

Synthesis and characterization of metal complexes of s-propanoyl (β -n-propanoyl) dithiocarbazate with some 3d-transition metal ions

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Synthesis of complexes containing tetradentate ligands, Especially the macrocyclic ones, has evoked much interest due to their unique properties and their relation to biologically important system. In the present piece of research work, syntheses and characterizations of some novel complexes N, S ligands with divalent (Cu^{++} , Ni^{++} , Co^{++} , Zn^{++}) and trivalent metal ions viz. Fe^{++} , and Cr^{+++} with S-propanoyl- (β -N-propanoyl) dithiocarbazate has been undertaken. After synthesis of the complexes spectroscopic studies such as electronic, IR were done alongwith magnetic moments, conductometric and ligand field parameters' evaluations. The results confirmed the four coordination of $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Cd}(\text{II})$ ions while $\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$ were found to be six coordinate, and nitrate thiocyanate unidently attached to metal inside the coordination sphere.

Introduction

Several reports 1-4 have appeared on the studies of triphenyl phosphine complexes with $\text{MM}'(\text{NCS})_4$ [Where $\text{M} = \text{Co}^{++}$, Ni^{++} , $\text{M}' = \text{Hg}^{++}$, $(\text{Ag}^+)_2$, $(\text{TI}^+)_2$]. It was observed that when PPH_3 is linked with a metal, further linkage of the ligand to the metal is very difficult probably due to the large steric hindrance of the ligand.

Despite the extensive physicochemical investigations on a variety of organic sulphur compounds, no unequivocal conclusion has been reached regarding the participation of the 3d orbitals of the sulphur atom in resonance interaction⁵. In the case of compounds containing the bivalent sulphur atom, it has been generally observed that significant (d - p) π type of resonance interaction involving the participation of the 3d orbitals of the sulphur atom takes place in the ground state as well as in the excited state in alkyl aryl sulphides, provided a sufficiently strong electron releasing group is present para to the alkylmercapto group⁶. A similar conclusion has also been reached for alkyl aryl sulphones from a study of dipole moments⁷, dissociation constants⁸ and UV absorption spectra⁹ of a number of alkyl aryl sulphones.

As a part of our general study of N, S ligands we have undertaken the synthesis and characterization of some new complexes of divalent Cu, Ni, Co, Zn and trivalent metal ions e.g. Fe, and Cr with S-propanoyl- (β -N-propanoyl) dithiocarbazate.

Experimental

a) $[\text{M}(\text{C}_7\text{H}_{11}\text{N}_2\text{S}_2\text{O}_2)_2]$ where $\text{M} = \text{Cu}^{+2}$, Co^{+2} , Ni^{+2} and Zn^{+2}

S-propanoyl (β -N-propanoyl) dithiocarbazate (0.008 mol) was added to aqueous potassium hydroxide (0.008 mol) in 30 mL water, stirred for five minutes and to the filtrate was added with stirring a solution of metal nitrate (0.004 mol) in water (20 mL) and refluxed on water bath for two hours. The resulting precipitate was filtered, washed with water and ethanol and dried in vacuo over P_4O_{10} .

b) $[\text{M}(\text{C}_7\text{H}_{11}\text{N}_2\text{S}_2\text{O}_2)_2(\text{X})(\text{H}_2\text{O})]$ - Where $\text{M} = \text{Fe}^{+3}$, Cr^{+3} and $\text{X} = \text{NO}_3$, or NCS S-propanoyl (β -N-propanoyl) dithiocarbazate (SPDTC) (0.008 mol) was added to aqueous potassium hydroxide (0.008 mol in 30 mL water) stirred for ten minute, filtered and to the filtrate was added with stirring a solution of Ferric/ Chromium nitrate (0.004 mol) in water (20 mL) and refluxed on water bath for two hours. The resulting precipitate was filtered, washed with water and ethanol and dried under vacuum.

In Order to get isocyanate complex first Ferric/ Chromium isocyanate were prepared as follows-

To a solution of hydrated metal nitrate (Ferric nitrate hexahydrate and chromium nitrate hexa hydrate/ (0.004 mol) in anhydrous methanol (25 mL) was added a solution of potassium thio cyanate (0.020 mol) in the same solvent (25 mL). The precipitated potassium nitrate was filtered, the filtrate added to an aqueous solution (25 mL) of SPDTC (S-propanoyl) (β -N-propanoyl) dithiocarbazate (0.004 mol) containing potassium hydroxide (0.008 mol).

The whole contents were refluxed for two hour to ensure the completion of reaction, the precipitate obtained was filtered, washed with water and ethanol and dried under vacuum over anhydrous calcium chloride.

Results and Discussions

All the complexes are stable to air and moisture. They decompose at higher temperatures. The complexes are insoluble in water and common organic solvents but soluble in DMF, DMSO. The negligibly low values of molar conductance around $5\text{-}6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ of these complexes in $1 \times 10^{-3} \text{ M}$ DMF solution suggest their non-electrolytic behavior. Elemental analysis indicates metal to ligand ratio as 1:2.

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Table 1. Analytical data of the bi- and trivalent metal complexes.

S.No	Complex	Colour	% Chemical analysis Found (Calculated)				Metal
			C	H	N	S	
1	[Cu(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂]	Greenish	32.63 (33.50)	3.93 (4.38)	10.70 (11.16)	24.84 (25.52)	11.93 (12.67)
2	[Co(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂]	Bluish	32.90 (33.80)	3.95 (4.42)	10.93 (11.26)	24.85 (25.75)	10.92 (11.85)
3	[Ni(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂]	Brown	32.92 (33.82)	3.98 (4.42)	10.96 (11.27)	24.86 (25.76)	10.83 (11.81)
4	[Zn(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂]	Colour less	32.86 (33.37)	3.82 (4.37)	10.92 (11.12)	24.90 (25.42)	11.90 (12.98)
5	[Cr(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	Dark Blue	28.79 (29.47)	3.83 (4.21)	11.85 (12.28)	21.88 (22.45)	8.65 (9.12)
6	[Fe(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	Reddish	28.89 (29.27)	3.85 (4.18)	11.93 (12.19)	21.88 (22.30)	8.93 (9.73)
7	[Cr(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	Dark Blue	30.88 (31.80)	3.93 (4.24)	11.94 (12.36)	27.87 (28.26)	8.89 (9.18)
8	[Fe(C ₇ H ₁₁ N ₂ O ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	Reddish	30.90 (31.58)	3.98 (4.21)	11.98 (12.28)	27.78 (28.87)	8.87 (9.80)

Zn(II) complex is diamagnetic, and the electronic spectra does not display absorption band in visible region. The observed magnetic moment value for the Cu(II) complex is 1.99 B.M. The electronic spectrum shows three bands at 16100, 18500 and 20,000 cm⁻¹ which can be assigned to ²B_{1g} → ²B_{2g}, ²B_{1g} → ²A_{1g} and ²B_{1g} → ²E_g transition (10) respectively indicating square planar geometry⁽¹¹⁾.

Moment value of Cr(III) complex are lower than the value required for d³-ion i.e. 3.86 B.M. and this can be explained in terms of the existence of antiferromagnetic⁽¹²⁻¹³⁾ interaction between two or more chromium atoms through the bridging group in a polymeric structure. The ligand field parameters Δ, and B-have been calculated by spectral procedure⁽¹⁴⁾. The positions of the bands assignable to transitions ⁴A_{2g} → ⁴T_{2g}(v₁), ⁴A_{2g} → ⁴T_{1g}(F)(v₂) and ⁴A_{2g} → ⁴T_{1g}(P)(v₃), the values of the parameters Δ and B-are characteristics of Octahedral geometry⁽¹⁵⁾.

The nephelauxetic ratio (β) which is the ratio of Racah inter electronic repulsion parameter (β) for the chromium ion in a complex to its value in the gaseous ion⁽¹⁶⁾ has been calculated and

this comes out to 0.72-0.62 indicating a covalent character of (Cr-S) bond in these derivatives.

For the Co(II) complex two strong bands at 7100 and 16360 cm⁻¹ may be assigned to the transition ⁴A_{2g} → ⁴T_{1g}(F)(v₂) and ⁴A_{2g} → ⁴T_{1g}(P)(v₃) respectively. The splitting of the v₂-band as seen in the case of oxygen donor tetrahedral complexes was not seen since the ligands α-substituted⁽¹⁷⁾.

The Ni(II) complex exhibit two bands at 7250 and 14100 cm⁻¹ attributable to the transitions ³A_{2g} → ³T_{1g}(v₂) and ³T_{1g}(v₃) → ³T_{1g}(P) respectively. The Δ= 3940 cm⁻¹ and for the Co(II) complex Δ = 4040 cm⁻¹ for the Ni(II) complex indicate tetrahedral geometries for these complexes⁽¹⁸⁻¹⁹⁾.

The values of magnetic moment observed for the present complexes 5.70-5.89 B.M are also in agreement with the octahedral geometry. The Ni(II) complex shows magnetic moment value of 5.9 BM which is in the range expected for octahedral complexes. The electronic spectrum shows three bands at 16160, 20000 and 21740 cm⁻¹ The first two are assigned to ³A_{2g} → ³T_{1g}(F) and ³A_{2g}

→ ${}^3T_2g(P)$ transition. The last weak band observed at 20000 cm^{-1} is assignable to spinforbidden ${}^3A_2g \rightarrow {}^1T_1g$ transition. On the basis of above observations Ni(II) complex is assigned octahedral geometry.

Electronic spectral studies

All the absorption bands observed in the reflectance spectra (using MgO as reference) of the present iron (III) complexes are of low intensity and those beyond 25000 cm^{-1} may be presumably due to charge transfer. The brownish red colour is usually ascribed to

the presence of one or more low lying charge transfer absorption bands⁽²⁰⁾ in the near infra-red region at approximately 11000 cm^{-1} which may be assigned to ligand field transition. The iron (III) ion in aqueous solution is very much subject to hydrolysis and yellowish brown colour commonly observed is not due to ligand field bands of $Fe(H_2O)^{+3}$ but rather to charge transfer band. Position and intensity of these bands are only sensitive to anions. Because of other very intense bands one does not usually observe d-d transition in the visible spectra of iron (III) compounds having the ground states 6s.

Table 2. Electronic spectra and magnetic moment data of s-propanoyl [β -n-propanoyl] dithio carbamate

S.NO.	Compound	λ_{max} (KK)			Δ_{kk}	B (Free ion = 1.03)	β	$\mu\text{-eff}$ (B.M)
		ν_1	ν_2	ν_3				
1.	$[Cr(C_7H_{11}N_2O_2S_2)_2(NO_3)(H_2O)]$	14.3	2260	32 30	14.3	64	62	3.84
2	$[Cr(C_7H_{11}N_2O_2S_2)_2(NCS)(H_2O)]$	14 27	21.5	32 50	1427	73	0.71	3.86

In the present iron (III) complexes the bands observed in the region $12870\text{-}14200\text{ cm}^{-1}$, $16310\text{-}19300\text{ cm}^{-1}$, $23300\text{-}25200\text{ cm}^{-1}$, $27300\text{-}31500\text{ cm}^{-1}$ and $36200\text{-}41600\text{ cm}^{-1}$ are tentatively assigned to $6A_1g \rightarrow {}^4T_1g$ (G)(d-d Transition), $6A_1g \rightarrow {}^4T_2g$ (G)(d-d Transition), $t_2g \rightarrow \pi^*$ (Charge-Transfer Transition), $\pi \rightarrow e_g$ (Charge Transfer Transition) and $\pi \rightarrow \pi^*$ respectively. Complete analysis of spectra of octahedral iron (III) is not possible due to complications which are beyond control.

or $Dq = 11.0$

B

The transition $6A_1g \rightarrow {}^4T_1g$ gives directly the values of $10Dq$ and B. The calculated values of $10Dq$, B, C and β_{35} from present iron (III) complexes presented in Table.

From absorption spectra of present iron (III) complexes ($\pi \rightarrow t_2g$) and ($e_g \rightarrow \pi^*$) are evaluated from charge transfer bands by using the following relations

$$(\pi \rightarrow e_g) - \Delta = (\pi \rightarrow t_2g) \text{ in KK} \quad (1)$$

$$(t_2g \rightarrow \pi^*) - \Delta = (e_g \rightarrow \pi^*) \text{ in KK} \quad (2)$$

$$(\pi \rightarrow t_2g) + (t_2g \rightarrow e_g) + (e_g \rightarrow \pi^*) = (\pi \rightarrow \pi^*) \quad (3)$$

Table 3. Electronic spectral data and relevant ligand field parameters

S.N.	COMPOUND	Observed Bands cm^{-1}	Assignments	$10Dq$ cm^{-1}	B cm^{-1}	c cm^{-1}	β_{35}
1	$[Fe(C_7H_{11}N_2O_2S_2)_2(NO_3)(H_2O)]$	13310	$6A_1g \rightarrow {}^4T_1g$ (G)	13310	1280	5120	0.93
		16340	$6A_1g \rightarrow {}^4T_2g$ (G)				
		24170	$t_2g \rightarrow \pi^*$				
		29030	$\pi \rightarrow e_g$				
		36635	$\pi \rightarrow \pi^*$				
2	$[Fe(C_7H_{11}N_2O_2S_2)_2(NCS)(H_2O)]$	13240	$6A_1g \rightarrow {}^4T_1g$ (G)	13240	1212	4848	0.92
		16560	$6A_1g \rightarrow {}^4T_2g$ (G)				
		24040	$t_2g \rightarrow \pi^*$				
		28030	$\pi \rightarrow e_g$				
		36710	$\pi \rightarrow \pi^*$				

Table 4. Relevant ligand field energy parameters in high-spin octahedral iron (iii) complexes

S.	Complex in Table I.	Δ K.K	F2 KK	F4 KK	$(\pi \rightarrow t_{2g})$ KK	$(e_g \rightarrow \pi^*)$ KK	$(\pi \rightarrow \pi^*)$ KK	ν	g
N.	1	2	3	4	5	6	7	8	9
1	[Fe(C7H11N2O2S2)2' (N03) (H20)]	13.20	92.39	66.71	15.80	10.95	39.95	47.44	1.9713
2	[Fe(C7H11N2O2S2)2 (NCS) (H20)]	13.21	97.63	60.33	14.80	10.80	38.80	22.55	1.8635

The assignments to different transition observed in the absorption spectra of the present ferric complex have been made by getting the best fit in the Tanabe-Sugano diagram for d^5 configuration.

$$\frac{6A_1g \rightarrow {}^4T_1g}{B} = 110$$

According to Miller et al.⁽²¹⁾ for simple one electron molecular orbital treatment the sum of $(\pi \rightarrow t_{2g})$, $t_{2g} \rightarrow e_g$ and $t_{2g} \rightarrow \pi^*$ in KK should be equal to energy of the $(\pi \rightarrow \pi^*)$ transition. The value of $t_{2g} \rightarrow e_g$ is commonly known as $10Dq$ and can also be evaluated by Figgis equation

$$\frac{6A_1g \rightarrow {}^4T_1g}{B} = 24$$

The observed and calculated values for the transition $(\pi \rightarrow \pi^*)$ are in the range 36.2-41.6 K.K. and 38.80-42.50 K.K. respectively. Thus the calculated and observed $(\pi \rightarrow \pi^*)$ energies are in good agreement.

The values of spin orbit coupling constant (λ) and Lande's splitting factor (g) for the present iron (III) complexes are calculated by using the following relations and their values are tabulated in table (III).

$$\mu = \mu_o (1 - \alpha\lambda/10Dq)$$

$$g = (2 - 8\lambda/10Dq)$$

μ_o = Observed magnetic moment in B.M.

μ = spin only value 5.92 BM

α = A constant depending on metal ion stereochemistry

Condon-Shortly Ligand field repulsion parameters F_2' and F_4' .

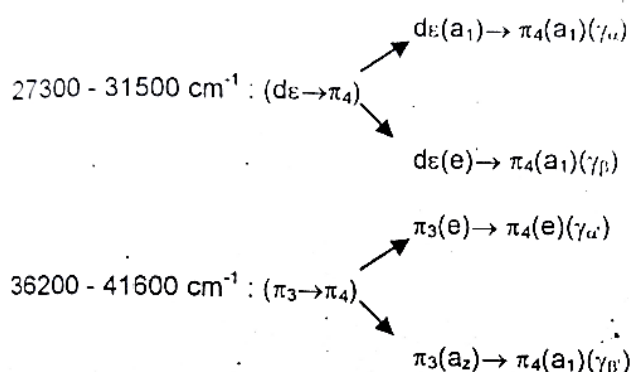
are also calculated by using the mathematical formulations given by Low and Rosengarton⁽²²⁾

$$C = 35F_4'/442 \text{ and } B = [F_2'/49 - 5F_4'/441]$$

The free ion value of F_2' and F_4' for iron (III) complexes are 80.80 KK and 4983 K.K. respectively, while the corresponding values for complexed iron (III) ion are found in the range 91.12, 97.63 K.K. and 60.33-66.71 K.K. respectively. The phenomenal increase in F_2' and F_4' values during complexation may be due to expanded radial functions of the d-electron⁽²³⁾

As reported by Carlo-Tos⁽²⁴⁾ very weak spin forbidden transition

in high spin outer octahedral iron(III) complexes observed in the region 28170-29150 cm^{-1} and 37600 - 38750 cm^{-1} are further splitted as well as expected to overlap. In our present iron (III) complexes the bands observed in the region 27300-31500 cm^{-1} and 36200-41600 cm^{-1} are also splitted as below



These splitted band ($\nu_{\alpha'}$ & ν_{β}) and (ν_{α} & $\nu_{\beta'}$) have about the same energy and are expected⁽²⁴⁾ to overlap 1000

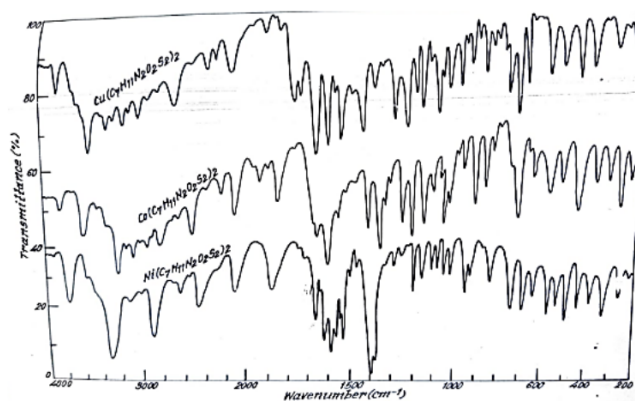


Figure 1. IR Spectra of complexes.

IR Studies

The ligand s-propanoyl (β -N-propanoyl) dithio carbazate is a potential bidentate ligand and sterically favourable three types of coordinations either through-CONH, C=O or $>C=S$. Ligand prepared complexes in the alkaline medium and the attempts to prepare complexes in the neutral medium did not gave fruitful results. This suggests that nucleophilicity of the ligand is greatly increased in alkaline medium probably due to creation of anionic site in situ.⁽²⁵⁻²⁷⁾

The ligand exists in thione and thiol tautomeric form and in alkaline medium the ligand is deprotonated and bonding occurs through the thiolate anion generated from thiol causing spin pairing in the complex. (28) The IR-spectra of the free ligand exhibit broad band at $\sim 3410\text{cm}^{-1}$ which have been assigned (29-30) to νSH and νNH respectively. The $\nu(\text{SH})$ disappears in the IR-spectra of the complexes while no significant change is noticed in νNH modes indicating that bonding is taking place through sulphur atom only and $-\text{NH}$ group is not involved in complexation.

The strong bands at 1605-1590, 1480-1490, 1360-1310 and 1260-1280 cm^{-1} in the IR-spectra of ligand and their metal complexes may be assigned to the combinations of $\nu\text{NH}+\text{C}=\text{C}$, $\text{CH}_2+\text{C}=\text{C}$, $\text{C}=\text{N}+\text{C}=\text{S}$ and mixing of $\nu(\text{C}=\text{S}+\text{C}=\text{N})$ respectively. (31-34)

In case of Dithiocarbamate complexes it has been suggested that when both the sulphur atoms of ligands are involved in bonding the $\nu_{\text{as}}(\text{CSS})$ mode (at $\sim 1000\text{cm}^{-1}$) does not split, whereas splitting of the band takes place when unidentate sulphur bonding is involved, the IR-spectra of the ligand does not exhibit any band around 1000 cm^{-1} but a strong band around 870 cm^{-1} appears to be due to $\nu_{\text{as}}(\text{CSS})$ mode. The appearance of only a single band in the range of 800-950 cm^{-1} in the metal complexes indicates that both the sulphur atoms of the ligands is taking part in bonding in these complexes. The band at about 610 cm^{-1} in the ligand and the corresponding metal complexes has been assigned to either $\nu_{\text{as}}(\text{CSS})$ or $\nu(\text{C}=\text{S})$. The new band appearing at 325-380 cm^{-1} may be assigned to $\nu(\text{M}-\text{S})$.

Aromatic in plane deformation vibration bands between 1230 and 960 cm^{-1} = CH - out of the plane vibration band near 860 cm^{-1} and aromatic (CH) out of plane vibrations between (35) 860 and 735 cm^{-1} in the ligand do not resemble the IR-spectra of the complexes. This is another support for complex formation.

The characteristic bands due to the (C=O) and (C=C) group of the complexes are found at 1630 and 1530 cm^{-1} respectively. The former one shifts to higher frequencies whereas the latter one shifts to lower frequencies. The bands appearing in the region 1720-1450 cm^{-1} , on complexation are difficult to assign as various bands fall in this region. However the bands have been assigned tentatively comparing the spectra of the respective ligand. (36)

A sharp band at 1600 cm^{-1} due to $\nu(\text{C}=\text{O})$ of the ligand do not shift in chelation suggesting non coordination of the ketonic oxygen. (37)

Besides the IR-spectra of the complex indicate shift of $\nu(\text{C}=\text{S})$ mode of the free ligand and a sharp strong band at 1570-1550 cm^{-1} attributable to $\nu(\text{C}=\text{N})$ mode. The π nitrogen coordination is evident from the shift $\nu(\text{NH})$ of the free ligand appearing at 3320 cm^{-1} to lower wave numbers (3080-3240 cm^{-1}). The far IR spectra of the complexes exhibit bands in the region 460-275 and 380-230 cm^{-1} on which are tentatively attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ modes respectively. (38-43)

The presence of coordinated water is indicated by the

appearance of a broad band at 3000-3250 cm^{-1} and a sharp peak (44-45) at 830 cm^{-1} .

The infra-red spectral bands due to νCN , νCS and δNCS indicates the presence of thiocyanate group (46-48) are in accordance with HSAB-principle (49)

The IR-spectra exhibit bands at about 1495, 1290, 1010 and 810 cm^{-1} characteristic of unidentate nitrate group. (50-54)

Conclusions

The complexes prepared were obtained in good yield and were stable at room temperature in air and moisture. They were found insoluble in water and common organic solvents but insoluble in DMF and DMSO. Their non-electrolytic behaviour was revealed from their low conductivity values. The colour in the complexes was attributed to d-d transitions. IR spectra showed presence of coordinated water molecules. From the studies it could be inferred that analytical, conductivity, magnetic measurements and spectral data of the complexes are consistent with four coordination of Cu(II), Ni(II), Co(II) and Cd(II) ions while Cr(III) and Fe(III) are six coordinate, and nitrate thiocyanate unidentate attached to metal inside the coordination sphere.

References

1. PP. Singh, S.A Khan & J.P. Pandey, *Cand J Chem.* 57 (1979), 3061
2. P.P. Singh, R.C. Verma & N. Singh, *J. Less Comm. Metal*, 70, (1980), 155 3.
3. PP. Singh, SA Khan and M U. Khan - *Jour Ind. Chem Soc.* 35 (1982) 59
4. R. Makhija, L Pazdernic and R. Rivest, *Cand J. Chem.*, 51 (1973), 438
5. (a) L Goodman & RW. Taft, *J. Amer. Chem. Soc.* 87, (1965), 4385
(b) G.L Bendazzoli and C. Zauli, *J. Chem. Soc.*, (1965) 6827.
6. V. Baliah and M. Uma, *Tetrahedron*, 19 (1963), 455
7. V. Baliah and S.P. Shanmuganathan- *Trans Faraday Soc.* 55 (1959), 232
8. S.P. Shanmuganathan & N Yanajakshi, *Proc Ind Academy of Sciences*, 69, (1969), 212
9. A. Mangini, *Pure and Applied Chemistry*, 1, (1963), 103
10. L Sacconi and M. Ciampolini, *J. Chem. Soc.*, 274 (1964), 78
11. A. Bose and R. Chatterjee, *Proc. Phys. Soc.*, 83 (1963), 23
12. R.G. Shulman, S. Sugano and K. Knox, *Phys. Rev.*, 130 (1963), 512
13. Dubicki, G.A. Kakos & G Winter, *Aust J. Chem.*, 21(1968) 1451.
14. E Konig, *The nephelauxetic effect in structure and bonding vol. 9* (Springer Verlag, Berlin Heiderberg) (1971).
15. DA. Brown, D. Conningham & W.K. Glass, *J. Chem. Soc. (A)* (1968) 1563.
16. S.K. Aggarwal, R.C. Mehrotra, *Inorg Chim Acta*, 112 (1966), 177.
17. S. Syoichi & S. Takachi, *Chem Pharm Bull*, 25 (1977) 3232
18. ABP Lever, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam). (1967).
19. J Abbot DML Goodgame & Jecves, *J Chem. Soc. Dalton Trans.* (1978) 880
20. James, Wroblewski and G.J. Long. *Inorg Chim Acta*, 36 (1979) 155)
21. NL Miller, T Allinger & J.C. Jai Jour, *Amer. Chem. Soc.* 88 (1966), 4495.
22. W.Low and G. Rosengarten, *Jour. Mol. Spectra* 12 (1964) 319
23. C.L Jain and R.C. Saxena *Curr. Sci.* 47 (1978) 32, 84, 766
24. Carco, Preeti and G. Tosi *Aust. Jour, Chem.* 33 (1980), 1203.
25. MTH Tarafder & MA. Ali, *Can J. Chem.* 56(1978) 2000
26. MTH Tarafder & MAJ Miah, R N Bose & M.A. Ali, *J inorg Nucl. Chem* 43 (1981) 3151

27. MTH Tarafder, M. Begum & M.L. Rahman, *Indian J. Chem.*, 25A(1986) 377
28. S.E. Livingstone, *Quart rev.*, 19 (1965) 386
29. B. Bordas, P. Sohar, G. Matoesly & P. Bachooi, *J. Org. Chem.*, 37 (1972) 1727
30. K. Nag & D.S. Jordar, *Inorg Chim Acta* 14(1975) 133.
31. M.L. Shankarnaryana & C.C. Patel, *Spectrochim Acta*, 21 (1965) 95
32. F. Bonate & R Ugo, *J Organometal Chem.*, 10 (1967) 257
33. M. Akbar all, S.E. Livingstone & D.J. Phillips, *Inorg. Chim Acta*, 5(1971) 119.
34. C. Batistoni, G. Mattgno, A. Moraci & F. Tarli, *J. inorg Nucl. Chem Lett.* 7 (1971) 1081
35. P. Teyssie and J.J. chretie, *Spectrochim. Acta* 9, (1963), 1406.
36. R.W. Hay and B. P. Caughley, *Aust. J. Chem.*, 20, (1967), 1829.
37. N.S. Birader & Y.H. Kulkarni, *J. inorg nucl. Chem.*, 33, (1971) 2451.
38. A.D. Westland & MTH Tarafder, *Inorg. Chem.*, 20 (1981) 3992.
39. A.D. Westland & MTH Tarafder, *Inorg. Chem.*, 21 (1982) 3228
40. MTH Tarafder & MAL Miah, *Inorg Chem*, 25 (1986) 2265
41. MTH Tarafder & A Ahmed, *Indian J Chem*, 25A(1986) 729
42. K. Nakamoto, *Infra Red Spectra of inorganic & coordination compounds* (John Wiley, New York) 1963.
43. DM Adams, *Metal-ligand & related vibrations* (Arnold, London) 1967
44. I. Gamo, *Bull Chim Soc. Japan* 34 (1961) 760
45. J.R. Ferraro, *Low frequency vibrations of inorganic and coordination compounds* (Plenum Press, New York) 1971
46. J.L. Burgeister, *Coord. Chem. Rev* 1, (1966), 205.
47. A. Turco & C. Pecile, *Nature*, 196, (1961), 66.
48. A. Sabatini & I. Bertini, *Inorg. Chem.*, 4 (1965), 1865.
49. R.G. Pearson *J. Chem. Edu* 45 (1968), 581, 641.
50. M.A. Ali, M. uddin, M.N. Uddin, D.A Chaudhary & MTH Tarafder, *Ind. J Chem*, 25A (1986) 238
51. K. Nakamoto, *Infrarad Spectra of inorganic & coordination compounds* (John Wiley, New York), 1963
52. Lallan Mishra & Ajay K Yadav, *Ind. Journal of Chemistry*, 39A (2000) 660
53. Nigamananda Das, Amitabh Dash & Prakash Mohanty *Indian Journal of Chemistry*, 39A (2000) 664.
54. V Anbalagan & T S Srivastava, *Indian Journal of Chemistry*, 39A, (2000)