

## INFRARED SPECTRA OF METAL COMPLEXES FROM 1,2-DIMORPHOLINOETHANE AND 1,3-DIMORPHOLINOPROPANE

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**Abstract.** The ligands, 1,2-Dimorpholinoethane (DME) and 1,3-Dimorpholinopropane (DMP) form tetrahedral complexes of stoichiometry,  $MLX_2$  where L, DME or DMP, M, Hg(II), Cd(II), Zn(II), Cu(II), Ni(II) and Co(II); X, Halogens and  $NO_3$ . The solid state IR data of these complexes generally support tetrahedral coordination  $MX_2 N_2$ . The splitting of the C—O—C bands in the complexes is caused by solid state effects such as packing and its influence on ring conformations or long range intermolecular interactions of the oxygen atoms. The effects of chelation on some characteristic bands are discussed and the solid state data are examined in the light of electronic spectra and conductance data of the complexes in solution.

The ligands 1,2-dimorpholinoethane (DME) and 1,3-dimorpholinopropane (DMP) form tetrahedral complexes with various metals<sup>1-4</sup> coordinating through nitrogen atoms only except in the case of gallium complex in which DME has been reported<sup>5</sup> to act as a tetradentate ligand. Although coordination through ethereal oxygen is not very common, a few such complexes have been reported in literature.<sup>6-9</sup> It is possible to detect coordinated ethereal oxygen by studying the changes in C—O—C IR stretching frequencies upon chelation. Similarly, metal—ligand stretching vibrations in the far IR regions could be used to investigate various coordination geometries in metal halide complexes.<sup>10</sup>

In spite of considerable interest in the coordination chemistry of DME and DMP, the IR spectra of these complexes have never been reported. In the present work such spectra over the range 4000—200  $cm^{-1}$  as nujol mulls, have been investigated. The effects of chelation on some characteristic bands were studied and the solid state data were examined in the light of electronic spectra and conductance data in solution.

### Experimental

#### Materials

The metal salts and all solvents were obtained from Merck except for morpholine which was from Matheson, Coleman and Bell. The salts were dried under reduced pressure at about 110°. The solvents were distilled before using. The ligands; DME and DMP were prepared according to the procedure given by Gero<sup>11</sup> and as reported earlier.<sup>4</sup>

#### Preparation of the Complexes and Physical Measurement

All complexes were prepared by the procedures

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reported earlier.<sup>4</sup> Satisfactory elemental analyses (C, H and N) were obtained for all complexes studied. The PMR spectra of the ligands were obtained on a Varian model EM-360 (60 MHz) spectrometer using TMS as external standard. Molar conductance were measured with a conductance bridge manufactured by Mullard Equipment, London. All measurements were done at room temperature. Magnetic susceptibilities were measured by the Guoy method at room temperature using Hg  $[Co(NCS)_4]$  as the standard. Elemental analyses were done at Microanalytical Laboratories, Harwell, England. Near IR and UV, visible spectra were recorded on a Cary Model 14 spectrophotometer with 1-cm matched quartz cells. IR spectra were recorded in the range 4000—200  $cm^{-1}$  on a Perkin-Elmer model 577 grating infrared spectrophotometer as nujol mulls supported on CsI plates.

### Results and Discussion

With DME and DMP, divalent mercury, cadmium, zinc, copper, nickel and cobalt forms complexes having the stoichiometry,  $MLX_2$  where L=DME or DMP and X, Halogens or nitrate ion. Some characteristic bands in the IR spectra of these ligands and their metal complexes are given in Tables 1 and 2, and some typical spectra are shown in Fig. 1-3.

In the free ligands, the bands at 1070 and 920  $cm^{-1}$  are tentatively assigned as C—O—C stretching vibration<sup>2,12</sup> and very strong absorption in the region of 1120  $cm^{-1}$  with a shoulder at 1130  $cm^{-1}$  is assigned to the C—N stretching vibration. In Hg(II), Cd(II), and Zn(II) complexes of DME, the C—N stretching vibrations are split into three distinct bands compared to the free ligands. Similarly, the C—O—C stretching vibrations are split into two each: one component having the frequencies observed for the ligand while the second with about 20  $cm^{-1}$  higher frequencies. In DMP complexes, the two C—O—C bands are split into two each with the ligand C—O—C absorption almost in the middle.

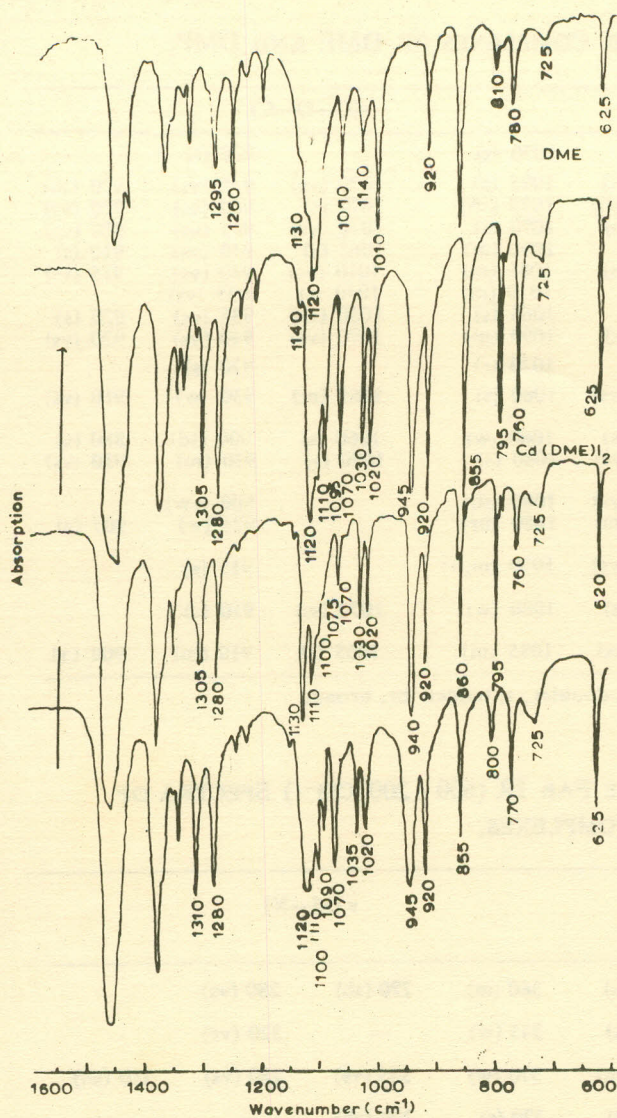


Fig. 1. IR Spectra of DME and its complexes as nujol mulls, showing characteristic bands at 600-1600  $\text{cm}^{-1}$  region.

Identical splittings and shifts in these bands are observed for Cu(II) halide complexes of DME and DMP. Although some of the bands in these complexes are relatively broad and weak, the general splitting pattern is the same. In the case of  $\text{Cu}(\text{DME})(\text{NO}_3)_2$ , one C—O—C band is shifted to lower frequency while the second is shifted to higher frequency.

The Ni(II) and Co(II) complexes of both ligands exhibit spectra having split  $\nu(\text{C}-\text{N})$  and  $\nu(\text{C}-\text{O}-\text{C})$  bands relative to the free ligands. The splitting for cobalt complexes is more evident compared to Ni(II) complexes.

The far IR spectra (Table 2, Fig. 3) of metal chloride complexes have three distinct sets of bands in the region of 480, 380 and 280  $\text{cm}^{-1}$ . Two  $\nu(\text{M}-\text{L})$  vibrations and two  $\nu(\text{M}-\text{X})$  vibrations are expected to be IR active for molecules of the type  $\text{MX}_2\text{L}$  where L, two monodentate ligand or a bidentate ligand.<sup>10</sup> The bands around 480 and 380  $\text{cm}^{-1}$ , therefore, could be assigned to  $\nu(\text{M}-\text{L})$

vibrations since these bands occur at approximately the same frequencies for both ligands and are independent of the halogens. The bands are split due to low site symmetry of the metal in the solid complex.<sup>14</sup> The observation of two distinct sets of bands for  $\nu(\text{M}-\text{L})$  vibrations in the complexes is noteworthy since no evidence for such vibrations above 200  $\text{cm}^{-1}$  has been found in complexes of heavy bidentate nitrogen donor ligands such as  $\alpha$ ,  $\alpha$ -bipyridyl and O, phenanthroline.<sup>15</sup> The set of bands around 280  $\text{cm}^{-1}$  is halogen dependent and can be assigned to  $\nu(\text{M}-\text{X})$  vibrations. This band was only observed for the metal chloride complexes. The second  $\nu(\text{M}-\text{X})$  vibration for the chloride complexes and the corresponding vibrations for the bromo- and iodo-derivatives are not observed. Such vibrations must either be too weak to locate or else below 200  $\text{cm}^{-1}$ . The  $\nu(\text{M}-\text{Cl})$  vibrations in cobalt complexes lie 10-40  $\text{cm}^{-1}$  above those of comparable zinc and mercury complexes as indeed is the case for the  $\nu(\text{M}-\text{X})$  vibrations of  $\text{MX}_4^{2-}$  anions.<sup>13</sup> A further point of interest is the intensity of  $\nu(\text{M}-\text{L})$   $\nu(\text{M}-\text{X})$  vibrations, which is higher for Hg(II)

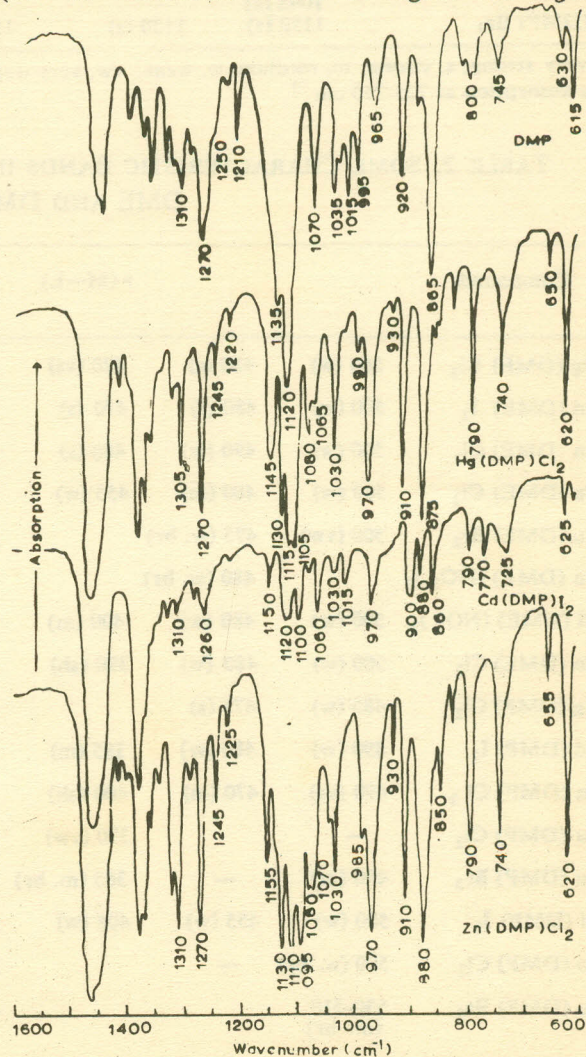


Fig. 2. IR spectra of DMP and its complexes as nujol mulls, showing some characteristic bands at 600-1600  $\text{cm}^{-1}$  region.

TABLE 1. INFRARED SPECTRAL DATA FOR COMPLEXES OF DME AND DMP.

Compound	$\nu(\text{C-N})$			$\nu(\text{C-O-C})$			
DME	1130 (sh)			1070 (s)		920 (s)	
Hg (DME) Cl <sub>2</sub>	1140 (w)	1120 (vs)	1110 (s)	1095 (s)	1070 (vs)	945 (vs)	920 (vs)
Cd (DME) I <sub>2</sub>	1130 (vs)	1110 (s)	1100 (sh)	1095 (sh)	1070 (s)	940 (vs)	920 (vs)
Zn (DME) Cl <sub>2</sub>	1120 (vs)	1110 (s)	1100 (s)	1090 (s)	1070 (vs)	945 (vs)	920 (vs)
Cu (DME) Br <sub>2</sub>	1120 (vs)	1110 (m)		1095 (m)	1065 (s)	940 (vs)	910 (s)
Cu (DME) Cl <sub>2</sub>	1120 (vs)	1110 (s)	1100 (s)	1085 (m)	1070 (vs)	940 (vs)	915 (vs)
Cu (DME) (NO <sub>3</sub> ) <sub>2</sub>	1140 (w)	1110 (vs)		1050 (m)	1040 (s)	935 (vs)	
Ni (DME) (NO <sub>3</sub> ) <sub>2</sub>	1120 (vs)	1105 (s)		1065 (s)	1050 (m)	935 (vs)	920 (s)
Co (DME) Cl <sub>2</sub>	1120 (vs)	1110 (s)	1100 (s)	1090 (m)	1070 (vs)	940 (vs)	920 (vs)
DMP	1135 (s-sh)	1120 (vs)		1070 (s)		920 (s)	
Hg (DMP) Cl <sub>2</sub>	1145 (s)	1130 (s)	1115 (vs)	1080 (s)	1065 (m)	930 (w)	910 (vs)
	1105 (vs)						
Cd (DMP) I <sub>2</sub>	1150 (s)	1120 (sd)	1100 (s)	1080 (w)	1060 (s)	900 (sd)	880 (s)
Zn (DMP) Cl <sub>2</sub>	1155 (s)	1130 (vs)	1110 (vs)	1080 (s)	1070 (s)	930 (m)	910 (vs)
	1095 (vs)						
Cu (DMP) Cl <sub>2</sub>	1150 (m)	1120 (m)	1105 (vs)	1080 (sh)		900 (vw)	
Cu (DMP) Br <sub>2</sub>	1150 (m)	1130 (sh)	1120 (m)	1080 (br)		925 (w)	905 (s)
	1105 (s)						
Ni (DMP) I <sub>2</sub>	1135 (w)	1120 (s)	1110 (vs)	1070 (m, t)		915 (s)	
	1100 (s)						
Co (DMP) Cl <sub>2</sub>	1155 (m)	1130 (vs)	1110 (s)	1080 (w)	1070 (w)	910 (s)	
	1095 (s)						
Co (DMP) Br <sub>2</sub>	1150 (s)	1120 (s)	1105 (vs)	1085 (m)	1065 (s)	910 (m)	900 (s)

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; d, doublet; t, triplet; br, broad.  
 NO<sub>3</sub> absorption at 725-750 cm<sup>-1</sup>.

TABLE 2. SOME CHARACTERISTIC BANDS IN THE FAR IR (600-200 CM<sup>-1</sup>) SPECTRA OF DME AND DMP COMPLEXES.

Compound	$\nu(\text{M-L})$				$\nu(\text{M-X})$			
Hg (DME) Cl <sub>2</sub>	500 (w)	480 (s)	470 (vs)	380 (s)	360 (m)	290 (sh)	280 (vs)	
Cd (DME) I <sub>2</sub>	500 (w)	480 (s)	470 (s)	380 (s)	345 (w)	—	320 (vs)	
Zn (DME) Cl <sub>2</sub>	500 (w)	490 (w)	480 (s)	385 (m)	370 (w)	335 (vs)	280 (vs)	310 (sh)
Cu (DME) Cl <sub>2</sub>	500 (w)	480 (m)	455 (w)	390 (s)	370 (s)	290 (sh)	—	—
Cu (DME) Br <sub>2</sub>	500 (vw)	475 (w, br)		385 (w)	360 (w, br)	—	—	
Cu (DME) (NO <sub>3</sub> ) <sub>2</sub>		480 (w, br)			350 (s)	—	—	
Ni (DME) (NO <sub>3</sub> ) <sub>2</sub>	500 (w)	480 (w)	400 (m)		370 (w, br)	—	—	
Co (DME) Cl <sub>2</sub>	500 (w)	480 (w)	390 (sh)		350 (m)	330 (vs)	320 (s)	
Hg (DMP) Cl <sub>2</sub>	485 (w)	475 (s)		380 (vs)	365 (m)	290 (vs)	260 (s)	
Cd (DMP) I <sub>2</sub>	490 (w)	480 (w)	385 (m)	370 (w)		—	—	
Zn (DMP) Cl <sub>2</sub>	490 (vs)	470 (m)	400 (sh)	380 (s, br)	370 (s)	325 (s, br)	300 (s)	
Cu (DMP) Cl <sub>2</sub>	—		370 (vw)			315 (m)	—	
Cu (DMP) Br <sub>2</sub>	490 (m)	—	365 (m, br)			—	—	
Ni (DMP) I <sub>2</sub>	500 (w)	455 (w)	405 (w)	380 (w)	360 (m)	—	—	
Co (DMP) Cl <sub>2</sub>	500 (w, br)	—		380 (w, br)		345 (vs)	320 (s)	
Co (DMP) Br <sub>2</sub>	530-510 (m, br)			430 (w)	390 (w)	—	—	

w, weak; vs, very strong; m, medium; s, strong; br, broad; sh, shoulder; vw, very weak.

and Zn(II) complexes compared to the other complexes studied.

A considerable shift with splitting of  $\nu(\text{C}-\text{N})$  stretching frequencies in the complexes compared to the free ligands, is clear evidence of coordination through nitrogen atoms. Similarly, such effects on  $\text{C}-\text{O}-\text{C}$  vibrations may be due to weak interactions of the metal atoms with the oxygen donors of the ligands. Such weak interactions are possible when morpholine moieties in DME or DMP molecules attain a boat conformation (Fig. 4) so that oxygen atoms are spatially well-oriented for coordination. Molecular models indicate that in this conformation a nearly square and almost planar arrangement of two oxygens and two nitrogens would be present when DME or DMP molecules are chelated to a metal ion. This arrangement probably would be more favoured in the case of DMP than in DME, since the former provides a more favourable (i.e. wider) bite angle than the latter. An increase in the size of the central chelate ring of linear tetradentate ligands has been shown to lessen chelate ring strain leading to increased stability of the metal complex depending upon the configurational requirements of the metal.<sup>16</sup> The solid state IR spectral data of the complexes indicate interactions of the metal atoms with the oxygen donor sites which may be merely the solid states effects or it may be due to long range intermolecular

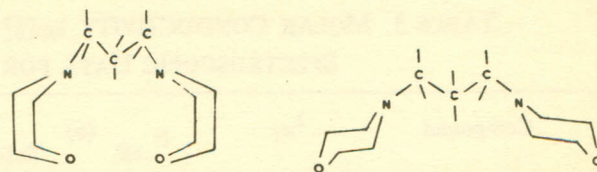


Fig. 4. Structures of DME and DMP.

interactions of the oxygen atoms. The  $\text{M}-\text{X}$  assignments are those expected for tetrahedral geometry. A change from 4-coordinate to 6-coordinate geometry would be expected to cause a decrease in  $\nu(\text{M}-\text{X})$ .<sup>17</sup>

The electronic spectral data, molar conductivities and other physical properties given in Table 3, substantiate tetrahedral coordination. Divalent zinc, cadmium and mercury form very stable, white crystalline complexes. Their solution spectra in nitromethane or acetone show no absorption in the range  $7,600-23,000 \text{ cm}^{-1}$ . These complexes are nonelectrolytes in ethanol and acetone which indicates coordination of the halogen atoms to the metal in agreement with tetrahedral symmetry. The green Cu(II) complexes are also nonelectrolytes and their solution electronic spectra show the usual unsymmetrical absorption (likely due to several overlapping transitions) from  $8,600$  to  $24,000 \text{ cm}^{-1}$ , with the strongest maxima at about  $14,700 \text{ cm}^{-1}$ . Similar visible spectra were observed for other Cu(II) complexes having a  $\text{CuN}_2\text{Cl}_2$  chromophore.<sup>18-19</sup> The  $d^9$  electron configuration makes Cu(II), would be octahedral environments, vulnerable toward Jahn-Teller distortions, which in extreme cases may lead to square arrangements. There is only a small barrier between square and tetrahedral configuration, which may be easily overcome by steric requirements placed by the ligands on the complex.<sup>20</sup> As a result, the geometric arrangement about Cu(II) is often not symmetrical and interpretation of its spectral properties are therefore complicated. This appears to be the case for copper-halide complexes. Nevertheless, the presence of several unsymmetric absorption bands indicates that the structure about the metal may not be perfectly tetrahedral.

The nonelectrolytic behaviour, high spin type magnetic moments and solution electronic spectra with strongest maxima at  $9,100$ , and  $15,630 \text{ cm}^{-1}$  are indicative of tetrahedral coordination geometry for the relatively unstable Ni(II) complexes in solution. In these complexes the maxima at  $9,100$  and  $15,630 \text{ cm}^{-1}$  can be assigned to the transition of  $T_d$  symmetry.<sup>21</sup> The blue Co(II) complexes are also nonelectrolytes in acetone and have magnetic moments around  $4.60 \text{ B.M.}$  These complexes exhibit two groups of multiple maxima which could be assigned to various transitions for Co(II) in tetrahedral symmetry.<sup>22</sup>

### Conclusion

Although solid state IR spectral data of DME and DMP complexes indicate weak interactions between the oxygen sites and the metal, the difficulty to observe such interactions in solution is illustrated

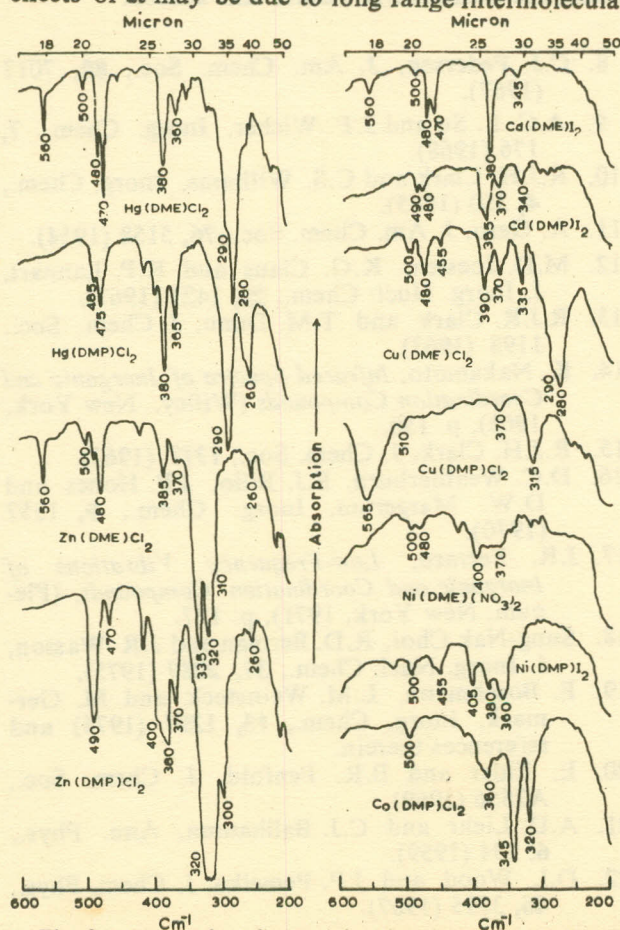


Fig. 3. Absorption frequencies ( $\text{cm}^{-1}$ ) of complexes of metal-halides with DME and DMP ( $600-200 \text{ cm}^{-1}$ ) range.

TABLE 3. MOLAR CONDUCTIVITY  $\lambda_m(\Omega^{-1} \text{ MOLE}^{-1} \text{ CM}^2)$ . MAGNETIC MOMENTS AND SPECTROSCOPIC DATA FOR DME AND DMP COMPLEXES.

Compound	$\lambda_m$	$\mu_{\text{eff}}$ (b)	Solvent (a)	$\lambda_{\text{max}} \text{ cm}^{-1}$	$\epsilon_{\text{max}}$ (v)
Cu (DME) Cl <sub>2</sub>	13.9	2.07	1	10750 (102),	19,500 (565)
Cu (DME) Br <sub>2</sub>	13.5	2.17	1	10400 (181),	19,600 (675)
Cu (DME) (NO <sub>3</sub> ) <sub>2</sub>	4.4	2.08	1	14700 (150),	23,260 (44)
Ni (DME) (NO <sub>3</sub> ) <sub>2</sub>	5.8	3.47	1	9100 (9), 25320 (41)	15,630 (20), 18200 (s)
Co (DME) Cl <sub>2</sub>	0.5	4.40	1	9800 (18),	15,380 (352), 15870 (33)
Cu (DMP) Cl <sub>2</sub>	42.0	2.18	2	10,750 (60), 14,100 (61)	11,750 (72), 12680 (58)
Cu (DMP) Br <sub>2</sub>	65.5	2.21	2	10,530 (70), 21,280 (257)	14,290 (112) 16670 (193)
Ni (DMP) I <sub>2</sub>	64.7	3.46	2	16,670 (24),	24,390 (46)
Co (DMP) Cl <sub>2</sub>	2.5	4.66	1	9,800 (18),	15,870 (630) 16500 (605)
			2	17,540 (5707), 9,760 (20), 22,730 (1131).	16,000 (215) 16950 (209)
Co (DMP) Br <sub>2</sub>	29.4	4.57	1	9,520 (11),	14,490 (490) 15870 (149)
			2	14,800 (675),	16,390 (183)

(a) (1)acetone nitromethane(2) conductance and spectral data were obtained in the same solvent.

(b)  $\mu_{\text{eff}}$  is in B.M. (c) spectra were run immediately after mixing, and intense charge transfer band at about 26,000  $\text{cm}^{-1}$  was observed in all complexes.

in this study. For tetradentate chelation, the morpholine moieties in these ligands must attain a rather constrained boat conformation which is probably not possible in solution state. The transition metal complexes having chelated 1, 4-diheterocyclohexanes as ligands with H, O, S, Se, P or a combination of these as hetroatoms are not known.<sup>23</sup> The steric requirements of DME and DMP are most suited for tetrahedral coordination with various metals.

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