters concerning transition metal complexes have been reported during the last decade. Much remains to be done, however, to arrive at a comprehensive theory underlying the relationship between X-ray absorption spectra and the nature of metal–ligand bond involved in the complexes. In this paper a number of cobalt complexes formed with a variety of ligands involving nitrogen, oxygen and sulphur as donors have been taken up for their K-absorption spectral investigations. The edge-shift and edge-width measurements have been interpreted to gauge the relative influence of the nature of metal–donor interactions on them. Optical data available for some of the complexes have been used to substantiate these conclusions.

Experimental

One set of compounds constitutes the divalent cobalt complexes: $H_2[Co(TDSA)\cdot 4H_2O]$, $Na_2[Co-(\alpha\text{-}MPA)_2\cdot 2H_2O]$, $Na_2[Co(DMAET)_2(OH)_2]\cdot 2H_2O$ and $Co(PhTT)_2$ where abbreviations TDSA, α-MPA, DMAET and PhTT are used for Thiodisalicylic acid, $C_6H_3(OH)(COOH)\cdot S\cdot C_6H_3(OH)(COOH)$, α-Mercaptopropionic acid, $CH_3\cdot CH(SH)\cdot COOH$, Dimethylaminoethanethiol, $N(CH_3)_2\cdot CH_2\cdot CH_2\cdot SH$ and 1-Phenyltetrazoline-5-thione, $C_7H_6N_4S$, respectively. The methods of preparation and the structures proposed for them are described elsewhere [6–9].

$CoSO_4\cdot 7H_2O$ has also been included for the sake of comparison. A second set of compounds comprises the trivalent amine complexes $[Co(NH_3)_4(CO_3)]NO_3$, $[Co(NH_3)_4(NO_2)_2]NO_3$ and $Co(NH_3)_3(NO_2)_3$ earlier described by Biltz and Biltz [10].

A Machlett sealed X-ray tube with a tungsten target was operated at 20 kV and 10 mA to get the continuous radiation. A 40 cm radius Cauchois type curved crystal spectrograph was used to record the spectra in the first order on Kodak X-ray films. The spectrographic set up, using (100) reflection planes of mica as analyser was able to resolve $MoK_{\beta 1,3}$ doublet which gave a dispersion of about 12 X.U. per mm amounting to 59 eV mm^{-1} in the region of cobalt K-edge. The reference lines used were $K_{\alpha 1,2}$ of nickel and copper which were present as impurities in the tungsten target. Details regarding the preparation of absorbing screen, microphotometering arrangement and method of measurements have been described elsewhere [11]. Actual measurements were made from the microphotometer records, having a magnification of 8.

Results and Discussion

Figure 1 is a typical microphotometric trace (8X) of $CoSO_4\cdot 7H_2O$. In Table I are given the shifts of Co K-absorption edge in various complexes. Table II shows the widths of the absorption edge *i.e.*, the energy difference between the main edge, K, and the principal absorption maximum, A (Fig. 1). Table III depicts ligand field splitting energy, 10 Dq, nephelauxetic ratio, β, and ligand field stabilization energy (LFSE) for divalent complexes.
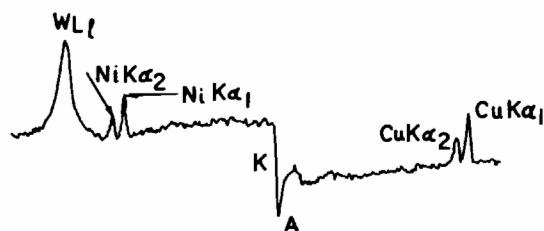

Fig. 1. Microphotometer record of K-absorption edge in $CoSO_4\cdot 7H_2O$.

TABLE I. Shifts in the K-Absorption Edge of Cobalt Sulphate and the Complexes.

Metal Ion	Compound	λ_K(X.U.) ± 0.05	$(\nu/R)_K$	$\Delta(\nu/R)$	Δ eV ± 0.6
Co(0)	Co (metal)	1604.7	567.87	–	–
Co(II)	Co–TDSA	1603.15	568.43	0.56	7.6
	Co–PhTT	1603.10	568.44	0.57	7.7
	Co–DMAET	1602.95	568.50	0.63	8.6
	Co–MPA	1602.85	568.53	0.66	8.9
	$CoSO_4 \cdot 7H_2O$	1602.55	568.64	0.77	10.4
Co(III)	$[Co(NH_3)_4(CO_3)]NO_3$	1602.44	568.67	0.80	10.8
	$[Co(NH_3)_4(NO_2)_2]NO_3$	1602.29	568.73	0.86	11.7
	$Co(NH_3)_3(NO_2)_3$	1601.59	568.98	1.11	15.1

TABLE II. Widths of the Absorption Edges.

Compound	λ_A(X.U.) ± 0.05	$(\nu/R)_A$	λ_K(K.U.) ± 0.05	$(\nu/R)_K$	$\Delta(\nu/R)$	Edge-width, eV ± 0.6
$CoSO_4 \cdot 7H_2O$	1601.42	569.04	1602.55	568.64	0.40	5.4
Co–TDSA	1601.95	568.85	1603.15	568.43	0.42	5.7
Co–MPA	1601.42	569.04	1602.85	568.53	0.51	6.9
Co–DMAET	1601.39	569.05	1602.95	568.50	0.55	7.4
$[Co(NH_3)_4(NO_2)_2]NO_3$	1600.91	569.22	1602.29	568.73	0.49	6.7
$[Co(NH_3)_4(CO_3)]NO_3$	1601.05	569.17	1602.44	568.67	0.50	6.8
Co–PhTT	1601.48	569.02	1603.10	568.44	0.58	7.8

TABLE III. Ligand Field Parameters of Some Cobalt Complexes.

Compound	Ligand Field Splitting Energy 10 Dq (cm^{-1})	Nephelauxetic Ratio (β)	Ligand Field Stabilization Energy (Kcal/mol)
Co–TDSA	11,110	0.77	18.99
Co–MPA	12,240	–	21.9
Co–DMAET	12,900	0.65	29.4
Co–PhTT	4842	0.61	–

As evident from Table I, the edge-shifts for the Co(III) complexes are significantly greater than that for $CoSO_4 \cdot 7H_2O$ and other Co(II) complexes. This, obviously, is the valency effect. Further, the energy difference of 4–5 eV between the two oxidation states agrees well with the results of other workers [12, 13]. A perusal of edge-width data would clearly show that the value for Co–PhTT is the largest amongst all the complexes under study. It is the only complex which has been shown [9] to be unusually tetrahedral whereas the rest of the complexes are octahedral. The larger values of edge-width for tetrahedral coordination than octahedral coordination was also reported by Keeling [14]; thus controversial coordination symmetry around Co^{2+} in $Co[Al_2]O_4$ was decided on this basis.

Observing the edge-shift and edge-width values for the complexes belonging to the same oxidation state,

it may be seen that edge-widths, unlike the edge-shifts, tend to show an increase in their magnitude with increase in the covalent character of the metal–ligand bond. The edge-shift due to $CoSO_4 \cdot 7H_2O$ is observed to be the highest whereas the edge-width is the smallest amongst all the complexes. This compound may well be expected to be comparatively more ionic than all the other complexes studied here. Further, comparing it with the Co–TDSA complex it is found that although the octahedron in either case consists of oxygen chromophore, CoO_6, the Co–TDSA complex is different in having a ring closure in which the bidentate ligand holds the metal ion through carbonyl groups. Ring closure is known to provide a somewhat enhanced covalent character of the metal–ligand bond. In the Co–MPA complex, two of the oxygens of CoO_6 chromophore in $CoSO_4 \cdot 7H_2O$ may be imagined to be replaced by two sulphur

TABLE IV. A Correlation between Edge-width and Coordination Stoichiometry in Some Cobalt Complexes.

No. on the Curve (Fig. 2)	Complex	Coordination Stoichiometry M:O:S:N	$\Sigma \|X_M - X_L\|$	Edge-width	$[(E.W) \cdot \Sigma \|X_M - X_L\|]^{\frac{1}{2}}$
1	$CoSO_4 \cdot 7H_2O$	1:6:−:−	10.2	5.4	7.4
2	Co−TDSA	1:6:−:−	10.2	5.7	7.6
3	Co−TLA	1:4:2:−	8.2	7.0	7.6
4	Co−DMAET	1:2:2:2	7.2	7.4	7.3
5	$[Co(NH_3)_4(NO_2)_2] \cdot NO_3$	1:2:−:4	8.2	6.7	7.4
6	$[Co(NH_3)_4(CO_3)]NO_3$	1:2:−:4	8.2	6.8	7.5
7	Co−PhTT	1:−:4:4[a]	7.6	7.8	7.7

[a] Computed from edge-width.

atoms, having lower electronegativity. In the Co−DMAET complex, the coordination sphere consists of two sulphur and two nitrogen atoms in addition to two oxygen atoms. The electronegativity difference between the central metal ion and the donors would thus be further lowered resulting in an overall increase in the covalent character of the bond. Thus, it is found that the sequence of decreasing edge-shifts for the complexes is the same as that of increasing edge-widths, the only exception being the Co−TDSA complex:

Edge shift: $CoSO_4 \cdot 7H_2O >$ Co−MPA >
Co−DMAET > Co−PhTT > Co−TDSA

Edge-width: $CoSO_4 \cdot 7H_2O <$ Co−TDSA <
Co−MPA < Co−DMAET < Co−PhTT

It is interesting to note that a comparison of the relevant optical data available for these complexes (Table III) also leads to a similar conclusion.

Considering the Co(III) complexes, it is seen that in $[Co(NH_3)_4(CO_3)]NO_3$ and $[Co(NH_3)_4(NO_2)_2]NO_3$, the metal ion is surrounded in each case by four nitrogen and two oxygen atoms and thus has a nearly resembling donor environment. The proximity in the magnitude of edge-shifts as well as edge-widths for the two complexes would thus be obvious. However, the smaller edge-shift in the case of $[Co(NH_3)_4-(CO_3)]NO_3$ may be attributed to a somewhat enhanced covalency resulting from ring formation by the bidentate carbonate group. In the complex $Co(NH_3)_3(NO_2)_3$, the number of oxygen donors is raised to three resulting in the increased overall ionic character of the metal−ligand bond and hence higher edge-shift for this complex.

The edge-width has earlier been qualitatively related [15, 16] to the overall electronegativity difference between metal and the donor atoms through an expression of the form

$[\text{Edge-width} \cdot \Sigma \|X_M - X_L\|]^{\frac{1}{2}} = $ a constant for a given metal in a given region (1)

provided $X_M \neq X_L$, where X_M and X_L are the Pauling electronegativities of the metal and the donors respectively. The summation on the left-hand side extends over all the atoms in the coordination sphere. The edge-width measurements of these complexes and their respective coordination stoichiometries are shown to obey the above relationship (Table IV). The corresponding rectangular hyperbola is shown in Fig. 2. The average value of the constant obtained
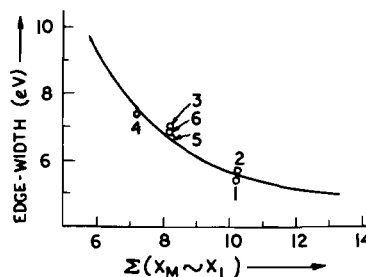

Fig. 2. Variation of $\Sigma \|X_M - X_L\|$ with edge-width of cobalt in some complexes.

here is in agreement with that found earlier (7.6) [15, 16]. It may be noted that the observed increase in the degree of covalency (which results from a decrease in the electronegativity difference) immediately follows from this relationship as well.

The Co−PhTT complex, however, shows deviation from this relationship. This complex has earlier been suggested to be unusually tetrahedral [9], the coordination sphere consisting of the group CoN_2S_2. Accordingly, the value obtained for $\Sigma \|X_M - X_L\|$ would be 3.8. However, the computed value, using the experimental edge-width (7.8 eV), is found to be 7.6. This edge-width value corresponds to the coordination stoichiometry Co:N:S = 1:4:4. Such a raising of the coordination number as a result of intermolecular interaction between N and S donors and cobalt ions from different molecules has been postulated earlier [17].
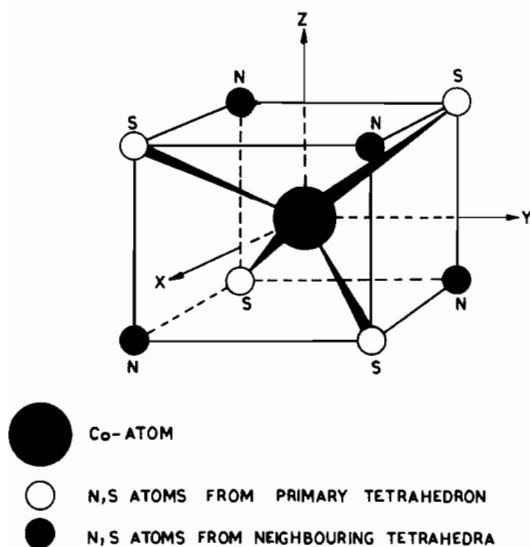
Fig. 3. The suggested coordination polyhedron of the Co–PhTT complex.

The suggested coordination polyhedron of the complex is shown in Fig. 3. The possibility of the intermolecular association envisaged here could not be verified due to lack of molecular weight data. The possibility of raising a coordination number due to molecular association has earlier been reported in some tetrahedral complexes of cobalt with bidentate monoanions like 1-phenyltetrazoline-5-thione [18, 19].

Conclusions

There are a number of factors which influence the nature and strength of the metal–ligand bond in a complex. Nyholm [20] in a comprehensive review has listed some factors which are of major importance in this regard. In the present investigations we have attempted to correlate the effects of two of these factors, *viz.*, (i) the difference between the effective electronegativities of the metal (M) and the donor (L), *i.e.* $|X_M - X_L|$ and (ii) the possibilities for ring formation.

The net effect of these factors on the degree of covalency of the bond and consequently on the magnitude of edge-shifts and edge-widths may now in view of the foregoing discussion be summed up in the following statement: "provided the valency of the metal ion is fixed, an increase in the overall covalent character of the metal–ligand bond, in general, results in a corresponding increase in the edge-width and a decrease in the edge-shift of the compound".

Acknowledgments

References

1 G. L. Glen and C. G. Dodd, *J. Appl. Phys.*, *39*, 5372 (1968).
2 B. K. Agarwal and L. P. Verma, *J. Phys.*, *C, 3*, 535 (1970).
3 H. L. Nigam and U. C. Srivastava, *Inorg. Chim. Acta*, *5*, 338 (1971).
4 V. G. Bhide and N. V. Bhat, *J. Chem. Phys.*, *48*, 3103 (1968).
5 W. Seka and H. P. Hanson, *J. Chem. Phys.*, *50*, 344 (1969).
6 P. C. Srivastava, K. B. Pandeya and H. L. Nigam, *J. Inorg. Nucl. Chem.*, *35*, 3613 (1973).
7 S. K. Srivastava, K. B. Pandeya and H. L. Nigam, *Ind. J. Chem.*, *13*, 498 (1975).
8 P. C. Jain and H. L. Nigam, *Ind. J. Chem.*, *7*, 280 (1969).
9 U. Agarwal, V. A. Narayan and S. K. Dikshit, *Can. J. Chem.*, *45*, 1057 (1967).
10 H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry", 2nd Ed., Wiley, London, pp. 179 and 183 (1927).
11 H. L. Nigam and U. C. Srivastava, *Zeit. für Naturforsch.*, *B26*, 997 (1971).
12 C. Mande and A. R. Chetal, *International Conference on X-ray Spectra and Chemical Binding, Leipzig*, 194 (1966).
13 R. M. Agarwal and A. N. Nigam, *Proc. Indian Acad. Sci.*, *Volume LXIII*, 200 (1966).
14 R. O. Keeling, Jr., "Developments in Applied Spectroscopy", Plenum Press, New York, Vol. 2, 263 (1963).
15 U. C. Srivastava and H. L. Nigam, *Indian J. Chem.*, *9*, 1301 (1971).
16 H. L. Nigam and U. C. Srivastava, *Chem. Comm.*, *14*, 761 (1971).
17 S. K. Dikshit, *Ph.D. Thesis*, Indian Institute of Technology, Kanpur (1968)
18 P. Pauling, G. B. Robertson and G. A. Rodley, *Nature*, *207*, 73 (1965)
19 F. A. Cotton and R. C. Elder, *Inorg. Chem.*, *4*, 1145 (1965).
20 R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).