CHAPTER IV

X-RAY ABSORPTION SPECTROSCOPIC STUDY

#### CHAPTER IV

#### 4.1 INTRODUCTORY DISCUSSION

Extensive X-ray spectroscopic work has been done on measurement of chemical shift and chemical effects on K and L absorption edges in different materials (1-12).

Bergenren (13) and Lindh (14) were the first to show that chemical combination influences X-ray emission and absorption spectra. An interesting problem in X-ray spectroscopy is to correctly relate the observed "chemical shift" in both emission lines and absorption edges, to the molecular and crystallographic structure of the emitter or absorber, and to the chemical state of its atoms.

Although the inner-shell electrons of an atom are not directly involved in the formation of a chemical bond, their energies are shifted slightly when the chemical or crystallographic environment of the atom is changed. This is because inner-shell binding energies do depend slightly upon Coulomb and exchange interactions with electrons in outer shells. In fact, chemical shifts are to be found not only in deep-lying electronic levels, but also in nuclear energy levels.

Such chemical shifts have been observed for a long time both in X-ray absorption edges, where we are concerned with the ionization of an inner electron, and in emission lines, seven an electron falls from outer-shell orbital into an inner shell

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orbital. Theoretical attempts have been made in order to interpret the observations. Such attempts are important because by a combination of theoretical calculations and experimental measurement we may hope to obtain valuable information about the nature of chemical bonds.

The observed X-ray absorption edge shift is shown to be related with many parameters like covalency, effective charge, electronegativity, coordination number, crystal structure etc. (15, 16). Agarwal and Verma (1) suggested an empirical rule for the absorption edge shift  $\triangle E$ : "In general, the chemical shift is towards the high-energy side of the metal edge; it increases progressively with increase of the valence of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of a metal-metal bonding". The first part of this rule namely the valence dependence of the shift is well known (17, 18). Boehm et al. (19), Mande and Chetal (20) and Miller (21) used this dependence to determine the valences of the absorbing ions in compounds. Sapre and Mande (2) tested this rule and found that the covalence suppresses the shift, not only for the cations but also for the anions. Moreover, anions show a negative (low-energy) shift.

Ovsyannikova <u>et al</u>. (22) and Dey and Agarwal (23, 24) suggested the following empirical formulae respectively.

$$\Delta E = const. [N - (1 - f_i) n] ... 4.1$$
  
 $\Delta E = N^2 f_i ... 4.2$ 

where N is the valence,  $f_i$  is the Pauling ionicity for a crystal, n is the coordination number and  $\Delta E$  the shift.

Batsanov and Ovsyannikova (25) have expressed the coordination effective charge 'g' as

 $q = N - nf_c$  ... 4.3 where N is the valency, n is the coordination number and  $f_c$  the covalency.

Comparison of (4.1) with (4.3) shows that  $\Delta E \triangleleft$  effective charge q. Quite often, Suchet's method of evaluating q has been employed to relate  $\Delta E$  with q (26).

Adhypak <u>et al</u>. (27) found that chemical shift of edge increases with increase in electronegativity difference of the combining atoms.

In general, ionic solids have been found to give rise to sharp edges, whereas in covalent compounds they are somewhat broadened (28).

Van Nordstrand (29, 30) has reported a large number of K-absorption curves of transition metal ions in different types of solids. He classifies these curves in four categories namely, type I spectra associated with an octahedral co-ordination in the common salts, hydrates, complexes and oxides, type II associated with an octahedral co-ordination shell constituted of linear ligands such as CN and C**O**, type III characteristic of metal and metallic phases and type IV associated with tetrahedral configu-

ration. The principal features of these curves have been explained by Sinha and Mande (31) on the basis of ligand field theory. On the basis of this explanation Mande and Chetal (32, 33) have distinguished octahedral and tetrahedral co-ordination in transition metal complexes. Studies on K-absorption edge width by Nigam and Shrivasthva (34) lead them to formulate an empirical correlation between edge width and co-ordination stoichiometry being expressed in terms of metal and nearest neighbour electronegativity difference. Nigam and Shrivasthva (35) have found that the edge width increases with increasing covalent character of the bond. Alok Kumar et al. (36), A.K. Singh and Kashyap (37), Shobha Mehta and Ankhindi (38), P.N.Koul et al. (39) have carried out studies on K-absorption edge shift of some transition metal complexes. They have discussed absorption edge shifts in terms of the effective nuclear charge and the nature of the ligand.

By obtaining the well resolved extended part of the fine structure on the high energy side of an absorption edge, solid state effects and chemical bonding can be studied. Many authors (40-43) have reported the fine structure extending upto several hundred electron volts on the high energy side of X-ray absorption edge of a number of metals, compound, complexes etc., since 1930. Different theories have been proposed to explain EFS. Essentially all the theories of fine structure which are more or less modifications of the basic theory due to Kronig (40) have been classified into two groups. In one, plane waves (Block functions) are used

to describe the ejected electron and the energies of the allowed final states in the crystal are calculated. Since this presupposes a three dimensionally ordered crystal such theories have been named as 'long range order (LRO) theories'. In the second treatment, the final states are considered to be those following the scattering of the electron by neighbouring atoms. Therefore, they have been named as 'short range order (SRO) theories'. Applying SRO theories to a compound a lot of information can be obtained about the factors such as interatomic distance, fractional covalency, co-ordination number etc.

Various theories proposed so far to explain EFS are most successful in predicting the relative energies at which maxima in the absorption curve occur, but are less successful in reproducing the actual spectral curves.

In the present work, we have selected a set of cobalt(III) complexes for the X-ray absorption spectroscopic study. The study of chemical shift of K-absorption edge and the EXAFS on the high energy side of the K-edge for the selected Co(III) complexes was undertaken with a view to understanding the role of the following in the X-ray absorption process.

i) gradual replacement of a bidentate ligand.

ii) gradual replacement of a monodentate ligand.

iii) cis-trans isomerism.

#### 4.2 <u>COBALT COMPLEXES</u>

In almost all cobalt compounds, valency of cobalt is either two or three. Valency designates the formal positive charge on the metal ion, whereas the co-ordination number describes the nearest neighbours bounded to the metal ion. The simple divalent cobalt salts are more stable than the corresponding compounds of trivalent cobalt, whereas cobaltic complexes are more stable than the cobaltous complexes (44).

#### 4.2(a) Cobaltic Complexes

In cobaltic complexes, the coordination number is always six. Cobaltic complexes are numerous because the trivalent state of cobalt is more stable in the complexes. The cobaltic ion in a complex can be the 'central atom' of a cation, neutral molecule or an anion. The chief donor atoms attached to trivalent cobalt in these complexes are (in order of diminishing strength of the link) nitrogen, carbon in cynides, oxygen and the halogens.

#### 4.2(b) Cobaltic Amines

The affinity of Co(III) ion for nitrogen is very strong; so that in aqueous solutions, amines can be very readily formed inspite of many water molecules present. The ammonia groups can be replaced partly or wholly by other amines and partly by water and large number of mono and divalent acid radicals like nitro, oxalic acid as well as the halogen (45). The amines can have

any number of amine groups from 6 to 2; the stability falls off as the number of amine groups deminishes the strength of the link. On the other hand, the formation of a chelate ring by molecule which have two amine groups, greatly increases the stability. The second effect is stronger than the first, so that the ethylene diamine (en) with two primary amine groups gives more stable compounds than the ammonia complex itself.

#### 4.3 OCTAHEDRAL\_COMPLEXES

There are three kinds of electronic structures that can be expected for the octahedral complexes  $MX_6$ , of the iron group transition metal elements.

i) The first kind is that in which no 3d orbitals might be involved and bonds can be formed by hybridized  $4s4p^3$ orbitals, which would resonate among the six positions. Besides, with these four orbitals, two 4d orbitals may be used to form bonds with  $sp^3d^2$  hybridization. In his earlier work, Pauling called these complexes as ionic (45) and was greatly criticized (46). Later he called these complexes as hypoligated (or high spin, weak field).

ii) In the second type, one of the 3d orbitals is used with  $sp^3$  orbitals for bond formation. The bonds are formed by  $dsp^3$  hybridization e.g. Fe in hemoglobin hydroxide. This type of structure occurs only rarely.

iii) In the third kind  $d^2sp^3$  bonds are formed, using two of the five 3d orbitals, leaving three for atomic electrons. Such complexes are named as hyperligated (45). They are also known as low-spin or high field complexes.

All of the cobalt(III) complexes with exception of  $[CoF_6]^{-3}$  are found to be diamagnetic. These complexes therefore show zero magnetic moment and the bonding is  $d^2sp^3$  type.

### 4.4 COBALT K-EDGE IN PURE COBALT METAL

The K-absorption curve studied for cobalt metal (hcp) by Barnes, Beeman and Friedman (47, 48) revealed considerable structure in it. It was pointed out by Barnes (47) that the observed effects might be associated with the presence of an incomplete 3d shell. The cobalt K-absorption edge splits into two components  $K_1$  and  $K_2$ . Whenever splitting of the discontinuity occurs, the measurements are made from the inflection point on the K<sub>1</sub> component (low energy absorption component). The original microphotometer record of Co-K-absorption discontinuity obtained has been reproduced in Fig. 4.1. For the metal, the inflection point on  $K_1$  corresponds to electronic jump 1s to Fermi level. The X-ray absorption process maps out the vacant energy levels of p symmetry in valence and conduction bands according to the dipole selection rules. Thus in the absorption spectrum of the metal, the coefficient of absorption is proportional to the product of density of allowed but unoccupied states and the probability of transition to these states,  $\mu(E) \triangleleft N(E).P(E)$ . Accordingly Beeman and Friedman (48) considering Krutter (49) and Slater's (50) energy band structure have concluded that there is considerable admixture of p function in the 3d and 4s bands of Cu. Extending this argument for Co, the inflection point on  $K_1$  can be taken as corresponding to a state of admixture of 3d-4s-4p, whereas the inflection point on  $K_2$  corresponds to pure p states. Recently Carter (51) has developed bidirectional orbital approach that can be used to obtain qualitatively the density of states distribution for transition metals.

## 4.5 <u>SHAPE, STRUCTURE AND CHEMICAL SHIFT OF CO-K EDGE</u> IN CO(III) COMPLEXES

The original microphotometer records of Co-K discontinuity in complexes studied in the present investigation are shown in Figs. 4.1 and 4.2. It has been observed that the edges do not show any structure or splitting which confirms octahedral coordination as reported by Van Nordstrand (29, 30).

The inflection point on the edges was taken as the position of the edge, which corresponds to the Fermi limit in the case of metals and to the first available vacant state in the case of compound. The shift of K-absorption edge of cobalt in a complex is measured in comparison with the K-absorption edge of cobalt in pure metallic state. Co-K edge shift in the complex with respect to that in pure metal is shown in Plate 4.I. The chemical shift data for the complexes under investigation are presented in Tables 4.1, 4.2 and 4.3.













A general observation of the tables 4.1, 4.2 and 4.3 indicates that in all the cobalt(III) complexes, the chemical shift is found towards high energy side of the metal edge, which is in accordance with the Agarwal and Verma's (1) empirical rule. It has been pointed out (52-54) that such chemical shift is mainly governed by the charge on the central absorbing atom; although there are other factors like co-ordination number, nature of ligand, symmetry, electro-negativity, polarizability etc. which affect the magnitude of the chemical shift.

The effective charge 'q' on cobalt ion in these complexes is estimated using a semi empirical method of Gianturco and Coulson (52, 55). Clementi and Roetti (56) obtained the theoretical binding energy (B.E.) for a large number of ions using an analytical self consistent RHF type calculation. A plot (Fig. 4.3) between these theoretical snifts in B.E. of an electron such as K electron and the oxidation number of cobalt atom obtained by Koul <u>et al</u>. (39) was used to determine the fractional oxidation number of the atom in a particular compound corresponding to the measured K-absorption edge shift. This quantity is defined (52) as the effective charge 'q' on the X-ray absorbing cobalt ion. The 'q' values for different complexes are also listed in Tables 4.1, 4.2 and 4.3. 4.5(a) Cobalt complexes of the form  $trans[Co(AA)_2(NO_2)_2]NO_3$ 

In Table 4.1 cobalt K-edge data for cobalt complexes with general formula,  $\operatorname{trans}[\operatorname{Co}(\operatorname{AA})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$ , where (AA) indicates the bidentate ligands ethylene diamine (en), trimethylene diamine (tn) and propylene diamine (pn) are given. It is seen that the chemical shift  $\triangle$  E varies in the following manner.

 $\Delta E \left\{ tr[Co(en)_2(NO_2)_2]NO_3 \right\} \Delta E \left\{ tr[Co(tn)_2(NO_2)_2]NO_3 \right\} \\ \Delta E \left\{ tr[Co(pn)_2(NO_2)_2]NO_3 \right\}$ 

The observed variation in chemical shifts can be explained on the basis of ring structure of the bidentate ligands en, tn and pn and spectrochemical series of ligands due to Fajans and Tsuchida (57, 57a). In this series ligands are arranged according to decreasing crystal field stabilization energy (CFSE). The bidentate ligands en, tn and pn form ring-like structures with metal ion called metal chelates.

The study of Parkovic and Meek (58) shows that the more bulky the metal chelate ring, the smaller is the crystal field splitting ( $\Delta$ ) and vice-versa.

The bidentate ethylenediamine (en) gives rise to a five membered chelate ring when it is co-ordinated with cobalt atom and the bidentate trimethylenediamine (tn) gives rise to six membered chelate ring when it is co-ordinated with cobalt atom. Further, the bidentate propylenediamine (pn) gives rise to five membered chelate ring, which is conjugated with an additional

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Table 4.

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S.No.	Absorber	Energy E(eV) ± 1 (eV)	Chemical shift E(eV)	Effective charge on Co'q'electron/atom ± 0,1 electron/atou
l •	Co-metal (Author)	7710.20	١	ł
2.	Co-metal (Bearden)	7709.54	ı	
°.	trans[Co(en) $_2(NO_2)_2$ ]NO $_3$	7727.36	17.16	1.85
4.	$trans[Co(tn)_2(NO_2)_2]NO_3$	7725 <b>.77</b>	15.57	1.62
ۍ•	trans[Co(pn) $_2(NO_2)_2$ ]NO $_3$	7724.63	14.43	1.575

C-CH<sub>3</sub> group, with cobalt metal atom (Fig. 4.4). Thus the bidentate ligand (en) on co-ordination with cobalt ion gives a less bulky metal chelate ring than that given by the ligands (tn) and (pn). Following Parkovic and Meek (58) a greater crystal field splitting ( $\Delta$ ) is expected for the complex trans[Co(en)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub> than the remaining two. So in the spectrochemical series of ligands the positions of tn and pn will be on the lower crystal field stabilization energy side with respect to that of en. It has been reported that greater the CFSE greater is the chemical shift (59). This explains the larger chemical shift fof the trans[Co(en)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub> complex in comparison with the other two complexes.

The number of atoms involved in the chelate rings due to th and pn is the same. However, for the complex  $\operatorname{trans}[\operatorname{Co}(\operatorname{tn})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$  the metal chelate ring is six membered whereas for the complex  $\operatorname{trans}[\operatorname{Co}(\operatorname{pn})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$  it is five membered in conjugation with an additional  $\operatorname{CH}_3$  group. The additional conjugated  $\operatorname{CH}_3$  group in case of  $\operatorname{trans}[\operatorname{Co}(\operatorname{pn})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$  may be responsible in making the chelate ring more bulky. As such CFSE for  $\operatorname{trans}[\operatorname{Co}(\operatorname{tn})_2(\operatorname{NO}_2)_2]$  $\operatorname{NO}_3$  will be greater than that for  $\operatorname{trans}[\operatorname{Co}(\operatorname{pn})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$  and hence greater shift is expected for the complex  $\operatorname{trans}[\operatorname{Co}(\operatorname{tn})_2(\operatorname{NO}_2)_2]$  $\operatorname{NO}_3$  than that for  $\operatorname{trans}[\operatorname{Co}(\operatorname{pn})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$ .

The stability of complexes of a particular metal atom with a fixed valency and with various multidentate ligands increases with the increase in the effective nuclear charge on the central metal atom (60). Thus we observe from Table 4.1 that the stability



Fig.4.4 STRUCTURE OF Co(III) COMPLEXES.

of the complexes increases in the following order  $trans[Co(en)_2(NO_2)_2]NO_3 > trans[Co(tn)_2(NO_2)_2]NO_3 > trans[Co(pn)_2(NO_2)_2]NO_3.$ 

This observation in connection with the stability of the complexes is strengthened by a remark due to Jorgenson (61) that a metal complex with a bidentate ligand (tn) is less stable than the complex of the same metal atom with bidentate ligand (en) though the donor strengths of (en) and (tn) are similar. Further examination of published data (62, 63) reveals that a metal complex with five membered metal chelate ring is more stable except when conjugation is present in the system. This suggests that stability of trans[Co(en)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub> is greater than that of trans[Co(pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>.

# 4.5(b) <u>Cobalt complexes of the form</u> $trans[Co(AA)_2(B)_2]^{+1}$

In Table 4.2 cobalt K-edge data for cobalt(III) complexes with general formula trans $[Co(AA)_2(B)_2]^{+1}$ , where (AA) indicates the bidentate ligands ethylenediamine (en), trimethylenediamine (tn) and (B) denotes the unidentate ligand NO<sub>2</sub> and Cl<sup>-</sup> are given. Comparison of chemical shifts for trans $[Co(tn)_2(NO_2)_2]NO_3$  and trans $[Co(tn)_2Cl_2]NO_3$  shows that the shift is suppressed when ligand NO<sub>2</sub> is replaced by Cl<sup>-</sup>. This may be probably due to (59) higher dipole moment due to NO<sub>2</sub> ligand or shorter Co-NO<sub>2</sub> distance or due to both. In either ways, the result appears to be the contraction of the electron cloud on the Ch(III) ion, corresponding to higher stability of the complex with NO<sub>2</sub> ligand. Consequently,

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complexes	nd B = NO,
in Co(III)	en, tn a
edge	( AA =
le 4.2 : Chemical shift of Co-K	$trans[Co(AA)_2(B)_2]^{+1}$
Tab.	

S.No.	Absorber	Energy E(eV) ± 1 (eV)	Chemical shift E(eV)	Effective charge on Co'q' electron/atom t oil electron/atom
<b>1</b> •	$trans[Co(tn)_2(NO_2)_2]NO_3$	7725.77	15.57	1.62
2.	trans[Co(tn) $_2$ Cl $_2$ ]NO $_3$	7723.75	13.55	1.475
°.	trans[Co(en) $_2(NO_2)_2$ ]NO $_3$	7727.36	17.16	1.85
4	$trans[co(en)_2 Cl_2]Cl$	7725.20	15.00	1.575

the binding energy of the K-electron increases, thereby giving rise to larger chemical shift for trans $[Co(tn)_2(NO_2)_2]NO_3$  than that for trans $[Co(tn)_2Cl_2]NO_3$ .

This result can also be explained on the basis of spectrochemical series of ligands. In the spectrochemical series of ligands due to Fajans and Tsuchida (57, 57a) the ligands are arranged according to decreasing crystal field stabilisation energy (CFSE). It is evident from this series that the crystal field due to Cl<sup>-</sup> ligand is less than that due to  $NO_2^-$  ligand and hence the suppression of chemical shift is observed when unidentate ligand  $NO_2^-$  is replaced by unidentate ligand Cl<sup>-</sup>.

The suppression of the chemical shift is in conformity with the electro-negativity series of ligands in which ligands are arranged in decreasing order of electronegativity. The ligand  $NO_2^-$  lies higher up in the electro-negativity series than the ligand Cl<sup>-</sup>, hence percentage ionic character of the bond Co-NO<sub>2</sub> is more than the percentage ionic character of the bond Co-Cl. Percentage ionic character of the bond is given by

$$f_i = 1 - e^{-0.25(X_M - X_L)^2}$$

where  $f_i \longrightarrow percentage ionic character of the bond,$  $(X_M - X_L) \longrightarrow electronegativity difference between metal atom and ligand.$ 

 $f_i$  increases as  $(X_M - K_L)$  increases. This again turns out to be a convincing explanation for the

larger shift for trans[Co(tn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub> than that for trans[Co(tn)<sub>2</sub>Cl<sub>2</sub>]NO<sub>3</sub>. Similarly shifts for trans[Co(en)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub> and trans[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl can be explained.

# 4.5(c) <u>cis-trans Isomers of cobalt complexes of the form</u> $\begin{bmatrix} Co(AA)_2 [NO_2)_2 \end{bmatrix}^{+1}$

In Table 4.3 cobalt K-edge data for cis-trans isomers of cobalt(III) complexes having general formula  $[Co(AA)_2(NO_2)_2]^{+1}$  are given. Here (AA) means the bidentate ligand (en), (tn), or (pn). It is seen that the chemical shift is less for cis-isomer than for the corresponding trans-isomer. This may be because of the percentage increase in co-valency of metal-ligand bonds in the cis form complexes. In the cis-isomer there is no centre of symmetry. Further, the cis-isomer is less symmetric than the corresponding trans form due to the considerable distortions in bond angles and the assymmetric distribution of electrostatic field. This may perhaps be the cause of decrease in percentage ionicity of the metal-ligand bond. As such the bonding becomes less ionic and hence more covalent in cis-isomers. Thus chemical shifts of the cobalt K-edge as observed in cis and trans forms are explained.

#### 4.6 EXAFS OF COBALT K-EDGE IN CO(III) COMPLEXES

The original microphotometer records of Co-K-absorption edges with the extended X-ray absorption fine structure (EXAFS) for Co(III) complexes investigated in the present work are shown

	general formula [Co(AA) <sub>2</sub> (NO,	2)2] <sup>+1</sup> (AA =	en, tn, pn)		-
S.No.	Absorber	Energy E <sub>(eV)</sub> ± 1 (eV)	Chemical shift E(eV)	Effective charge on Co 'q' electron/atom ±o.1 electron/atom	
<b>1</b> •	$trans[Co(en)_2(NO_2)_2]NO_3$	7727.36	17.16	1.85	
2.	cis[Co(en) $_{2}(NO_{2})_{2}]NO_{3}$	7725.40	15.20	1.587	
ຕື	$trans[Co(tn)_2(NO_2)_2]NO_3$	7725,77	15.57	1.62	
4.	$cis[co(tn)_{2}(NO_{2})_{2}]CI$	7724.42	14.22	1.512	
<b>ي</b>	$trans[Co(pn)_2(NO_2)_2]NO_3$	7725.00	15.00	1.575	
6.	cis[Co(pn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]Cl	7723.70	13.50	1.475	

isomers of Co(III) complexes hav	
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Fig.4.5 (a) EXAFS OF Co-K EDGE IN Co(III) COMPLEXES.



Fig.4.5 (b) EXAFS OF Co-K EDGE IN Co(III) COMPLEXES.



Fig.4.5 (c) EXAFS OF Co-K EDGE IN Co(III) COMPLEXES.



Fig.4.5(d) EXAFS OF Co-K EDGE IN Co(III) COMPLEXES.

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Table 4.4 : Energy values (E) in eV of maxima from Co-K EXAFS in Co(III) complexes.

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	Energy	values of r	naxima in e	V with avera	age error <u>+</u>	L eV
Absorber	A			D	1 1 1 1 1 1 1 1 1 1 1	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
$trans[Co(en)_2(NO_2)_2]NO_3$	17.46	67.35	113.4	142.0	169.0	188.1
$trans[Co(tn)_2(NO_2)_2]NO_3$	11.05	63 <b>.</b> 86	108.06	135.08	152.0	175.0
$trans[Co(pn)_2(NO_2)_2]NO_3$	15.26	53.10	79.8	104.5	138.5	180.6
$trans[Co(en)_2Cl_2]Cl$	19.21	73.56	117.2	155.2	187.1	219.5
$trans[Co(tn)_2 Cl_2]NO_3$	19.20	70.82	94.76	122.4	155.1	173.28
cis[Co(en) $_{2}(NO_{2})_{2}]NO_{3}$	11.72	72.31	87.03	105.9	131.9	169.08
$cis[co(tn)_2(NO_2)_2]$ Cl	12.28	62.77	79.08	94.56	124.03	144.9
cis[ $co(pn)_2(NO_2)_2$ ] C1	12.03	56.49	74.66	89•64	109.29	

in Figs. 4.5.a, 4.5.b, 4.5.c and 4.5.d. The microphotometer records the transmitted intensity and therefore the minima and the maxima on the microphotometer record should correspond to the actual absorption maxima and minima respectively.

In Table 4.4 are presented the energies (eV) of the absorption maxima in the EXAFS by the Co(III) complexes. These energy values are measured with respect to the inflection point on the main discontinuity. The interesting features of the X-ray K absorption spectra of the complexes are discussed in the following sections.

#### 4.6(a) Low Energy Absorption

The X-ray K-absorption process involves the ejection of 1s electron to a vacant p level. The strongest peak or main peak 'A' (maximum absorption) for the first row transition metals is attributed to 1s  $\longrightarrow$  4p transitions. Occasionally a few weaker peaks occur on the low energy side of the main peak. This occurrence of weaker peaks on the low energy side of the main peak is called the low energy absorption.

For all the complexes investigated in the present work, the low energy absorption feature is found to be absent. Mitchel and Beeman (8) have associated the presence or absence of low energy absorption feature with the presence or absence of unfilled 4p orbitals of metal ions in covalently bonded complexes of the transition elements according to the Pauling's hybridization theory. For the complexes studied in the present work, the bonding orbitals are  $3d^24sp^3$  hybrid (low spin type). According to the Pauling's hybridization theory, the present complexes do not have unfilled 4p orbitals and therefore it may be expected from Mitchell and Beeman's consideration (8) given earlier that the low energy absorption feature should be absent for all the complexes under investigation. Further on the basis of Pauling's hybridization theory, the main peak 'A' may be assigned to  $ls \longrightarrow 5p$  transition as is done by Bhat et al. (64).

## 4.6(b) MO Energy Level Diagram for Octahedral Complexes of Co(III)

The electronic distribution in complexes can be best explained on the basis of molecular orbital theory (46). It is possible to set up an energy level diagram for the Co(III) octahedral complexes and the resulting diagram is only qualitatively correct. The 3d, 4s and 4p orbitals on  $Co^{3+}$  and six hybrid orbitals of ligands are to be considered for the construction of mos. By using the symmetry properties, the nine metal orbitals can be combined with the six ligand orbitals to give the molecular orbitals of the complex. It can be seen from symmetry considerations that certain atomic orbitals can overlap in certain ways to have positive overlap integrals, and lead to the formation of bonding molecular orbital. Changing the orientation of the orbitals or changing the symmetry type can result in zero or negative overlap. This can be done elegantly by means of group theory (65). It is certain that overlap of 4s and 4p orbitals



Fig.46:MO energy level diagram of low spin Co(III) complexes illustrating electron distribution.

with the ligands is considerably better than the 3d orbitals. As a result, the  $a_{1g}$  and  $t_{1u}$  molecular orbitals are the lowest in energy and the corresponding  $a_{1g}^*$  and  $t_{1u}^*$  antibonding orbitals, the highest in energy. The  $e_g$  and  $e_g^*$  orbitals arising from the 3d orbitals are displaced less from their barycenter because of poorer overlap. The  $t_{2g}$  orbitals are nonbonding (in type bonding) and not displaced. The total number of eighteen electrons, six from Co central atom and twelve from the ligands are now placed in different molecular orbitals starting from the lowest energy. The resulting energy level diagram appears as given in Fig. 4.6.

The appearance of all the edges of the complexes is marked by a strong absorption peak. This main absorption peak 'A' corresponds to an electron transition from 1s core level to the first available unoccupied molecular orbital. The available unoccupied molecular orbitals are  $e_g^*$ ,  $a_{1g}^*$  and  $t_{1u}^*$ . Since transition from 1s to  $e_g^*$  or  $a_{1g}^*$  are not allowed by the electric dipole selection rules, the first absorption maximum 'A' is assigned to an electron transition, 1s  $\longrightarrow t_{1u}^*$ .

## 4.6(c) Diagnosis of cis-trans Isomers

The octahedral complexes having general formula  $[M(AA)_2(B)_2]X$  show geometric isomerism and often it is not possible to distinguish between the isomers by simple techniques. A cursory look at the spectra of cis-trans isomers shows that, the main absorption peak appears a relatively broad structure in

case of cis isomer. This broadening of 'A' peak in the cis form may be due to the lowering in symmetry of the cis-form. Such broadening of the main absorption peak due to the lowering of symmetry has been reported by Obashi (66). A general observation of EFS of all the cis and trans compounds reveals that well defined maxima and minima are observed in case of trans compounds whereas they are not so well defined and are flattened in case of the cis compounds. This may be due to more complicated distortion in cis-compounds than that in the corresponding trans-compounds.

#### 4.6(d) Application of Levy's Method

Kozelenkev who attributed the EFS to the variation in transition probabilities, used a simple square well potential to develop an expression for the absorption cross-section of the absorber. This expression was simplified by Levy (67) to calculate the distance  $r_1$  characterising the first co-ordination sphere of the ligands around the absorbing atom using the energy values of the prominent fine structure maxima and minima. He further simplified the treatment and arrived at an expression for the radius of the first co-ordination sphere in terms of  $\Delta E$ , the energy difference between the second absorption maxima (B) and the subsequent minima ( $\beta$ ). The relation between  $\Delta E$  and  $r_1$  is as given below.

$$r_1 = \left(\frac{151}{\Delta E}\right)^{1/2} \dots 4.4$$

Table 4.5 : Metal-ligand distance ( $\mathscr{T}_1$ ) obtained from the fine structure of K-absorption spectra of Co(III) complexes from Levy's theory.

Absorber	$\frac{\Delta E(\beta - B)}{\pm 1 \text{ eV}}(\text{eV})$	$\gamma'_{1} = \left(\frac{151}{\Delta E}\right)^{1/2} A^{\circ}$
trans[Co( <b>en</b> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]NO <sub>3</sub>	34.95	2.0786
$trans[Co(tn)_2(NO_2)_2]NO_3$	20.87	2.6898
$trans[Co(pn)_2(NO_2)_2]NO_3$	17.95	2.900
trans[Co(en) <sub>2</sub> Cl <sub>2</sub> ]Cl	31.14	2.202
$trans[Co(tn)_2Cl_2]NO_3$	14.962	3.1768

The radius  $r_1$  gives the average bond length. The average bond length  $r_1$  calculated using this method for some complexes are presented in Table 4.5.

### 4.6(e) Application of Lytle's Theory

Lytle (68-70) has introduced a phenomenological theory to account for X-ray absorption edge fine structure. According to him the allowed energy values for the ejected photoelectron can be calculated quantum mechanically by considering a spherical Wigner-Seitz cell around the absorbing atom. For solving the Schrodinger equation it is assumed that the potential inside the cell is zero and infinite outside it. According to Lytle, the absorption maxima in the fine structure which correspond to energy levels are given by

$$E = \frac{h^2}{8mr_s^2} \times Q$$
 ... 4.5

where, 'E' denotes the position of energy maxima,

- 'h' the Plank's constant,
- 'm' the mass of electron,
- 'Q' the zeroth root of the half order Bessel function appearing in the radial part of the solution of the Schrodinger equation for the ejected photoelectron and 'r<sub>s</sub>' the radius of the sphere of equivalent volume.

Since the dipole selection rules (  $\Delta 1 = \pm 1$ ) are inherent in this model, the transitions are restricted from any initial

- 10



Fig.4.7 (a) LYTLE PLOTS ( E vs Q ) FOR Co(III) COMPLEXES.





Fig. 47(b) LYTLE PLOTS ( E vs Q) FOR Co(111) COMPLEXES.



Fig. 47 (c) LYTLE PLOTS (E vs Q) FOR Co(III) COMPLEXES.





Fig.4.7 (d) LYTLE PLOT ( E vs Q ) FOR Co(III) COMPLEXES.

symmetry to a specific set of Q values. For example, the transition for the K-absorption will be to the levels of p symmetry with Q values,

 $Q = 2.04, 6.04, 12, 20, 30, \dots$  etc.

Equation 4.5 predicts a linear relation between E and Q values, such that the slope of the line can be used to evaluate the radius of the first co-ordination sphere. Substituting the values of 'h' and 'm' in equation 4.5,  $r_c$  can be written as,

$$r_s = \left(\frac{37.6}{M}\right)^{1/2}$$
 ... 4.6

where 'M' is the slope of E versus Q plot.

The plots of E versus Q for the complexes under present investigation are shown in Figs. 4.7.a, 4.7.b, 4.7.c and 4.7.d. The plots are seen to be linear as is predicted by the Lytle's theory. However the E versus Q plots for the complexes do not pass through the origin which is similar to that observed by Ballal and Mande (71). It has been shown by Kondavor and Mande (72) and Deshmukh <u>et al</u>. (73) that only in the case of metals and compounds with metallic character, the E versus Q plots pass through the origin while in case of insulators they do not. The intercept ( $V_c$ ) on the E axis is a measure of effective nuclear charge or electronegativity (74). The r<sub>s</sub> values, the intercepts ( $V_c$ ) on the E axis for the complexes are presented in Table 4.6 alongwith the 'q' values. The variation in the values of

of Co(III) com	lexes.			
Absorber	Slope of E Vs Q plot 'M'	Intercept on the E axis 'Vc' eV	Metal-ligand distance 'rs' A <sup>o</sup>	Effective atomic charge q electron/atom ± 0.1 electron/atom
$trans[Co(en)_2(NO_2)_2]NO_3$	8.2	13.0	2.1413	1.85
$trans[Co(tn)_2(NO_2)_2]NO_3$	8•0	0*6	2.1679	1.62
$trans[Co(pn)_2(NO_2)_2]NO_3$	6•0	5.5	2.5033	1.575
$trans[Co(en)_2(NO_2)_2]NO_3$	8.2	13.0	2.1413	1.85
$trans[co(en)_2 Cl_2]Cl$	6•1	0*6	2.1816	1.575
$trans[Co(tn)_2(NO_2)_2]NO_3$	8•0	0*6	2.1679	1.62
$trans[Co(tn)_2 Cl_2]NO_3$	7.5	4•5	2•239	1.475
$trans[Co(en)_2(NO_2)_2]NO_3$	8.2	13.0	2.1413	1.85
cis[Co(en) $_2(NO_2)_2$ ]NO $_3$	6.1	8.0	2.4827	1.587
$trans[Co(tn)_{2}(NO_{2})_{2}]NO_{3}$	8•0	0.6	2.1679	1.62
$cis[co(tn)_2(NO_2)_2]Cl$	5.9	3•0	2.5244	1.512
$trans[Co(pn)_{2}(NO_{2})_{2}]NO_{3}$	6 <b>.</b> 0	5.5	2.5033	1.575
cis[Co(pn) $_{2}(NO_{2})_{2}$ ]Cl	5.6	4 • 5	2.5912	1.475

Table 4.6 : Application of Lytle's theory to the fine structure of the K-absorption spectra

intercept on the E axis is consistent with the effective atomic charge 'q' and hence with chemical shift (sections 4.5(a), 4.5(b), 4.5(c)).

For the sake of comparison, the values of average bond lengths (metal-ligand distance) calculated using Levy's and Lytle's methods are shown in Table 4.7. There is good agreement between the results from the two methods. Further, the metalligand distances calculated from Levy's and Lytle's methods seem to be reliable because it has been reported by Levy (67) that for the octahedral Co(III) complexes such as  $[Co(NH_3)_6]^{3+}$ ,  $[Co(en)_3]^{3+}$ ,  $[Co(NO_2)_6]^{3-}$  wherein the bonding to the central cobalt metal ion is through nitrogen, the average metal-ligand distance is of the order of  $2A^0$ .

For the complexes having general formula  $trans[Co(AA)_2(NO_2)_2]$ NO<sub>3</sub> where (AA) indicates (en), (tn), (pn), the bond length increases in the following order (Table 4.6).  $trans[Co(en)_2(NO_2)_2]NO_3 \ \ trans[Co(tn)_2(NO_2)_2]NO_3 \ \ trans[Co(pn)_2(NO_2)_2]NO_3$ .

The above variation in the bond length may be due to the outstretching of the metal-ligand bond due to the substitution of a less bulky bidentate ligand by a more bulky bidentate ligand (refer section 4.5.a).

For the complexes of the type  $trans[Co(AA)_2(B)_2]^{1+}$  where (AA) indicates (en) or (tn) and B indicates  $NO_2^-$  and  $Cl^-$ , it is observed that keeping the bidentate ligand same i.e. en or tn,

Metal-ligand distance (A <sup>0</sup> )		
Levy's method	Lytle's method	
2.0786	2.1413	
2.6898	2.1679	
2.900	2.5033	
2.202	2.1816	
3.1767	2.239	
	Metal-ligand Levy's method 2.0786 2.6898 2.900 2.202 3.1767	

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Table 4.7 : Metal-ligand distances in Co(III) complexes from Levy's and Lytle's methods the replacement of NO<sub>2</sub> ligand by Cl<sup>-</sup> ligand causes increase in the average metal-ligand distance (Table 4.6). As seen earlier (section 4.5.b) the monodentate ligand NO<sub>2</sub> offers a greater crystal field than that offered by the monodentate ligand Cl<sup>-</sup>. Consequently, trans[Co(AA)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>1+</sup> represents a compressed octahedron whereas trans[Co(AA)<sub>2</sub>Cl<sub>2</sub>]<sup>1+</sup> represents an elongated octahdron.

### 4.6(f) Application of Lytle, Sayers and Stern's (LSS) Theory

For the understanding of the structure of the condensed matter by X-ray absorption process, it was proposed by E.A.Stern (75) for the first time that it is necessary to take the account of the partial scattering of the ejected photoelectron by atoms in the neighbourhood of the absorbing atom. Lytle, Sayers and Stern (76) have given the theory of extended fine structure by considering the partial scattering of the ejected photoelectron by atoms in the neighbourhood of the absorbing atom (SRO theory). The fluctuations of the absorption coefficient arise as a result of interference between photo-excited outgoing electron waves and those same waves that have been back scattered from near by neighbouring atoms to near the origin where the overlap with the initial state occurs. The interference is either constructive or destructive, depending on the wave number of the electron. When the waves add constructively, there is an absorption maximum and when they add destructively, there is a minimum. Lytle et al. (76) including the effects of the thermal motion of the lattice,

the attenuation of the photo-excited electron as it moves away from the parent atom and the change of the wave vector that is produced by multiple scattering showed that, the normalized oscillatory part of the absorption rate is,

$$\lambda(K) = \frac{m}{4\pi h^{2}K} \sum_{j}^{M} \frac{N_{j}}{r_{j}^{2}} s_{j}^{(K)} \sin[2kr_{j} + 2 \int_{j}^{M} (k)] \cdot e^{-2r_{j}/\lambda} \cdot e^{-2k^{2} S_{j}^{2}} \cdots 4.7$$

where,  $s_j$  is the back-scattering amplitude from each of the N<sub>j</sub> neighbouring atoms in the jth shell,  $\lambda$  is the mean free path of the electron, and  $e^{-2k^2} \delta_j^2$  is the Debye-Waller factor that takes into account thermal vibrations of the positions of the atoms. The factor  $e^{-2r_j/\lambda}$  describes the decay of the photoelectron.  $S_j(K)$ , is the phase shift caused by the potential of the absorbing atom which is counted twice because both the outgoing and the back-scattered electron waves experience this shift.

The electron wave vector (K) in the equation 4.7 is related to the kinetic energy E of the K-shell photo-electron (energy measured from the X-ray edge) by

 $K = (0.263 E)^{1/2} \dots 4.8$ 

Lytle <u>et al</u>. (76) proposed a simple graphical method to determine the nearest neighbour distances and phase-shifts. The basic idea is that, usually, scattering from the first shell dominates the EFS curve. The  $Sin[2kr_j + 2S_j(K)]$  factor arises from the phase change felt by the wave-function on its outward and return trips (77) plus the phase-shifts  $S_j(k)$  caused  $S_{j}(k)$  caused

central atom. Lytle et al. (76) assume that  $S_i$  is linear in K,

where  $\textbf{q}_j$  and  $\beta_j$  are constants. Substituting this into the argument of the sine, we can define an  $n_j$  given by,

$$2Kr_{j} - 2a_{j}K + 2\beta_{j} = \frac{1}{2}n_{j}\pi$$
 ... 4.10

where,  $n_j = 0, 2, 4, \ldots$  for maxima and

 $n_{j} = 1, 3, 5, \dots$  for minima.

For the first co-ordination shell

 $2K(R_1 - q_1) + 2 \beta_1 = \frac{1}{2} n_1 \pi$  ... 4.11 A straight line plot of  $n_1$  against K (in  $A^{o^{-1}}$ ) for the observed maxima and minima determines  $(R_1 - q_1)$  from the slope M. The relation between M and  $(R_1 - q_1)$  is,

 $M = \frac{4}{\pi} (R_1 - q_1) \qquad \dots 4.12$ Once  $q_1$  is evaluated for a standard material,  $R_1$  the interatomic distance for the unknown compounds can be calculated.

The LSS theory is applied to the complexes having general formula  $\operatorname{trans}[\operatorname{Co}(\operatorname{AA})_2(\operatorname{NO}_2)_2]\operatorname{NO}_3$  where AA = en, tn, pn. In Table 4.8 are given the values of EXAFS maxima and minima for these complexes. Using these values the K values are calculated using the relation,

$$K = (0.263 \text{ E})^{1/2} \qquad \dots 4.13$$

The K values are also included in Table 4.8. The graphs of n versus K are plotted Fig. 4.8, the slopes 'M' of which are related with the chemical bonding parameter  $q_1$  by the relation

$$M = \frac{4}{\pi} (R_1 - \alpha_1) \qquad \dots \quad 4.14$$

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Table	

c	Peak	Trans[Co(en)	2 (N02)2 ]N03	Trans[Co(tn)	2 (NO2)2 ]NO3	Trans[Co(pn)	2 (NO2)2 ]NO3
		E(eV) +1 eV	K <sub>(A</sub> °)-1	E(eV) +1 eV	K(A°)-1	E(eV) +1 eV	K (A°) <sup>-1</sup>
0	A	17.46	2.143	11.05	1.71	15.26	2.00
Г	Ծ	41.90	3.32	39 30	3.22	39•90	3.24
2	В	67.35	4.20	63.86	4.10	53.10	3.74
e	θ	102.30	5.19	84.73	4.72	71.05	4.32
4	U	113.4	5.46	108.06	5.34	79.8	4.58
ß	حر	124.8	5.73	125.75	5.75	96.77	5.05
9	D	142.0	6.11	135.08	5.96	104.5	5.24
L	م,	164.6	6 <b>.</b> 58	140.73	6.08	116.0	5.52
8	យ	169.0	6.67	152.00	6.32	138.5	6•04
6	Ű	178.5	6 <b>.</b> 85	157.18	6.43	162.1	6.53
10	ſĽ	188.1	7.03	175.00	6.78	180.6	6•89



Fig.46 VARIATION OF n WITH K FOR Co(III) COMPLEXEX.

The M values in each case are used to get  $(R_1 - q_1)$  values. Knowing  $R_1$ , the metal-ligand distance from crystallographic data,  $\mathbf{q}_1$  in each case can be determined. However, as crystallographic data for these complexes are not available, we have used the metal-ligand distance R1 calculated from Levy's method to determine the set of  $q_1$  values. The  $(R_1 - q_1)$  and  $q_1$  values for the complexes are presented in Table 4.9 in which the average metalligand distance 'd' as calculated using LSS theory and the 'q' values are also included. Such a set of  $\boldsymbol{\alpha}_1$  values for the present complexes would immediately reflect the change in the bonding with the ligand substitution. It has been assumed in the theory developed by Lytle et al. (76) that the  $a_1$  value for a given crystal structure should not vary. However, such variations for the same type of crystal structure have been reported by Lokhande et al. (78) which are attributed to the changing iono-covalent bonding. The variation in 4 also reflects change in the valence of the absorbing atom as suggested by Barhate et al. (79). Thus for the compounds in which the valence of the absorbing atom does not change, like Co<sup>+3</sup> in the present case, the change in the iono-covalent character of metal-ligand bond can be determined by correlating variation of  $\boldsymbol{q}_1$  with the effective atomic charge 'q'. Thus, we observe from the Table 4.9 that increase in the  $\boldsymbol{\mathtt{q}}_1$  value corresponds to increase in the covalent character of the metal-ligand bond.

The average metal-ligand distance (bond length)  $\mathbf{d}_{\mathbf{J}}$  can be calculated by taking average  $\mathbf{q}_{1}$  for these complexes on the

complexes.
$\texttt{trans[Co(AA)_2(NO_2)_2]NO_3}$
theory to
Lytle <u>et al</u> .'s
Application of
Table 4.9 :

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Absorber	Slope 'M' of n K plot	R1 A <sup>0</sup> from Levy's method	( <sub>R1</sub> - 4) <sub>A</sub> o	a <sub>1</sub> Ao	Bond length d A <sup>o</sup>	Effective atomic charge g electron/atom t o.1 electron/atom
$trans[Co(en)_2(NO_2)_2]NO_3$	2.0833	2.0786	1.6362	0.4424	2.1417	1.85
$trans[Co(tn)_{2}(NO_{2})_{2}]NO_{3}$	2.75	2.6898	2.1598	0.5300	2.6653	1.62
$trans[Co(pn)_2(NO_2)_2]NO_3$	3.00	2.9003	2.3562	0.5441	2.8617	1.575

assumption that the structure being the same, the chemical bonding parameter  $\mathfrak{q}_1$  should be constant for the crystal as a whole (LRO approach). The average  $\mathfrak{q}_1$  is then added to the  $(R_1 - \mathfrak{q}_1)$  value of each complex to get the average metal-ligand distance 'd'.

#### REFERENCES

- 1. Agarwal, B.K. and J. Phys. C. Solid st. Phys., <u>3</u>, Verma, L.P. 535, (1970).
- Sapre, V.B. and J. Phys. C. Solid st. Phys., <u>5</u>, Mande, C. 793, (1972).
- 3. Hanson, H. and The Phys. Rev., <u>76</u>, 118-121, (1949).
  Beeman, W.W.
- 4. Mande, C. and The Proc. of Indian Academy of Nigavekar, A.S.
  Sciences, <u>67</u>, (1968).
- 5. Kondawar, V.K. and J. Phys. C. Solid st. Phys., <u>9</u>, (1976). Mande, C.
- 6. Chetal, A.R. and J. Phy. F. Metal Phys., <u>5</u>, (1975). Sarode, P.R.
- 7. Sarode, P.R. and J. Phy. Soc. of Japan, <u>40</u>, 6, (1976). Chetal, A.R.
- 8. Mitchel, C. and J. Chem. Phy., <u>20</u>, 1298, (1952). Beeman, W.E.
- 9. Sapre, V.B. and J. Phy. Chem., <u>34</u>, 1351-56, (1973). Mande, C.
- 10. Mande, C. and The Proc. of the Indian Academy of Chetal, A.R. Science, <u>62</u>, (1965).

- 11. Deshmukh, P. and Praman4, vol. 2, No.3, p. 138-147, Mande, C. (1974).
- 12. Pendharkar, A.V. Chem. Phy. <u>7</u>, 244-54, (1975). and Mande, C.
- 13. Bergengren, J. Zeit. f. Physik, <u>3</u>, 287 (1920).
- 14. Lindh, A.E. Zeit.f. Physik, <u>6</u>, 303, (1921).
- 15. Sarode, P.R., J. Phy. C., <u>12</u>, 2439, (1979). Ramsesha, S., Madhusudan, W.H. and Rao, C.N.R.
- 16. Pendharkar, A.V. Pramana, <u>1</u>, 104, (1973). and Mande, C.
- 17. Cauchois, Y. "Les Spectras de Rayons X et al la structure Electronique de la Matiere" Gauthier-Villars Company, Paris (1948).
- 18. Kunzl, V. Coll. Trav. Chim. Tchecoslovaquie, <u>4</u>, 213, (1932).
- 19. Boehm, G., Naturforsch, <u>96</u>, 509, (1954). Faessler, A. and Ruttmayer, G.
- 20. Mande, C. and Chetal, A.R. Karl-Marx Univ. Leipzig (1966).

21. Miller, A. J. Phys. Chem. Soc., <u>29</u>, 633, (1968).

- 22. Ovsyannikova, I.A., Bull. Acad. Sci. USSR. Phys. Ser. <u>31</u>, Batsanov, S.S., 936, (1971). Nanonova, L.I., Batsanova, L.R. and Nekrasova, E.A.
- 23. Dey, A.K. and J. Chem. Phys., <u>59</u>, 1397, (1973). Agarwal, B.K.
- 24. Dey, A.K. and Nuovo Cimento Lett., <u>1</u>, 803, (1971). Agarwal, B.K.
- 25. Batsanov, S.S. and In Chemical Bonds in Semiconductors Ovsyannikova, I.A. and Thermodynamics, ed. by N.N.Sirota. (Consultants Bureau, New York 1968) P. 65.
- 26. Sapre, V.B. J. Phys. C5, 793, (1972). and Mande, C.
- 27. Adhyapak, S.V., Nuovo Cimento 35B, 179, (1974). Kanetkar, S.M., Nigavekar, A.S.
- 28. Hanson, H.P. Developments in Applied Spectroscopy, <u>26</u>, 254, (1963).
- 29. Van Nordstrand, R.A. Advances in Catalysis, <u>12</u>, New York, (1960).

- 30. Van Nordstrand, R.A. Conf. Non-crystalline solids, New York (1960).
- 31. Sinha, K.P. and Ind. J. Phy., <u>37</u>, 257, (1963). Mande, C.
- 32. Mande, C. and International conference on X-ray Chetal, A.R. spectra and chemical binding, Leipzig, East Germany, (1965).
- 33. Chetal, A.R. International Conference on X-ray processes in Matter. P.104. Helisinki Univ. of Tech., Otaniemi, Finland, (1974).
- 34. Nigam, H.L., and Chem. Comm., <u>14</u>, 761, (1971). Shrivastava, U.C.
- 35. Nigam, H.L. and Ind. J. Chem., <u>9</u>, 1301, (1971). Shrivastava, U.C.
- 36. Alok Kumar <u>et al</u>. J. Phys. C. Solid St. Phys., <u>13</u>, 3523, (1980).
- 37. Singh, A.K. and J. Phys. F. Metal Phys., <u>5</u>, (1975). Kashyap, B.M.S.
- 38. Mehta, S. and Phys. Letters, vol.70A, <u>2</u>, (1979). Anikhindi, R.G.
- 39. Koul, P.N. <u>et al</u>. J. Phys. Soc. of Japan, Vol.50, No.1, p. 246-250, (1981).

40. Kronig, R. de L. Z. Phys., <u>75</u>, 486, (1932). 41. Paratt, L.G. Rev. Mod. Phys., <u>31</u>, 616, (1950). Phil. Mag., <u>40</u>, 345, (1979). 42. Gurman, S.J. and Pettiger, R.F. 43. Saxena, K.N., Phys. Letts., <u>78</u>, 325, (1980). Saxena, C.P., Anikhindi, R.G. and Kaveshwar, A.S. The chemical elements and their 44. Sidgwick, N.V. compounds, 1, Oxford Uni. Press, Amen House, London, (1962). 45. Pauling, L. "The Nature of Chemical Bond", 3rd ed.

Cornell Uni. Press, Ithaca, New York, (1960).

46. Huheey, J.S. Inorganic Chemistry, Principles of structure and reactivity. Harper and Row Publishers N.Y. (1972).

47. Barnes, A.H. Phys. Rev., <u>44</u>, 141, (1933).

48. Beeman, W.W. and Phys. Rev., <u>56</u>, 392, (1939). Friedman, H.

49. Krutter, H.M. Phys. Rev., <u>48</u>, 664, (1935).

50. Slater, J.C. Phys. Rev., <u>49</u>, 537, (1936).

- 51. Carter, F.L. NBS Special Publication No.323, P. 385, (1971).
- 52. Gianturco, F.A. Mol. Phys., <u>14</u>, 223, (1968). and Coulson, C.A.
- 53. Nigam, A.K. and J. Phys. F., <u>3</u>, 1251, (1973). Gupta, M.K.
- 54. Agarwal, B.K. X-ray spectroscopy, Springer-Verlag, Berlin Heidelburg, New York, (1979).
- 55. Ghatikar, M.N., J. Phys. C. Solid st. Phys., <u>10</u>, Padalia, B.D. and 4173, (1977). Nayak, R.M.
- 56. Clementi, E. and Atomic Data and Nuclear Data, <u>14</u>, Roetti, C. 177-478, (1974).
- 57. Fajans, K. Naturwissenschaften, <u>11</u>, 165, (1923).
- 57a. Tsuchida, R. Bull. Chem. Soc., Japan, <u>13</u>, 338, 436, 471, (1938).
- 58. Parkovic, S.F. and Inorg. Chem., <u>4</u>, 20, (1965). Meek, D.W.
- 59. Khasbardar, B.V. Ph.D. thesis, Shivaji University, Kolhapur, (1978).
- 60. Day, M.C. andTheoretical Inorganic chemistry,Selbin, J.Litton Educational Publishing INC.

- 61. Kazuo, Nakamoto, Spectroscopy and structure of metal Paul, McCarthy. chelate compounds. John Wiley and Sons, INC, New York.
- 62. Chaberek, S. and "Organic sequestering Agents", John Martell, A.E. Wiley and Sons, Inc., New York, 1959.
- 63. Sillen, L.G. and Stability constants of Metal-Ion Martell, A.E. complexes, The chemical society, London, 1964.
- 64. Bhat, N.V., Spectrochemica Acta, <u>35</u> B, 489, (1980). Syamal, A., Salvi, S.V. and Umadikar, P.H.
- 65. Cotton, F.A. Chemical Applications of Group Theory, 2nd ed. Wiley, New York, (1970).
- 66. Obashi, M. Jap. J. App. Phys. vol. 16, <u>1</u>, p. 167-171, (1977).
- 67. Levy, R.M. J. Chem. Phys., <u>43</u>, 1846, (1965).

69. Lytle, F.W.

70. Lytle, F.W.

- 68. Lytle, F.W. Phys. noncryst. solids. Proc. Int. Conf. Delft. (Amsterdam) p. 12 (1964).
- - Develop. Appl. Spectr., <u>2</u>, 285, (1963).

Advance X-ray Anal., 9, 398, (1966).

- 71. Ballal, M.M. and Jap. J. Appl. Phys., <u>16</u>, 2169, (1977). Mande, C.
- 72. Kondavar, V.K. X-ray Spectrometry, <u>5</u>, 2, (1976). and Mande, C.
- 73. Deshmukh, P., Pramana, <u>6</u>, 305, (1976). Deshmukh, P.C. and Mande, C.
- 74. Agarwal, B.K. J. Phys. Cl0, 3213, (1977). and Johri, R.K.
- 75. Stern, E.A. Phys. Rev. <u>B.10</u>, 3027, (1974).
- 76. Lytle, F.W., Phys. Rev., <u>B.11</u>, 4825, (1975). Sayers, D.E. and Stern, E.A.
- 77. Lee, P.A. and Pendry, Phys. Rev., <u>B-11</u>, 2795, (1975). J.B.
- 78. Lokhande, N.R. Jour. of Phys. Soc. Jap., <u>47</u>, 614, and Chetal, A.R. (1979).
- 79. Barhate, A.V., Solid state Communications, <u>36</u>, Pendharkar, A.Y., 473, (1980). Sapre, V.B. and Mande, C.