

Complexes of a Schiff base formed by the Condensation of S-benzyl dithiocarbazate and benzoyl acetone

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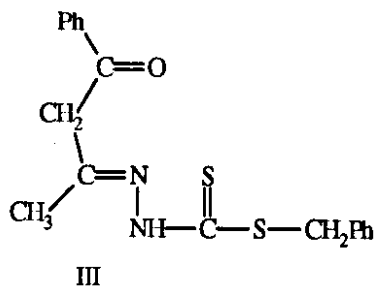
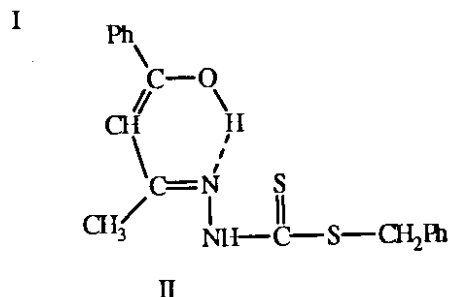
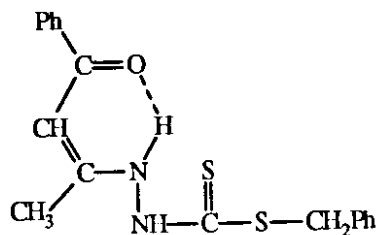
Summary: The synthesis and characterization of Co^{2+} , Ni^{2+} , Cu^{2+} , Pd^{2+} , Cd^{2+} and Hg^{2+} complexes of benzoyl acetone hydrazine-S-benzyl dithiocarbazate [H_2BATC] are reported. Elemental analysis, magnetic moment and spectral [IR, UV-vis $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$] measurements have been used in characterize the complexes. The spectral data show that the ligand behaves in bidentate or tridentate manner. The stereochemistry of these complexes is discussed based upon their spectral and magnetic properties. The antibacterial activities of the ligand and its metal complexes toward various types of bacteria are also reported.

Introduction

Dithiocarbazate and its derivatives as well as their metal complexes are frequently used as anticancer [1,2], antitumor, antituberculosis [3], antibacterial [4], antifungal [5,6] and antipyretic agents [7]. Complexes of schiff base ligand formed salicylaldehyd or substituted salicylaldehyd with S-alkyldithiocarbazate [8-10] were studied and recently the complexes of schiff base derived from condensation of S-benzyl dithiocarbazate with 2-aminoacetophenone [11], biacetylmonoxime [12], benzilmonoxime [13] and dimedone [14] have been reported. Relatively little work is reported on the corresponding metal complexes of schiff base formed by condensation of β -diketone with derivatives of dithiocarbazate.

In this paper we report the preparation and characterization of some new metal complexes derived from benzoylacetone hydrazine-S-benzyl dithiocarbazate [H_2BATC]. The ligand may possess any of the structure I-III shown below [14] or they may exist as tautomeric equilibrium mixture of these forms.

Metals such as cadmium, copper, nickel and mercury are toxic to microorganisms [16-18]. Their toxicity, however, can be affected by abiotic factors

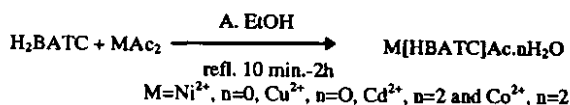
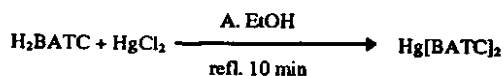
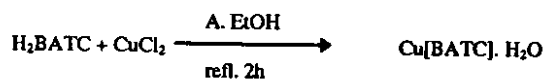
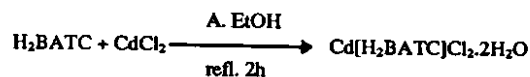
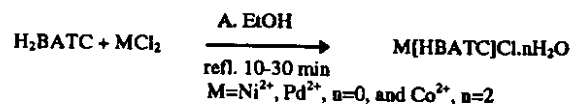


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such as pH, Eh, temperature, organic materials, or clay minerals [19]. Further, it can be affected by microbial action such as redox reaction or conversion into organic form [20]. This study reports the variation of antibacterial activity of these metals upon their complexation with [H₂BATC].

Results and Discussion

The major reactions are as follow:



The analytical and physical data for the metal complexes are listed in Table-2.

The ¹H-NMR spectrum of H₂BATC in [DMSO] shows five signals at δ=2.06, 3.29, 4.26, 4.39 and 7.29 relative to TMS may be assigned to methyl protons (CH₃-), methylene protons of the -S-benzyl moiety (S-CH₂Ph), methylene proton of benzoyl acetone (-CH₂-CPh), the imino and aromatic protons respectively. In ¹³C-NMR spectrum of the ligand, three signals are observed at δ = 183.5, 158.5, and 142.4 which attributed to the C=S, C=O and C=N group respectively. The above observation indicate that the ligand actually exists in thione form.

The principle IR bands of H₂BATC and its metal complexes are listed in Table-3. The IR spectrum of H₂BATC shows band at 3358 cm⁻¹ which may be assigned to ν(OH) or (NH) stretching vibrations [21,22]. The appearance of

Table-1: Bacterial strains and their code identity and source

Organism	Code identity	Code meaning
<i>Staphylococcus aureus</i>	CBSC 15-5554A	Carolina Biological Supply Compny, U.S.A.
<i>Streptococcus faecalis</i>	NCTC 370	Nationaal Collection of type Culture, England
<i>Yersinia enterocolitica</i>	ATCC 23715	American Type Culture Collection, U.S.A.
<i>Escherichia coli</i>	ATCC E 11775	-do-

this band is an indication that the ligands are largely if not completely in an enolized form even in the solid state [15]. The double weak bands at 2916 and 2970 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibration of S-CH₂Ph [23,24]. The three intense bands at 1629, 1601 and 981 cm⁻¹ are assigned to ν(C=O) or ν(C=C) [15], ν(C=N) and ν(N-N) [25] stretching vibrations respectively. The thioamide groups bands [26] I-IV are 1558, 1257, 920 and 940 cm⁻¹. The bands assigned to thioamide vibration are not pure and have substantial contribution from ν(C-N), δ(C-H), δ(N-H). The band at 1105 cm⁻¹ is assigned to ν(C-O). The possibility of thione - thiol tautomerism (NH-C-S → N=C-SH) is ruled out, since no band characteristic of thiol group (2500-2650 cm⁻¹) is found in the spectrum of the ligand.

The H₂BATC behaves as mononegative tridentate ligand coordinating via the azomethine nitrogen, the CS and the deprotonated enolic group as in structure IV. This behavior is found in Ni[HBATC]Cl, Co[HBATC]Cl.2H₂O, Pd[HBATC]Cl, Ni[HBTAC]Ac, Cd[HBTAC]Ac. 2H₂O, Cu[HBATC]Ac, and Co[HBATC]Ac.2H₂O. This mode of complexation is supported by the shift in ν(C=N) to lower and ν(N-N) to higher frequency indicating coordination through the azomethine group [27]. Also the shift in ν(C-O) to lower energy and the disappearance of ν(OH) indicating that the enolic proton is lost upon complexation and the involvement of this oxygen in bonding to

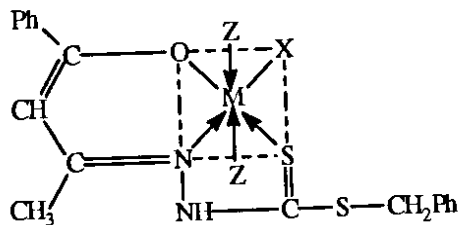
Table-2: Analytical and physical data for the complexes derived from H₂BATC

Compound	Empirical Formula	Colour	mp (°C)	Found (Calc.) %				M _{cal} (BM)
				C	H	M	Cl	
H ₂ BATC	C ₁₃ H ₁₈ N ₂ O ₂ S ₂	white	133	63.44 (63.31)	4.9 (5.29)	-	-	-
Ni[HBATC]Cl	NiC ₁₃ H ₁₇ N ₂ O ₂ S ₂ Cl	orange	232	50.2 (49.63)	4.5 (3.92)	13.6 (13.47)	8.5 (8.13)	diam.
Co[HBATC]Cl.2H ₂ O	CoC ₁₃ H ₂₁ N ₂ O ₃ S ₂ Cl	black	148	46.61 (45.82)	5.13 (4.48)	12.20 (12.49)	7.1 (7.51)	1.54
Pd[HBATc]Cl	PdC ₁₃ H ₁₇ N ₂ O ₂ S ₂ Cl	pale brown	224	44.1 (44.73)	2.98 (3.54)	21.8 (22.01)	7.12 (7.33)	diam.
Cd[HBATC]Cl ₂ .2H ₂ O	CdC ₁₃ H ₂₂ N ₂ O ₃ S ₂ Cl ₂	cream	>350	39.2 (38.5)	4.3 (3.94)	20.4 (20.0)	13.28 (12.62)	diam.
Ni[HBATC]Ac	NiC ₂₀ H ₂₀ N ₂ O ₃ S ₂	brown	254	52.80 (52.31)	5.1 (4.35)	13.2 (12.78)	-	1.0
Co[HBATC]Ac.2H ₂ O	CoC ₂₀ H ₂₄ N ₂ O ₃ S ₂	dark green	163	50.35 (48.48)	4.6 (4.8)	11.45 (11.89)	-	1.47
Cd[HBATC]Ac.2H ₂ O	CdC ₂₀ H ₂₄ N ₂ O ₃ S ₂	beige	188	44.23 (43.36)	5 (4.37)	19.0 (20.47)	-	diam.
Cu[HBATC]Ac	CuC ₂₀ H ₂₀ N ₂ O ₃ S ₂	olive green	155	52.1 (51.76)	4.30 (4.31)	13.5 (13.69)	-	1.23
Cu[BATc].H ₂ O	CuC ₁₃ H ₁₈ N ₂ O ₂ S ₂	olive green	127	51.6 (51.12)	5.10 (4.29)	16.0 (15.06)	-	1.97
[Hg(BATC)] ₂	Hg ₂ C ₃₆ H ₃₂ N ₄ O ₂ S ₄	yellow	>350	- (39.95)	- 2.95	37.8 (37.07)	-	diam.

Table-3: IR spectral bands of H₂BTC and its metal complexes

Compound	Thioamide bands				ν(OH)	ν(C=N)	ν(N-N)	ν(C=S)	ν(N=C-S)
	I	II	III	IV					
H ₂ BATC	1558	1257	921	940	3358	1601	981	-	-
Ni[HBATC]Cl	1558	1244	926	970	-	1575	1017	-	-
Co[HBATC]Cl.2H ₂ O	1511	1239	917	969	-	1557	1026	-	-
Pd[HBATC]Cl	1557	1243	903	966	-	1584	1027	-	-
Cd[HBATC]Cl ₂ .2H ₂ O	1540	1240	914	963	3380	1567	1026	-	-
Ni[HBATC]Ac	1541	1240	910	977	-	1585	1000	-	-
Co[HBATC]Ac.2H ₂ O	1558	1254	906	967	-	1580	1025	-	-
Cd[HBATC]Ac.2H ₂ O	1557	1239	946	960	-	1572	1001	-	-
Cu[HBATC]Ac	1551	1239	901	969	-	1584	1000	-	-
Cu[BATC].H ₂ O	1557	-	922	-	-	1575	1029	698	1635
[Hg(BATC)] ₂	1558	-	922	-	-	1575	-	699	1620

the metal ion. This enolic behavior is quite common to most of the schiff bases derived from β-diketone and mono or diamine [15].



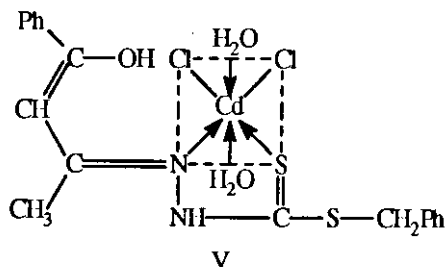
— M = Ni²⁺, Co²⁺, Cd²⁺, Cr²⁺ and Pd²⁺

— X = Cl or Ac Z = H₂O for Co²⁺ and Cd²⁺

IV

H₂BATC behaves as binategative tridentate ligand coordinating via the imine nitrogen, the deprotonated enolic group and CS in the thiol form, with the displacement of hydrogen atom from the latter group. This behavior is found in Cu[BATC].H₂O and [Hg(BATC)]₂ complexes. The ν(C=N) band shift to lower wavenumber by about (25 cm⁻¹) confirming the participation of azomethine nitrogen in coordination. Also the disappearance of ν(OH) band and thioamide bands, structure (II,IV), with simultaneous appearance of new band in the region 1620-1635 and 699 cm⁻¹ assigned to ν(N=C-S) and ν(C-S) respectively [28], indicate that the involvement of this oxygen and sulphur in bonding to the metal ion.

Additionally, H₂BATC behaves as neutral bidentate ligand coordinating through the thion sulphur and nitrogen of the azomethine group as in structure V. The behavior is found in Cd[HBATC]Cl₂·2H₂O. This mode is confirmed by the following observation, the strong band at 3380 cm⁻¹, similar to the ligand which indicates that the enolic hydrogen remains intact in the Cd²⁺ complex. The ν(C=N) and ν(C=S) bands shift to lower and higher frequency in the complex spectrum with the shift to higher frequency for ν(N-H), all this indicates that H₂BATC behaves as neutral bidentate ligand in this case.



The observed new bands in the complexes at between 540-480, 470-400, 390-348 and 330-280 cm⁻¹ are tentatively assigned to ν(M-O) [29], ν(M-N) [30], ν(M-S) [30] and ν(M-Cl) [12] respectively. The two new bands at ~ 1530 and 1430 cm⁻¹ are characteristic for the monodentate acetate group [26]. The water of crystallization was determined from the mass loss observed upon heating the complexes in an oven at 120°C for four hours.

Magnetic and spectral studies

In the Co[HBATC]Ac·2H₂O and Co[HBATC]Cl₂·2H₂O the μ_{eff} values are 1.54 and 1.47 BM, respectively. These values are lower than expected value (1.8 BM) for low spin octahedral or square planar (2.2 BM) [31] complexes. This lowering may arise on account of (i) the presence of cobalt III species (ii) the covalent nature of metal-ligand bond (iii) the presence of low symmetry component and (iv) an equilibrium between high spin and low spin (⁴A₂ ↔ ⁴T₂) state [32]. The electronic spectrum of the cobalt II complexes, Co[HBATC]Ac·2H₂O show band at 18518, 24271 and 27624 cm⁻¹ which are assigned

to ⁴A_{2g} ← ⁴T_{2g}(F) ν₂, ⁴T_{1g} ← ⁴T_{1g}(P) ν₃ and charge transfer respectively [33]. Also in the Co[HBATC]Cl₂·2H₂O complex the electronic spectrum shows two bands at 14836 and 26880 cm⁻¹ assigned to ⁴A_{2g} ← ⁴T_{1g}(F) ν₂ and charge transfer transition. Thus the magnetic values and electronic spectra suggest octahedral geometry for both cobalt complexes.

The nickel II complexes Ni[HBATC]Cl and Ni[HBATC]Ac are both diamagnetic. The electronic spectra of these complexes show bands in the regions 17064 - 19038 and 27 624 cm⁻¹ which are referred [34] to ν₂ and ν₃ bands. The fact that there is no band observed below 10000 cm⁻¹ and the diamagnetic behaviour indicate square planar geometry for these complexes [34]. The square planar in presence of sulphur ligand exhibit an additional well defined band lower in energy than ν₂ and around 11000 cm⁻¹, which is referred to as ν₁. In the present complexes the 17064 - 19083 cm⁻¹ bands (ν₂) may be assigned to ¹A_{2g} ← ¹A_{1g} transition (b_{1g} ← b_{2g}).

The magnetic moments of Cu[BATC]·H₂O and Cu[HBATC]Ac are 1.97 and 1.23 BM at room temperature, respectively. The value observed for Cu[BATC]·H₂O is in the range of high spin copper II complexes having monomeric structure [35]. The low value of μ_{eff} for Cu[HBATC]Ac than the standard value reported for one unpaired electron (1.7 - 2.2 BM), may be due to the covalent nature of the metal sulphur bond or copper - copper interaction [36] in a dimeric or polymeric structure. The electronic spectra of copper II complexes in DMF show bands at 27624 and 19083 cm⁻¹ which are assigned to charge transfer and ²E_g ← ²T_{2g} transition respectively [31]. The band positions are in good agreement with those generally observed for square planar copper II complexes [37-39].

The palladium II complex Pd[HBATC]Cl is diamagnetic and the electronic spectrum of this complex shows band at 25252 cm⁻¹ assigned to ¹B_{1g} ← ¹A_{1g} transition [39] which suggest square planar geometry for this complex.

Antibacterial activity

It is well known that heavy metals are toxic to microorganism [18], but the activities of these

Table-4: Antibacterial activities of H₂BATC and its metal complexes.

Compound	Actual inhibition zone diameter (mm)			
	Staphylococcus aureus	Streptococcus Faecalis	Yersinia enterocolitica	Escherichia coli
H ₂ BATC	6	8	-	7
Cd[H ₂ BATC]Cl ₂ .2H ₂ O	-	8.5	6	11
Cd[HBATC]Ac.2H ₂ O	5.5	8	-	9
Cu[HBATC]Ac	-	14.5	-	11
Ni[HBATC]Cl	6	9.5	6	8
Ni[HBATC]Ac	6	14	-	11.5
[Hg(HBATC)] ₂	6	7.5	21	12

metals upon their complexation with some ligands need further study. The antibacterial activities of H₂BATC and its metal complexes are given in Table-4. Four bacterial genera were used in this study. These genera include two gram-negatives (*E. coli* and *Y. enterocolitica*) and two gram-positives (*S. aureus* and *St. faecalis*). The data clearly illustrate that some metal complexes under study increase the potency of the ligand and another attenuated its activity. The incorporation of Ni²⁺ and Hg²⁺ has no effect on the potency of the ligand whereas Cu²⁺ and Cd²⁺ attenuated its activity towards *Staphylococcus aureus*. The antibacterial activities against *Streptococcus faecalis* decrease in the order Cu[HBATC]Ac > Ni[HBATC]Ac > Ni [HBATC]Cl > Cd[H₂BATC]Cl₂.2H₂O > Cd [HBATC]Ac. 2H₂O = H₂BATC > [Hg (HBATC)]₂.

The [Hg(HBATC)]₂, Ni[HBATC]Ac and Cd[H₂BATC]Cl₂.2H₂O complexes have activity against *Yersinia enterocolitica*, while, the ligand and other complexes do not have any such activity. Also we report activities against *Escherichia coli* by all complexes under study higher than the ligand. Finally, the results clearly show that some complexes have antibacterial activities which are higher than those of the ligand.

Experimental

All chemicals used are of analar grade.

Synthesis of [H₂BATC]

The hydrazine-S-benzylidithiocarbamate was synthesized according to the general literature [15]. The schiff base was prepared by heating equimolar amount of benzoyl acetone (16.2 g, 0.1 mol) and the ester (20 g, 0.1 mol) in 100 mL absolute ethanol in presence of few drops of glacial acetic

acid and refluxed for 0.5 hour. The pale yellow crystals appeared which were separated and crystallized from absolute ethanol (m.p. 133°C) (found C, 63.44; H, 4.9; N, 8.92. Calc. for C₁₈H₁₈N₂O₂S₂ C, 63.31; H, 5.29; N, 8.81%; yield 27.36 g, 80%).

Synthesis of metal chelates

All complexes were prepared by refluxing equimolar amount (0.01 mol) of H₂BATC in 70 mL absolute ethanol and the hydrated metal chloride (0.01 mol) in 30 mL absolute ethanol or metal acetate (0.01 mol) in 20 mL doubly distilled water, from 10 min. to 2 hours. The resulting solid complexes were filtered off hot, washed with hot ethanol, then diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride. The solid complexes isolated are quite stable in air and insoluble in common organic solvents but soluble in dimethyl sulphoxide [DMSO]. Elemental analyses were performed by the Micro analytical unit at Cairo university. The metal halide were determined by standard method [40]. All measurements were carried out as described earlier [13].

Bacterial strain

The bacterial strains used in this study are shown in Table-1. The strains were grown on blood agar-base (Difco) slants and maintained at 4°C with monthly transfer.

Effect of chemical agents

The bacterial strains were grown in Muller-Hinton broth (Merck) for 8 hours at 37°C. Each culture was then spread on Muller-Hinton agar (Merck) plates (0.1 mL/plate). An equivalent amount of each chemical was absorbance onto sample application piece (LKB) for 5 min. The

sample application pieces were then placed on the surface of the Muller-Hinton agar plates immediately after their inoculation with the test bacterium. The plates were incubated for 24 hours of 37°C and the diameter (mm) of the inhibition zone was recorded.

References

1. F.P. Dwyer, E. Mayhew, E.M.F. Roe and A. Shulman, *Br. J. Cancer*, **19**, 195 (1965).
2. M. Das and S.E. Livingstone, *Inorg. Chim. Acta*, **19**(1), 5 (1976).
3. R. Donvick, F. Panzy, G. Stryker and J. Bornsein, *J. Bact.*, **59**, 667 (1950).
4. M.A. Ali, M.C. Haroon, T.M. Tarafder and M.A. Khair, *Transition Met. Chem.*, **17**(2), 133 (1992).
5. M.E. Hossain, J. Begum, N. Mohammad and M.A. Ali, *Transition Met. Chem.*, **18**(5), 497 (1993).
6. M. Rahman, M.A. Mridha and M.A. Ali, *Transition Met. Chem.*, **19**(2), 237 (1994).
7. W.I. Summerford, W.H. Horting and G.L. Jankis, *J. Am. Chem. Soc.*, **63**, 2082 (1940).
8. M.P. Degaonkar, S. Gopinathan and C. Gapinathan, *Indian J. Chem. Sect. A*, **28A**(8), 678 (1989).
9. S.V. Singh and R.V. Singh, *Indian J. Chem. Sect. A*, **28A**, (9), 804 (1989).
10. M.A. Ali and R.N. Bose, *J. Inorg. Nucl. Chem.*, **30**, 265 (1977).
11. G.M. Abu El-Reash, F.I. Taha, A.M. Shallaby and O.A. El-Gamal, *Bull. Soc. Chim. Fr.*, **127**, 01 (1990).
12. G.M. Abu El-Reash, F.I. Taha, A.M. Shallaby and O.A. El-Gamal, *Synth. React. Inorg. Met-Org. Chem.*, **20**(7), 887 (1990).
13. M.A. S. Monshi and N.M. Abd El-Salam, *J. Chem. Soc. Pak.*, (in press).
14. G.M. Abu El-Reash, F.I. Taha, A.M. Shallaby and O.A. El-Gamal, *Synth. React. Inorg. Met-Org. Chem.*, **21**(4), 697 (1991).
15. M.A. Ali and S. G. Teoh, *J. Inorg. Nucl. Chem.*, **40**, 451 (1978).
16. A. Abbas and C. Edwards, *Applied and Environmental Microbiology*, **55**, 2030 (1989).
17. J.J. Nieto, A. Ventosa and F. Ruiz-Berraquero, *Applied and Environmental Microbiology*, **53**, 1199 (1987).
18. G.M. Gadd and A.J. Griffiths, *Microbial Ecology*, **4**, 303 (1978).
19. H. Babich and G. Stotzky, *Crit. Rev. Microbiol.*, **8**, 99 (1980).
20. T.D. Brock, D.W. Smith and M.T. Madigan, "Biology of Microorganisms", 4th ed., Prentice-Hall International Inc., USA (1984).
21. K. Ueno and A.E. Martell, *Phys. Chim.*, **59**, 998 (1955).
22. B. Khim, C. Miyake and S. Inoto, *J. Inorg. Nucl. Chem.*, **37**, 963 (1975).
23. A. El-Dissouki, G.B. Mohamad and A.Z. El-Sonbati, *Inorg. Chim. Acta*, **74**, 279 (1983).
24. M.M. Abou-Sekkina, A. El-Dissouki and A.Z. El-Sonbati, *Acta. Chim. Hung.*, **114**, 29 (1983).
25. A. Braibanti, F. Delvalla, M.A. Pellinghelli and E. Leporati, *Inorg. Chem.*, **7**, 1430 (1968).
26. C.N. Roa and R. Venkatoghavan, *Spectrochim. Acta*, **18**, 541 (1962).
27. A.A. El-Asmy and T.Y. El-Ansi, *Synth. React. Inorg. Met-org. Chem.*, **19**(4), 309 (1989).
28. L.J. Bellany, "The Infrared Spectra of Complex Molecules", Methuen, London, (1954).
29. B.B. Kaul and K.B. Pandeya, *J. Inorg. Nucl. Chem.*, **40**, 1035 (1977).
30. M.P. Teotia, D.K. Rastogi and W.U. Malik, *Inorg. Chim. Acta*, **7**, 339 (1973).
31. S.F.A. Kettle, "Coordination Compound", CECIAL Misstear, Associate, Britain (1969).
32. M.A. Ali, S.E. Livingstone and D.J. Philip, *Inorg. Chim. Acta*, **5**, 493 (1971).
33. C.K. Jorgenson, *J. Inorg. Nucl. Chem.*, **24**, 1521 (1962).
34. A.B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, (1968).
35. M. Paulaniandavar and C. Natarajan, *Aust. J. Chem.*, **33**, 737 (1980).
36. M. Kato, H.B. Jonassen and J.C. Fanning, *Chem. Rev.*, **64**, 99 (1964).
37. B.N. Figgis, "Introduction to Ligand Fields Theory", Wiley Interscience, New York (1966).
38. L. Sacconi and M. Ciampolin, *J. Chem. Soc.*, 276 (1964).
39. K. Hussain Reddy and D. Venkata Reddy, *Indian J. Chem.*, **V24A**, 154 (1985).
40. A.I. Vogel, "Quantitative Inorganic Chemistry", Longman, London (1961).