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### CYCLOSERINE DERIVATIVES AS LIGANDS. COBALT(II), NICKEL(II), COPPER(II), ZINC(II) AND CADMIUM(II) HALIDE COMPLEXES OF $N_4, N'_4$ -TEREFTAL-BIS(CYCLOSERINE)

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## CYCLOSERINE DERIVATIVES AS LIGANDS. COBALT(II), NICKEL(II), COPPER(II), ZINC(II) AND CADMIUM(II) HALIDE COMPLEXES OF $N_4, N'_4$ -TEREFTAL-BIS(CYCLOSERINE).

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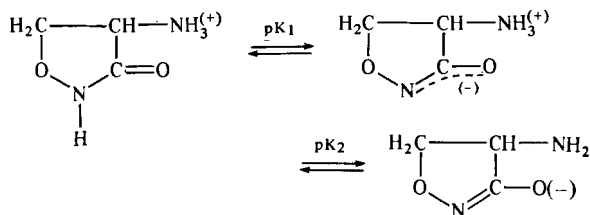
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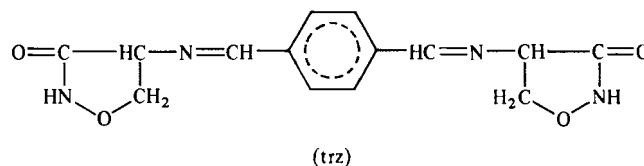
Transition metal(II) complexes of the cycloserine derivative,  $N_4, N'_4$ -tereftalbis(cycloserine) or Terizidone, were prepared and investigated by means of magnetic measurements, electronic and infrared spectroscopy and conductivity measurements. The magnetic moments and electronic spectra of the Co(II) compounds are consistent with pseudotetrahedral and pseudooctahedral symmetries, whereas the Ni(II) complexes had a pseudotetrahedral geometry. The various ligand field parameters  $Dq$ ,  $B'$  and  $\beta$  have been evaluated; the  $B'$  values suggest a strong covalency in the metal–ligand  $\sigma$  bond and the  $Dq$  values show a medium-strong ligand field. The position and multiplicity of the metal–halide stretching frequencies are discussed and used as a guide to the stereochemistry. Tetrahedral and octahedral structures are present in the zinc(II) and cadmium(II) complexes. The ligand was monodentate  $O$ -bonded or bidentate  $O, O'$ -bonded through the oxygen of the keto groups. We have never observed a metal-induced cycloserine ring opening under the present experimental conditions.

### INTRODUCTION

The transition metal complexes of cycloserine, 4-amino-3-isoxazolidone, have been investigated in considerable detail<sup>1–3</sup> obtaining complexes in different metal : ligand stoichiometric ratios and with the ligand always monodentate, but through the different donor sites. The above ligand exists in aqueous solution, indicated by potentiometric titrations, as a dipolar ion according to the equilibrium with the  $pK_1$  and  $pK_2$  values equal to 4.4 and 7.4 respectively.



Our interest in the coordination properties of the cycloserine was recently extended to the study of the chemical reactivity and linkage isomers of the coordination compounds of the derivatives of this ligand. We started with the  $N_4, N'_4$ -tereftal-bis-(cycloserine) or 1,4-bis(3-oxy-4-isoxazolidinylimino-methyl)-benzene, commercially known as Terizidone



(hereafter abbreviated *trz*), in which the above reported equilibria are absent.

The Terizidone molecule has wide application as a drug commonly used in clinical therapeutics, being a typical example of a sustained-release pharmaceutical preparation, whose action is attributed to a slow production of cycloserine *in vivo*.

Furthermore, this study has been stimulated by the fact that the metal complexes with ligands showing biological activity are more active than the free ligands.<sup>4,5</sup> The use of Terizidone as a metal complex instead of the free molecule could represent a better route of administration associated with a smaller risk of toxic side effects and could serve as a good double sustained-release pharmaceutical preparation.

Another ramification of this research is the correlation of the actions and effects of drugs with their chemical structures. Such structural activity relationships are an integral link in the analysis of drug action, and exploitation of this relationship

among established therapeutic agents has often led to the development of improved drugs. Finally, we have to bear in mind the possible interactions between drugs and metal containing enzymatic systems, because these interactions are very often dangerous to living organisms.

In this paper we have considered the coordination properties of Terizidone with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) halides.

## RESULTS AND DISCUSSION

The analytical results, magnetic susceptibility data and decomposition points are reported in Table I. The room temperature magnetic moments of the complexes are in the range expected for high-spin tetra-coordinate and hexa-coordinate Co(II) derivatives and tetrahedral Ni(II) complexes, corresponding to pseudotetrahedral and pseudooctahedral symmetries (6). The  $\mu_{eff}$  values of the copper derivatives correspond to one unpaired electron, confirming the presence in the complexes of copper(II) ( $S = 1/2$ ).

The electronic spectral data and the ligand field parameters of the complexes are given in Table II. The assignments of the relevant infrared bands, made by comparing the free ligand and the complexes spectra, are reported in Tables III and IV.

The compounds are microcrystalline or powder-like, soluble in DMF, nitro-methane and acetonitrile; all these derivatives are non-conducting in the above solvents, being the  $\Lambda_M$  values below 20,

35 and 75  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  in DMF, nitromethane and acetonitrile, respectively.<sup>7</sup>

### Electronic Spectral Study and Magnetic Susceptibility Measurements

With the cobalt(II) halides, complexes of essentially pseudotetrahedral and octahedral geometries are formed and their solid state electronic spectra and magnetic moment values are in accord for their stereochemistries.

The room temperature magnetic moments for the tetrahedral derivatives are in the 4.6–4.8 B.M. range. The solid state electronic spectra show a three-fold splitting of the electronic transitions  $\nu_3$  and  $\nu_2$  in Table II, with two sets of three bands between 15550 and 12900  $\text{cm}^{-1}$  and between 8160 and 6270  $\text{cm}^{-1}$  respectively. This behaviour is typical of a distorted tetrahedral coordination and the actual symmetry of the complexes will be  $C_{2v}$  or lower.<sup>8-10</sup> These bands are located at lower energies on passing from the chloro- to the iodo-derivative. We have calculated the ligand field parameters  $Dq$ ,  $B'$  and  $\beta$  using the frequency values corresponding to the centres of gravity of the split  $\nu_3$  and  $\nu_2$  absorption bands. The wavenumber of the  $\nu_1$  was not identified from the experiments because an unambiguous assignment was not possible in the near infrared region; its calculated values are reported in Table II.

As for the two octahedral derivatives of cobalt(II) ( $\mu_{eff} = 5.4$  and  $5.6$  B.M.), the solid state electronic spectra are both similar and consist of two bands at about 21000 and 8000  $\text{cm}^{-1}$ , corresponding to the

TABLE I  
Analytical data and other physical properties.

Compound	Colour	Found %			Required %			$\mu$ B.M.	Dec. Point (°C)
		C	H	N	C	H	N		
Co(trz)Cl <sub>2</sub>	turquoise	38.7	3.3	13.2	38.9	3.3	13.0	4.6	168–173
Co(trz)Br <sub>2</sub> · H <sub>2</sub> O	pale blue	31.2	2.9	10.2	31.2	3.0	10.4	4.8	178–183
Co(trz) <sub>4</sub> Br <sub>2</sub> · 2H <sub>2</sub> O	pink	46.2	4.4	15.4	45.9	4.1	15.3	5.4	> 300
Co(trz)I <sub>2</sub> · 4H <sub>2</sub> O	olive green	24.9	3.2	8.0	24.5	3.2	8.2	4.7	189–194
Co(trz) <sub>2</sub> I <sub>2</sub> · 2H <sub>2</sub> O	pink	35.1	3.6	11.3	35.3	3.4	11.7	5.6	158–163
Ni(trz)Cl <sub>2</sub> · 3H <sub>2</sub> O	yellow	34.2	3.9	11.5	34.6	4.1	11.5	3.5	140–145
Ni(trz)Br <sub>2</sub> · 3H <sub>2</sub> O	yellow	28.9	3.4	9.6	29.3	3.5	9.7	4.0	160–165
Cu(trz) <sub>2</sub> Cl <sub>2</sub> · 3H <sub>2</sub> O	pale green	42.4	4.3	13.8	42.4	4.3	14.1	2.0	195–200
Cu(trz) <sub>2</sub> Br <sub>2</sub> · H <sub>2</sub> O	olive green	39.8	3.7	13.6	39.8	3.6	13.2	1.9	224–229
Zn(trz)Cl <sub>2</sub> · H <sub>2</sub> O	pale yellow	37.3	3.6	12.6	36.8	3.5	12.3	dia.	187–192
Zn(trz) <sub>2</sub> Br <sub>2</sub> · 3H <sub>2</sub> O	pale yellow	38.1	3.9	12.5	38.1	3.9	12.7	dia.	198–203
Zn(trz) <sub>4</sub> I <sub>2</sub> · 4H <sub>2</sub> O	yellow	41.6	4.0	13.9	42.0	4.0	14.0	dia.	162–167
Cd(trz)Cl <sub>2</sub> · 4H <sub>2</sub> O	white	30.0	3.9	9.7	30.2	4.0	10.0	dia.	148–153
Cd(trz) <sub>2</sub> Br <sub>2</sub> · 4H <sub>2</sub> O	yellow	35.4	3.7	11.6	35.4	3.8	11.8	dia.	156–161
Cd(trz) <sub>4</sub> I <sub>2</sub>	yellow	43.1	4.0	14.3	42.7	3.6	14.2	dia.	177–182

Table II.  
Solid state electronic spectra and ligand field parameters ( $\text{cm}^{-1}$ )

Compounds	Assignments	$Dq$	$B'$	$\beta$	$Z^*$
	${}^4A_2(F) \rightarrow {}^4T_1(F)$				
Co(trz)Cl <sub>2</sub>	8160, 7470, 6450	432	620	0.64	0.09
Co(trz)Br <sub>2</sub> ·H <sub>2</sub> O	8010, 7300, 6330	424	588	0.61	0.08
Co(trz) <sub>2</sub> ·4H <sub>2</sub> O	7850, 7280, 6270	420	581	0.60	0.07
	${}^4T_1g(F) \rightarrow {}^4A_2g(F)^a$				
Co(trz) <sub>2</sub> Br <sub>2</sub> ·2H <sub>2</sub> O	17690	944	933	0.96	1.74
Co(trz) <sub>2</sub> I <sub>2</sub> ·2H <sub>2</sub> O	17330	925	928	0.96	1.72
	${}^3T_1(F) \rightarrow {}^3T_1(F)$				
Ni(trz)Cl <sub>2</sub> ·3H <sub>2</sub> O	13040				
Ni(trz)Br <sub>2</sub> ·3H <sub>2</sub> O	6780	367	699	0.67	0.57
	d-d bands				
Cu(trz) <sub>2</sub> Cl <sub>2</sub> ·3H <sub>2</sub> O	12500	355	669	0.64	0.49
Cu(trz) <sub>2</sub> Br <sub>2</sub> ·H <sub>2</sub> O	13420, 9240				

<sup>a</sup>Calculated values.

B is taken to be 967 and 1041  $\text{cm}^{-1}$  for the Co<sup>2+</sup> and Ni<sup>2+</sup> free gaseous ions respectively.

spin-allowed transitions  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ,  $\nu_3$  and  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ , corresponds to a two-electron jump and as consequence it will have a much lower oscillator strength than the other two bands and will be much weaker; in fact this band has not been observed in our spectra. Using the equations proposed by Eilbeck and coworkers,<sup>8</sup> which have been derived from the energy matrix of the two  ${}^4T_{1g}$  levels, the values of  $Dq$ ,  $B'$  and  $\beta$  have been evaluated from the position of the  $\nu_1$  and  $\nu_3$  bands. Using the relationship  $\nu_2 = \nu_1 + 10Dq$ , the energy of the  $\nu_2$  band has been calculated and is reported in Table II together with the ligand field parameters. The calculated  $\nu_2$  band lies at some 17500  $\text{cm}^{-1}$ ; a very weak shoulder does occur on the  $\nu_3$  band in this region, but this may arise from spin-orbit splitting of the  $\nu_3$  band. The calculation does suggest that the shoulder at about 16650  $\text{cm}^{-1}$  is not due to the  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  transition and is likely to be the spin-forbidden  ${}^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$  transition.

The nickel(II) derivatives are pseudotetrahedral; the magnetic moment measurements (3.5–4.0 B.M.) and solid state electronic spectra are all in very good agreement with this.<sup>6,13,15,16</sup> The spectral data and the values chosen for the energies  $\nu_2$  and  $\nu_3$ , from which the values of the parameters  $Dq$ ,  $B'$  and  $\beta$  have been derived, are presented in Table II. Because of the ambiguous assignment of  $\nu_1$ , we have reported in Table II its calculated values only.

By comparing with  $Dq$  values reported for [CoL<sub>4</sub>]<sup>2+</sup> cations,<sup>11</sup> we can see that  $Dq$  lies in the 447–538  $\text{cm}^{-1}$  range for CoN<sub>4</sub> chromophores; the corresponding range for CoO<sub>4</sub> chromophores is 410–470  $\text{cm}^{-1}$ .<sup>12</sup> In the case of [CoL<sub>6</sub>]<sup>2+</sup> cations, the  $Dq$  values for CoO<sub>6</sub> chromophores are in the 920–980  $\text{cm}^{-1}$  range, while the values corresponding to CoN<sub>6</sub> chromophores are higher than 1000  $\text{cm}^{-1}$ .<sup>13,14</sup> The  $Dq$  values for our both tetrahedral and octahedral cobalt(II) complexes agree very well with CoO<sub>2</sub>X<sub>2</sub> and CoO<sub>4</sub>X<sub>2</sub> chromophores.

A comparison of the electronic spectra of the tetrahedral nickel(II) derivatives with those of other complexes having Ni-N and Ni-O bonds suggests that the complexes are O-bonded, the band energies being at lower values than for N-bonded derivatives.<sup>13,15,16</sup>

Regarding the effective positive charges,  $Z^*$ , which decrease with decreasing values of  $\beta$ , using the equation connecting for the first row transition metals  $B'$  with  $Z^*$  and  $q$  (the occupation number of the  $d$  shell),<sup>17</sup> we have obtained the values reported in Table II, which, with the exception of the octahedral cobalt(II) derivatives, are considerably below the formal +2 oxidation state of these metals.

TABLE III.  
 Most important infrared bands of Terizidone complexes (4000–600 cm<sup>-1</sup>)

Compounds	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	Form ring vibrational modes	
				Stretchings ( $\omega$ )	Bendings
Terizidone	3130m	1705vs	1640vs	1562, 1455, 1385, 1160	1030, 850
Co(trz)Cl <sub>2</sub>	3140m	1700vs	1598vs	1540, 1455, 1368, 1167	1012, 854
Co(trz)Br <sub>2</sub> ·H <sub>2</sub> O	3180m	1696vs	1602vs	1540, 1452, 1370, 1170	1011, 862
Co(trz) <sub>4</sub> Br <sub>2</sub> ·2H <sub>2</sub> O	3200s	1702vs	1645m, 1590vs	1540, 1442, 1369, 1161	1016, 822
Co(trz)I <sub>2</sub> ·4H <sub>2</sub> O	3230s	1700s	1600vs	1540, 1451, 1370, 1168	1011, 857
Co(trz) <sub>2</sub> I <sub>2</sub> ·2H <sub>2</sub> O	3205s	1704ms	1586vs	1518, 1440, 1370, 1160	1010, 820
Ni(trz)Cl <sub>2</sub> ·3H <sub>2</sub> O	3220s	1692vs	1610vs	1562, 1452, 1380, 1164	1030, 850
Ni(trz)Br <sub>2</sub> ·3H <sub>2</sub> O	3230s	1693vs	1607vs	1548, 1450, 1370, 1165	1028, 848
Cu(trz) <sub>2</sub> Cl <sub>2</sub> ·3H <sub>2</sub> O	3140m	1702vs	1650vs, 1600s	1562, 1463, 1380, 1163	1031, 850
Cu(trz) <sub>2</sub> Br <sub>2</sub> ·H <sub>2</sub> O	3200s	1699vs	1645m, 1610s	1540, 1445, 1369, 1161	1020, 821
Zn(trz)Cl <sub>2</sub> ·H <sub>2</sub> O	3190ms	1700vs	1600vs	1540, 1450, 1364, 1166	1012, 865
Zn(trz) <sub>2</sub> Br <sub>2</sub> ·3H <sub>2</sub> O	3210s	1702vs	1600vs	1538, 1449, 1360, 1162	1012, 870
Zn(trz) <sub>4</sub> I <sub>2</sub> ·4H <sub>2</sub> O	3240ms	1702vs	1650m, 1600vs	1536, 1452, 1360, 1161	1013, 869
Cd(trz)Cl <sub>2</sub> ·4H <sub>2</sub> O	3135m	1703vs	1638vs, 1580ms	1560, 1457, 1385, 1162	1032, 851
Cd(trz) <sub>2</sub> Br <sub>2</sub> ·4H <sub>2</sub> O	3240ms	1702vs	1589vs	1539, 1450, 1361, 1164	1012, 830
Cd(trz) <sub>4</sub> I <sub>2</sub>	3260m	1702vs	1645m, 1582vs	1538, 1452, 1361, 1162	1012, 840

 TABLE IV.  
 Far-infrared spectra (600–50 cm<sup>-1</sup>).

Compounds	$\nu(\text{M}-\text{X})$	$\nu(\text{M}-\text{L})$	Bendings	Other bands
Terizidone	—	—	—	336m, 299mw, 238ms, 181m, 146m
Co(trz)Cl <sub>2</sub>	305vs, 280vs	460m, 390m	116m, 81m	292m, 243m, 179mw, 154m
Co(trz)Br <sub>2</sub> ·H <sub>2</sub> O	252m, 224ms	448m, 375m	76m, 67m	293m, 241m, 176mw, 149m
Co(trz) <sub>4</sub> Br <sub>2</sub> ·2H <sub>2</sub> O	219mw	410ms	—	297m, 244m, 177mw, 151m
Co(trz)I <sub>2</sub> ·4H <sub>2</sub> O	219m, 203ms	445ms, 388m	65m, 58m	298m, 243m, 179mw, 149m
Co(trz) <sub>2</sub> I <sub>2</sub> ·2H <sub>2</sub> O	202ms	418ms, 349m	—	295m, 243m, 172mw, 149m
Ni(trz)Cl <sub>2</sub> ·3H <sub>2</sub> O	324m, 275ms	442m, 368m	106m, 76m	298m, 240ms, 179m, 149m
Ni(trz)Br <sub>2</sub> ·3H <sub>2</sub> O	254ms, 225ms	445m, 360m	72m, 65m	294m, 239m, 184m, 142m
Cu(trz) <sub>2</sub> Cl <sub>2</sub> ·3H <sub>2</sub> O	315m, 289ms	420m, 388m	—	300m, 239m, 181m, 150m
Cu(trz) <sub>2</sub> Br <sub>2</sub> ·H <sub>2</sub> O	254m, 224m	418m, 390m	—	298m, 244m, 174mw, 149m
Zn(trz)Cl <sub>2</sub> ·H <sub>2</sub> O	320m, 282m	507m, 368m	120m, 107m	296m, 247m, 175mw, 151m
Zn(trz) <sub>2</sub> Br <sub>2</sub> ·3H <sub>2</sub> O	225vs	504m, 355m	104m	298m, 250m, 179mw, 152m
Zn(trz) <sub>4</sub> I <sub>2</sub> ·4H <sub>2</sub> O	203ms	500m	91m	301m, 251m, 176mw, 149m
Cd(trz)Cl <sub>2</sub> ·4H <sub>2</sub> O	209ms <sub>t</sub> , 172m <sub>b</sub>	418ms, 361vs,	106m, 98m	298m, 235m, 180m, 152m
Cd(trz) <sub>2</sub> Br <sub>2</sub> ·4H <sub>2</sub> O	189m	410m, 349m	89m	301m, 233m, 179mw, 150m
Cd(trz) <sub>4</sub> I <sub>2</sub>	168m	416m	78m	298m, 242m, 177mw, 149m

A pseudotetrahedral geometry can be attributed to the copper(II) derivatives on the basis of the solid state electronic spectra, that show bands at *ca.* 13500 and 9200 cm<sup>-1</sup>, Table II.<sup>18</sup> For a truly tetrahedral complex, the crystal-field theory predicts only one transition, <sup>2</sup>T<sub>2</sub> → <sup>2</sup>E, but a flattening of the tetrahedron results in the splitting of both the ground and excited levels and, as a consequence, four d-d transitions should be expected.<sup>19,20</sup> The above reported bands can be assigned to crystal-field transitions of copper(II) on the basis of their

frequencies and their relatively low intensities. The other two expected bands may be located below 5000 cm<sup>-1</sup> or may be hidden by the intense bands at *ca.* 20500 cm<sup>-1</sup>, probably due to a charge-transfer or to an intra-ligand transition. This pseudo-tetrahedral structure assignment is supported by the room temperature magnetic susceptibility values. Table I shows that the copper complexes have  $\mu_{\text{eff}}$  values equal to 1.97 and 1.94 B.M., higher than those of the planar compounds reported in the literature (1.80–1.86 B.M.), in accordance with the higher

orbital contribution to the moment expected for a tetrahedral arrangement of the ligands.<sup>21</sup>

### Infrared Spectral Studies

The infrared spectra of the free ligand and its metal derivatives (in the 4000–600  $\text{cm}^{-1}$  range) are reported in Table III. The ring modes stretchings ( $\omega$ ) and the two bendings due to the cycloserine ring lie in the ranges 1562–1160  $\text{cm}^{-1}$  and 1032–820  $\text{cm}^{-1}$ , respectively.<sup>22</sup> Regarding the vibrational modes  $\nu(\text{NH})$ ,  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{O})$ , going from the free ligand to the complexes, we observe a spectral pattern significantly different, Table III. The band attributed to  $\nu(\text{NH})$  undergoes blue shifts, the  $\nu(\text{C}=\text{N})$  mode is unchanged at the same value as in the free ligand or shows very small shifts towards lower energies, whereas  $\nu(\text{C}=\text{O})$  undergoes red shifts or is split into two bands at higher and lower energies depending on the stoichiometry of the complex. This behaviour is clearly indicative of a metal-ligand interaction *via* one or two oxygen atoms and is in accordance with the above reported conclusions reached from the electronic spectra studies.

In the complexes having a 1 : 1 metal : ligand molar ratio, with the exception of the cadmium chloro-derivative, the  $\nu(\text{C}=\text{O})$  falls in the 1610–1598  $\text{cm}^{-1}$  with a red shift of about 37  $\text{cm}^{-1}$ .

As for the 1 : 2 complexes, in the derivatives  $\text{Co}(\text{trz})_2\text{I}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}(\text{trz})_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cd}(\text{trz})_2\text{Br}_2 \cdot 4\text{H}_2\text{O}$  the  $\nu(\text{C}=\text{O})$  vibrational mode occurs between 1600 and 1586  $\text{cm}^{-1}$ , with a shift to lower energies of *ca.* 48  $\text{cm}^{-1}$ .

In the octahedral 1 : 4 cobalt(II) derivative, in the 1 : 4 zinc(II) and cadmium(II) complexes, in the 1 : 2 copper(II) derivatives and in the 1 : 1 cadmium chloro-derivative the  $\nu(\text{C}=\text{O})$  is split into two bands of higher and lower energies.

Starting from these results we can propose a coordination of the ligand *via* one or two oxygens of the keto group depending if the  $\nu(\text{C}=\text{O})$  vibrational mode is present as split or unsplit band, respectively.

The small negative shift observed in some cases of the  $\nu(\text{C}=\text{N})$  can be described as the electron withdrawing from the oxygen atom in the metal–ligand bond formation, thus affecting the carbon–nitrogen bond, which has, as a consequence, less double bond character, *i.e.* modes coupled.

The infrared results as regards  $\nu(\text{OH})$  and  $\delta(\text{HOH})$  for all the water containing complexes, clearly confirm the presence of lattice water and exclude the presence of coordinated water, lacking the vibrational

modes such as wagging, twisting and rocking, activated by coordination to the metal.

### Far-infrared Spectral Studies

In the far-i.r. spectra of the complexes, the bands of the free ligand are still present at *ca.* the same wavenumbers, with the exception of the vibrational mode at 336  $\text{cm}^{-1}$  which is absent in all the complexes as already observed in the previously reported cycloserine metal complexes.<sup>1,2</sup>

**Cobalt(II) complexes.** In the  $\text{Co}(\text{trz})\text{X}_2$  complexes, the cobalt-halogen stretching frequencies may be readily picked out by comparing the spectra of the different complexes; the couple of bands present in the 305–203  $\text{cm}^{-1}$  range, Table IV, may be attributed to the  $\nu(\text{Co}-\text{X})$ . These fall in the ranges expected for the proposed pseudotetrahedral stereochemistry and imply covalent metal–halogen bonds for terminal halides. This statement is confirmed by the frequency ratios  $\nu(\text{Co}-\text{Br})/\nu(\text{Co}-\text{Cl}) = 0.81$  and  $\nu(\text{Co}-\text{I})/\nu(\text{Co}-\text{Cl}) = 0.72$ , that fall in the ranges usually accepted for complexes with similar structures bearing terminally bonded halide atoms.<sup>23</sup> In the remaining 1 : 4 bromo- and 1 : 2 iodo-derivatives the reported  $\nu(\text{Co}-\text{X})$  values are lower than those observed for the 1 : 1 derivatives, but in agreement with those found for  $\nu(\text{Co}-\text{X})$  in octahedral complexes, according to the fact that in a change of stereochemistry with an increasing in the coordination number there is a decrease in the frequency values of the metal-halide stretchings.

New halogen independent bands are present in the 460–349  $\text{cm}^{-1}$  region, absent in the spectra of the starting materials used in this study, and they can be assigned to  $\nu(\text{Co}-\text{O})$  vibrational modes.<sup>24–26</sup>

**Nickel(II) complexes.** The nickel-halide stretching vibrations, present as medium or medium-strong bands at 324 and 275  $\text{cm}^{-1}$ , and at 254 and 225  $\text{cm}^{-1}$  in the chloro- and bromo-derivatives respectively, are in good agreement with the literature data for pseudotetrahedral complexes.<sup>24,25,27</sup> The ratio  $\nu(\text{Ni}-\text{Br})/\nu(\text{Ni}-\text{Cl})$ , equal to 0.80 (using average values of  $\nu(\text{Ni}-\text{X})$  frequencies), agrees well with the literature data for pseudotetrahedral complexes<sup>27</sup> and gives further confirmation that in these 1 : 1 complexes the halide atoms are not bridged.

New medium bands, due to  $\nu(\text{Ni}-\text{O})$ , are present in the 445–360  $\text{cm}^{-1}$  range in all the complexes.<sup>24–26</sup>

**Copper(II) complexes.** In the copper(II) derivatives two  $\nu(\text{Cu}-\text{X})$  are present in the far-i.r. region at 315 and 289  $\text{cm}^{-1}$  and at 254 and 224  $\text{cm}^{-1}$  for the chloro- and bromo-complex respectively. These values are typical of pseudotetrahedral copper(II) complexes. The ratio  $\nu(\text{Cu}-\text{Br})/\nu(\text{Cu}-\text{Cl})$ , using average values of the  $\nu(\text{Cu}-\text{X})$  frequencies, is 0.79 and matches very well the literature data reported for the above suggested stereochemistry.<sup>27</sup> The new bands, present in the spectra of the complexes only, at 420–388  $\text{cm}^{-1}$  are to be due to  $\nu(\text{Cu}-\text{O})$ .

**Zinc(II) and cadmium(II) complexes.** The chloro-derivatives were of the 1 : 1 type, whereas the bromo- and iodo-complexes were 1 : 2 and 1 : 4 respectively both for zinc and cadmium.

The 1 : 1 halide complexes may have halogen-bridged dimeric tetrahedral structures permitting two sets of metal-halogen modes (terminal and bridging), but terminally bonded ligands, or ligand bridges and terminal halogens. In the spectra of our zinc chloro-complex, the bands at 320 and 282  $\text{cm}^{-1}$  are due to terminal chloride,<sup>24,28</sup> while bridging and terminal  $\nu(\text{Cd}-\text{Cl})$  are present at 172 and 209  $\text{cm}^{-1}$  respectively in the  $\text{Cd}(\text{trz})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  derivative.<sup>28,29</sup> This fact agrees very well with the above discussed  $\nu(\text{C}=\text{O})$  mode, which was indicative of a bidentate behaviour of the ligand *via* both the oxygens of the keto groups in the zinc derivative and of a monodentate behaviour in the cadmium one. Furthermore, these results eliminate the possibility that the compounds can be regarded as polymeric halogen- and ligand-bridged octahedral complexes. Two bands are present in these complexes at 120 and 107  $\text{cm}^{-1}$  and at 106 and 98  $\text{cm}^{-1}$  for the zinc- and cadmium-complex respectively, which can be assigned to the  $\delta(\text{Cl}-\text{M}-\text{Cl})$  bending modes.

In the zinc and cadmium 1 : 2 and 1 : 4 derivatives the  $\nu(\text{M}-\text{X})$  are at the expected wavenumbers for terminal halides in octahedral complexes.

A consistent feature of the zinc and cadmium complexes spectra is that all the derivatives show bands in the 507–351  $\text{cm}^{-1}$  region, which do not appear in the spectrum of the free ligand, and which we consider to arise from metal-ligand vibrations, Table IV. These values are in the expected ranges for zinc-oxygen and cadmium-oxygen vibrations<sup>2,24,25</sup>

## CONCLUSIONS

The complexes reported in this study were always O-bonded with the ligand acting as mono- or bidentate; the presence of a very strong  $\nu(\text{C}=\text{O})$  mode

shifted in the complexes towards lower energies in comparison to the free ligand spectrum, or of two bands split towards higher and lower energies confirm the above behaviour of the ligand. In the far-i.r. spectra no bands are present in the ranges where  $\nu(\text{M}-\text{N})$  usually lies for these metals.

We can propose a pseudotetrahedral geometry for the complexes having a 1 : 1 metal : ligand stoichiometric ratio and for the copper derivatives, whereas for all the remaining derivatives a pseudooctahedral geometry can be suggested. It is worthy of note that in the case of the cobalt bromo- and iodo-derivatives only, the reaction is particularly dependent on the solvent employed; in fact if the reaction is carried out in acetone the 1 : 1 derivatives only can be obtained, while working in ethanol the reaction leads to the hexacoordinated compounds.

Far-i.r. spectroscopy enables us to distinguish between the different geometries and between terminal and bridging halides; the relationship between  $\nu(\text{M}-\text{X})$  vibrations and stereochemistry is outlined and shown to have potential application to the diagnosis of the stereochemistry and coordination number of the new metal halide complexes. This is particularly important where the metal ions have a closed shell of valence electrons and hence the techniques of electronic absorption spectroscopy and magnetism may yield no unambiguous informations on the stereochemistry.

A formulation of the type  $[\text{ML}_2][\text{MX}_4]$  for the complexes having only one coordinated ligand *per* metal ion must be ruled out because these compounds behave as nonelectrolytes and because these compounds do not show in the infrared spectra the typical vibrations of the tetrahalogroup  $[\text{MX}_4]^{2-,24,25,30-32}$

With the exception of the  $\text{Cd}(\text{trz})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  complex, in which terminal and bridging halide atoms are present, all the remaining 1 : 1 complexes and the copper(II) derivatives have a  $\text{C}_{2v}$  symmetry; in fact in the far-i.r. spectra two terminal  $\nu(\text{M}-\text{X})$  vibrations,  $a_1 + b_1$ , and two  $\nu(\text{M}-\text{L})$  vibrations,  $a_1 + b_2$ , have been found to be i.r.-active, as expected for molecules of this type.

The compounds  $\text{Co}(\text{trz})_2\text{I}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}(\text{trz})_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cd}(\text{trz})_2\text{Br}_2 \cdot 4\text{H}_2\text{O}$  have a polymeric octahedral symmetry, in fact just one  $\nu(\text{M}-\text{X})$ ,  $a_g + a_u$ , and two  $\nu(\text{M}-\text{L})$ ,  $2a_g + 2a_u$ , are i.r.-active, in accordance with a  $\text{C}_i$  symmetry group, although each repeat unit approximates to  $D_{4h}$  symmetry.<sup>26</sup>

We can propose for the 1 : 4 derivatives a trans-octahedral  $D_{4h}$  symmetry; in fact only one

$\nu(\text{M}-\text{X})$  vibration,  $a_{2u}$ , and only one  $\nu(\text{M}-\text{L})$  vibration,  $e_u$ , are seen in the infrared spectra, while if the complexes were cis-octahedral,  $C_{2v}$  symmetry, we should have found two  $\nu(\text{M}-\text{X})$  vibrations,  $a_1 + b_1$ , and four  $\nu(\text{M}-\text{L})$  vibrational modes,  $2a_1 + b_1 + b_2$ .

The solubility of these complexes in solvents suitable for cryoscopic freezing point measurements was too small for accurate molecular weight determinations, and so we are not able to decide if the ligand, when acting as bidentate, behaves as chelating ligand in monomeric complexes or as a bridging ligand in dimeric or polymeric complexes; however, on the basis of the above reported discussion regarding the far-i.r. spectra, we can propose the presence of monomeric complexes, with the exception of the derivatives for which a  $C_i$  symmetry has been suggested and of the cadmium chloro-complex, for which a pseudotetrahedral halide-bridged dimeric structure could be suggested.

We can exclude a metal-induced ring opening of the heterocyclic part of the ligand molecule; in fact in the infrared spectra we have never observed the typical bands of the derivatives obtained by the hydrolysis of the cycloserine ring;<sup>1,2</sup> furthermore, the terizidone ligand can be recovered (as pale yellow powder) by chemical decomposition of the complexes.

## EXPERIMENTAL

The Terizidone ligand, kindly supplied by Bracco Chemical Ind. (Milan), was in high purity grade and was used without further purification.

### *Preparation of the Complexes*

The complexes were obtained by adding 2.0 mmoles of the hydrated metal salts dissolved in 25 ml of acetone or ethanol to a suspension of the ligand in 30 ml of the same solvent (metal : ligand molar ratios from 1 : 1 to 1 : 6). Upon being heated under reflux for about 1 hour, the mixture became clear and was filtered in order to remove the unreacted ligand. The filtered solution was further refluxed under vigorous stirring for about 2 hours and the compounds precipitated spontaneously. They were filtered, washed with acetone or ethanol, diethyl ether and dried overnight over  $\text{P}_4\text{O}_{10}$ . We have obtained complexes only in the metal : ligand ratios reported in Table 1, and the yields for all the complexes were in the

90–95% range. Repeated syntheses and elemental analyses gave reproducible results. The ligand is very stable in the solvents used, under the experimental conditions.

### *Infrared Measurements*

The i.r. spectra have been recorded in the 4000–50  $\text{cm}^{-1}$  range with a Perkin-Elmer 180 spectrophotometer of the Instruments Centre of Modena University. The spectra in the 4000–400  $\text{cm}^{-1}$  range were measured for KBr discs or nujol mulls. Far-i.r. spectra were measured for nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

### *Electronic Spectra*

The electronic spectra have been recorded with a Shimadzu MPS-50L spectrophotometer in the solid state in the 4000–30000  $\text{cm}^{-1}$  range using the method of Venanzi and co-workers.<sup>3,3</sup>

### *Magnetic Susceptibility Measurements*

These were carried out by Gouy's method at room temperature. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of the Pascal's constants.

### *Conductivity Measurements*

These measurements were carried out with a WTW LBR type conductivity bridge at 25°C for  $10^{-3}\text{M}$  solutions in DMF, acetonitrile and nitromethane.

### *Analyses*

Carbon, nitrogen and hydrogen have been determined with a Perkin-Elmer 240 elemental analyzer.

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