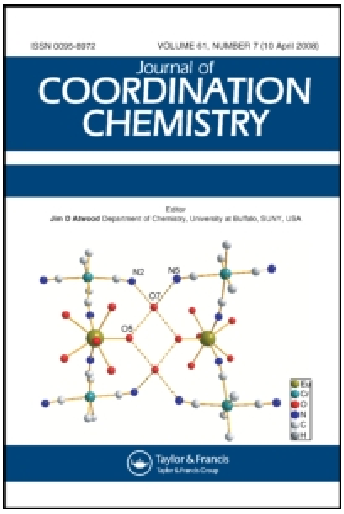

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COORDINATION CHEMISTRY OF CYCLOSERINE DERIVATIVES. COMPLEXES OF IRON(II), IRON(III), MANGANESE(II) AND PALLADIUM(II) WITH $N_{4-}N'_{4-}$ TEREFTAL-BIS(CYCLOSERINE)

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To cite this Article Preti, Carlo , Tassi, Lorenzo , Tosi, Giuseppe , Zannini, Paolo and Zanoli, Aline Franca(1983) 'COORDINATION CHEMISTRY OF CYCLOSERINE DERIVATIVES. COMPLEXES OF IRON(II), IRON(III), MANGANESE(II) AND PALLADIUM(II) WITH $N_{4-}N'_{4-}$ TEREFTAL-BIS(CYCLOSERINE)', Journal of Coordination Chemistry, 12: 3, 177 — 186

To link to this Article: DOI: 10.1080/00958978308073846

URL: http://dx.doi.org/10.1080/00958978308073846

COORDINATION CHEMISTRY OF CYCLOSERINE ERIVATIVES. COMPLEXES OF IRON(II), IRON(III), IANGANESE(II) AND PALLADIUM(II) WITH N_4-N'_4-TEREFTAL-BIS(CYCLOSERINE)

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(Received April 4, 1982; in final form July 1, 1982)

thetic and other studies of iron(II), iron(III), manganese(II) and palladium(II) complexes with the oserine derivative, N_4, N'_4-tereftal-bis(cycloserine) or Terizidone, are reported. The methods used the characterization of the compounds include elemental analyses, molar conductance, magnetic nents, electronic and infrared spectroscopy and thermal analyses (TG and DTG). From the netic properties it was concluded that the above ligand forms low-spin complexes with pallan(II) and high-spin complexes with iron(II), iron(III) and manganese(II). The wavelengths of the cipal absorption bands have been accounted for quantitatively in terms of the crystal field theory manganese(II) and tetrahedral iron(III) complexes. The values of *B* and *C* in the iron(III) derivatives less than in the corresponding manganese(II) complexes. Far-infrared spectra have been extensively ied and the relationship between metal-halogen stretching vibrations and stereochemistry of the plexes is outlined and shown to have potential application in the assignment of the stereochemistry coordination number of these new metal-halide complexes. The ligand is always monodentate onded through the nitrogen of the imino group of the isoxazole ring. Under our experimental litions no metal-induced cycloserine ring opening was observed.

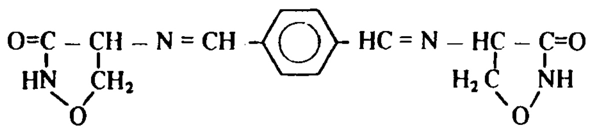
'RODUCTION

dies have been recently made on complex formation of antibiotics as ligands, such as loserine, 4-amino-isoxazolidin-3-one[1–3] and its derivative Terizidone, N_4, N'_4-tereftal-cycloserine).[4,5] These molecules have wide application in the pharmaceutical industry are drugs commonly used in clinical therapeutics, the first being a broad-spectrum biotic and the latter a typical example of a sustained-release pharmaceutical prepara-, whose action is attributed to a slow production of cycloserine *in vivo.*

t is well known that antibiotics interact with metal ions and this interaction is of a plex nature; the belief that the antibiotic action of the tetracyclines, for example, is ted to the ability of these compounds to form metal complexes with metal ions has ulated a great deal of investigation concerning the complexing properties of the tetralines as ligands.[6]

The most important factor in stimulating our interest in the coordination properties of loserine and Terizidone towards transition metal ions is the fact that metal complexes ligands which have biological activity are more active than the free ligands.[7,8] We hope t study of the stereochemistries and the chemical reactivity of coordination comnds of the drugs will help to determine what relationship exists between chemical cture and biological activity. Furthermore, the use of Terizidone as a metal complex ld represent a better route of administration associated with smaller risk of toxic side cts and could be a good double sustained-release pharmaceutical preparation.

In previous studies we reported the Terizidone derivatives of chromium(III), cobalt(II), kel(II), copper(II), zinc(II), ruthenium(III), rhodium(III) and cadmium(II) halides; in



this paper we consider the coordination properties of Terizidone, N_4, N'_4-tereftal-bis-(cycloserine) (trz) with the metal ions iron(II), iron(III), manganese(II) and palladium(II).

RESULTS AND DISCUSSION

According to the methods reported in the Experimental section we have obtained the complexes shown in the Table 1, together with their analytical data, colours and room temperature magnetic moments. Working with manganese(II) we have obtained complexes in the metal:ligand stoichimetric ratios 1:4 and 1:6, and the derivative $[Mn(trz)_2Br_2] \cdot 3H_2O$. Starting with $FeX_3 \cdot nH_2O$ (X = Cl, Br) and $FeI_2 \cdot nH_2O$ we have obtained compounds of general formula $Fe(trz)_nX_3$ (X = Cl n = 2, 3; X = Br n = 1, 4, 6) and $[Fe(trz)_4]I_2$, while palladium(II) complexes are of the type $[Pd(trz)_4]X_2$ (X = Cl, NO_3).

The principal features of the visible absorption spectra are given in Tables 2 and 3, while the most important i.r. data in the 4000-50 cm^{-1} range are shown in Tables 4 and 5.

The compounds are microcrystalline or powder-like, soluble in nitromethane and *N, N'*-dimethylformamide (DMF). Conductivity measurements carried out in DMF demonstrate that *i*) iron complexes of the type $[Fe(trz)_n]Br_3$ (n = 4, 6) are 1:3 electrolytes, Λ_M being in the range 205-230 ohm^{-1} cm^2 $mole^{-1}$; *ii*) the manganese derivatives with a metal:ligand ratio of 1:6, the iron iodo-derivative and the palladium complexes are 1:2 electrolytes, Λ_M values being in the 140-165 ohm^{-1} cm^2 $mole^{-1}$ range; *iii*) the iron(III) chloro-complex having a 1:2 metal:ligand molar ratio is a 1:1 electrolyte, Λ_M = 76 ohm^{-1} cm^2 $mole^{-1}$; *iv*) the 1:2 and 1:4 manganese complexes and the remaining iron derivatives were non conducting in the same solvent indicating the covalent nature of the compounds and the absence of ionic species in solution (Λ_M below 30 ohm^{-1} cm^2 $mole^{-1}$).[9]

Electronic Spectra and Magnetic Measurements

Manganese(II) complexes. Manganese(II) has a d^5 configuration, hence the same type of energy-level diagram applies both for tetrahedral and octahedral environment of the metal. The energies of the ${}^6A_1 \rightarrow {}^4E({}^4D)$ and of the ${}^6A_1 \rightarrow {}^4E, {}^4A_1({}^4G)$ transitions are independent of Dq and depend only on B and C. Therefore, once an assignment of the bands of the spectra has been made, the calculation of the values of B and C is easily performed by use of the expressions for the energies of the excited states relative to the ground state:

$$ {}^4E, {}^4A_1({}^4G) = 10B + 5C $$

$$ {}^4E({}^4D) = 17B + 5C $$

These values of B and C, (Table 2), were then used in solving the secular equation of Tanabe and Sugano[10] to evaluate a single value of Dq. By standard treatment[11] we found the best value of C and consequently the best values of B and $10Dq$ that fitted the energy levels, and finally, by a least-squares method, the ligand field parameters. In this way

TABLE 1
Analytical data and other physical properties

Compound	Colour	Found%			Calcd.%			μ_{eff}
		N	C	H	N	C	H	B.M.
$[Mn(trz)_6]Cl_2$	white	17.6	52.8	4.5	17.3	52.0	4.4	5.9
$[Mn(trz)_6]Br_2$	ivory	17.0	50.0	4.4	16.6	49.7	4.2	5.8
$[Mn(trz)_6]I_2$	pale grey	16.4	48.0	4.3	15.8	47.5	4.0	6.0
$[Mn(trz)_4Cl_2]$	pale ivory	17.0	50.1	4.4	16.8	50.4	4.2	5.8
$[Mn(trz)_4Br_2]$	ivory	16.0	46.6	4.1	15.7	47.2	4.0	6.1
$[Mn(trz)_4I_2]$	pale orange	15.3	44.2	4.0	14.8	44.3	3.7	6.2
$[Mn(trz)_2Br_2]\cdot 3H_2O$	hazel brown	13.1	38.8	4.0	12.8	38.5	3.9	6.4
$[Fe(trz)_3Cl_3]$	brown	15.6	47.0	3.9	15.7	47.2	4.0	6.0
$[Fe(trz)_2Cl_2]Cl\cdot 2H_2O$	brown	13.9	41.8	4.0	14.0	41.9	4.0	5.5
$[Fe(trz)_6]Br_3$	brown	15.9	47.6	4.0	15.9	47.8	4.0	5.9
$[Fe(trz)_4]Br_3\cdot 4H_2O$	brown	14.7	42.7	4.1	14.2	42.7	4.1	5.7
$[Fe(trz)Br_3]$	dark orange	9.4	28.4	2.3	9.4	28.1	2.4	5.8
$[Fe(trz)_4]I_2$	dark orange	15.0	44.2	3.8	14.8	44.3	3.7	5.1
$[Pd(trz)_4]Cl_2$	pale yellow	16.6	49.0	4.2	16.2	48.5	4.1	dia.
$[Pd(trz)_4](NO_3)_2\cdot 3H_2O$	yellow	16.4	45.4	4.4	16.9	45.0	4.2	dia.

good agreement between calculated and observed energies has been found for all the states (Table 3). The differences are of the order of 1.46% for the state $^4T_1(^4G)$, 2.17% for the state $^4T_1(^4P)$ and 1.18% for the state $^4T_1(^4F)$.

The nephelauxetic parameter β, in the 0.88–0.76 range (Table 2), does not differ greatly from unity, in keeping with the commonly accepted opinion that manganese(II) complexes are quite ionic. In addition, decreasing values of β are associated with a reduction in the effective positive charge of the cation and with an increasing tendency to be reduced; in the case of the first row transition metals, the equation

$$B'\,(\text{cm}^{-1}) = 384 + 58q + 124(Z^* + 1) - 540/(Z^* + 1)$$

links the variation of the Racah parameter with the effective cationic charge Z^* and the number q of electrons in the partly filled d shell.[2] The effective ionic charges for the manganese(II) complexes range between 1.11 and 1.55.

The effective magnetic moment values are in the range expected for five unpaired electrons, $S = 5/2$ and these μ_{eff} values are very close to the spin-only value irrespective of whether the ligand arrangement is of octahedral or tetrahedral symmetry.[12]

Iron complexes. According to the conductivity values and i.r. results (see below) we propose a pseudotetrahedral structure for $[Fe(trz)_2Cl_2]Cl\cdot 2H_2O$, $[Fe(trz)Br_3]$, $[Fe(trz)_4]Br_3\cdot 4H_2O$ and $[Fe(trz)_4]I_2$ and a pseudooctahedral symmetry for the other two iron(III) derivatives; electronic spectra confirm these stereochemistries.

Five of the ten transitions expected from an Orgel diagram of a d^5 system[13] for tetrahedral complexes of iron(III) have been detected in the electronic spectra of our derivatives (Tables 2 and 3). The first two bands at 14350–15100 cm^{-1} and in the 16530–16900 cm^{-1} range are assigned to transitions to the ^4G sub-levels, $^4T_1$ and ^4E, $^4A_1$,

TABLE 2
Ligand field parameters and *Dq* independent bands of Mn(II) and Fe(III) derivatives (cm^{-1})

Compound	${}^6A_1 \rightarrow {}^4E, {}^4A_1 ({}^4G)$	${}^6A_1 \rightarrow {}^4E({}^4D)$	B^a	C	$\overline{10Dq}$	β
$[Mn(trz)_6]Cl_2$	26600	32050	779	3762	7210	0.88
$[Mn(trz)_6]Br_2$	26450	31850	771	3748	7210	0.87
$[Mn(trz)_6]I_2$	26315	31750	776	3711	6980	0.87
$[Mn(trz)_4Cl_2]$	26300	31050	679	3902	7410	0.76
$[Mn(trz)_4Br_2]$	25840	30770	704	3760	7230	0.79
$[Mn(trz)_4I_2]$	25450	30670	746	3598	7720	0.84
$[Mn(trz)_2Br_2]\cdot 3H_2O$	26100	31250	736	3748	7470	0.83
$[Fe(trz)_2Cl_2]Cl\cdot 2H_2O$	16660	18620	280	2772	3580	0.26
$[Fe(trz)_4]Br_3\cdot 4H_2O$	16530	18940	344	2618	2930	0.32
$[Fe(trz)Br_3]$	16900	18870	281	2818	2970	0.26

[a] B is taken to be 890 and 1080 cm^{-1} for the free gaseous Mn^{2+} and Fe^{3+} ions respectively.

TABLE 3
Electronic spectra of Mn(II) and Fe(III) derivatives: observed and calculated bands (cm^{-1}).

	${}^6A_1 \rightarrow {}^4T_1 ({}^4G)$		${}^6A_1 \rightarrow {}^4T_1 ({}^4P)$		${}^6A_1 \rightarrow {}^4T_1 ({}^4F)$	
Compound	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
$[Mn(trz)_6]Cl_2$	22420	21908	35985	35749	44250	44201
$[Mn(trz)_6]Br_2$	22075	21755	36040	35590	43860	43935
$[Mn(trz)_6]I_2$	21650	21800	35970	35240	43480	43732
$[Mn(trz)_4Cl_2]$	21760	21580	36540	35930	42900	43108
$[Mn(trz)_4Br_2]$	21100	21180	36225	35109	41500	42607
$[Mn(trz)_4I_2]$	21050	20215	35975	34734	41150	42507
$[Mn(trz)_2Br_2]\cdot 3H_2O$	21280	21195	34480	35460	43750	43261
$[Fe(trz)_2Cl_2]Cl\cdot 2H_2O$	14550	14847	22830	22812	25840	25929
$[Fe(trz)_4]Br_3\cdot 4H_2O$	14350	15142	21980	21915	25970	26100
$[Fe(trz)Br_3]$	15100	15576	23000	22787	26000	26138

respectively. The next transition between 18620 and 18940 cm^{-1} could be due to the ${}^4E({}^4D)$, while the remaining two transitions between 21980 and 23000 cm^{-1} and in the 25840-26000 cm^{-1} range are to the ${}^4P$ and ${}^4F$ levels.

Using the same method of calculation described above for the manganese(II) complexes we have obtained the best values of *C*, *B* and 10*Dq* that fit the energy levels; these values are reported in Table 2, while the calculated absorption maxima are given in Table 3. The differences between calculated and observed energies are of the order of 3.43% for the state ${}^4T_1({}^4G)$, 0.44% for the state ${}^4T_1({}^4P)$ and 0.46% for the state ${}^4T_1({}^4F)$. The β values, Table 2, are in the range normally accepted for tetrahedral iron(III) complexes.

By comparing the results obtained for the manganese(II) and iron(III) complexes we observe that the values of *B* and *C* in the iron derivatives are lower than in the corresponding manganese compounds. The parameter 10*Dq* is significantly lower for the iron(III) complexes than for manganese(II) and shows the order Cl > Br. In the octahedral iron(III) halide complexes the very weak spin-forbidden transitions are obscured by charge-transfer bands at 38900 and 35100 cm^{-1}, and at 39400 and 35450 cm^{-1} in the

TABLE 4
Most important infrared bands of Terizidone complexes (4000–650 cm^{-1}).

Compound	ν_{NH}	$\nu_{C=N}$	$\nu_{C=O}$	Ring vibrational modes	
				Stretchings	Bendings
Terizidone	3130m	1705vs	1640vs	1562, 1455, 1385, 1160	1030, 850
$[Mn(trz)_6]Cl_2$	3140m, 3045s	1708vs	1640vs	1563, 1457, 1389, 1165	1031, 852
$[Mn(trz)_6]Br_2$	3140m, 3045s	1705vs	1638vs	1561, 1456, 1387, 1163	1030, 851
$[Mn(trz)_6]I_2$	3138m, 3040s	1706vs	1640vs	1562, 1456, 1388, 1165	1032, 851
$[Mn(trz)_4Cl_2]$	3140m, 3040s	1705vs	1635vs	1563, 1457, 1389, 1161	1030, 850
$[Mn(trz)_4Br_2]$	3140m, 3040s	1702vs	1635vs	1560, 1453, 1385, 1162	1030, 850
$[Mn(trz)_4I_2]$	3145m, 3050ms	1708s	1640s	1562, 1454, 1390, 1162	1030, 851
$[Mn(trz)_2Br_2]\cdot 3H_2O$	3150m, 3038ms	1703vs	1638vs	1565, 1452, 1390, 1165	1031, 850
$[Fe(trz)_3Cl_3]$	3150ms, 3040m	1710s	1643ms	1540, 1450, 1390, 1170	1040, 828
$[Fe(trz)_2Cl_2]Cl\cdot 2H_2O$	3136m, 3020ms	1701vs	1635vs	1561, 1451, 1385, 1160	1030, 850
$[Fe(trz)_6]Br_3$	3170m, 3060m	1705s	1638s	1555, 1450, 1385, 1175	1030, 828
$[Fe(trz)_4]Br_3\cdot 4H_2O$	3139ms, 3035s	1700vs	1635vs	1561, 1455, 1390, 1160	1030, 850
$[Fe(trz)Br_3]$	3160m, 3030m	1700vs	1639ms	1570, 1450, 1395, 1165	1040, 830
$[Fe(trz)_4]I_2$	3135m, 3030ms	1701vs	1635vs	1570, 1453, 1385, 1160	1029, 850
$[Pd(trz)_4]Cl_2$	3135m, 3040m	1706s	1635s	1560, 1452, 1350, 1150	1030, 848
$[Pd(trz)_4](NO_3)_2\cdot 3H_2O$	3140m, 3045ms	1700s	1630vs	1560, 1450, 1350, 1162	1031, 850

chloro- and bromo-derivatives, respectively. The band at some 39000 cm^{-1} could be assigned to a $\pi_3 \rightarrow \pi_4$ transition of the type $\pi_3(e) \rightarrow \pi_4(e)$ and/or $\pi_3(a_2) \rightarrow \pi_4(a_1)$; both have about the same energy and are expected to overlap. The second band near 35000 cm^{-1} could be a $d_\epsilon \rightarrow \pi_4$ transition of the type $d_\epsilon(a_1) \rightarrow \pi_4(e)$ and/or $d_\epsilon(e) \rightarrow \pi_4(a_1)$ which, as previously reported should have both the same energy and are expected to overlap.[14]

As for the iron(II) iodo-derivative, the crystal-field theory predicts that spin-free iron(II) complexes with six *d* electrons will form tetrahedral complexes in which the ground state has the electronic configuration $t_{2g}^3e_g^3$. The solid state electronic spectrum of the complex $[Fe(trz)_4]I_2$ exhibits a broad band in the near i.r. region at 5620 cm^{-1} that is assignable to the $^5E \rightarrow {}^5T_2$ transition, showing that the complex has a tetrahedral symmetry, the position of the band maximum excluding other geometries. The spectrum is also characterized by an intense band at 43100 cm^{-1}, attributed to a ligand to metal charge transfer.

The magnetic susceptibility values at room temperature for the iron(III) derivatives are consistent with the proposed tetrahedral and octahedral stereochemistries. Iron(II) has a $^5D_4$ ground state which under the influence of the cubic field of a tetrahedral arrangement of ligands splits into a lower doublet, ^5E, and an upper triplet, $^5T_2$, so that only a small orbital contribution to the magnetic moment above that of the spin-only value of 4.90 B.M. is predicted; in accordance, the μ value for the present iodo-derivative is 5.1 B.M. (Table 1).[12]

Palladium(II) complexes. The solid state electronic spectra of the palladium derivatives are indicative of square-planar geometry.[15] The bands at 23530 and at 23920 cm^{-1} in the chloro- and nitrato-derivatives respectively may be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition,

TABLE 5
Far-infrared bands of Terizidone complexes (450–50 cm^{-1}).

Compound	ν_{M-X}	ν_{M-L}	Other bands
Terizidone			336m, 299mw, 238ms, 181m, 146m
$[Mn(trz)_6]Cl_2$		218m, 207m	337m, 299w, 238s, 180m, 150m
$[Mn(trz)_6]Br_2$		216m, 206w	335m, 300mw, 237ms, 178m, 148m
$[Mn(trz)_6]I_2$		220m, 206m	339m, 298mw, 238ms, 180m, 148m
$[Mn(trz)_4Cl_2]$	226m	206m	337m, 299m, 238ms, 180m, 148m
$[Mn(trz)_4Br_2]$	185m	210m	338m, 300m 238ms, 179m, 150m
$[Mn(trz)_4I_2]$	140ms	205m	336m, 299m, 236ms, 180m, 148mw
$[Mn(trz)_2Br_2]\cdot 3H_2O$	200w, 190m	218m, 211mw	335m, 297m, 237ms, 179m, 149m
$[Fe(trz)_3Cl_3]$	355m	208m	340m, 301m, 243ms, 182m, 148m
$[Fe(trz)_2Cl_2]Cl\cdot 2H_2O$	380ms, 362ms	229ms, 217m	338m, 299m, 239ms, 181m, 147m
$[Fe(trz)_6]Br_3$		209m	335m, 298m, 236ms, 181m, 147m
$[Fe(trz)_4]Br_3\cdot 4H_2O$		211m	338m, 300m, 237ms, 180m, 148m
$[Fe(trz)Br_3]$	286ms, 268sh	212m	346m, 302m, 236ms, 182m, 150m
$[Fe(trz)_4]I_2$		219m	335m, 297m, 235ms, 180m, 147m
$[Pd(trz)_4]Cl_2$		262m	335m, 298m, 239m, 183m, 150m
$[Pd(trz)_4](NO_3)_2\cdot 3H_2O$		254m	333m, 302m, 237m, 184m, 150m

from which, by assuming a value of $F_2 = 10F_4 = 600$ for the Slater-Condon interelectronic repulsion parameters,[16] it is possible to derive the values of Δ_1 (25640 and 26020 cm^{-1} respectively).

Infrared Spectra

The infrared spectra of the free ligand and its metal derivatives (in the 4000-50 cm^{-1} range) are reported in Tables 4 and 5. The ring stretching modes, ω, are in the 1570-1150 cm^{-1} range, while the two bendings due to the cycloserine ring lie in the 1040-828 cm^{-1} region.[4,17] By comparing the free ligand spectrum with those of the complexes, we observe, as regards the vibrational modes ν_{NH}, $\nu_{C=N}$ and $\nu_{C=O}$, that the ν_{NH} stretch is split into two bands, while $\nu_{C=O}$ is unchanged or shows very small positive shifts. The $\nu_{C=N}$ mode is practically unchanged compared with the uncomplexed ligand. This behaviour is clearly indicative of a metal-ligand interaction *via* one imino nitrogen atom.

The infrared results as regards ν_{OH} and δ_{HOH} for all the complexes containing water 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. These results have been fully confirmed by thermogravimetric studies.

As for the complex $[Pd(trz)_4](NO_3)_2\cdot 3H_2O$, by the use of i.r. spectroscopy it is possible to determine whether or not the anions are coordinated to the metal. Coordination, in fact, lowers the original symmetry of the free ion and this is reflected in the number and intensity of its fundamental vibrations. This compound behaves in DMF solution as an 1:2 electrolyte and its i.r. spectrum shows the typical bands of a non-bonded nitrato group; D_{3h} symmetry, ν_3 (doubly degenerate stretch) as a very strong band at 1381 cm^{-1}, ν_2 (out-of-plane deformation) and ν_4 (double degenerate in-plane bending) in the 850-750 cm^{-1} range.[18]

Thermogravimetric studies

The thermal decomposition of the complexes was studied by TG and DTG techniques. The results exclude the presence of coordinated water in the complexes containing water, Table 1, and unambiguously confirm the presence of lattice water. The observed and calculated weight losses in the 50-130° range agree with the loss of three molecules of water in the manganese(II) complex and in the palladium nitrato-derivative, and of two and four molecules in the 1:2 iron chloro-derivative and 1:4 iron bromo-derivative, respectively.

The following decomposition step is quite complicated and most likely involves thermal breakdown of the ligand as confirmed by the absence of any clear distinction between loss of the Terizidone and conversion of the remaining halide into the corresponding oxide.

Far-infrared Spectra

Manganese(II) complexes. The compounds of the type $[Mn(trz)_6]X_2$ show, in the far-i.r. spectra (Table 5) two bands in the 220-206 cm^{-1} range. These vibrational modes, absent in the spectra of the starting materials, can be assigned to manganese-ligand interactions through the nitrogen atom of the imino group.[19-23] In these derivatives metal-halogen absorptions are not found in the range usually observed for manganese derivatives containing covalently bonded halide atoms. This fact is in accord with the conclusions reached from the conductivity measurements and electronic spectra.

As for the 1:4 derivatives, comparison of the spectra of these complexes with those of the 1:6 ones reveals some new bands whose frequency becomes progressively lower as the mass of the halogen increases and can therefore be assigned to the vibrations ν_{Mn-X}, in good agreement with literature data for other manganese(II) halide complexes.[20,23,24] In all these derivatives a single band is present near 210 cm^{-1} and this can be assigned to ν_{Mn-N} stretching vibrations. In the 1:2 compound, two ν_{Mn-Br} and two ν_{Mn-N} vibrations have been found in the 218-190 cm^{-1} range, (Table 5).

Iron and palladium complexes. In the 1:4 and 1:6 bromo derivatives of iron(III), in the iron(II) iodo-derivative and in the palladium(II) complexes, metal-halogen absorptions have not been found in the usually observed ranges, in agreement with the conductivity measurements. In these complexes a single band is present in the 219-209 cm^{-2} range in the case of iron and in the 262-254 cm^{-1} region for the palladium derivatives, attributed to the ν_{M-N} vibrational modes.[19,23-26]

Comparison of the spectra of the complexes $[Fe(trz)_2Cl_2]Cl \cdot 2H_2O$ and $[Fe(trz)Br_3]$, enables us to assign the medium or medium-strong bands occurring at 380 and 362 cm^{-1} in the chloro-derivative and at 286 and 268 cm^{-1} in the bromo-complex to iron-halogen stretching vibrations, by analogy with other related assignments in this region.[26-29] These values are indicative of tetrahedral coordination of the iron(III) ion in the complexes; the ratio ν_{Fe-Br}/ν_{Fe-Cl} equals 0.75.[29] The vibrational modes in the range 229-217 cm^{-1} and at 212 cm^{-1} in the two complexes respectively are due to the ν_{Fe-N} stretching modes. In the octahedral derivative $[Fe(trz)_3Cl_3]$ a band is present at 208 cm^{-1}, ν_{Fe-N}, and at 355 cm^{-1}, ν_{Fe-Cl}. The vibrational mode ν_{Fe-X} in this octahedral complex is at lower wavenumbers than in the tetrahedral ones, since with an increase of coordination number there is a decrease in the M-X stretch.

The complexes of trz obtained are always *N*-bonded through the nitrogen atom of the imino group; the ligand acts as a monodentate in spite of the presence of many potential donor atoms in the molecule. The study of high-spin coordination compounds of manganese(II) is quite difficult owing to the electronic structure of the metal, $t_{2g}^3e_g^2$, in particular if we consider the electronic spectra (having doubly forbidden transitions) and the stability of the complexes (the crystal field stabilization energy being absent). However, taking into account that the ν_{Mn-X} stretching frequencies depend on the stereochemistry of the complexes and that an increase of the coordination number is accompanied by a decrease of the ν_{M-X} values we conclude that our ν_{Mn-X} values confirm an octahedral coordination around the central atom[30] in agreement with the conductivity measurements. In the far i.r. region we have found just one ν_{Mn-X} and one ν_{Mn-L} for the 1:4 complexes; we can propose for these complexes octahedral geometries with *trans*-isomers with D_{4h} symmetry. In fact for octahedral compounds of the $[ML_4X_2]$ type with C_{2v} symmetry, *cis*-isomers, just two ν_{M-X}, $a_1 + b_1$, and four ν_{M-L}, $2a_1 + b_1 + b_2$, modes are i.r. active.

For the manganese and iron 1:2 derivatives we suggest a distorted tetrahedral C_{2v} symmetry on the basis of the presence of two ν_{M-X} vibrations, $a_1 + b_1$, and two ν_{M-L} vibrations, $a_1 + b_2$, in the far i.r. spectra.

The 1:1 iron bromo-derivative shows in its spectrum two ν_{Fe-X} and one ν_{Fe-L} stretching modes and we suggest a pseudotetrahedral geometry for the metal ion with C_{3v} symmetry. In fact for this symmetry just two ν_{M-X}, $a_1 + e$, and one ν_{M-L}, a_1, modes are i.r. active. For the 1:4 and 1:6 iron derivatives the suggested geometries are tetrahedral and octahedral respectively. The palladium derivatives are square-planar, D_{4h}.

EXPERIMENTAL

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

Preparation of the complexes.

The manganese(II) complexes were obtained by adding the hydrated metal halides dissolved in ethanol to a suspension of the ligand in the same solvent (metal: ligand molar ratios from 1:1 to 1:6). Upon being heated under reflux for about 20 minutes, the mixture became clear and was filtered in order to remove any unreacted ligand. The filtered solution was further refluxed with vigorous stirring for about 1 hr. and the compounds precipitated spontaneously. The iron and palladium derivatives have been prepared in chloroform and acetone respectively, under the same experimental conditions, the only difference being the fact that the palladium derivatives were obtained at room temperature. The complexes were filtered, washed with ethanol, acetone or chloroform, diethyl ether and dried overnight over P_4O_{10}.

We obtained complexes only in the metal:ligand ratios reported in Table 1. Repeated syntheses and elemental analyses gave reproducible results. The ligand is very stable under the experimental conditions in the solvents used.

Physical measurements.

The i.r. spectra were recorded in the 4000-50 cm^{-1} range with a Perkin-Elmer 180 spectrophotometer of the Instruments Centre of Modena University. The spectra in the 4000-400 cm^{-1} range were measured using KBr discs or nujol mulls. Far-i.r. spectra were measured using nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen. The electronic spectra were recorded with a Shimadzu-MPS-50L spectrophotometer in the solid state in the 5000-45000 cm^{-1} range using the method of Venanzi and co-workers.[31] Molecular susceptibilities obtained using Gouy's method were corrected for diamagnetism of the component atoms by use of Pascal's constants. Conductivity measurements were carried out with a WTW LBR type conductivity bridge at 25° for 10^{-3} M solutions in *N, N'*-dimethylformamide. The TG and DTG curves were recorded with a Mettler TA 3000 thermal analysis system equipped with a TC 10 processor. Open Al_2O_3 crucibles were used at a heating rate of 10° min^{-1}. Carbon, nitrogen and hydrogen were determined with a Carlo Erba 1106 elemental analyzer.

Acknowledgements. We thank Dr. A. Alessandrini for his experimental work, Bracco Chemical Industry of Milan for the kind supply of the Terizidone ligand, Mr. G. Pistoni for elemental analyses and the National Research Council (C.N.R.) of Italy for financial support.

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