THE COORDINATING BEHAVIOUR OF BENZOXAZOLE-2-THIONE TOWARDS SOME TRANSITION METAL HALIDES IN THE LIGHT OF SPECTROSCOPIC INVESTIGATIONS

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Some benzoxazole-2-thione (*bot*) complexes of manganese(II), iron(III), iron(II), ruthenium(III) and osmium(III) have been prepared and their conductivities, electronic spectra, magnetic susceptibility data and i.r. spectra are reported and discussed. The metal—halogen stretching modes in the far i.r. region resulted particularly useful in distinguishing between the *mer*- and *fac*-isomers in the ruthenium and osmium compounds of the type ML_3X_3. From the magnetic properties it was concluded that the above ligand forms low-spin complexes with ruthenium(III) and osmium(III) and high-spin complexes with manganese(II), iron(II) and iron(III). The wavelengths of the principal absorption peaks have been accounted for quantitatively in terms of the crystal field theory for manganese(II), tetrahedral iron(III), ruthenium(III) and osmium(III) derivatives. The values of B and C in the iron(III) derivatives are less than in the corresponding manganese(II) complexes. The charge-transfer observed in the ruthenium(III). osmium(III) and iron(III) derivatives is considerably lower than the corresponding one in the iron(II) iodo-derivative.

INTRODUCTION

The present work is part of a research program in the field of the study of the coordination behaviour of benzoxazole-2-thione, (*bot*). Here we report the results of our studies on manganese(II), iron(III), iron(II), ruthenium(III) and osmium(III) with the above ligand. We embarked on this study for two reasons; first because this ligand exists as two tautomeric conformations, the thioketo form and the thiol form involving —NH—C=S and —N=C—SH groups in a thione—thiol equilibrium:

Thioketo form   Thiol form
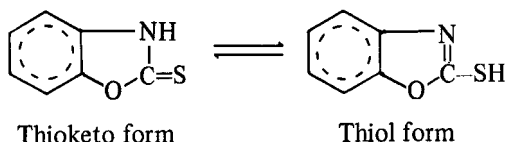
The complexing properties of the HNCS group with metal ions have been studied for some time in our laboratory[1-5] in order to further our present knowledge in the field of the ligands which exhibit the above reported thiol—thione equilibrium. It appears, from previous papers,[2-5] that in acid or neutral medium the *bot* molecule coordinates through the nitrogen heteroatom. When operating in basic medium the ligand bonds *via* sulphur and nitrogen; this behaviour could be explained by

admitting first an attack of the sulphur anion of the molecule in the thiol form, followed by the coordination of the cyclic nitrogen.

Our second purpose was to examine the benzoxazole group because of its importance as an analytical reagent, in biological systems, in industry and medicine; furthermore this molecule plays an important role as a regulator for plant growth and development.[6-10]

According to the methods reported in the Experimental section we have obtained microcrystalline compounds that are listed in Table I together with elemental analyses, conductivity measurements results and effective magnetic moment values. The solid state electronic spectra and ligand field parameters are shown in Tables II—V. The most important i.r. data both for the ligand and its metal complexes in the range 4000—90 cm^{-1} are listed in Tables VI and VII. The far infrared spectra of these complexes have been recorded and the factors affecting ruthenium- and osmium—halide stretching frequencies are discussed because the vibrational spectroscopy should enable us to differentiate between *fac*- and *mer*-isomers of [Mbot$_3$X$_3$] (M = Ru,Os; X = Cl,Br,I).

From the magnetic properties it was concluded that the ligand here studied forms low-spin complexes with ruthenium(III) and osmium(III), while all the remaining derivatives resulted high-spin.

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TABLE I
Analytical data and other physical properties

Compounds	Colour	Found %			Required %			Dec. point °C	μ B.M.
		C	H	N	C	H	N		
[Mnbot$_2$Cl$_2$]	white	39.6	2.4	6.8	39.3	2.4	6.5	201–206	5.4
[Mnbot$_2$Cl$_2$]·2H$_2$O	pink-white	36.1	2.9	6.0	36.2	3.0	6.0	190–195	5.6
[Mnbot$_2$Br$_2$]·H$_2$O	pale yellow	31.1	2.4	5.0	31.4	2.3	5.2	198–203	5.8
[Mnbot$_2$I$_2$]·H$_2$O	dark yellow	26.4	1.9	4.3	26.7	1.9	4.4	145–150	5.7
[Febot$_2$Cl$_2$]Cl [a]	green	36.5	2.3	5.9	36.2	2.2	6.0	135–140	5.5
[Febot$_3$Cl$_3$]·H$_2$O	dark green	39.5	2.7	6.6	39.8	2.7	6.6	90–95	6.0
[FebotBr$_3$]·2H$_2$O	brown	17.4	1.8	2.7	17.4	1.9	2.9	>340	5.8
[Febot$_2$Br$_2$]Br [a]	brown	28.3	1.7	4.7	28.1	1.7	4.7	130–135	6.1
[Febot$_3$Br$_3$]·2H$_2$O	red-brown	32.2	2.6	5.5	32.1	2.4	5.3	89–94	5.9
[Febot$_2$I$_2$]	dark brown	27.7	1.9	4.5	27.5	1.6	4.6	130–135	5.4
[Rubot$_3$Cl$_3$]·2H$_2$O	brown	35.7	2.5	6.1	36.2	2.7	6.0	>340	1.8
[Rubot$_3$Br$_3$]·H$_2$O	dark green	31.0	2.1	5.1	31.0	2.1	5.2	191–196	1.7
[Rubot$_3$I$_3$]·3H$_2$O	yellow	25.3	2.2	4.3	25.5	2.1	4.2	155–160	1.8
[Osbot$_3$Cl$_3$]·2H$_2$O	brown	31.6	2.4	5.3	32.1	2.4	5.3	213–218	2.0
[Osbot$_3$Br$_3$]·2H$_2$O	dark brown	27.0	1.9	4.7	27.4	2.1	4.6	128–133	1.9
[Osbot$_3$I$_3$]	grey-black	25.1	1.5	4.1	24.6	1.5	4.1	146–151	2.1

[a] The Λ_M values for 10^{-3} M solutions in nitromethane are 98.90 and 65.77 $ohm^{-1}\ cm^2\ mole^{-1}$ for the chloro- and bromo-derivative respectively.

TABLE II
Ligand field parameters and Dq independent bands of tetrahedral manganese(II) and iron(III) derivatives (cm^{-1})

Compounds	$^4E_g,^4A_1g(^4G) \leftarrow ^6A_1$	$^4E_g(^4D) \leftarrow ^6A_1$	B	C	$\overline{10Dq}$
[Mnbot$_2$Cl$_2$]	26740	31250	644	4060	7730
[Mnbot$_2$Cl$_2$]·2H$_2$O	26880	31750	696	3984	7100
[Mnbot$_2$Br$_2$]·H$_2$O	26670	31050	626	4082	6870
[Mnbot$_2$I$_2$]·H$_2$O	26310	31000	670	3922	7580
[Febot$_2$Cl$_2$]Cl	17390	19570	311	2856	3620
[FebotBr$_3$]·2H$_2$O	16260	18080	260	2732	2940
[Febot$_2$Br$_2$]Br	16180	17860	240	2756	2970

RESULTS AND DISCUSSION

All the complexes resulted non-conducting in nitromethane with the exception of the chloro- and bromo-derivative of iron(III) whose conductivity values, Λ_M, resulted 98.90 and 65.77 $ohm^{-1}\ cm^2$ $mole^{-1}$ respectively, Table I.

ELECTRONIC SPECTRAL STUDY AND MAGNETIC MEASUREMENTS

Manganese(II) Derivatives

Since manganese(II) has a d^5 electronic configuration the same type of energy-level diagram applies both

TABLE III

Electronic spectra of tetrahedral manganese(II) and iron(III) derivatives: observed and calculated absorption bands (cm^{-1})

Compounds	$^4T_{1g}(^4G) \leftarrow {}^6A_1$		$^4T_{1g}(^4P) \leftarrow {}^6A_1$		$^4T_{1g}(^4F) \leftarrow {}^6A_1$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
[Mnbot$_2$Cl$_2$]	21980	21850	37060	36850	43480	43560
[Mnbot$_2$Cl$_2$]·2H$_2$O	21970	22470	36300	36420	43860	43950
[Mnbot$_2$Br$_2$]·H$_2$O	22470	22560	36700	36320	42920	43090
[Mnbot$_2$I$_2$]·H$_2$O	20530	21450	36360	36090	42735	43100
[Febot$_2$Cl$_2$]Cl	15925	15569	23430	23650	27400	27174
[FebotBr$_3$]·2H$_2$O	14925	14935	21275	22030	25510	25080
[Febot$_2$Br$_2$]Br	14815	14845	21050	22050	25770	24825

for tetrahedral and octahedral environment of the metal. The intensities of the electronic transitions from the ground state ^6S to state of fourfold multiplicity are very weak. The energies of $^6A_1 \rightarrow {}^4E$, $^4A_1(^4G)$ and $^6A_1 \rightarrow {}^4E(^4D)$ depend only on B and C and are independent on Dq.

The values of B and C have been derived from the expression:[11]

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

$$^4E(^4D) \quad = 17B + 5C$$

once the assignments of the bands of the spectrum have been made. These values of B and C were then used in solving the secular equations of Tanabe and Sugano[11,12] to evaluate a single value of Dq. Using the determinant of the Tanabe and Sugano 3×3 matrix of interaction for the three energy levels of $^4T_{1g}$ symmetry which are derived from ^4G, ^4P and ^4F levels of manganese(II) by a crystal field of cubic symmetry of the type:

$$\begin{vmatrix} -10Dq+10B+6C-E & -3\sqrt{2}B & C \\ -3\sqrt{2}B & 19B+7C-E & -3\sqrt{2}B \\ C & -3\sqrt{2}B & 10Dq+10B+6C-E \end{vmatrix} = 0$$

the values of the energies of the new levels have been obtained.

The values of the parameters B, C and 10Dq reported in Table II have been determined by choosing C as unity of energy and the values of E are then a function of the two parameters B and 10Dq only. According to Heidt and co-workers[11] we found the best values of C and consequently the best values of B and 10Dq that fitted the energy levels and finally by the least squares method the ligand field parameters.

In this way good agreement between calculated and observed energies has been found for all the states, Table III. The differences are of the order of 1.87% for the state $^4T_1(^4G)$, 0.66% for the state $^4T_1(^4P)$ and 0.40% for the state $^4T_1(^4F)$.

Low values of B are associated with a reduction in the effective positive charge of the cation and with an increasing tendency to be reduced to a lower oxidation state. For 3d transition metals the variation of Racah interelectronic repulsion parameter with the cationic charge Z* and the number q of electrons in the partly filled d shell is expressed by the relation:[13]

$$B = 384 + 58q + 124(Z^*+1) - 540/(Z^*+1)$$

where B is cm^{-1}.

The effective ionic charges of the manganese(II) complexes are in the range 0.90–1.18, considerably below the formal+2 oxidation state of the metal.

The μ values are in the range expected for five unpaired electrons S=5/2, and these magnetic moments are very close to the spin-only value irrespective of whether the ligand arrangement is of octahedral, tetrahedral or lower symmetry.[14]

Iron Derivatives

According to the conductivity measurements values and i.r. results (see below), we could propose a pseudotetrahedral structure for [Febot$_2$Cl$_2$]Cl, [FebotBr$_3$]·2H$_2$O and [Febot$_2$Br$_2$]Br and a pseudo-octrahedral symmetry for the other two iron(III) derivatives; the electronic spectra confirm these stereochemistries.

From Orgel's diagram of d^5 systems,[15] there are ten expected transitions for tetrahedral complexes of iron(III); five of these transitions are visible in the

TABLE IV

Electronic spectra and ligand field parameters of low-spin Ru(III) and Os(III) complexes (cm^{-1}). First approach

Compounds	$^2T_{2g} \to {}^4T_{1g}$	$^2T_{2g} \to {}^4T_{2g}$	$^2T_{2g} \to {}^2A_{2g}, {}^2T_{1g}$	B	C	10Dq
[Rubot₃Cl₃]·2H₂O	14705	18350	24815	456	1824	27551
[Rubot₃Br₃]·H₂O	14325	17950	24390	453	1812	27108
[Rubot₃I₃]·3H₂O	14265	17825	23530	445	1780	26200
[Osbot₃Cl₃]·2H₂O	16890	20490	26740	450	1800	29440
[Osbot₃Br₃]·2H₂O	17180	20660	26955	435	1740	29565
[Osbot₃I₃]	17240	20000	28010	345	1380	30080

TABLE V

Electronic spectra and ligand field parameters of low-spin Ru(III) and Os(III) complexes (cm^{-1})

Compounds	$^2T_{2g} \to {}^2A_{2g}, {}^2T_{1g}$	$^2T_{2g} \to {}^2E_g$		$^2T_{2g} \to {}^2T_{1g}, {}^2T_{2g}$		$^2T_{2g} \to {}^2A_{1g}$		$\overline{B}$	$\overline{C}$	$\overline{10Dq}$
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.			
[Rubot₃Cl₃]·2H₂O	24815	28820	28775	31055	30975	33110	33175	440	1760	27455
[Rubot₃Br₃]·H₂O	24390	28735	28170	30865	30270	32465	32370	420	1680	26910
[Rubot₃I₃]·3H₂O	23530	27470	27400	29940	29550	31645	31700	430	1720	26110
[Osbot₃Cl₃]·2H₂O	26740	30675	30628	32785	32788	34965	34948	432	1728	29332
[Osbot₃Br₃]·2H₂O	26955	—	31023	33060	33283	35320	35543	452[a]	1808[a]	29667[a]
[Osbot₃I₃]	28010	31445	31340	33220	33190	35090	35040	370	1480	30230

[a]Values evaluated using the transitions $^2T_{2g} \to {}^2T_{1g}, {}^2T_{2g}$ and $^2T_{2g} \to {}^2A_{1g}$ only.

TABLE VI
Most important infrared absorption bands (cm^{-1})

Compounds	ν(NH)	Thioamide I	ν(C=S) + δ(NCS)	Thioamide II	ν(COC) asym.	Thioamide III	ν(COC) sym.	Thioamide IV
bot solid	3250s	1505vs	1282s	1245ms	1095vs	1010s	820ms	745vs
bot CHCl$_3$ sol.	3450s	—	1285s	—	1100s	1013s	—	—
[Mnbot$_2$Cl$_2$]	3180vs	1510s	1285s	1248s	1097s	1012ms	820ms	750vs
[Mnbot$_2$Cl$_2$]·2H$_2$O	3160vs	1512s	1290s	1248s	1102s	1018ms	820ms	750vs
[Mnbot$_2$Br$_2$]·H$_2$O	3190s	1510s	1285s	1245ms	1097s	1010ms	820ms	748vs
[Mnbot$_2$I$_2$]·H$_2$O	3240s	1512s	1289s	1250s	1103s	1017s	820ms	750vs
[Febot$_2$Cl$_2$]Cl	3240s	1510s	1288ms	1255s	1105ms	1018m	815m	750vs
[Febot$_3$Cl$_3$]·H$_2$O	3130ms	1515ms	1290m	1253m	1102m	1015m	820m	750s
[FebotBr$_3$]·2H$_2$O	3260ms	1490ms	1330m	1248m	1105ms	1010sh	810m	755vs
[Febot$_2$Br$_2$]Br	3260s	1512ms	1288m	1252ms	1100ms	1015m	810m	750vs
[Febot$_3$Br$_3$]·2H$_2$O	3250s	1512s	1290ms	1250ms	1102s	1017ms	820ms	750vs
[Febot$_2$I$_2$]	3250s	1510s	1287ms	1252s	1100s	1015ms	812m	750vs
[Rubot$_3$Cl$_3$]·2H$_2$O	3090ms	1513s	1290s	1250vs	1110s	1018ms	820ms	750vs
[Rubot$_3$Br$_3$]·H$_2$O	3080ms	1510vs	1290s	1255vs	1105s	1015ms	818ms	750vs
[Rubot$_3$I$_3$]·3H$_2$O	3200ms	1512s	1290s	1250ms	1102ms	1015ms	820m	750vs
[Osbot$_3$Cl$_3$]·2H$_2$O	3080m	1520s	1292ms	1255s	1108s	1015ms	820m	748vs
[Osbot$_3$Br$_3$]·2H$_2$O	3100m	1515s	1290ms	1255ms	1105ms	1015ms	820m	750vs
[Osbot$_3$I$_3$]	3180m	1510s	1288m	1245m	1100m	1015m	820m	750vs

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TABLE VII
Most important far infrared bands (450–90 cm^{-1})

Compounds	ν (M–X)	ν (M–L)	Other bands
bot	–	–	425ms,264m,237m,101m
[Mnbot$_2$Cl$_2$]	230m	219m,212m	428ms,264m,237m,100mw
[Mnbot$_2$Cl$_2$]·2H$_2$O	229m	218m,211m	427ms,264m,237m,98sh
[Mnbot$_2$Br$_2$]·H$_2$O	204m	217m,213m	428ms,265m,238m,102m
[Mnbot$_2$I$_2$]·H$_2$O	145m	216m,206m	432ms,262m,238mw,102mw
[Febot$_2$Cl$_2$]Cl	383m,367m	228ms	424ms,270mw,232m,104w
[Febot$_3$Cl$_3$]·H$_2$O	339m	230ms	422ms,268mw,239mw,97mw
[FebotBr$_3$]·2H$_2$O	288ms	228m	423m,269m,233mw,103w
[Febot$_2$Br$_2$]Br	287ms	227m	425m,266m,233m,101m
[Febot$_3$Br$_3$]·2H$_2$O	262ms	228m	424ms,270vw,234mw,104w
[Febot$_2$I$_2$]	170m	232ms	422ms,269mw,239m,103w
[Rubot$_3$Cl$_3$]·2H$_2$O	346m,338m,332m	294m,282m,255m	428m,276mw,240m,97m
[Rubot$_3$Br$_3$]·H$_2$O	219m,212m,198m	297m,285m,256m	424ms,270m,238m,98w
[Rubot$_3$I$_3$]·3H$_2$O	195m,164m,130m	292m,282m,255m	426m,269m,241m,100w
[Osbot$_3$Cl$_3$]·2H$_2$O	330m,319m,305m	293m,284m,259ms	423ms,270m,236m,98w
[Osbot$_3$Br$_3$]·2H$_2$O	204m,191m,172m	295m,285m,260ms	425ms,272mw,237m,104m
[Osbot$_3$I$_3$]	165m,135m,120mw	293m,283m,259ms	425m,270m,235m,100mw

electronic spectra of our complexes, Tables II and III. Comparison of analogous iron(III) and manganese(II) derivatives should help in a correct assignment. The transitions in the manganese complexes occur between 20530 and 43860 cm^{-1}. Five of the ten transitions of iron(III) complexes are observed between 14815 and 27400 cm^{-1}, which means a large decrease in term separations due to more covalency associated in the bonding in the higher charged tetrahedral ions. The first two bands at 14815–15925 cm^{-1} and in the range 16180–17390 cm^{-1} are assigned to transitions to the ^{4}G sub-levels, to ^{4}T$_1$ and ^{4}E,^{4}A$_1$ respectively. The next transition between 17860–19570 cm^{-1} could be due to the ^{4}E(^{4}D), while the remaining two transitions between 21050 and 23430 cm^{-1} and in the range 25510–27400 cm^{-1} are to the ^{4}P and ^{4}F levels.

A first value of B and C has been obtained from the transitions to the levels ^{4}E,^{4}A$_1$(^{4}G) and ^{4}E(^{4}D) equal to 10B+5C and 17B+5C respectively. Using the same method of calculation above described for the manganese(II) complexes we have obtained the best value of C, B and 10Dq that fitted the energy levels which are reported in the Tables II and III together with the calculated absorption maxima. The differences between calculated and observed energies are of the order of 0.85% for the state ^{4}T$_1$(^{4}G), 2.96% for the state ^{4}T$_1$ (^{4}P) and 2.11% for the state ^{4}T$_1$(^{4}F).

By comparing the results obtained for manganese (II) and iron(III) complexes we observe that the values of B and C in the iron(III) derivatives are less than in the corresponding manganese(II) complexes; hence the transitions depending only on B and C lie at lower energies in the iron complexes. The crystal field parameter 10Dq is significantly lower for iron(III) complexes than for manganese(II); the 10Dq parameter shows an order Cl > Br.

In the octahedral iron(III)–halide complexes the very weak spin-forbidden transitions are obscured by charge-transfer bands at 40000 and 35335 cm^{-1} in the chloro-derivative and at 35520 and 38760 cm^{-1} in the bromo-derivative. The band at some 40000 cm^{-1} could be assigned to a $\pi_3 \rightarrow \pi_4$ transition of the type π_3(e) $\rightarrow \pi_4$(e) and/or π_3(a$_2$) $\rightarrow \pi_4$(a$_1$); both have about the same energy and are expected to overlap. The second band at 35335 cm^{-1} and 35520 cm^{-1} in the two complexes 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$_1$) that as previously reported should have both the same energy and are expected to overlap.[16]

As for the iron(II) iodo-derivative with a 1:2 metal:ligand ratio, 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$_{2g}^3$e$_g^3$. The solid state electronic spectrum of the complex [Febot$_2$I$_2$] exhibits a broad band in the near i.r. region at 5760

cm^{-1}; this band is assignable to the $^5E \rightarrow {}^5T_2$ transition showing that the complex may have pseudotetrahedral symmetry, the position of the band maximum excluding other geometries. The spectrum is characterized by an intense band at $45455\ cm^{-1}$ attributed to a ligand—metal charge-transfer.

The magnetic susceptibility values, at room temperature, for the iron(III) derivatives are in the range 5.8—6.1 B.M.; the μ value of the complex [Febot$_2$Cl$_2$]Cl, 5.5 B.M., resulted a bit lower than that expected for high-spin complexes perhaps because of the hygroscopicity of this derivative that could interfere giving an anomalous μ value, as obtained in previously reported complexes that resulted to have an anomalous μ value whenever the compounds were hygroscopic.[17, 18]

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 non-magnetic doublet (^5E) and an upper triplet ($^5T_2$), so that a magnetic behaviour similar to that of octahedral Cu(II) is to be expected.[14] Thus only a small orbital contribution to the magnetic moment above that of the spin-only value of 4.90 B.M. is predicted for a pseudotetrahedral complex, in accord with the μ value reported for the iodo-derivative, 5.4 B.M., Table I.

Ruthenium(III) Derivatives

The ground state of ruthenium(III) in the derivatives here reported has only one unpaired spin[19] corresponding to the configuration t_{2g}^5. The strong-field electrostatic matrices of Tanabe and Sugano[20] predict eight transitions from the ground state t_{2g}^5 to the doublet states of the configuration $t_{2g}^4 e_g^1$, and two transitions from the ground state to the quartet states of $t_{2g}^4 e_g^1$.

Utilizing a single electron model in the strong crystal field limit, we may think of the d levels as being split into a lower triply degenerate t_{2g} level, and a much higher doubly degenerate e_g level. For five electrons, all will go into the lower t_{2g} level, not quite filling it up. Therefore, both the lower t_{2g} level and the higher e_g level may act as acceptor level. In general the lowest charge-transfer band will be into the t_{2g} level. This same reasoning explains why, for strong crystalline fields, the first charge-transfer absorption in d^5 ions is consistently lower than the corresponding one in d^6 ions. In the d^6 ions, the t_{2g} level is completely filled, and so only the considerably higher e_g level can act as an acceptor.

In the spectra of our complexes, taken in nujol mulls, there are six maxima; two appear as broad

bands (weak) in the ranges 14265—14705 cm^{-1} and 17825—18350 cm^{-1}. The other bands appear in the ranges 23530—24815 cm^{-1}, 27470—28735 cm^{-1}, 29940—31055 cm^{-1} and 31645—33110 cm^{-1}. The low intensity of these transitions suggests they are crystal field transitions and they appear to be characteristic of octahedral complexes of ruthenium (III).[19, 21] The two broad low intensity bands are assigned to the two spin-forbidden transitions, while the remaining bands are assigned to transitions to doublet states.

The energy levels are:[22]

$^2T_2$	t^5	0
$^4T_1$	$t^4 e$	10Dq$-$5B$-$4C
$^4T_2$	$t^4 e$	10Dq+3B$-$4C
$^6A_1$	$t^3 e^2$	20Dq$-$15B$-$10C
$^2A_2, {}^2T_1$	$t^4 e$	10Dq$-$2B$-$C
^2E	$t^4 e$	10Dq+7B$-$C
$^2T_1, {}^2T_2$	$t^4 e$	10Dq+12B$-$C
$^2A_1$	$t^4 e$	10Dq+17B$-$C

The assignments are given in Tables IV and V and we have deducted from these bands values for 10Dq and B.

Let us first note that the intensity of the $^2T_2(t^5) \rightarrow {}^6A_1(t^3 e^2)$ transition would hardly be measurable since it corresponds to the highly forbidden transition of a double electron excitation ($\Delta S = +2$). We therefore disregard it in the calculations.

The two spin-forbidden transitions $^2T_2 \rightarrow {}^4T_2$ and $^2T_2 \rightarrow {}^4T_1$ should be separated by 8B; by assuming $C = 4B$[20] we can calculate B and C, then 10Dq using the transition $^2T_2 \rightarrow {}^2A_2, {}^2T_1$, Table IV. Using these values of B, C and 10Dq we have calculated the energies of $^2T_2 \rightarrow {}^2E$, $^2T_2 \rightarrow {}^2T_1, {}^2T_2$ and $^2T_2 \rightarrow {}^2A_1$ in order to check the exact assignment of the d—d bands in our complexes. By standard treatment we have found the best values of B and C and 10Dq that fitted the energy levels and finally we give, in Table 5, the values for all the levels of the Orgel's diagram, computed with the above values.

The absorption bands are usually broad; this is expected because of the lowering of the symmetry of the crystal field, whence most of the degenerate levels will be split.

A series of intense absorptions is present in all the complexes above 33500 cm^{-1} and can be assigned to charge-transfer transitions of the type $L \rightarrow t_{2g}$.

Strong covalent bonding certainly occurs between the central metal and the ligand; this is shown by the considerable decrease in the value of the Racah

electron repulsion parameter B from that of the free ion.[23] The overall effect of some covalent bonding will be an increase in the observed value of Dq; high values of Dq are usually associated with considerable electron delocalization, *i.e.*, covalent bonding.

For 4d transition metals the effective positive ionic charge can be evaluated by the relation:[13]

$$B = 472 + 28q + 50(Z^*+1) - 500/(Z^*+1)$$

where B is in cm^{-1}. The values obtained for the ruthenium(III) derivatives resulted between 1.20—1.74 against the formal +3 oxidation state of this metal ion.

The observed values of the effective magnetic moments of ruthenium(III) complexes are in the range 1.7—1.8 B.M., Table 1. For low-spin trivalent ruthenium in octahedral coordination the spin-orbit coupling constant λ is $-1180\ cm^{-1}$, and μ_{eff} is expected to be about 2.0 B.M.[14] The low values of the observed magnetic moments are in accord with the above indicated lowering of the crystal field symmetry.

Osmium(III) Derivatives

As for the osmium(III) derivatives of low-spin type, having the metal in the strong-field a t_{2g}^5 configuration, the two bands at lower wave numbers, $17000\ cm^{-1}$, and in the range $20000-20660\ cm^{-1}$ are assigned to the two spin-forbidden transitions $^2T_2 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_2$, Table 4. The low intensity bands between 26740 and $28010\ cm^{-1}$, near $31000\ cm^{-1}$, and in the ranges $32785-33220\ cm^{-1}$, $34965-35320\ cm^{-1}$ are transitions from the ground state to doublet states of $t_{2g}^4 e_g^1$. All these transitions are characteristic of osmium(III) octahedral complexes.

We have used the same type of calculation carried out on the ruthenium(III) derivatives and the results are reported in Tables IV and V. Even for these complexes we can suggest the presence of a strong covalency in the metal—ligand bond as shown by the values of B and Dq, that resulted of the same order of those obtained for ruthenium(III) complexes, Table V.

The intense absorptions present above $36000\ cm^{-1}$ in the three derivatives are due to ligand to metal charge-transfer bands. These bands, as in the ruthenium(III) derivatives, fall at lower wave numbers than in the iron(II) iodo-derivative.

The magnetic moment values resulted in the range 1.9—2.1 B.M., at room temperature, and this result matches very well with the fact that the magnetic moment of osmium(III) complexes would be expected to fall near 2.0 B.M. using a spin-orbit coupling constant $\lambda = -3500\ cm^{-1}$, which has been estimated for the free ion.[14]

The calculations of the ligand field parameters for manganese(II), tetrahedral iron(III), ruthenium(III) and osmium(III) derivatives have been carried out on a Hewlett Packard 9100B computer.

INFRARED SPECTRA

It is known from infrared spectral data[24] that the ligand *bot* exists in the solid state as hydrogen bonded thioamide complex; this hydrogen bond partially breaks down in CCl_4 solution. The i.r. spectrum shows a strong absorption at $3400\ cm^{-1}$ corresponding to $\nu(NH)$ vibrational mode, while a peak in the region near $2500\ cm^{-1}$, attributable to $\nu(SH)$, is not present.

It is possible that in this molecule only two atoms could act as bonding sites, *i.e.* the cyclic nitrogen atom and the sulphur exocyclic atom. Since the lone pairs on the oxygen atom present in the skeleton of the ring are involved in the resonating structures of the molecule, it is expected that it should have very weak coordinating ability.[25]

It is worthwhile examining the fact that the mode of coordination of the ligand can be distinguished by the analysis of the positions and intensities of the thioamide bands and of the bands at $1095\ cm^{-1}$ and $820\ cm^{-1}$ attributed to the prevailing contribution of $\nu(COC)$ asym. and sym. The directions of the shifts of all the bands in the spectra of the complexes are the same and this fact clearly indicates that the bonding pattern in all the complexes must be the same.

The spectra of the ligand in the solid state and in chloroform solution show a difference in the position of the $\nu(NH)$ stretching frequency, clearly indicating intermolecular or intramolecular hydrogen bonding between the hydrogen of the NH group and the sulphur of the thioketo group. In order to avoid the hydrogen bonding effect we have compared the spectra of the complexes in the solid state with that of a dilute solution in chloroform of the ligand.

The $\nu(NH)$ in the complexes is shifted towards lower wave numbers by about $270\ cm^{-1}$, Table VI, clearly indicating coordination through the nitrogen atom.

According to previously reported data[2,26] a sharp NH band in the metal complexes is indicative of absence of hydrogen bonding and a comparison of these values with the $\nu(NH)$ solution frequency of the free ligand can be used as evidence of coordination through the nitrogen atom. In our complexes sharp bands are present in the range $3250-3080\ cm^{-1}$ and a comparison with the $\nu(NH)$ value of $3450\ cm^{-1}$ clearly indicates a M—N coordination.

The band at 1505 cm^{-1}, thioamide I, being due to the normal coordinates having major contributions from δ(NH) + δ(CH) + ν(C=N), shows in the complexes shifts to higher energies and there is ample evidence that this band shifts to higher wave numbers whenever the coordination takes place through the nitrogen atom.[2, 3, 26] The thioamide II, having contribution from ν(C$\doteq$N) + δ(NH) + δ(CH) + ν(C=S), undergoes a blue shift, while in the case of sulphur coordination should be shifted to lower wave numbers. Furthermore the thioamide bands III and IV, having their main contribution from ν(C=S), do not show a red shift, thus excluding the possibility of the presence of a metal—sulphur bond.[26-32]

The bands at 1095 and 820 cm^{-1}, attributed to the prevailing contribution of ν(COC) asym. and sym., are in the complexes at the same wave numbers as in the free ligand, or show small blue shifts, and so a coordination through the oxygen atom of the oxazole ring can be excluded, Table VI.

Medium absorption bands are present in all the water containing complexes in the ranges expected for ν(OH) and δ(HOH), clearly confirming the presence of water of crystallization. We can exclude the presence of coordinated water because from a detailed analysis of the infrared spectra the other vibrational modes such as wagging, twisting and rocking activated by coordination to the metal have not been found in the expected ranges.[33]

In the far infrared spectra no bands are present in the ranges where ν(M—S) and ν(M—O) usually lie for these metals,[17, 34-37] but new halogen independent bands are present in ranges expected for ν(Mn—N), ν(Fe—N), ν(Ru—N) and ν(Os—N) respectively, Table VII.[18,34,36-38]

The comparison of the spectra of the halo-derivatives of manganese(II) shows some bands whose frequency becomes progressively lower as the mass of the halogen increases and are therefore assigned to vibrations involving manganese—halide bonds.[34, 36, 37]

By intercomparison of the spectra of the complexes [Febot$_2$Cl$_2$] Cl, [FebotBr$_3$]·2H$_2$O and [Febot$_2$Br$_2$] Br, the medium or medium-strong bands occurring at 383 and 367 cm^{-1} in the chloro-derivative and near 288 cm^{-1} in the bromo-derivatives could be attributed as the iron—halogen stretching vibrations ν(Fe—Cl) and ν(Fe—Br) respectively by analogy with other related assignments in this region.[18, 39-42] These values are indicative of tetrahedral coordination of the iron(III) ion in the complexes and the ratio ν(Fe—Br)/ν(Fe—Cl) equals to 0.78.[41] In the octahedral derivatives [Febot$_3$Cl$_3$]· H$_2$O and [Febot$_3$Br$_3$]·2H$_2$O the iron—halogen

stretching vibrations are present at 339m and 262ms cm^{-1} respectively with a ratio ν(Fe—Br)/ν(Fe—Cl) of 0.77. The vibrational modes ν(Fe—X) in the octahedral complexes are at lower wave numbers than in the tetrahedral ones, according with the fact that in an increasing of the coordination number there is a decrease in the M—X stretching vibration.

In the iron(II) derivative [Febot$_2$I$_2$] the ν(Fe—I) has been located at 170 cm^{-1}.[37]

The complexes of ruthenium(III) and osmium(III) resulted octahedral of the type [Mbot$_3$X$_3$] (M = Ru,Os; X = Cl,Br,I). A further guide to the stereochemistry of these complexes can in principle be obtained from a study of the metal—halogen stretching vibrations. These complexes can exist as *mer*- and *fac*-isomers; the bands due to ruthenium—halide and osmium—halide were easily identified by intercomparison of the spectra of the chloride, bromide and iodide derivatives respectively and reported data on other similar compounds.[36, 37, 43-49] Three M—X and three M—N stretching vibrations are present in the spectra of all the complexes, Table VII.

The greatest attainable symmetry is C$_{2v}$, *mer*-isomers, with 2a$_1$+b$_1$ representations for the MX$_3$ and MN$_3$ stretching vibrations. In *fac*-isomers, with C$_{3v}$ symmetry, only two ν(M—X) and two ν(M—N) vibrations are infrared active, a$_1$+e. We thus assign the two bands at higher energies to the two vibrations involving predominantly the mutually *trans*-halides and the band at lower wave number to the metal—halide stretching mode of the halide in *trans*-position to the nitrogen atom.

CONCLUSIONS

The obtained complexes of *bot* resulted always N-bonded, with the ligand acting as monodentate only, in spite of the presence of three potential donor atoms in the molecule. The manganese(II) compounds are tetrahedral with a μ_{eff} value corresponding to five unpaired electrons and very close to the spin-only value. The iron(III) derivatives are tetrahedral or octahedral, while [Febot$_2$I$_2$] is tetrahedral.

In the manganese(II) derivatives the 10Dq values are in the order Cl > Br; the surprising high value for the iodo-derivative, 7580 cm^{-1}, is out of line with respect to the usual spectrochemical order of the halides. A formulation of the type [Mnbot$_2$(H$_2$O)I] I, that could justify the high 10Dq value, must however be excluded because the water resulted non-coordinated to the metal and because the complex is non-conducting in nitromethane.

It might be worth noting that the C/B ratios are in the range 5.72–6.52 for the manganese(II) complexes and between 9.18 and 11.48 for the tetrahedral iron(III) derivatives; we are aware that this fact is quite strange.

The compounds of ruthenium(III) and osmium(III) are low-spin type with only one unpaired electron corresponding to the configuration t_{2g}^5; the field produced by the ligands resulted strong enough to coupling the d-electrons in these metal ions. These complexes were characterized as covalent with the octahedral structure d^2sp^3. All the ruthenium and osmium complexes have *mer*-configurations and the observed i.r. spectra and the assignments of M–X stretching vibrations (M = Ru,Os; X = Cl,Br,I) point out the utility of the far infrared spectra as an aid in the structural assignment of complexes of the type reported here.

EXPERIMENTAL

Purification of the Ligand

Benzoxazole-2-thione (*bot*), supplied by Fluka, was purified by recrystallization from ethanol (m.p. 195–196°C, lit. 196°C).[50]

Preparation of the Complexes

The manganese(II) complexes were all prepared by reaction of the appropriate manganese salt with a small excess of the molten ligand, preliminary studies having shown that in each case only a single product was formed, regardless of the presence of excess ligand. The compunds have been purified by means of repeated washing with ethanol and diethyl ether.

The other derivatives were obtained as above reported for manganese complexes starting with $MX_3 \cdot nH_2O$ (M = Fe; X = Cl,Br; M = Ru,Os; X = Cl,Br,I) and $FeI_2 \cdot nH_2O$. The purification has been carried out by washing with ethanol and diethyl ether.

U. V.-visible Spectra

The electronic spectra have been recorded with a Shimadzu MPS–50L spectrophotometer in the solid state in the range 4000–47000 cm^{-1}.

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.

Infrared Measurements

The i.r. spectra have been recorded in the range 4000–90 cm^{-1} with Perkin Elmer 457 and 225 and Hitachi–Perkin Elmer FIS3 spectrophotometers. The spectra in the range 4000–400 cm^{-1} were measured for KBr discs or $CHCl_3$ solution. The far i.r. spectra were measured for nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing dry nitrogen.

Conductivity Measurements

These were carried out with a WTW LBR conductivity bridge for 10^{-3}M solutions in nitromethane.

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