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Synthesis and Spectroscopic Characterization of Cr(III), Mn(II), Fe(III) AND Co(II) Complexes with Bis-Bidentate Ligands

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Abstract: Cr(III), Mn(II), Fe(III) and Co(II) complexes of 2,4-dihydroxy-5-acetylacetophenone (H_2L), 2,4-dihydroxy-5-acetylacetophenonedihydrazone (H_2L') and 2,4-diydroxy-5-acetylacetophenonedioxime (H_2L'') were synthesized. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, thermal, infrared, electronic spectra, magnetic susceptibility and conductivity measurements. The ligands behave as dibasic bis-bidentates yielding polymeric complexes. An octahedral geometry was suggested for all the complexes.

Keywords: Bis-bidentate donor; polymeric complexes, octahedral geometry.

INTRODUCTION

Polynucleating ligands are a growing class of compounds. This term, firstly coined as "dinucleating ligands" by Robson (1) in 1970, defines a class of ligands able to simultaneously bind two or more metal ions thus forming di- or polynuclear metal complexes. In this field, not only the ligands, but also their coordination compounds were extensively investigated allowing the understanding of the basic metal–metal interactions (2-6). The possible applications of the complexes formed by this type of ligands vary from the biomimetic studies of dinuclear metalloproteins or hosting and carrying of small molecules to their interesting catalytic properties. The importance of polynucleating ligands and their transition metal complexes prompted us to undertake the study of the coordination properties of such ligands. Regarding this, earlier we have reported the synthesis and characterization of 2,4-dihydroxy-5-acetylacetophenone, 2,4-dihydroxy-5-acetylacetophenone dihydrazone and 2,4-dihydroxy-acetylacetophenonedioxime and also on the synthesis and characterization of their Nickel (II) and Copper (II) chelates [7]. This paper reports on the syntheses and structures of Chromium(III), Manganese(II), Iron(III) and Cobalt(II) chelates of 2,4-dihydroxy-5-acetylacetophenone (H_2L), its dihydrazone (H_2L') and dioxime (H_2L'') derivatives (Figure 1).

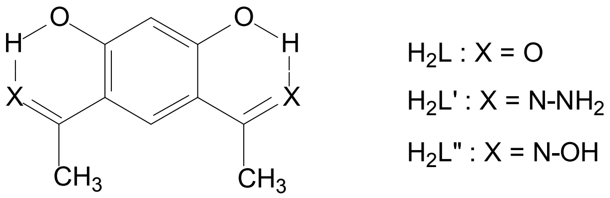

Figure 1.

[Structure of the ligands]

(H_2L- 2,4-dihydroxy-5-acetylacetophenone
H_2L'- 2,4-dihydroxy-5-acetylacetophenonedihydrazone
H_2L''- 2,4-dihydroxy-5-acetylacetophenonedioxime)

EXPERIMENTAL

The reagents and chemicals used were of BDH (AR) or E. Merck (AR) grade. All solvents were distilled under anhydrous conditions before use. The mass spectra of the ligands were recorded on a VG-Micromass 7070-H spectrometer. Elemental analyses were carried out by micro analytical methods. Metal contents were determined using a Varian Spectra 30/40 atomic absorption spectrometer, employing the necessary standards. DTA studies were carried out on a Leeds and Northrup, U.S.A. instrument. Thermal decompositions were effected at normal atmosphere in Robert–Grimshaw ceramic sample holders at a testing rate of 10^0 C/min using α–alumina as reference. Conductance measurements were carried out on a Digisun D1-909 digital conductometer. IR spectra were recorded on a Perkin-Elmer-783 spectrophotometer using KBr pellets. Reflectance electronic spectra were recorded in Nujol mulls on a Cary 2390 UV spectrometer. Magnetic susceptibilities were measured on a vibrating sample magneto meter of EG & G Princeton, research model.

Synthesis of Ligands

The ligands were prepared by reported procedures. (7, 8).

Synthesis of Complexes

A general method was adopted for the preparation of all the complexes. A methanolic suspension of the ligand was added in small increments to a methanolic solution of the metal chloride. After complete addition the metal to ligand mole ratio was always kept as 1:1. A distinct lowering of the pH was observed. The pH of the solution was then increased to 6 using a methanolic ammonia solution and the contents were refluxed for 6 h. The separated solid complex was filtered, washed with methanol, petroleum ether and dried in vacuum. The purities of ligands and metal complexes were checked by TLC using 1:1 ethyl acetate and methanol mixtures. The analytical data and proposed formulae for the complexes are given in Table 1.

RESULTS AND DISCUSSION

The complexes are colored and stable in air. They are insoluble in common organic solvents but soluble in 1, 4-dioxane, THF, DMSO and DMF. They do not melt or decompose until 350^o C.

Elemental, conductance and thermal analysis of metal complexes

Analytical data indicate that the metal to ligand stoichiometry is 1:1 in all the complexes, metal to chlorine ratio is 1:1 in trivalent metal complexes (Table 1). From the conductivity data, it can be concluded that the chloride ion is in coordination sphere (9). The higher ratios of hydrogen and oxygen in Mn(II) and Co(II) complexes of H_2L indicate the probable presence of water molecules. It is established by thermal analysis. Thermal analysis has revealed an endotherm at 180^0C and 160^0C in Mn(II) and Co(II) complexes of H_2L, respectively. These endotherms indicate the presence of coordinated water per mole of metal ion (10).

Table 1: Analytical Data of Metal Complexes

Complexes with molecular formula	Calcd. (Found) %					Λ_M
	Metal	Carbon	Hydrogen	Nitrogen	Chloride	(mho cm^2 mole^{-1})
$[Cr(L)Cl]_n$ $(CrC_{10}H_8O_4Cl)_n$	18.60 (18.23)	42.93 (41.86.)	2.86 (2.83)	–	12.70 (12.62)	9
$[Mn(L)H_2O]_n$ $(MnC_{10}H_{10}O_5)_n$	20.74 (20.40)	45.29 (44.70)	3.77 (3.73)	–	–	12
$[Fe(L)Cl]_n$ $(Fe\ C_{10}H_8O_4Cl)_n$	19.71 (19.39)	42.35 (41.76)	2.82 (2.79)	–	12.53 (12.37)	15
$[Co(L)H_2O]_n$ $(Co\ C_{10}H_{10}O_5)_n$	21.91 (21.47)	44.62 (43.95)	3.72 (3.67)	–	–	8
$[Cr(L')Cl]_n$ $(CrC_{10}H_{12}O_2\ N_4Cl)_n$	16.91 (16.66)	39.02 (38.48)	3.90 (3.85)	18.21 (17.96)	11.54 (11.40)	21
$[Mn(L')]_n$ $(MnC_{10}H_{12}O_2N_4)_n$	19.98 (19.71)	43.65 (43.01)	4.36 (4.31)	20.37 (19.98)	–	18
$[Fe(L')Cl]_n$ $(FeC_{10}H_{12}O_2\ N_4Cl)_n$	17.94 (17.69)	38.54 (38.07)	3.85 (3.80)	17.99 (17.75)	11.40 (11.23)	20
$[Co(L')]_n$ $(CoC_{10}H_{12}O_2N_4)_n$	21.13 (21.08)	43.02 (42.49)	4.30 (4.24)	20.08 (19.79)	–	18
$[Cr(L'')Cl]_n$ $(CrC_{10}H_{10}O_4\ N_2Cl)_n$	16.80 (16.00)	38.77 (37.80)	3.23 (3.16)	9.05 (8.83)	11.47 (11.22)	15
$[Mn(L'')]_n$ $(MnC_{10}H_{10}O_4\ N_2)_n$	19.84 (19.34)	43.33 (42.46)	3.61 (3.53)	10.11 (9.88)	–	12
$[Fe(L'')Cl]_n$ $(FeC_{10}H_{10}O_4\ N_2Cl)_n$	17.82 (17.40)	38.29 (37.42)	3.19 (3.15)	8.94 (8.73)	11.22 (11.21)	15
$[Co(L'')]_n$ $(CoC_{10}H_{10}O_4\ N_2)_n$	20.98 (20.46)	42.72 (41.73)	3.56 (3.45)	9.97 (9.74)	–	8

IR spectra

IR spectral data of the ligands and complexes are given in Table 2. The $\nu_{(OH)}$ bands identified in the free ligands were absent in the IR spectra of all the complexes. This is attributed to deprotonation of phenolic groups during complexation (11). Further, a shift in the $\nu_{(C\text{-}O)}$ band by 10–20 cm^{-1} to higher frequency confirms coordination through the phenolic oxygen in the ligands (12). The carbonyl stretching vibration in H_2L and the azomethine stretch in H_2L' and H_2L'' have under-gone shifts to lower frequency confirming their participation in coordination. (13, 14). While the $\nu_{(NH2)}$ bands in the complexes of $H_2L'$and the $\nu_{(OH)}$(oxime) band in the complexes of H_2L'' have broadened and undergone a shift to lower frequency as compared with the free ligand. This is attributed to intramolecular hydrogen bonding (15). Based on these observations the ligands are concluded to be dibasic and bis-bidentate donors. H_2L coordinates through the carbonyl and phenolic oxygens. H_2L' and H_2L'' coordinate through the azomethine nitrogen and phenolic oxygen.

In Mn(II) and Co(II) complexes of H_2L, a broad band was observed in the range of 3500–3000 cm^{-1}. This clearly indicates the presence of coordinated water molecules, as supported by the thermal analysis. Further, an additional band has been identified at 840 cm^{-1} and 820 cm^{-1} respectively in these two complexes, which are assignable to the rocking motion of coordinated water molecule (16). Non-ligand bands observed in the region of 840–440cm^{-1} in the complexes are assigned to M–O and M–N vibrations (17, 18). The additional bands observed at 320 – 260 cm^{-1} in Cr(III) and Fe(III) complexes of all the ligands are due to M-Cl vibrations (19).

Magnetic Moments and Electronic spectra

Magnetic susceptibility observed at room temperature and magnetic moments calculated show strikingly subnormal values. The observed and expected magnetic moments are given in Table 3.

The sub normality in magnetic moments has been ascribed to antiferromagnetism which is due to the interaction between electronic spins on neighboring metal ions. It is generally accepted that mechanism of the exchange interaction involves the mutual pairing of electronic spins via some form of orbital overlap. Antiferromagnetic exchange may be metal-metal interaction or super exchange.

Metal-metal interaction involves direct overlap of orbitals containing the unpaired electrons, which influences the magnetic behaviour where as super exchange involves the interaction of electrons with opposite spins on the two interacting ions via an intermediate diamagnetic anion(s) which results ineffective pairing leading to a minimum number of unpaired spins in the ground state of the system.

Both the mechanisms seem to be operative in the complexes as a consequence of their polymeric nature and stacked arrangements (20).

The absorption maxima for the complexes and the corresponding assignments of the electronic transitions are included in table 3. On the basis of the data octahedral geometries have been proposed for all complexes (21, 22).

CONCLUSIONS

The ligands are dibasic bis-bidentate ligands. H_2L behaves as a dibasic bis bidentate OO-OO donor. H_2L’ and H_2L” behave as dibasic bis-bidentate ON-ON donor. All the metal complexes are paramagnetic but they are strikingly showing subnormal magnetic moments probably due to metal-metal interaction and super exchange phenomena. Based on analytical, thermal, conductivity, magnetic and spectral data, octahedral geometries have been proposed for all the complexes. (Fig 2-6).

Table 2: Characteristic Infra Red Frequencies Of Ligands & Complexes (cm^{-1})

Compound	$\nu_{(NH2)}$	$\nu_{(OH)}$ phenolic	$\nu_{(OH)}$ oxime	$\nu_{(C=O)}$	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(N-O)}$	$\nu_{(N-N)}$	New Bands
H_2L	_	2700-3000 b		1650 s		1180 s			
[Cr(L)Cl]$_n$		_		1580 s		1190 s			720 w, 680 w, 300 w.
[Mn(L)H_2O]$_n$		_		1600 s		1190 s			3450-3000 b, 840 m, 790 w, 750 w, 660 w.
[Fe(L)Cl]$_n$		_		1580 s		1190 s			770 w, 720 w,260 w.
[Co(L)H_2O]$_n$		_		1600 s		1190 s			3500-3000 b, 820 m, 730 w, 620 w.
H_2L’	3400 s	2550 b			1610 s	1170		1050 s	
[Cr(L’)Cl]$_n$	3300-3000 b	_			1560 b	1190 s		1040 s	680 w, 640 w, 600 w, 320 w
[Mn(L’)]$_n$	3300-3200 b	_			1560 b	1200 s		1030 s	780 w, 560 w, 480 w, 460 w
[Fe(L’)Cl]$_n$	3100-2900 b	_			1550 b	1200 s		1040 s	750 w, 540w, 300 w
[Co(L’)]$_n$	3300-3100 b	_			1550 b	1200 s		1030 s	790 w, 670 w, 610 w
H_2L”		2600-3100 b	3400 s		1660 s	1190 s	960 s		
[Cr(L”)Cl]$_n$		_	3400 b		1530 s	1200 s	960 s		690w, 600 w, 320 w
[Mn(L”)]$_n$		_	3400 b		1570 s	1180 s	940 s		660 w, 580 w
[Fe(L”)Cl]$_n$		_	3400 b		1520 s	1190 s	960 s		620 w, 560 w,280 w
[Co(L”)]$_n$		_	3200 b		1530 s	1180 s	940 s		640 w, 560 w

Table 3: Magnetic and Electronic Spectral Data of Complexes.

Complex	μ_{eff} (BM) (observed)	μ_{eff} (BM) (expected)	Band position (cm^{-1})	Assignment
$[Cr(L)Cl]_n$	1.49	3.88	31250 24390 17540	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(P)$
$[Mn(L)H_2O]_n$	4.17	5.92	23640-14930	-
$[Fe(L)Cl]_n$	2.83	5.7 - 5.92	25000-16000	-
$[Co(L)H_2O]_n$	3.44	4.7 – 5.2	18520 15150 8690	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{2g}$
$[Cr(L')Cl]_n$	1.53	3.88	33330 21280 16670	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(P)$
$[Mn(L')]_n$	2.04	5.92	22630-14860	-
$[Fe(L')Cl]_n$	1.33	5.7 - 5.92	24390-11700	-
$[Co(L')]_n$	1.48	4.7 – 5.2	18520 15150 8690	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{2g}$
$[Cr(L'')Cl]_n$	3.64	3.88	30000 26320 17540	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(P)$
$[Mn(L'')]_n$	3.58	5.92	23810-8620	-
$[Fe(L'')Cl]_n$	4.59	5.7 - 5.92	23260-9440	-
$[Co(L'')]_n$	3.59	4.7 – 5.2	24390 16660 9500	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{2g}$

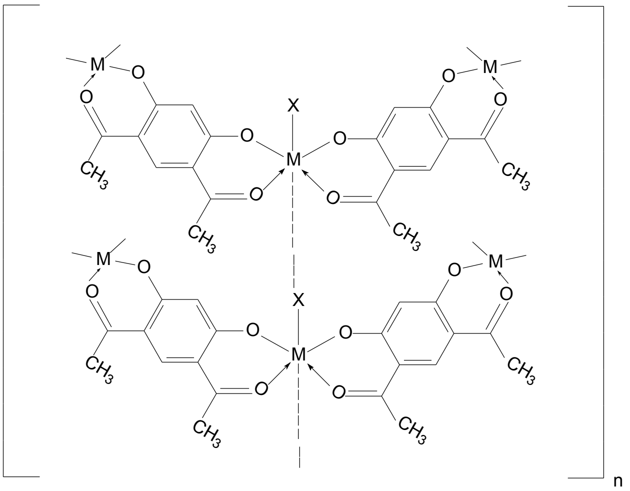

Figure 2.:[Structure of metal complexes of H_2L], (M=Cr(III), Fe(III), X=Cl M=Mn(II), Co(II), X=H_2O)

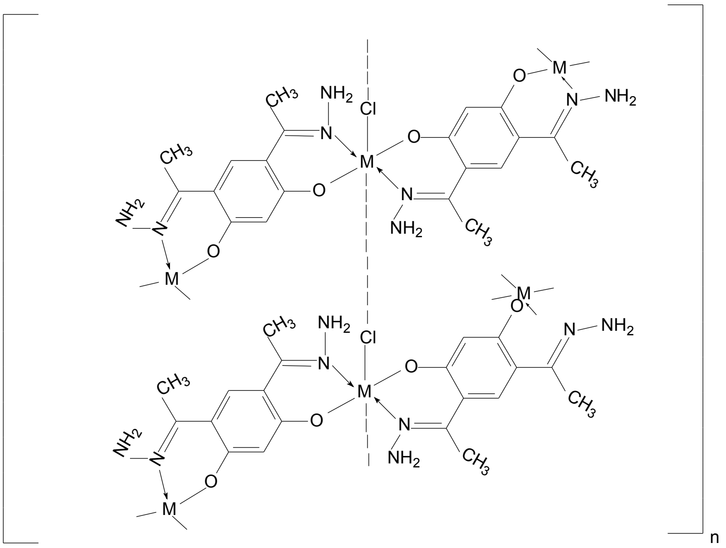

Figure 3.: [Structure of Cr(III), Fe(III) complexes of H_2L']

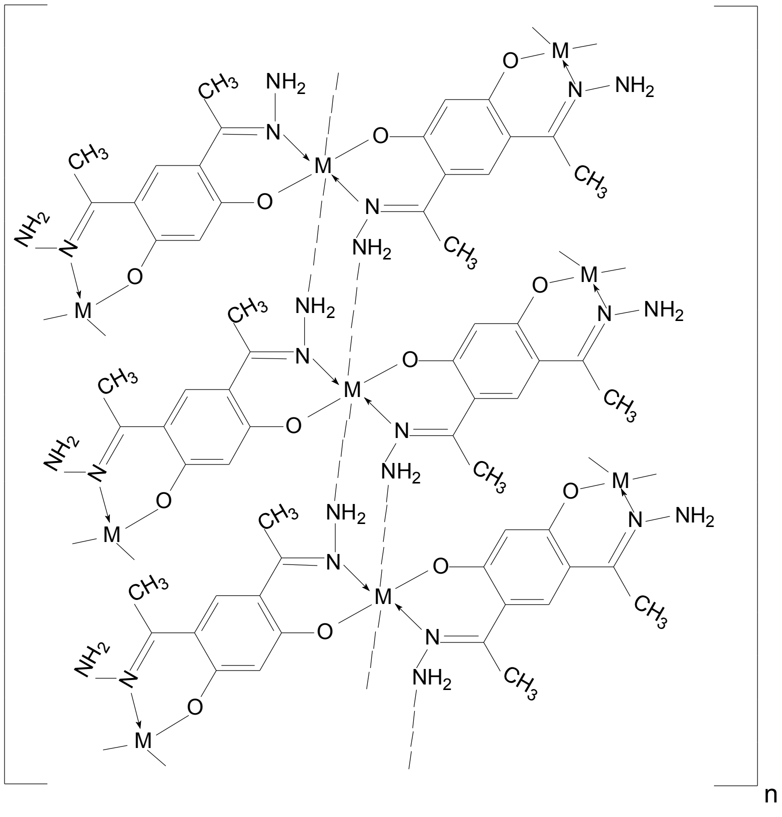

Figure 4.: [Structure of Mn(II), Co(II) complexes of H_2L']

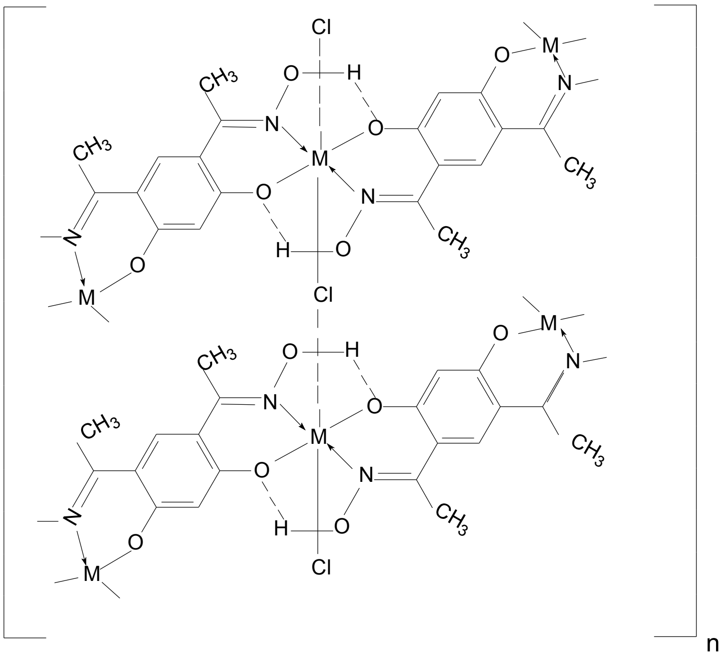

Figure 5.:[Structure of Cr(III), Fe(III) complexes of H_2L"]

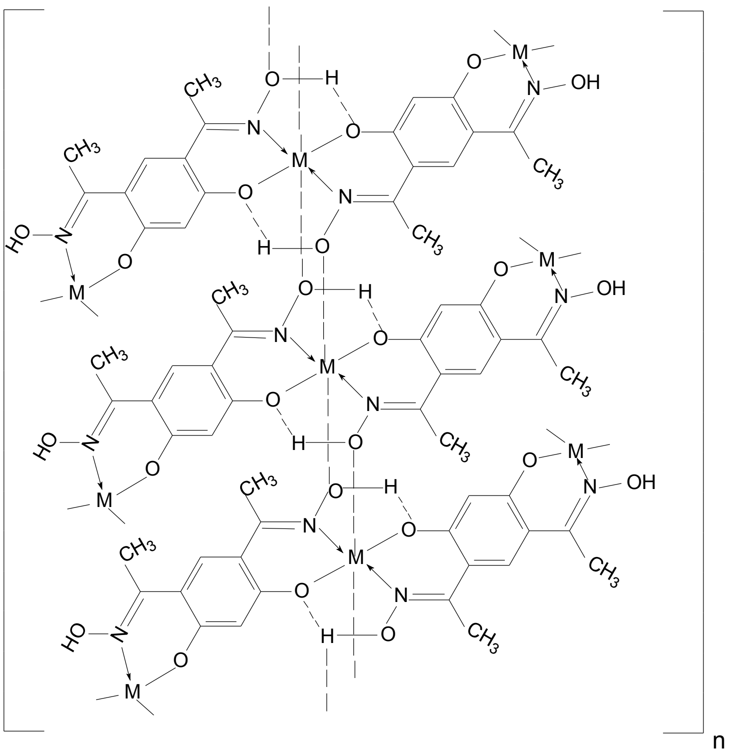

Figure 6.:[Structure of Mn(II), Co(II) complexes of H_2L"]

REFERENCES

1.Pilkington N.H and Robson R., Aust. J. Chem. 1970, 23, 2225.

2.Noboru Y, Hiroki O and Tasuku I., Chem. Commun.1998,63

3. Singh K, Barwa M.S and Tyagi P., Eur. J. Med. Chem. 2006, 41, 147.

4. Moussa D, Ibrahima T, Mohamed G, Abdou S.S and Aliou H.B., Acta Chim. Slov. 2006, 53, 417.

5. Aswar A.S, Bansod V.S, Aswale V and Mandlik V., Indian J.Chem. 2004, 43A, 1892.

6. Rani D.S, Lakshmi P.V.A and Jayatyagaraju V., Trans. Met. Chem. 1994, 19 (1), 75.

7. Shyamala B.S and Jayatyagaraju V., Syn. Met. Org. 2003 , 33,63,

8. Anjaneyulu A.S.R, Rama Prasad A.V and Sivakumar Reddy D., Curr. Sci. 1979, 48,300.
9. Angelici, R.J., Synthesis and Technique in Inorganic Chemistry, Saunders, Philadelphia, 1969.
10. Nikolaev A.V, Logvinenko V.A and Mayachina L.I., Thermal Analysis, Academic Press, New York, 1969.
11.Ceccanti N, Formica M, Fusi V, Giorgi L, Micheloni M, Pardini R, Pontellini R and Tin M.R., Inorg. Chim. Acta. 2001, 321,153.
12. Mishra, A.P and Pandey L. R., Indian J. Chem A. 2005, 44(1), 94
13. Ananthalakshmi P.V, Sandhyarani D and Jayatyagaraju V., Asian J.Chem. 1995,7, 296
14. Nejati, K and Rezvani Z., New Journal of Chemistry. 2003, 27(11) 1665
15. Colthup N.B, Daly L.H and Wiberley S.E., Introduction to Infrared and Raman Spectroscopy, 3rd Ed., Academic Press, New York, 1990.
16. Ochocki J, Zurowska B, Mroziñski J, Kooijman H, Spek A.L and Reedijk J., Eur. J. Inorg. Che.1998, 1998 (2) 169.
17..Agarwal R.K, Singh L, Sharma D.K and Singh R., Turk. J. Chem. 2005, 29,309.
18. Ananthalakshmi P.V, Sarithareddy P and Jayatyagaraju V., Bull. Chem. Soc. Ethiop. 2008, 22(3), 385.
19. Getova V.T, Pantcheva I.N, Ivanov D.S, Mehandjiev D.R, Skumryev V and Bontchev P.R. Cent. Eur. J. Chem. 2007, 5,118
20. Sarithareddy P, Susheela T and Tyagaraju V.J., Ind. J. Chem. 2004, 43A, 341.
21. Figgs B. N., Introduction to Ligand Field, Wiley, New York, 1966 .
22. Lever A.B.P., Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, Amsterdam, 1984.

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