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# Spectroscopic characterization and EPR spectral studies on transition metal complexes with a novel tetradentate, 12-membered macrocyclic ligand

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#### Abstract

Complexes of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) containing a tetradentate macrocyclic N-donor ligand have been prepared via template reaction of 2,3-pentanedione, ethylene-di-ammine and transition metal ions. The complexes have been characterized on the basis of the elemental analysis, molar conductance, magnetic moment susceptibility, IR, electronic and EPR spectral studies. The complexes are of high spin type and possess four coordinate tetrahedral five coordinate square pyramidal and six coordinated octahedral/tetragonal geometry.

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## 1. Introduction

The tetraaza macrocyclic ligands and their metal complexes have attracted interest among the coordination chemists [1]. The metal ions directs the reaction preferentially towards cyclic rather than oligomeric or polymeric products [2]. The study of synthetic macrocyclic compounds is a very important area of chemistry in view of their presence in many biological significant naturally occurring metal complexes [3]. Keeping in mind the importance of such type of compounds, in this paper we report the synthesis and characterization of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) complexes with a new macrocyclic ligand (L) (Fig. 1).

#### 2. Experimental

Synthesis of macrocyclic ligands often involved multi-step process and the products are generally obtained in poor yields. The use of metal templates in the preparation of macrocyclic complexes has been well established as a simple method by which high yields of the target compound can be obtained.

All chemicals used, were of AnalaR grade and procured from Fluka (USA) and E. Merck (Germany). Metal salt were

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## 2.1. Preparation of complexes

A template reaction was carried out for the formation of the complexes. A hot ethanolic solution (20 ml) of the metal salt (0.025 mol) was mixed with a hot ethanolic solution (20 ml) of ethylene-di-ammine (0.05 mol). Then an ethanolic solution (20 ml) of 2,3-petanedione (5.0 g, 0.05 mol) in the presence of ethanolic lithium hydroxide solution (0.42 g, 0.01 mol) was added to the resultant solution under constant stirring. This solution was refluxed for 8 h. On cooling a colored complex precipitated out. The complexes were filtered, washed with cold ethanol and dried under vacuum over  $P_4O_{10}$ .

## 2.2. Physical measurements

The C, H and N were analysed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on a ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO<sub>4</sub>·5H<sub>2</sub>O as a callibrant. IR spectra (KBr) were recorded on a Perkin-Elmer FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMF on a Shimadzu UV mini-1240 spectrophotometer. EPR spectra of all the complexes were recorded as polycrystalline sample on E<sub>4</sub>-EPR spectrome-

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Fig. 1. Structure of the ligand (L).

ter using the DPPH as the *g*-marker. The purity of the compounds has been checked on high performance liquid chromatography (HPLC), Waters Alliance Model 2695, by using Thermo-Hypersil BDS (250 mm long, i.d. 4.6  $\mu$ m and particle size 5  $\mu$ m) column. The mixture of potassium-dihydrogen-orthophosphate buffer (pH 4.5) and acetonitrile in the ratio of 70:30, used as mobile phase, with the flow rate of 1.0 ml min<sup>-1</sup>.

# 3. Results and discussion

On the basis of elemental analysis, complexes were assigned the composition shown in Table 1. The molar conductivity values of the complexes recorded at room temperature in DMSO solvent. The complexes of Cr(III) are found to be 1:1 electrolyte [4] and may be formulated as [Cr(L)X<sub>2</sub>]X, where  $X = Cl^$ and NO<sub>3</sub><sup>-</sup>. All other complexes, except the cobalt nitrate, are non-electrolytic in nature while cobalt nitrate is 1:2 electrolyte [5], these complexes may be formulated as [M(L)X<sub>2</sub>] and [Co(L)](NO<sub>3</sub>)<sub>2</sub>, respectively.

In the IR spectra of the complexes the absence of the bands characteristic for free carbonyl group ( $\sim 1720 \text{ cm}^{-1}$ ) and primary ammines ( $\sim 3400 \text{ cm}^{-1}$ ) suggests that the complete condensation had occurred. The appearance of a new, strong intensity, band in the region 1620–1660 cm<sup>-1</sup>, attributed to the characteristic stretching frequencies of the imino linkage  $\nu$ (C=N) [6], provides strong evidence in favor of the formation of cyclic product. Another IR spectral peak in the region 405–475 cm<sup>-1</sup>,

 Table 1

 Elemental analysis, color and molar conductance data of the complexes



Fig. 2. IR spectral bands of the complexes.

attributed to v(M-N), which provides strong evidence for the involvement of nitrogen in coordination [6]. Hence, we conclude out that the ligand is tetradentate coordinating through four nitrogen atoms.

## 3.1. IR bands due to anions

The IR spectra of the Cr(III) nitrate complex exhibit bands corresponding to coordinated as well as uncoordinated nitrate group. The cobalt nitrate complex shows the peak at 1385 cm<sup>-1</sup> corresponding to uncoordinated nitrates (Fig. 2), while other nitrato complexes are found to be coordinated to the central metal ion in unidentate manner (Table 2). In the IR spectra of the thiocyanato complexes the peaks in the range ~2089–2092, ~855–865 and ~410–498 cm<sup>-1</sup> could be assigned to  $\nu$ (N=C),  $\nu$ (C=S) and  $\nu$ (NCS) bending vibrations, respectively. The position of the bands is in favor of monodentate coordination through the N-atom of the NCS group. The positions of IR peaks in the sulphato complexes are in the tune of monodentate coordinated sulphate group.

### 3.2. Chromium(III) complexes

Cr(III) complexes shows magnetic moments corresponding to three unpaired electrons, i.e. 3.72–3.82 B.M. Expected

Complex	Yield (%)	Color	Molar conductance $(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$	Calculated (found) (%)				
				C	Н	Ν	М	
[Cr(L)Cl <sub>2</sub> ]Cl CrC <sub>14</sub> H <sub>24</sub> N <sub>4</sub> Cl <sub>3</sub>	77	Green	92.23	41.34 (41.27)	5.95 (5.91)	13.78 (13.67)	12.78 (12.84)	
[Cr(L)(NO <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub> CrC <sub>14</sub> H <sub>24</sub> N <sub>7</sub> O <sub>9</sub>	66	Grey	84.86	34.57 (34.51)	4.97 (4.86)	20.16 (20.22)	10.69 (10.76)	
$[Mn(L)Cl_2]MnC_{14}H_{24}N_4Cl_2$	78	Light brown	10.42	44.94 (44.92)	6.46 (6.53)	14.97 (15.03)	14.68 (14.59)	
$[Co(L)Cl_2] CoC_{14}H_{24}N_4Cl_2$	65	Pink	12.24	44.46 (44.53)	3.73 (3.81)	14.81 (14.88)	15.58 (15.63)	
[Co(L)(NCS)2] CoC16H24N6S2	82	Redish brown	16.96	45.38 (45.47)	5.71 (5.84)	19.85 (19.96)	13.91 (14.02)	
[Co(L)](NO <sub>3</sub> ) <sub>2</sub> CoC <sub>14</sub> H <sub>24</sub> N <sub>6</sub> O <sub>6</sub>	70	Grey	205.95	38.99 (38.76)	3.27 (3.33)	19.48 (19.56)	13.66 (13.72)	
$[Co(L)SO_4] CoC_{14}H_{24}N_4SO_4$	78	Pink	12.08	41.69 (41.72)	5.99 (6.04)	13.89 (13.97)	14.61 (14.76)	
[Ni(L)Cl <sub>2</sub> ] NiC <sub>14</sub> H <sub>24</sub> N <sub>4</sub> Cl <sub>2</sub>	62	Dark brown	12.84	44.49 (44.62)	6.40 (6.46)	14.82 (14.95)	15.53 (15.67)	
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ] NiC <sub>14</sub> H <sub>24</sub> N <sub>6</sub> O <sub>6</sub>	62	Brown	12.56	39.01 (39.08)	5.61 (5.67)	19.49 (19.59)	13.61 (13.67)	
[Ni(L)(NCS)2] NiC16H24N6S2	72	Green	14.92	45.41 (45.54)	5.71 (5.79)	19.86 (19.82)	13.86 (13.97)	
$[Cu(L)Cl_2] CuC_{14}H_{24}N_4Cl_2$	82	Brown	14.45	43.93 (44.12)	6.32 (6.45)	14.64 (14.89)	16.60 (16.82)	
$[Cu(L)(NO_3)_2]$ CuC <sub>14</sub> H <sub>24</sub> N <sub>6</sub> O <sub>6</sub>	73	Light green	17.06	38.57 (38.65)	5.55 (5.62)	19.28 (19.34)	14.58 (14.66)	
$[Cu(L)SO_4] CuC_{14}H_{24}N_4SO_4$	66	Black	13.65	41.22 (41.34)	5.93 (5.98)	13.73 (13.91)	15.58 (15.67)	

Table 2IR spectral bands of the complexes

Complexes	ν(C=N)	ν( <b>M</b> — <b>N</b> )	v(M-X)	ν(CH)	
[Cr(L)Cl <sub>2</sub> ]Cl	1625	420	362	3003	
$[Cr(L)(NO_3)_2]NO_3$	1632	450	1236, 1033, 802	2958	
$[Mn(L)Cl_2]$	1640	440	-	2900	
$[Co(L)Cl_2]$	1620	470	316	2940	
$[Co(L)(NCS)_2]$	1648	410	2089, 855	2976	
$[Co(L)](NO_3)_2$	1660	425	1230, 1030, 800	2950	
[Co(L)SO <sub>4</sub> ]	1624	405	940, 1040, 1188	2948	
$[Ni(L)Cl_2]$	1644	424	304	2956	
$[Ni(L)(NO_3)_2]$	1628	435	1235, 1028, 802	2987	
[Ni(L)(NCS) <sub>2</sub> ]	1640	475	2092, 865	2943	
$[Cu(L)Cl_2]$	1650	452	-	2980	
$[Cu(L)(NO_3)_2]$	1638	438	1232, 1024, 806	2995	
[Cu(L)SO <sub>4</sub> ]	1656	455	946, 1048, 1192, 640	2978	

Table 3

Electronic spectral and magnetic moment data of the complexes

Complexes	$\lambda_{\text{Max}}$ (cm <sup>-1</sup> )	$\mu_{\rm eff}$ (at room temperature)	
[Cr(L)Cl <sub>2</sub> ]Cl	14347, 21367, 28688	3.82	
[Cr(L)(NO <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	15772, 23201, 26315	3.72	
$[Mn(L)Cl_2]$	18270, 24650, 28930, 30487	5.94	
$[Co(L)Cl_2]$	8090, 16500, 20921	5.05	
$[Co(L)(NCS)_2]$	8650, 15480, 21300, 34450	5.08	
[Co(L)](NO <sub>3</sub> ) <sub>2</sub>	5400, 14706, 22222, 30824	4.66	
[Co(L)SO <sub>4</sub> ]	12400, 15504, 21368	4.98	
[Ni(L)Cl <sub>2</sub> ]	11402, 18620, 25500	3.12	
$[Ni(L)(NO_3)_2]$	9450, 18692, 21277	3.04	
[Ni(L)(NCS) <sub>2</sub> ]	9860, 18797, 22650, 29540	3.20	
$[Cu(L)Cl_2]$	13600, 22422	1.90	
$[Cu(L)(NO_3)_2]$	11050, 17452	2.02	
[Cu(L)SO <sub>4</sub> ]	12500, 20600	1.94	

to high spin octahedral Cr(III) complexes [7]. The electronic spectra recorded in DMSO solution gives well resolved three peaks (Table 3 and Fig. 3), which may be assigned to the  ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F), {}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F) \text{ and } {}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(P)$  transition, respectively. The energy of the first spin allowed transition  ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ , directly gives the value of the 10 Dq. The values of the Racah parameter 'B' have been calculated by using the formula:  $B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_3)/(15\nu_2 - 27\nu_1)$ . The low 'B' values indicate the greater degree of the co-valance in M–N bond.

Table 4Ligand field parameters of the complexes

Complexes	$Dq (cm^{-1})$	$B (\mathrm{cm}^{-1})$	β	LFSE (kJ mol <sup>-1</sup> )
[Cr(L)Cl <sub>2</sub> ]Cl	1494	659	0.72	21400
$[Cr(L)(NO_3)_2]NO_3$	1577	796	0.86	226.00
$[Mn(L)Cl_2]$	824	749	0.79	_
$[Co(L)Cl_2]$	948	987	0.88	90.60
$[Co(L)(NCS)_2]$	1013	1055	0.90	96.82
$[Co(L)](NO_3)_2$	301	684	0.61	43.15
[Ni(L)Cl <sub>2</sub> ]	1140	660	0.63	163.44
$[Ni(L)(NO_3)_2]$	945	775	0.74	135.48
[Ni(L)(NCS) <sub>2</sub> ]	986	791	0.76	141.36

The EPR spectra recorded as polycrystalline sample at room temperature and the *g*-values has been calculated by using the expression:  $g = 2.0023(1 - 4\lambda/10 \text{ Dq})$ , where  $\lambda$  is the orbit spin coupling constant for the metal ion in the complexes. The *g*-values are 1.97–1.99.

#### 3.3. Manganese(II) complex

The room temperature magnetic moment of the complex is 5.94 B.M. It corresponds to the five unpaired electrons, high spin octahedral configuration [8]. The electronic spectra of the complexes give four weak intensity peaks (Table 3), which may be assigned to the transitions, characteristic to the octahedral geometry  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}G)$ ,  ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}{}^{4}A_{1g}({}^{4}G)$ ,  ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}({}^{4}D)$  and  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}P)$ , respectively. By the help of above transitions various ligand field parameters have been calculated and are listed in Table 4.

The EPR spectrum of the complex recorded as polycrystalline sample and in DMSO solution at room temperature. The polycrystalline sample gives one broad isotropic signal centered at 1.9892, it is near to the free electron value, i.e. 2.0023 (Table 5).

## 3.4. Cobalt(II) complexes

The magnetic moment of the cobalt(II) complexes recorded at room temperature lies in the range 4.66–5.08 B.M. It may be possess for the four coordinated tetrahedral, five coordinated square pyramidal and six coordinated octahedral geometry. The geometry of the present complexes have been elucidated on the basis of electronic spectra, discussed below.



Fig. 3. Electronic spectra of the complexes.

Table 5
EPR spectral data of the complexes

Complexes	Temperature	$g_{  }$	$g_\perp$	$g_{ m iso}$	<i>g</i> 3	<i>g</i> <sub>2</sub>	$g_1$	R	G
[Cr(L)Cl <sub>2</sub> ]Cl	RT	_	_	1.982	_	_	_	_	_
$[Cr(L)(NO_3)_2]NO_3$	RT	_	_	1.984	_	-	_	_	_
$[Mn(L)Cl_2]$	RT	_	_	1.982	_	-	_	_	_
$[Co(L)Cl_2]$	LNT	5.871	5.871	4.002	_	-	_	_	_
$[Co(L)(NCS)_2]$	LNT	4.254	4.254	2.854	-	-	_	_	_
$[Co(L)](NO_3)_2$	LNT	3.902	3.902	2.715	_	-	_	_	_
[Co(L)SO <sub>4</sub> ]	LNT	4.232	4.232	2.731	_	-	_	_	_
$[Cu(L)Cl_2]$	RT	2.271	2.061	2.131	_	-	_	_	4.45
$[Cu(L)(NO_3)_2]$	RT	2.308	2.075	2.177	-	-	_	_	4.13
[Cu(L)SO <sub>4</sub> ]	RT	-	-	2.231	4.424	2.177	2.092	0.344	-

RT, room temperature; LNT, liquid nitrogen temperature.

## 3.5. $Co(L)Cl_2$ and $Co(L)(NCS)_2$

The electronic spectra of complexes prepared from CoCl<sub>2</sub> and Co(NCS)<sub>2</sub> are characteristic of octahedral cobalt(II) [9–10]. They show three peaks (Table 3), corresponding to  ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{2g}({}^{4}F)$ ,  $\nu_{1}$ ;  ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F)$ ,  $\nu_{2}$  and  ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)$ ,  $\nu_{3}$  transitions, respectively. The EPR spectra of the complexes under study were recorded at liquid nitrogen temperature because we found that the rapid relaxation of Co(II) broadened the lines at higher temperature  $(g_{||} = 4.254 - 5.871$  and  $g_{\perp} = 2.154 - 3.067$ ). The large deviations of the *g*-values from the spin only value (g = 2.0023) is due to the large angular momentum contribution.

# 3.6. $Co(L)(NO_3)_2$

The electronic spectra of the tetrahedral and octahedral cobalt(II) complexes are almost similar. The remarkable difference is the presence of a band at  $\sim$ 5000 cm<sup>-1</sup>, in the tetrahedral complexes, which is absent in the octahedrals. In the present case the presence of the band at 5400 cm<sup>-1</sup>, suggests tetrahedral geometry of this complex [11].

## 3.7. Co(L)SO<sub>4</sub>

The electronic spectra of the sulphate complex display three bands at ~12,400 cm<sup>-1</sup>,  $\nu_1$ ; ~15,504 cm<sup>-1</sup>,  $\nu_2$ ; ~21,368 cm<sup>-1</sup>,  $\nu_3$ , corresponding to the square pyramidal geometry [9]. Ligand field parameters for the complex have been calculated and are in the tune of the results published earlier [12].

## 3.8. Nickel(II) complexes

All complexes are of high spin type and show room temperature magnetic moments in the range 3.04–3.20 B.M. (Table 3), correspond to two unpaired electrons. High spin Ni(II) complexes may be four coordinated tetrahedral and six coordinated octahedral. The observed  $\mu_{eff}$  values are low for tetrahedral Ni(II) complexes, which is known to show magnetic moments in the range 3.40–4.12 B.M. The electronic spectra are in favor of octahedral geometry [13]. It shows three bands (Table 3) which are assignable to octahedral configuration transitions:  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$ ,  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ , respectively.

The Naphelauxetic parameter  $\beta$  is calculated by using the relation:  $\beta = B_{(Complex)}/B_{(Free ion)}$ , where *B* is the Racah interelectronic repulsion parameter. The values of *B*, lowered than the free Ni(II) ion, i.e. 1041 cm<sup>-1</sup>, suggesting 24–37% covalent character in the M–N linkage. Other ligand field parameter are also calculated and are listed in Table 4.

#### 3.9. Copper(II) complexes

The room temperature magnetic moment values of the Cu(II) complexes (1.90–2.02 B.M.) indicates the monomeric nature of the complexes. The values correspond to one unpaired electron and the complexes may be considered as tetragonal geometry, except the sulphato complex which possess five coordinated square pyramidal geometry and Cu<sup>2+</sup> ion and anions occupies the axial position. The chloro and nitrato complexes of the Cu(II) gives two electronic peaks (Table 3) assigned to the  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  transitions, characteristic for tetragonal geometry. The copper(II) sulphato complex gives the electronic peaks comparable with five coordinate square pyramidal geometry.

The complexes have anisotropic EPR spectra, characteristic to tetragonal geometry [14]. The *g*-values have been calculated by the method published earlier [15–16], and are summarized in Table 5. The value of  $G = (g_{||} - 2)/(g_{\perp} - 2)$  which measure the exchange interaction between the copper centers in polycrystalline samples. If the value of G > 4, the exchange interaction is negligible but the G < 4 value suggest considerable interaction between the solid complex. The value of G in the complexes reported here is G > 4, suggesting that there is no interaction between the copper centers.

Five coordinated copper(II) complex may possess two geometries, i.e. trigonal bi-pyramidal and square pyramidal [17], which are characterized by ground states  $d_{x^2-y^2}$  or  $d_{z^2}$ , respectively [18]. The EPR spectra provides an excellent basis for distinguishing between these two ground states. For system with  $g_3 > g_2 > g_1$  the ratio  $(g_2 - g_1)/(g_3 - g_2)$  called the parameter '*R*', is very useful for this purpose. If the ground state predominantly,  $d_{z^2}$ , the value of *R* is greater than 1, and the value of *R* less than 1 is in the case of  $d_{x^2-y^2}$  ground state. The value of  $g_1, g_2, g_3$  and *R* (Table 5) for the complex under study suggest the  $d_{x^2-y^2}$  ground state (square pyramidal geometry) around the Cu(II) ion.

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# References

- [1] M. Shakir, S.P. Varkey, T.A. Khan, Indian J. Chem. 34 (1995) 72.
- [2] R. Machida, E. Kimura, M. Kodama, Inorg. Chem. 22 (1983) 2055.
- [3] K.R. Adam, M. Antolovich, D.S. Baldwin, L.G. Brigden, P.A. Duckworts, J. Chem. Soc., Dalton Trans. (1992) 1869.
- [4] K.M. Thimmaiah, W.D. Lloyd, G.T. Chandrapa, Inorg. Chim. Acta 106 (1985) 81.
- [5] C.R.K. Rao, P.S. Zacharias, Polyhedron 16 (1997) 1201.
- [6] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley/Interscience, New York, 1970;
  - S. Chandra, L.K. Gupta, Sangeetika, Spectrochim. Acta A 62 (2005) 453.

- [7] B.N. Figgis, Introduction to Ligand Field Theory, Wiley, New York, 1978.
- [8] N.K. Singh, S.K. Kushwaha, Indian J. Chem. 39 (2000) 1070.
- [9] A.B.P. Lever, Electronic Spectra of Inorganic and Coordination Compounds, John Wiley, New York, 1968.
- [10] E.Q. Gao, S. Bi, H. Sun, S. Liu, Synth. React. Inorg. Met.-Org. Chem. 27 (1997) 1115;
  - S. Chandra, L.K. Gupta, Spectrochim. Acta A 60 (2004) 1563.
- [11] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley/Interscience Publication, New York, 1988.
- [12] S. Chandra, L.K. Gupta, Spectrochim. Acta A 60 (2004) 1751;
   S. Chandra, L.K. Gupta, Spectrochim. Acta A 60 (2004) 2767.
- [13] M. Shakir, A.K. Mohamed, O.S.M. Nasman, Polyhedron 15 (1996) 3490.
- [14] R. Pilbrow, Transition Ion Electron Paramagnetic Resonance, Oxford Science Publication, Oxford, 1990;
- S. Chandra, L.K. Gupta, D. Jain, Spectrochim. Acta A 60 (2004) 2411. [15] F.K. Kneubuhl, J. Chem. Phys. 33 (1960) 1074;
- S. Chandra, L.K. Gupta, Spectrochim. Acta A 62 (2005) 307.
   [16] S. Chandra, L.K. Gupta, Spectrochim. Acta A 61 (2005) 1181;
   S. Chandra, L.K. Gupta, Spectrochim. Acta A 60 (2004) 3079.
- [17] L. Sacconi, in: R.L. Carlin (Ed.), Transition Metal Chemistry, vol. 4, Marcel Dekker, New York, 1978, p. 221;
- S. Chandra, L.K. Gupta, Spectrochim. Acta A 61 (2005) 2139. [18] R. Barbucci, A. Bencini, D. Gatteschi, Inorg. Chem. 16 (1977) 2117;
  - S. Chandra, L.K. Gupta, Spectrochim. Acta A 61 (2005) 2549.