

Complexes of 1,2-dipiperidinoethane with Transition and Representative Metals

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Summary: 1,2-Dipiperidinoethane (DPE) reacts with divalent first row transition and representative metals to give complexes of the stoichiometry, MLX_2 when $L=DPE$. $M=Cu(II)$, $Ni(II)$, $Co(II)$, $Zn(II)$, $Cd(II)$ and $Hg(II)$ $X = Cl, Br, I$ and NO_3 . The ligand and complexes have been characterized by elemental analysis, conductivity measurements, room temperature magnetic moment studies, proton NMR, electronic and IR spectra. The ligand in these complexes behaves as bidentate like substituted ethylenediamine coordinating through nitrogen atoms. The solid state IR study and other data support distorted tetrahedral geometry of the type MN_2X_2 .

Introduction

Metal complexes, where coordination can occur between a variety of metal ions and a wide range of ligands play an important role in many biological systems [1-3]. It has been observed that metal ions have considerable effect on the antimicrobial activity of antibiotics [4-14]. Similarly metal complexes are known for their antitumour activity [15-16]. Our present work is of the same nature and concerns with the coordinating ability of 1,2-dipiperidinoethane (DPE) [1]. Which is a biologically active molecule, has been used as a neurotoxic agent due to *in vivo* conversion to a selective cholinesterase inhibitor. Administration products seizures and central nervous system lesions. Cholinergic origin of DPE toxicity has also long been investigated. It is both an acetylcholinesterase (AChE) inhibitor and muscarinic antagonist. This dual action negates most of the toxic effects of compound *in vivo*. The neurotoxicity is believed to arise from oxidative conversion to 1-N-oxide which selectively inhibits AChE. Since binding parameters were unchanged following *in vivo* exposure, cytotoxicity does not involve muscarinic neurons [17-20].

In spite of considerable importance of this molecule no work has been done on the synthesis of metal complexes of this ligand in solid state. Therefore, present work was undertaken with specific view to synthesize, isolate, and characterize solid complexes of transition and representative metals with 1,2-dipiperidinoethane.

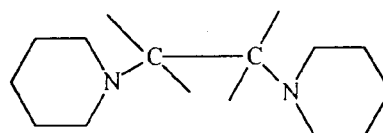


Fig. 1

1,2-Dipiperidinoethane (DPE)

Results and Discussion

Several complexes of 1,2-dipiperidinoethane with the first row transition and representative metals have been synthesized and studied. The characterization and assignment of their geometry was based on the elemental analysis, conductance measurements, magnetic susceptibilities and spectral measurements. Proton NMR of DPE in D_2O with TMS as internal standard showed a singlet at 1.55 ppm for terminal hydrogens, a singlet at 1.75 ppm for 8 hydrogens attached to the ring carbons, a singlet at 3.20 ppm for 8 hydrogens attached to the ring carbons adjacent to nitrogen atoms and a singlet for 4 ethyl hydrogens at 3.70 ppm. The infrared spectrum of piperidine exhibits a strong absorption band at 3600 cm^{-1} assigned to N-H stretching vibration, which is not present in DPE spectrum. The absorption bands in the region $1255\text{-}1050\text{ cm}^{-1}$ assigned to C-N stretching vibrations of piperidine have been shifted and splitted showing substitution on nitrogen atoms of piperidine ring. The IR spectrum of DPE showed C-H stretching vibrations in the range $2990\text{-}2880\text{ cm}^{-1}$ and C-N stretching vibrations at $1228\text{-}1070\text{ cm}^{-1}$. A mass peak of

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moderate intensity at m/z 196 corresponding to molecular ion $(C_{12}H_{24}N_2)^+$ was observed in the spectrum of DPE. The base peak at m/z 98 is probably due to the formation of *N*-methyl piperidine cation radical, while the signals at m/z 112 could be assigned to *N*-ethyl piperidine fragment due to loss of piperidine moiety which appeared at m/z 84. The ligand DPE behaves as a bidentate ligand and bears resemblance to 1,2-dimorpholinoethane (DME) in terms of chromophoric environment [21-23]. Analytical data shown in Table-1 indicates that only

one DPE molecule like DME is found to coordinate with metal ion and form complexes of the general formula $[M(DPE)X_2]$, $M=Cu(II)$, $Ni(II)$, $Co(II)$, $Zn(II)$, $Cd(II)$ and $Hg(II)$ $X = Cl^-$, Br^- , I^- and NO_3^- . The complexes are soluble in DMSO and in acetone where as some of these complexes are soluble in nitromethane.

In Table-2 are listed molar conductance and magnetic moments values for DPE complexes. The molar conductance values ranges from 3.36 to 9.14

Table-1: Analytical data for DPE and its metal complexes

Compound	Dec. Pt. °C	Colour	%Metal Found (Calc.)	%Anion Found (Calc.)	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)
DPE(HBr) ₂	340	White	-	-	40.33 (40.32)	7.75 (7.32)	7.56 (7.82)
[Zn(DPE)Cl ₂]	245	White	19.21 (19.67)	21.05 (21.34)	43.78 (43.31)	7.43 (7.28)	8.64 (8.42)
[Zn(DPE)Br ₂]	238	White	15.83 (15.52)	37.91 (37.94)	34.46 (34.17)	5.82 (5.74)	6.46 (6.65)
[Zn(DPE)(NO ₃) ₂]	241	White	16.37 (16.96)	32.39 (32.18)	37.15 (37.34)	6.97 (6.80)	14.31 (14.52)
[Cd(DPE)Cl ₂]	276	White	28.66 (28.29)	17.36 (17.85)	38.14 (37.94)	6.58 (6.38)	7.56 (7.38)
[Cd(DPE)Br ₂]	254	Dirty white	24.38 (24.01)	34.09 (34.13)	31.10 (30.74)	5.03 (5.16)	6.11 (5.98)
[Cd(DPE)I ₂]	247	Dirty white	19.63 (19.99)	44.87 (45.14)	-	-	-
[Cd(DPE)(NO ₃) ₂]	266	white	25.72 (25.99)	28.13 (28.67)	33.13 (33.29)	5.67 (5.59)	13.23 (12.95)
[Hg(DPE)Cl ₂]	129	White	42.80 (42.91)	15.50 (15.17)	30.44 (30.79)	5.38 (5.17)	6.16 (5.99)
[Hg(DPE)Br ₂]	122	White	36.27 (36.05)	28.09 (28.62)	26.19 (25.87)	4.51 (4.35)	5.25 (5.03)
[Hg(DPE)I ₂]	113	White	30.99 (30.84)	39.13 (39.02)	-	-	-
[Hg(DPE)(NO ₃) ₂]	126	White	37.16 (37.24)	23.29 (23.02)	27.26 (27.65)	4.35 (4.65)	10.97 (10.75)
[Co(DPE)Cl ₂]	257	Blue	18.30 (18.09)	21.94 (21.76)	44.31 (44.17)	7.60 (7.42)	8.81 (8.59)
[Co(DPE)Br ₂]	243	Bluish Green	14.13 (14.21)	38.27 (38.53)	34.98 (34.70)	5.99 (5.83)	6.97 (6.75)
[Co(DPE)I ₂]	232	Bluish Green	11.27 (11.59)	49.72 (49.89)	-	-	-
[Co(DPE)(NO ₃) ₂]	207	Bluish Green	15.37 (15.51)	32.49 (32.64)	38.22 (37.98)	6.21 (6.38)	15.09 (14.77)
[Ni(DPE)Cl ₂]	273	Green	17.81 (18.03)	21.99 (21.78)	44.45 (44.19)	7.68 (7.42)	8.77 (8.59)
[Ni(DPE)Br ₂]	240	Green	14.46 (14.16)	38.57 (38.55)	35.03 (34.72)	6.02 (5.83)	6.93 (6.75)
[Ni(DPE)I ₂]	235	Green	11.59 (11.55)	49.73 (49.91)	-	-	-
[Ni(DPE)(NO ₃) ₂]	179	Green	15.27 (15.50)	32.41 (32.74)	38.27 (38.00)	6.55 (6.38)	15.13 (14.75)
[Cu(DPE)Cl ₂]	143	Green	19.45 (19.23)	21.60 (21.46)	43.81 (43.55)	7.50 (7.32)	8.69 (8.47)
[Cu(DPE)Br ₂]	139	Blue	15.45 (15.15)	38.39 (38.11)	34.65 (34.32)	5.98 (5.77)	6.83 (6.67)
[Cu(DPE)(NO ₃) ₂]	210	Green	16.26 (16.57)	32.06 (32.33)	37.09 (37.53)	6.49 (6.30)	14.85 (14.59)

Table-2: Conductance and magnetic data of DPE complexes

Complex	Solvent	Molar Conductance (mS) mol ⁻¹	μ_{eff} (BM)
[Zn(DPE)Cl ₂]	Acetone	6.33	-
[Zn(DPE)Br ₂]	Acetone	7.29	-
[Zn(DPE)(NO ₃) ₂]	Acetone	9.63	-
[Cd(DPE)Cl ₂]	Acetone	5.82	-
[Cd(DPE)Br ₂]	Acetone	6.35	-
[Cd(DPE)I ₂]	Acetone	8.76	-
[Cd(DPE)(NO ₃) ₂]	Acetone	9.88	-
[Hg(DPE)Cl ₂]	Acetone	8.96	-
[Hg(DPE)Br ₂]	Acetone	6.68	-
[Hg(DPE)I ₂]	Acetone	10.44	-
[Hg(DPE)(NO ₃) ₂]	Acetone	10.91	-
[Co(DPE)Cl ₂]	DMSO	12.22	4.24
[Co(DPE)Br ₂]	DMSO	10.87	4.78
[Co(DPE)I ₂]	DMSO	10.64	4.75
[Co(DPE)(NO ₃) ₂]	DMSO	12.16	7.34
[Ni(DPE)Cl ₂]	DMSO	9.70	3.44
[Ni(DPE)Br ₂]	DMSO	10.49	3.43
[Ni(DPE)I ₂]	DMSO	10.83	3.29
[Ni(DPE)(NO ₃) ₂]	DMSO	12.32	3.15
[Cu(DPE)Cl ₂]	Nitromethane	12.98	2.07
[Cu(DPE)Br ₂]	Nitromethane	12.30	2.08
[Cu(DPE)(NO ₃) ₂]	Nitromethane	12.71	2.22

mS. This shows that the complexes of DPE are non-electrolytic in these solvents, which indicates that anions are coordinated with the metal atoms.

The magnetic moments of Co(II) complexes vary in the range 4.24 to 4.78 B.M., which is characteristic value for the presence of three unpaired electrons. While that for Ni(II) complexes is 3.15 to 3.44 B.M., indicating the presence of two unpaired electrons. The magnetic moments of Cu(II) lies in the range 2.07 to 2.22 B.M., characteristic for the presence of a single unpaired electron.

The [Co(DPE)Cl₂] complex is blue while [Co(DPE)Br₂] and [Co(DPE)(NO₃)₂] are bluish green. The magnetic moments range from 4.24 to 4.78 B.M. These complexes are non-electrolyte in DMSO.

The solution spectra of the three complexes in DMSO are similar. The spectra are shown in Fig. 2 and the data is presented in Table-3. The chloride complex exhibits three bands at 14930 cm⁻¹, 15000 cm⁻¹ and 17240 cm⁻¹. Similar bands were observed for bromide complex with minor variations. Nitrate complex was slightly different and only two bands at 15270 and 17540 cm⁻¹ were observed. These bands could be assigned to transition ⁴A₂(F) → ⁴T₁(P), ν_3 in

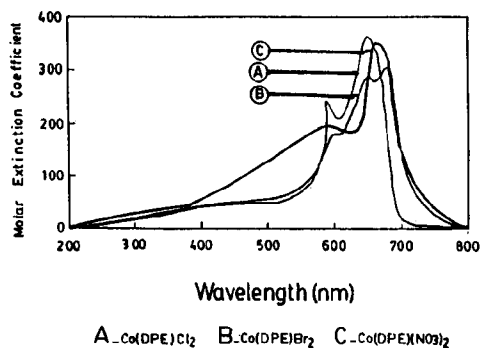


Fig. 2: Visible absorption spectra of DPE complexes in dimethylsulphoxide.

Table-3: Electronic absorption spectral data of DPE complexes in DMSO

Complex	λ_{max} (nm)	$\nu(\text{cm}^{-1})$	ϵ_{max} (M ⁻¹ cm ⁻¹)
[Co(DPE)Cl ₂]	580	17240	275
	645	15500	353
	670	14930	337
[Co(DPE)Br ₂]	595	16810	208
	650	15380	314
	690	14490	339
[Co(DPE)(NO ₃) ₂]	570	17540	185
	655	15270	367
	405	24690	57
[Ni(DPE)Cl ₂]	665	15040	178
	410	24390	52
[Ni(DPE)Br ₂]	675	14810	194
	385	25970	49
[Ni(DPE)(NO ₃) ₂]	645	15500	158
	510	19610	243
	665	15040	177
[Cu(DPE)Cl ₂]	780	12820	122
	525	19050	256
	695	14390	162
[Cu(DPE)Br ₂]	785	12740	113
	445	22470	155
	685	14600	65

Td symmetry. The low energy transition ⁴A₂(F) → ⁴T₂(F), ν_2 was not observed. The intensities and bandwidths are in accordance with the Td symmetry [24].

The solution spectra of [Ni(DPE)Cl₂], [Ni(DPE)Br₂] and [Ni(DPE)(NO₃)₂] complexes in DMSO are very much similar in band positions and intensities. The spectra are shown in Fig. 3 and data in Table-3. The non-electrolytic behaviour and the high spin type magnetic moments of 3.15 to 3.44 B.M. are clearly indicative to Td coordination geometry with nitrate ion as unidentate ligand. The strong bands observed at about 15500 cm⁻¹ can be

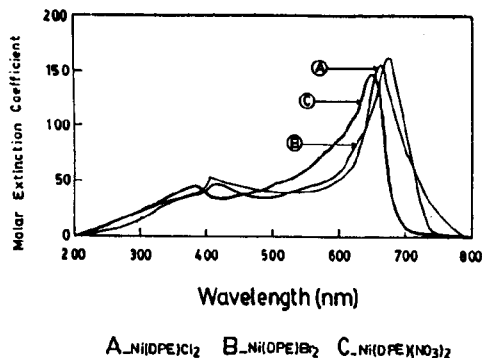


Fig. 3: Visible absorption spectra of DPE complexes in dimethylsulphoxide.

assigned to transition ${}^3T_1(F) \rightarrow {}^3T_1(P)$, ν_3 and the band at about 24500 cm^{-1} to transition ${}^3T_1(F) \rightarrow {}^3T_2(F)$, ν_1 in tetrahedral symmetry [25].

The solution spectra of chloride and bromide complexes of Cu(II) in DMSO are similar with some variation in band positions and intensities. The spectra are shown in Fig. 4 and data in Table-3. They exhibit clearly three absorption bands between 12000 to 22000 cm^{-1} , while only two bands were observed for nitrate complex. The complexes are non-electrolyte in nitromethane and have magnetic moments of 2.07 to 2.22 B.M. at room temperature. The electronic transitions observed in these complexes are consistent with C_{2v} symmetry. In this symmetry four transitions could be expected [26]. The fourth transition is not being observed as in the case of some previous investigations [27,28]. Similar spectra were observed for other Cu(II) complexes having CuN_2X_2 chromophore [24].

The characteristic bands in the infrared spectra (4000 - 600 cm^{-1}) of DPE and its metal complexes are given in Table-4. The infrared spectrum of the free ligand, $DPE(HBr)_2$ in KBr exhibits a strong absorption band at 1150 cm^{-1} and a weak band at 1135 cm^{-1} . These bands are assigned to C-N stretching vibrations [29,30].

In case of Zn(II) only three complexes $[Zn(DPE)Cl_2]$, $[Zn(DPE)Br_2]$, and $[Zn(DPE)(NO_3)_2]$ were synthesized. The iodide complex was unstable and could not be isolated in solid state. In these complexes the bands at 1150 and 1135 cm^{-1} assigned

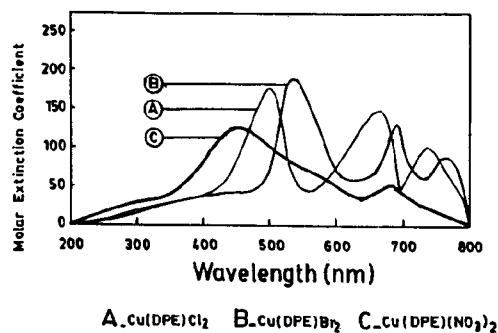


Fig. 4: Visible absorption spectra of DPE complexes in dimethylsulphoxide.

Table-4: Principal infrared bands (cm^{-1}) for DPE and its metal complexes

Compound	$\nu(\text{C-N})$
DPE	1150s, 1135w
$[Zn(DPE)Cl_2]$	1175m, 1165w, 1135vw, 1110vs
$[Zn(DPE)Br_2]$	1175m, 1162w, 1138vw, 1108vs
$[Zn(DPE)(NO_3)_2]$	1175w, 1165vw, 1135vw, 1110vs
$[Cd(DPE)Cl_2]$	1170w, 1160w, 1130sh, 1112vs
$[Cd(DPE)Br_2]$	1168w, 1158w, 1130sh, 1115vs
$[Cd(DPE)I_2]$	1172w, 1160w, 1130w, 1108vs
$[Cd(DPE)(NO_3)_2]$	1175m, 1165vw, 1138vw, 1110s
$[Hg(DPE)Cl_2]$	1170w, 115vw, 1135sh, 1110vs
$[Hg(DPE)Br_2]$	1175m, 1158vw, 1130sh, 1118vs
$[Hg(DPE)I_2]$	1172w, 1155w, 1135sh, 1125vs
$[Hg(DPE)(NO_3)_2]$	1170m, 1155sh, 1125vs
$[Co(DPE)Cl_2]$	1170w, 1155vw, 1135sh, 1122s
$[Co(DPE)Br_2]$	1172w, 1155vw, 1135sh, 1118s
$[Co(DPE)I_2]$	1170w, 1160vw, 1130sh, 1120vs
$[Co(DPE)(NO_3)_2]$	1175m, 1165w, 1130vw, 1105s
$[Ni(DPE)Cl_2]$	1172w, 1160vw, 1130sh, 1110s
$[Ni(DPE)Br_2]$	1170w, 1155vw, 1130vw, 1110s
$[Ni(DPE)I_2]$	1175w, 1160vw, 1132vw, 1115vs
$[Ni(DPE)(NO_3)_2]$	1172m, 1165vw, 1135sh, 1112s
$[Cu(DPE)Cl_2]$	1175m, 1160w, 1135w, 1110vs
$[Cu(DPE)Br_2]$	1175w, 1165vw, 1135vw, 1108vs
$[Cu(DPE)(NO_3)_2]$	1175m, 1165vw, 1135sh, 1112vs

to C-N stretching vibrations is split into four distinct bands. The strong one move to lower frequency side and is observed at about 1110 cm^{-1} whereas the other two weak bands shifts towards higher frequency side and appeared at 1175 and 1165 cm^{-1} .

Four complexes of Cd(II), $[Cd(DPE)Cl_2]$, $[Cd(DPE)Br_2]$, $[Cd(DPE)I_2]$ and $[Cd(DPE)(NO_3)_2]$ were synthesized. Similar complexes of Hg(II) were also isolated. In these complexes the bands attributed to C-N stretching vibrations like Zn(II) complexes is split into four bands with the exception of $[Hg(DPE)(NO_3)_2]$, where three bands were observed. The strong band observed at 1150 cm^{-1} in the free

ligand suffers a red shift by 25 to 40 cm^{-1} and other band moves to higher frequency side in comparison to the free ligand.

The behaviour of Cd(II) and Hg(II), DPE complexes is similar to Zn(II) complexes. The strong band at 1150 cm^{-1} shifts to lower frequency side and other bands move to higher frequency side. The shifts are almost to the same extent with minor variation in position and intensities.

Four complexes of Co(II), [Co(DPE)Cl₂], [Co(DPE)Br₂], [Co(DPE)I₂] and [Co(DPE)(NO₃)₂] were synthesized and isolated in solid state. In all these complexes the bands attributed to C-N stretching vibrations is split into four distinct bands as compared to the free ligand. Two bands suffer blue shift while the rest of two bands move to lower frequency side. The strong absorption band located at 1150 cm^{-1} undergoes a considerable red shift by 28 to 45 cm^{-1} in these complexes.

The complexes of Ni(II), [Ni(DPE)Cl₂], [Ni(DPE)Br₂], [Ni(DPE)I₂] and [Ni(DPE)(NO₃)₂] behave exactly like Co(II) complexes. The bands at 1150 and 1135 cm^{-1} attributed to C-N stretching vibrations are split into four bands. Two move to higher frequency side and other two move to lower frequency side. The strong band undergoes a red shift by 35 to 40 cm^{-1} .

In complexes of Cu(II), the bands attributed to C-N stretching vibrations suffer changes exactly like Co(II) and Ni(II) complexes. The strong absorption peak move considerably to lower frequency side. Infrared spectra of metal complexes clearly indicate that C-N stretching frequencies are shifted to lower and some to higher frequencies with changes in sharpness and intensities. This is caused by the withdrawal of electron density from the C-N band where nitrogen atom is coordinated to the metal ion. Thus 1,2-dipiperidinoethane behaves as bidentate ligand like substituted ethylenediamine coordinating through nitrogen atoms.

Experimental

Materials

Metal salts used were of reagent grade and used without further purification. The partial

dehydration of the salt was done by drying the hydrated salts in vacuum oven for several hours at 80-100°C. All solvents were distilled at least once before using.

Preparation of ligand

The ligand 1,2-dipiperidinoethane (DPE) was synthesized by the procedure [31]. Piperidine (0.25 mole) in absolute alcohol (40 ml) was added dropwise to 0.1 mole of 1,2-dibromethane in alcohol (20 ml). The contents were refluxed for about 8 hours at 80°C. The reaction mixture was left overnight to get piperidinium bromide crystals (m.p. 340°C). About 83% yield was obtained. Anal. (Found: C, 40.326; H, 7.751; N, 7.563. Calculated for C₁₂H₂₄N₂(HBr)₂: C, 40.223; H, 7.586; N, 7.821).

Preparation of ligand solution

The ligand 1,2-dipiperidinoethane dihydrobromide was dissolved in minimum amount of methanol, to which a calculated amount of alcoholic potassium hydroxide was added in order to remove precipitated potassium bromide. The filtrate was used as ligand solution.

Preparation of solid complexes

All the complexes were prepared using similar general procedure. Approximately 10 m moles of partially dehydrated salt was dissolved in minimum amount of anhydrous solvent. Methanol was used as solvent for the preparation of CoCl₂, CuBr₂ and NiCl₂ complexes and ethanol for the synthesis of rest of the metal complexes. The ligand DPE, and excess over 1:2 metal to ligand ratio was also dissolved in minimum amount of the same solvent and slowly added to the hot metal salt solution with constant stirring. The mixture was stirred and kept at 50°C for half an hour, then cooled for about 20 minutes. The metal complexes precipitated either immediately or on cooling. The complexes were washed three times with ether and dried at 40°C in vacuum oven.

Instrumentation

Infrared spectra were taken in the range of 4000 to 600 cm^{-1} on PYE UNICAM IR spectrophotometer as KBr disc.

Proton NMR spectra were recorded with Bruker (AM-300) instrument using tetramethylsilane as internal standard. Chemical shifts are reported as δ (ppm) values. Mass spectra were recorded with MAT 312 mass spectrophotometer.

Ultra violet and visible absorption spectra of the complexes in the range 200-900 nm using different solvents were obtained on DMS-200 UV/VIS spectrophotometer with 1cm matched quartz-cells.

Molar conductance of the solution of metal complexes were carried out with a conductivity meter type HI 8333. All measurements were done at room temperature on freshly prepared solutions.

Magnetic susceptibilities were measured by Guoy method at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard. The magnetic moments were calculated [28].

The elemental analysis were carried out at HEJ Research Institute of Chemistry, University of Karachi.

Conclusion

The stoichiometry of the complexes indicates that one DPE molecule is found to coordinate with metal ion. Therefore, it is evident that the ligand, under the existing conditions, prefer to form only mono complexes. The conductance measurements studies carried out in various solvents shows that all the complexes are non-electrolyte in nature further reveal the fact that anions are coordinated to the metal ion. The solid state IR spectra favours the formation of nitrogen coordination and thus support the bidentate behaviour of the ligand to form tetrahedral complexes of the type $[\text{MLX}_2]$. The magnetic moment studies and the solution electronic spectra further substantiate the distorted tetrahedral coordination geometry around the central metal ion.

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