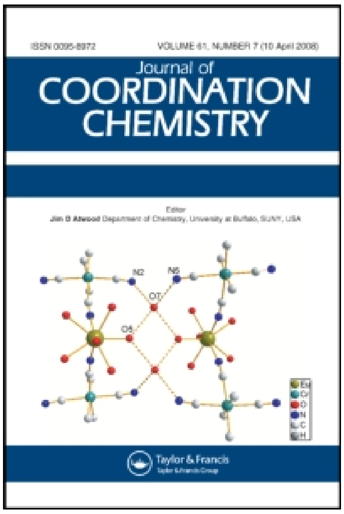

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NEW RHODIUM(III), IRIDIUM(III), PALLADIUM(II) AND PLATINUM(II) COMPLEXES CONTAINING BENZOXAZOLE-2-THIONE AS LIGAND

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NEW RHODIUM(III), IRIDIUM(III), PALLADIUM(II) AND PLATINUM(II) COMPLEXES CONTAINING BENZOXAZOLE-2-THIONE AS LIGAND

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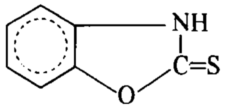
A series of benzoxazole-2-thione (*bot*) complexes of general formula [Mbot$_3$X$_3$], M=Rh(III), Ir(III) X=Cl, Br, I; [Mbot$_2$X$_2$], M=Pd X=Cl, Br, M=Pt X=Cl, Br, I and the complex [Pdbot$_4$]I$_2$ have been prepared and characterized by chemical analysis, infrared and electronic spectra, conductivity data and magnetic susceptibility measurements. From the magnetic properties it was concluded that the above ligand forms low-spin compounds. The position and multiplicity of the metal-halide stretching frequencies are discussed and used as a guide to the stereochemistry. The crystal field parameters are also calculated.

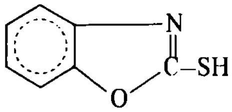
INTRODUCTION

The benzoxazole group is important as analytical reagent, in biological systems, in industry and medicine; furthermore this molecule plays an important role as a regulator for plant growth and development.[1–5]

The benzoxazole-2-thione, *bot*, is quite a peculiar ligand, the complexation potentially could occur through either the oxygen or the nitrogen atom of the oxazole ring or *via* the sulphur atom. The behaviour of isoxazole or substituted isoxazoles or oxazole containing ligands with transition metal ions is being studied for some time in our laboratory.[6–16] The 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

It results from i.r. spectral studies [17] that this ligand exists in the solid state as hydrogen bonded thioamide complex; this hydrogen bond partially breaks down in carbon tetrachloride solution. The i.r. spectrum does not show the ν(SH) peak near 2500 cm^{-1} but shows a strong absorption at 3450 cm^{-1} due to the ν(NH) stretch. It appears, from previous papers,[15,16] that in acid medium the *bot* molecule coordinates through the nitrogen heteroatom. When operating in basic medium the ligand bonds *via* sulphur and nitrogen.[18] This behaviour is obtained first by an attack of the sulphur anion of the molecule in the thiol form, followed by the coordination of the cyclic nitrogen.

We report here the compounds listed in Table I, together their analytical data and other physical properties. They have been characterized through elemental analyses, conductivity measurements, electronic spectroscopy, Table II, and infrared spectra in the range 4000–50 cm^{-1}, Tables III and IV. The far infrared spectra of these complexes have been studied in detail and factors affecting metal–halide stretching frequencies discussed; these data are also useful in assigning stereochemistries. From the magnetic properties it was concluded that the above ligand forms low-spin complexes. 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.[19]

RESULTS AND DISCUSSION

Electronic Spectra and Conductivity Measurements

The positions of the solid state electronic absorption bands and their most probable assignments are given in Table II. The diamagnetic nature of rhodium(III) and iridium(III) complexes indicates an octahedral surroundings of the donor atoms around the metal ions producing a strong field.

Rhodium derivatives show a band at 27320–27470 cm^{-1} and a second at some 33000 cm^{-1}. These two peaks are the two expected spin allowed transitions to the $t_{2g}^5e_g^1$ configuration. The ligand field bands are not obscured by charge transfer absorptions. The values of 10Dq and B′ as calculated from the positions of these bands[20] are reported in Table II and are well within those found for other trivalent rhodium complexes[21–25]. These bands are in the wavelength range expected for RhN_3X_3 chromophores (compare absorptions of the complexes RhL_3X_3, L = ε-thiocaprolactam, N,N′-dimethylformamide, pyridine[26–28] and of the chromophores RhO_6, RhS_6 and $RhCl_6^{3-}$ using the "law of the average environment"[21,29,30]).

As for the iridium complexes, the two observed absorption bands are in the ranges expected for the two spin allowed transitions from the ground state $^1A_{1g}$.

The ratios of the energies of ν_2 and ν_1 are in the range 1.20–1.21 in the rhodium complexes and are 1.13 in the iridium derivatives. In the iridium derivatives too, the bands are in the range typical of IrN_3X_3 chromophores;[21,29,30] the 10 Dq and B′ values are reported in Table II.

The B′ values are of the order of 52–55% and of 37–40% of the free ions value in rhodium and iridium derivatives respectively, suggesting that there is a considerable orbital overlap with a strong covalency in the metal–ligand σ bond. The nephelauxetic parameter shows an order with respect to the

TABLE I
Analytical data and other physical properties

Compounds	Colour	Found % C	Found % H	Found % N	Required % C	Required % H	Required % N	Dec. point °C
$[Rhbot_3Cl_3]$	brown	37.8	2.4	6.2	38.0	2.3	6.3	161–166
$[Rhbot_3Br_3]\cdot H_2O$	red-brown	31.0	2.0	5.2	31.0	2.1	5.2	149–154
$[Rhbot_3I_3]\cdot 3H_2O$	black	25.3	2.0	4.4	25.4	2.1	4.2	173–178
$[Irbot_3Cl_3]$	orange	33.7	2.1	5.7	33.5	2.0	5.6	166–171
$[Irbot_3Br_3]\cdot H_2O$	dark yellow	27.8	2.0	4.8	27.9	1.9	4.6	171–176
$[Irbot_3I_3]\cdot 2H_2O$	yellow	23.6	2.0	3.7	23.7	1.8	4.0	> 340
$[Pdbot_2Cl_2]$	brown	35.4	1.9	6.0	35.1	2.1	5.8	> 340
$[Pdbot_2Br_2]\cdot 2H_2O$	brown	27.6	2.1	4.5	27.8	2.3	4.6	> 340
$[Pdbot_4]I_2^a$	black	34.8	2.4	5.9	34.8	2.1	5.8	196–201
$[Ptbot_2Cl_2]\cdot H_2O$	yellow	28.5	1.9	4.7	28.7	2.1	4.8	> 340
$[Ptbot_2Br_2]$	hazel-brown	25.6	1.5	4.3	25.6	1.5	4.3	188–193
$[Ptbot_2I_2]$	brown	22.8	1.3	3.7	22.4	1.3	3.7	> 340

[a] Λ_M for 10^{-3} M solution in N,N′-dimethylformamide is 146.15 $ohm^{-1}\ cm^2\ mole^{-1}$.

TABLE II
Electronic spectra and ligand field parameters (cm^{-1})

Compounds	d–d bands $^1A_{1g}\rightarrow{}^1T_{1g}$	d–d bands $^1A_{1g}\rightarrow{}^1T_{2g}$	ν_2/ν_1	Ligand field parameters Δ	Ligand field parameters B′	Ligand field parameters β	Ligand field parameters Z*
$[Rhbot_3Cl_3]$	27470	33310	1.21	28960	393	0.55	0.54
$[Rhbot_3Br_3]\cdot H_2O$	27320	33000	1.21	28375	382	0.53	0.50
$[Rhbot_3I_3]\cdot 3H_2O$	27400	32950	1.20	28915	372	0.52	0.46
$[Irbot_3Cl_3]$	30030	34040	1.13	31682	262	0.40	
$[Irbot_3Br_3]\cdot H_2O$	29720	33700	1.13	31547	260	0.39	
$[Irbot_3I_3]\cdot 2H_2O$	29630	33415	1.13	30687	247	0.37	
	$^1A_{1g}\rightarrow{}^1B_{1g}$	C.T.					
$[Pdbot_2Cl_2]$	22885	33925		24985			
$[Pdbot_2Br_2]\cdot 2H_2O$	22720	33700		24820			
$[Pdbot_4]I_2$	22370	33560		24470			
$[Ptbot_2Cl_2]\cdot H_2O$	26455	31745, 34720		28555			
$[Ptbot_2Br_2]$	25190	32465, 34965		27290			
$[Ptbot_2I_2]$	26315	32680, 35210		28415			

B is taken to be 720 and 660 cm^{-1} for the Rh^{3+} and Ir^{3+} free ions respectively.

metals Rh(III) > Ir(III). The β values of our complexes were compared with the β values of other rhodium(III) and iridium(III) derivatives in order to find out the position of the ligand in the nephelauxetic series. Our ligand can be placed in the middle of this series and at the bottom end of the nitrogen donors and we suggest the following order: $F > X\text{–}PhSeO_2^- > H_2O > (CH_3)_2SO \simeq CH_3CONH_2 > (NH_2)_2CO > NH_3 \simeq$ *bot* $> S > (C_2H_5O)_2PSe_2^- > Cl^- > Br^- \ldots$

It is known that 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 to a lower oxidation state. For 4d transition metals the variation of Racah interelectronic repulsion parameter with cationic charge Z* and the number q of electrons in the partly filled d shell is expressed by the relation:[20]

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

where B′ is in cm^{-1}.

The effective ionic charges of the rhodium complexes here studied have been calculated, Table II; these values are in the range 0.46–0.54, considerably below the formal 3+ oxidation state of rhodium.

The electronic spectra of the diamagnetic palladium(II) and platinum(II) derivatives are indicative of square planar geometries.[31–33] Three spin allowed d–d transitions are expected corresponding to transitions from the three lower lying d levels to the empty $d_{x^2-y^2}$ orbitals; the ground state is $^1A_{1g}$ and the excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in order of increasing energy. The bands in the range 22370–22885 cm^{-1} and 25190–26455 cm^{-1} in the palladium and platinum derivatives respectively may be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$, Table II. Other intense bands are observed on the higher energy side of the d–d transitions; these last bands are undoubtedly charge transfer in nature.

By assuming a value of $F_2 = 10F_4 = 600$ for the Slater Condon interelectronic repulsion parameters both for palladium and platinum,[34] it is possible to derive from the first spin allowed d–d transition the values of Δ_1, Table II. The splitting parameter increases in the expected order Pt > Pd.

The iodo-derivative of palladium(II) with a metal:ligand ratio of 1:4 is 1:2 electrolyte in N,N′-dimethylformamide, Table I, while all the remaining complexes resulted non-electrolytes in the same solvent.[35]

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

Compounds	ν (NH)	Thio-amide I	ν (C=S) + δ (NCS)	Thio-amide II	ν (COC) asym.	Thio-amide III	ν (COC) sym.	Thio-amide IV
solid	3250s	1505vs	1282s	1245ms	1095vs	1010s	820ms	745vs
bot								
$CHCl_3$ sol.	3450s	–	1285s	–	1100s	1013s	–	–
$[Rhbot_3Cl_3]$	3200s	1512vs	1288s	1250s	1102s	1018s	821ms	750vs
$[Rhbot_3Br_3] \cdot H_2O$	3200s	1510vs	1290s	1252s	1100s	1012ms	822m	750vs
$[Rhbot_3I_3] \cdot 3H_2O$	3160s	1505vs	1285s	1252s	1097s	1010ms	820m	748vs
$[Irbot_3Cl_3]$	3080s	1515vs	1290s	1260s	1105s	1017ms	823ms	750vs
$[Irbot_3Br_3] \cdot H_2O$	3170s	1517s	1290ms	1260ms	1105m	1017m	820m	750vs
$[Irbot_3I_3] \cdot 2H_2O$	3100s	1512s	1290ms	1260ms	1105m	1005m	820sh	750vs
$[Pdbot_2Cl_2]$	3080s	1510ms	1297m	1265vs	1108vs	1015s	825s	750vs
$[Pdbot_2Br_2] \cdot 2H_2O$	3140s	1508vs	1290s	1267ms	1107s	1011m	820m	755vs
$[Pdbot_4]I_2$	3170m	1510s	1285ms	1248ms	1098ms	1010m	820m	750vs
$[Ptbot_2Cl_2] \cdot H_2O$	3080ms	1515m	1295m	1270vs	1110s	1017s	830ms	750vs
$[Ptbot_2Br_2]$	3080m	1517s	1290s	1270vs	1108ms	1015m	820m	750vs
$[Ptbot_2I_2]$	3070m	1508s	1290s	1265vs	1100s	1010s	822ms	745vs

TABLE IV
Far infrared spectra (400–50 $\mathrm{cm^{-1}}$)

Compounds	ν(M–X)	ν(M–L)	Other bands
bot	–	–	425ms, 264m, 237m, 101m, 70m
$[\mathrm{Rhbot_3Cl_3}]$	348mw, 332ms, 295m	250m, 230m, 217m	425ms, 264m, 237m, 100w, 73w
$[\mathrm{Rhbot_3Br_3}] \cdot \mathrm{H_2O}$	208m, 188sh, 170ms	248m, 226m, 218m	424ms, 257m, 233m, 102m, 71m
$[\mathrm{Rhbot_3I_3}] \cdot 3\mathrm{H_2O}$	149s, 132ms, 121m	251m, 225m, 215m	427ms, 263m, 240m, 105m, 70m
$[\mathrm{Irbot_3Cl_3}]$	342m, 317m, 300m	270m, 250m, 216m	425ms, 260m, 235m, 97m, 70mw
$[\mathrm{Irbot_3Br_3}] \cdot \mathrm{H_2O}$	212m, 198m, 175m	268m, 250m, 219m	426ms, 262m, 232m, 99m, 72m
$[\mathrm{Irbot_3I_3}] \cdot 2\mathrm{H_2O}$	146m, 133w, 119m	270m, 251m, 217m	425ms, 259m, 236m, 104m, 69m
$[\mathrm{Pdbot_2Cl_2}]$	330ms, 312m	295m, 257vs	425s, 268m, 232m, 98m, 71mw
$[\mathrm{Pdbot_2Br_2}] \cdot 2\mathrm{H_2O}$	274ms, 248m	296ms, 255m	423s, 264m, 235m, 97m, 73sh
$[\mathrm{Pdbot_4}]\mathrm{I_2}$	–	250m	432ms, 264m, 101m, 68m
$[\mathrm{Ptbot_2Cl_2}] \cdot \mathrm{H_2O}$	340m, 315m	251m, 224m	423ms, 264m, 243m, 103mw, 70mw
$[\mathrm{Ptbot_2Br_2}]$	228m, 207m	250m, 224m	425ms, 261m, 242m, 104m, 72m
$[\mathrm{Ptbot_2I_2}]$	194m, 166m	250m, 228m	424s, 263m, 238m, 102m, 71m

Infrared Spectral Studies

Thione compounds containing the H–N–C=S skeleton give rise to four thioamide bands: around 1550, 1300–1200, 1000 and 750–800 $\mathrm{cm^{-1}}$.[36–39] The presence of i.r. bands in such regions indicates that our ligand exists in the thione form in the solid state, Table III.

The spectra of the ligand in the solid state and in chloroform solution show a noticeable difference in the position of the ν(NH) stretching frequency, clearly indicating intermolecular hydrogen bonding between the hydrogen of the NH group and the sulphur atom of the thioketo group. The ν(NH) in the complexes is shifted towards lower energies by about 320 $\mathrm{cm^{-1}}$ using as reference the value of 3450 $\mathrm{cm^{-1}}$ for ν(NH) for the free ligand in chloroform solution, or by about 120 $\mathrm{cm^{-1}}$ using the 3250 $\mathrm{cm^{-1}}$ value obtained from the solid phase spectrum of the free ligand. The extensive hydrogen bonding disappears after dissolution in chloroform and after complexation.

According to previously reported data[15,40] a sharp NH band in the metal derivatives is indicative of the absence of hydrogen bonding and a comparison of these values with the ν(NH) solution frequency of the free ligand could be used to suggest a coordination through the nitrogen heteroatom. In the complexes here reported sharp bands are present in the range 3200–3070 $\mathrm{cm^{-1}}$ and a comparison with the ν(NH) value of 3450 $\mathrm{cm^{-1}}$ would indicate a M–N coordination.

This red shift in the NH stretching frequency clearly suggests a coordination through the nitrogen atom in all the complexes, but further confirmation of the mode of bonding can be reached by an analysis of the positions and intensities of the thioamide bands. The shifts in the positions of these bands are, in fact, a function of the position of coordination in the ligand molecule by the metal ion. The directions of the shifts in the position of all the bands in the spectra of the complexes are the same. This fact indicates that the bonding pattern in the complexes must be similar.

The band at 1505 $\mathrm{cm^{-1}}$, thioamide I, having contribution from $\delta(\mathrm{NH}) + \delta(\mathrm{CH}) + \nu(\mathrm{C{=}N})$ shows in the complexes small positive shifts; the thioamide II, having contribution from $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) + \delta(\mathrm{NH}) + \delta(\mathrm{CH}) + \nu(\mathrm{C{=}S})$ 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), are not shifted towards lower energies, while a red shift should be present if the sulphur atom were involved in the coordination to the metal.[36–46]

The bands at 1095 and 820 $\mathrm{cm^{-1}}$, attributed to the prevailing contribution of ν(COC) asym and sym, are at the same wave numbers or show small blue shifts, thus excluding the possibility of coordination through the oxygen of the oxazole ring.

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,[21,29,47–50] but new halogen independent bands are present in the ranges expected for ν(Rh–N), ν(Ir–N), ν(Pd–N) and ν(Pt–N) respectively, Table IV, in very good agreement with the literature data[50–52] and with the conclusions from the electronic spectra.

The octrahedral complexes of rhodium and iridium of the type $[\mathrm{ML_3X_3}]$ can exist as *mer*- and *fac*-isomers and the far infrared spectra of these complexes should provide significant structural informations. The bands due to rhodium–halide and iridium–halide stretching modes were identified by intercomparison of the spectra of the chloride, bromide and iodide derivatives respectively and reported data on other similar compounds.[51,53] Three M–N stretching vibrations and three M–X stretching vibrations are present in all the complexes (the spectra are summarized in Table IV).

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, $a_1 + e$. As for the ν(M–X) vibrations, we assign the two bands at higher frequencies to the two vibrations involving predominantly the mutually *trans*-haldes and the band at lower energy to the metal–halide stretching mode of the halide in *trans*-position to nitrogen.

Passing to the palladium and platinum derivatives, the spectra of ML_2X_2-type complexes show metal–halogen stretching frequencies whose position and multiplicity are indicative of *cis* square planar C_{2v} stereochemistry with terminal halides. As is clear from Table IV, these complexes show two ν(M–X) vibrations, $a_1 + b_1$ and two ν(M–L) vibrations, $a_1 + b_1$.

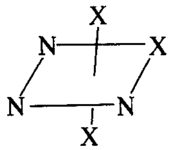
In the far i.r. spectrum of the complex $[Pdbot_4]I_2$ no bands are present in the expected range where ν(Pd–I) mode usually lies, but only a medium absorption band clearly due to ν(Pd–N); this is the vibration of e_u symmetry in the D_{4h} symmetry point group. The absence of palladium–iodine stretching mode is in accord with the conductivity measurements results that gave for this complex a typical value of 1:2 electrolyte.

The medium-strong bands present in the range 3450–3470 cm^{-1} (broad), ν(OH) and around 1650 cm^{-1}, δ(HOH) in the water containing complexes confirm the presence of water of crystallization, which is purely lattice and not coordination water as confirmed by the absence of wagging, twisting and rocking modes typical of coordinated water.[54]

CONCLUSIONS

The complexes of *bot* resulted always diamagnetic N-bonded, with the ligand acting as monodentate only, in spite of the presence of three potential donor atoms in the ligand molecule. The complexes were characterized as covalent, with the octahedral structure d^2sp^3 for the rhodium(III) and iridium(III) complexes and with the square planar structure dsp^2 for the palladium(II) and platinum(II) derivatives.

All the rhodium and iridium complexes have *mer*-configurations, *i.e.* the three nitrogen atoms of the ligands lie in a plane as in the configuration:



while the palladium and platinum derivatives have a *cis* square planar stereochemistry.

EXPERIMENTAL

Purification of the Ligand

Bot, supplied by Fluka was purified by recrystallization from ethanol (m.p. 192–194°C, lit. 193°C).[55]

Preparation of the Complexes

The rhodium and iridium derivatives have been obtained by reaction of RhX_3 and $(NH_4)_3IrX_6$, X = Cl, Br, I, in molten ligand in the required stoichiometrical ratio. The complexes have been purified by means of repeated washing with ethanol and ethyl ether in the case of rhodium and with water, ethanol and ethyl ether in the case of iridium.

The palladium and platinum complexes were obtained by reaction in aqueous/ethanol solution between K_2MCl_4 (where M = Pd, Pt) and *bot* in small excess in the presence of HX, X = Cl, Br, I, as in the following scheme:

$$K_2MCl_4 + bot \xrightarrow{HX} Mbot_nX_2$$

$$M = Pd; X = Cl, Br; n = 2$$

$$M = Pd; X = I; n = 4$$

$$M = Pt; X = Cl, Br, I; n = 2$$

In the case of the palladium–iododerivative we have obtained only the complex $[Pdbot_4]I_2$ even working in a 1:2 ratio metal:ligand.

The complexes separated out spontaneously during the reaction and were purified by washing with water, ethanol and ethyl ether.

Electronic Spectra

Solid-state electronic spectra have been recorded with a Shimadzu MPS–50L spectrophotometer by the method of Venanzi and co-workers.[56]

Magnetic Susceptibility Measurements

These were carried out by Gouy's method. 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 for 10^{-3} M solutions in N,N'-dimethylformamide at 25 ± 0.1°C.

Infrared Measurements

The infrared spectra were recorded in the range 4000–50 cm^{-1} with Perkin–Elmer models 457, 225 and Hitachi Perkin–Elmer FIS3 spectrophotometers. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen. The spectra in the range 4000–400 cm^{-1} were measured for KBr discs and in chloroform solution. Far i.r. spectra were measured for Nujol mulls supported between polyethylene sheets.

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REFERENCES

1. D. E. Ryan, *Anal. Chem.*, **22**, 599 (1950).
2. M. Tamura, H. Hada, J. Noguchi and S. Hayashi, *J. Phys. Chem.*, **66**, 559 (1962) and references therein.
3. P. Bassignana, C. Cogrossi and M. Gandino, *Spectrochim. Acta*, **19**, 1885 (1963).
4. C. Runti, *Fondamenti di Chimica Farmaceutica*, vol. I, II and III, Lint Inc., Trieste (1971).
5. L. S. Goodman and A. Gilman, *The Pharmacological Basis of Therapeutics*, Macmillan Company, Toronto (1971).
6. A. Cristini, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, **36**, 2473 (1974).
7. R. Pinna, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, **37**, 1681 (1975).
8. G. Devoto, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, **37**, 1635 (1975).
9. M. Massacesi, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, **37**, 1641 (1975).
10. M. Massacesi, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, **38**, 1556 (1976).
11. G. Devoto, G. Ponticelli, C. Preti, and G. Tosi, *J. Inorg. Nucl. Chem.*, **38**, 1744 (1976).
12. C. Preti, G. Tosi, M. Massacesi and G. Ponticelli, *Spectrochim. Acta, 32A*, 1778/1876).
13. G. Devoto, M. Massacesi, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem.*, **39**, 271 (1977)
14. R. Pinna, G. Ponticelli, C. Preti and G. Tosi, *Transition Met. Chem*, **1**, 173 (1976).
15. C. Preti and G. Tosi, *Can. J. Chem.*, **54**, 85 (1976).
16. C. Preti and G. Tosi, *J. Inorg. Nucl. Chem.*, **38**, 1125 (1976).
17. M. St. C. Flett, *J. Chem. Soc.*, 347 (1953).
18. C. Preti and G. Tosi, *Can. J. Chem.*, in press.
19. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon Inc., Boston (1963).
20. C. K. Jorgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).
21. E. Bertelli, C. Preti and G. Tosi, *J. Inorg. Nucl. Chem.*, **37**, 1421 (1975).
22. C. K. Kalia and A. Chakravorty, *Inorg. Chem.*, **8**, 2586 (1969).
23. C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 500 (1956).
24. C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, London (1964).
25. C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York (1962).
26. P. Dini, J. C. J. Bart, E. Santoro, G. Cum and N. Giordano, *Inorg. Chim. Acta*, **17**, 97 (1976)
27. M. Donati, D. Morelli, F. Conti and R. Ugo, *Chim. e Ind.* (Milan), **50**, 231 (1968).
28. R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1224 (1964).
29. G. Marcotrigiano, G. C. Pellacani, C. Preti and G. Tosi, *Bull. Chem. Soc. Japan*, **48**, 1018 (1975).
30. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1968).
31. P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).
32. P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1298 (1972).
33. R. M. Alcock, F. R. Hartley and D. E. Rogers, *J. Chem. Soc. Dalton Trans.*, 1070 (1973).
34. A. R. Latham, V. C. Hascall and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965).
35. W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
36. E. Lieber, C. N. R. Rao, C. N. Pillai and R. D. Hites, *Can. J. Chem.*, **36**, 801 (1958).
37. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley, New York (1966).
38. C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).
39. C. N. R. Rao, R. Venkataraghavan and T. R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).
40. P. P. Singh and R. Rivest, *Can. J. Chem.*, **46**, 2361 (1968).
41. D. De Filippo and C. Preti, *J. Chem. Soc. (A)*, 1904 (1970).
42. U. Agarwala, V. A. Narayan and S. K. Dikshit, *Can. J. Chem.*, **45**, 1057 (1967).
43. U. Agarwala and S. K. Dikshit, *J. Inorg. Nucl. Chem.*, **30**, 1248 (1968).
44. B. Singh and R. Singh, *J. Inorg. Nucl. Chem.*, **34**, 3449 (1972).
45. B. Singh and K. P. Thakur, *J. Inorg. Nucl. Chem.*, **36**, 1735 (1974).
46. U. Agarwala and L. Agarwala, *J. Inorg. Nucl. Chem.*, **34**, 241 (1972).
47. D. M. Adams and J. B. Cornell, *J. Chem. Soc. (A)*, 1299 (1968).
48. U. Agarwala and B. Singh, *J. Inorg. Nucl. Chem.*, **33**, 598 (1971).

49. A. Nakamura, Y. Tatsuno and S. Otsuka, *Inorg. Chem.*, 11, 2058 (1972).
50. J. R. Ferraro, *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York (1971).
51. R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 4, 350 (1965).
52. E. R. Birnbaum, *J. Inorg. Nucl. Chem.*, 35, 3145 (1973).
53. P. L. Goggin and J. R. Knight, *J. Chem. Soc. Dalton Trans.*, 1489 (1973).
54. C. Preti and G. Tosi, *Spectrochim. Acta*, 31A, 1139 (1975).
55. R. C. Weast (Editor), *Handbook of Chemistry and Physics*, 49th ed., The Chemical Rubber Co., Cleveland, Ohio, 1968–69 p. C204.
56. G. Dyer, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).