Inorganica Chimica Acta, 14 (1975) 195–200

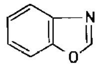
Isoxazole as a Ligand

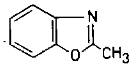
N. M. KARAYANNIS*, C. M. MIKULSKI**, S. D. SONSINO, E. E. BRADSHAW and L. L. PYTLEWSKI
Department of Chemistry, Drexel University, Philadelphia, Pa. 19104, U.S.A.
Received January 4, 1975

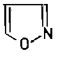
A number of divalent 3d metal chloride and perchlorate complexes with isoxazole were obtained by interaction of salt and ligand in triethyl orthoformate–ethanol. Characterization of these complexes was based on spectral (ir–electronic), magnetic and conductance evidence. The metal perchlorate complexes are of the following types (L = isoxazole): $[FeL_2(OH_2)_4](ClO_4)_2$, $[CoL_3(OH_2)_3](ClO_4)_2$, $[NiL_4(OH_2)_2](ClO_4)_2$ *and* $[CuL_3(OH_2)](ClO_4)_2$. *The former three cationic complexes are low-symmetry hexacoordinated, while the Cu(II) complex is distorted square-planar. Isoxazole acts as a monodentate N-ligand in these compounds.* $NiCl_2$ *forms a 1:2 complex with isoxazole, containing both terminal and bridging chloro and isoxazole (N- and O,N-bonded) ligands. This compound is polynuclear, hexacoordinated* ($[NiL_2Cl_2]_x$). $CuCl_2$ *yields a 1:1 complex with this ligand. This compound is binuclear, square planar, involving terminal chloro and bridging, O,N-bonded, isoxazole* ($[Cl_2Cu(OC_3H_3N)_2CuCl_2]$).

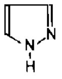
Introduction

A number of studies dealing with the syntheses and characterization of metal complexes of substituted oxazoles[1–3], thiazole[4] and derivatives[2,5], and isothiazole[6] appeared recently in the literature. Thiazole and isothiazole were found to form N-bonded complexes with divalent 3*d* metal ion (M = Co(II), Ni(II), Cu(II)) salts[4,6]. Benzothiazole and 2-methylbenzothiazole also form N-bonded 3*d* metal complexes[2], while 2-aminothiazole coordinates through the amino group rather than the ring nitrogen[5]. Benzoxazole (I) yields N-bonded complexes of the type ML_2X_2 (M = Co, Ni, Cu, Zn; X = Cl, Br, NO_3)[1,2]; thermal decomposition of the metal halide complexes of this type at 140° C, affords the species MLX_2, which involve bridging, N,O-bonded, bidentate benzoxazole ligands[3]. 2-Methylbenzoxazole (II), on the other hand, acts in most cases as a monodentate O-ligand towards the same metal ions; a complex involving bridging, O,N-bonded 2-methylbenzoxazole with $NiCl_2$ has also been reported[1,2]. It was of interest to us to explore the possibility of synthesizing and characterizing metal complexes with a similar ligand, namely isoxazole (III), as an extention of our recent studies of metal complexes with ligands containing both nitrogen and oxygen coordination sites[7–9]. The investigation of the ligand properties of isoxazole were thought to be of interest, since this compound has two neighboring potential donor atoms (O and N), and also resembles the extensively studied pyrazole ligand (IV)[10–15], which contains an NH group in place of the oxygen of isoxazole. The present paper deals with the syntheses and characterization of complexes of 3*d* metal chlorides and perchlorates with isoxazole.


(I)


(II)


(III)


(IV)

Experimental

Chemicals and Synthetic Procedure

The isoxazole used was a product of Eastman Organic Chemicals (b.p. 93–95° C). Its ir spectrum was in satisfactory agreement with literature values[16,17], and the ligand was utilized as received. The purest commercially available hydrated metal salts and organic solvents were generally utilized.

The synthetic procedure followed involved dissolution of the metal salt in a 1:1 (V/V) mixture of triethyl orthoformate (a dehydrating agent[18])–ethanol, at *ca.* 50° C, and the resulting solution was gently stirred for *ca.* 1 hr at this temperature (approximately 40 ml of solvent mixture per g of salt were used). Then, isoxazole was added to this solution at a ligand to salt ratio of 6:1, for the metal perchlorates, or 4:1, for the metal chlorides, and the resulting mixture was allowed to stir at 50° C, until precipitation occurred. Under these conditions, $NiCl_2$ and $CuCl_2$ yielded crystalline precipitates within 10–15 min from the addi-

---

* Present Address: Amoco Chemicals Corp., Naperville, Ill. 60540.

** Present Address: Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19174.

tion of the ligand, whereas in the cases of $M(ClO_4)_2$ (M = Fe, Co, Ni, Cu) solid precipitates were formed after 2–3 hr of stirring. Analytical (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., Table I) and spectral (Tables II and III) data shows that the above products are true complexes of isoxazole. These compounds were filtered, washed with ligroin (boiling range 63–75° C) and stored in an evacuated desiccator over calcium chloride. Under similar experimental conditions, a number of other divalent 3*d* metal chlorides (M = Mn, Fe, Co, Zn) and perchlorates (M = Mn, Zn) also gave solid products, which appeared to be mixtures of over 80% uncomplexed metal salt and less than 20% isoxazole metal complex, as suggested by analytical results. Small variations of the experimental procedure (changes of the ligand to metal ratio, concentration of the reaction mixture, temperature of operation, *etc.*) failed to produce pure isoxazole complexes with the latter metal salts. Different synthetic approaches have not been explored so far for these syntheses.

Solubilities and Characterization Studies

The six new metal complexes are soluble in various polar organic solvents, such as nitrobenzene, nitromethane, N,N-dimethylformamide and acetone. The metal perchlorate complexes dissolve much more readily in these media than the metal chloride complexes. Characterization of these compounds was based on magnetic susceptibility and conductance measurements (Table I), and infrared (Table II) and electronic (Table III) spectra, which were obtained by methods previously described[19].

Discussion

Stoichiometries of the New Metal Complexes

Lower than one would expect isoxazole to metal ratios are observed in the new complexes. In fact, pyrazole forms readily complexes of the types $[ML_6](ClO_4)_2$ [M = Mn through Ni, Zn), $[CuL_4](ClO_4)_2$, ML_4Cl_2 and CuL_2Cl_2[10–15]. For thiazole and isothiazole, species of the above stoichiometries have been isolated; in addition, these ligands also form complexes of the type CoL_2Cl_2[4,6]. Even the relatively bulkier benzoxazole and 2-methylbenzoxazole ligands generally form 2:1 complexes with divalent 3*d* metal halides[1], and the 1:1 analogs can only be obtained by thermal decomposition of these complexes[3], as already mentioned. Hence, it was rather unexpected to obtain a 2:1 $NiCl_2$ and a 1:1 $CuCl_2$ complex (Table I) with unsubstituted isoxazole. This is not surprising, however, as the only well known isoxazole metal complex is a 1:1 adduct with $CdCl_2$, which has been used extensively during the synthesis of isoxazole[20,21]. The isoxazole to metal ratios in the new metal perchlorate

TABLE I. Analyses, Magnetic Moments (300° K) and Molar Conductivities (10^{-3} *M* solutions in nitromethane, at 25° C) of Isoxazole Metal Complexes.

Complex[a]	Color	Analysis								$10^6\chi_M$cor, cgsu	μ_{eff}, BM	Λ_M, Ω^{-1} cm^2 mol^{-1}
		C %		H %		N %		Metal %				
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found			
NiL_2Cl_2	yellow–green	26.92	26.23	2.26	2.57	10.46	9.88	21.93	22.41	4,211	3.19	46
$CuLCl_2$	yellow	17.71	17.39	1.49	1.74	6.88	6.52	31.22	31.45	1,517	1.92	34
$FeL_2(ClO_4)_2 \cdot 4H_2O$	buff	15.50	15.04	3.04	3.37	6.03	5.96	12.01	12.11	11,224	5.21	164
$CoL_3(ClO_4)_2 \cdot 3H_2O$	orange	20.83	20.30	2.91	2.65	8.10	7.76	11.36	11.23	9,904	4.90	173
$NiL_4(ClO_4)_2 \cdot 2H_2O$	violet	25.29	25.15	2.83	3.05	9.83	10.01	10.30	9.86	4,298	3.22	167
$CuL_3(ClO_4)_2 \cdot H_2O$	dark blue	22.92	22.77	2.35	2.55	8.91	9.28	13.47	13.30	1,632	1.99	180

[a] L = isoxazole.

TABLE II. Infrared Spectra (Nujol Mull) of Isoxazole Metal Complexes (cm^{-1}).

Compound	4000–600 cm^{-1} region	$\nu_{M-ligand}$ (L, Cl, OH_2)[a]	ν_{ligand} and ν_{OH_2}(wag) (600–200 cm^{-1})
Isoxazole = L[b]	3160w, 3129w, 3116w, 3092vw, 2968vw, 2642vw, 2593vw, 2244vw, 2162w, 1808w, 1748w, 1653w, 1564m, 1492w, 1432vs, 1366s, 1259vw, 1219m, 1177vw, 1129s, 1087m, 1028m, 917s, 906w, 843s, 777vs, 632s		593s, 568s, 540m, 511w, 470w, 430w, b, 380vw, 360vw, 331vw, 320vw, 309vw, 295vw, 286vw, 272vvw, 260vvw, 215vw, 209vw
NiL_2Cl_2	3120w, 3086w, b, 2640w, b, sh, 2540vw, b, 2325vw, b, 1755vw, 1611vw, 1554vw, 1541vw, 1440vs, sh, 1357s, sh, 1260vw, sh, 1228m, 1172vw, 1138m, 1085w, 1057w, 1040w, 945m, 911m, 898w, 880w, 805vw, sh, 777vs, 724m, 627s	290s, sh(c), 281s(l), 240s(l), 233s(l), 220s(c)	584s, 570m, sh, 493w, 400vw, b, 380vw, b, 345vw, b
$CuLCl_2$	3170w, 3140w, 3120w, 3085w, 2600w, vb, 2550vw, b, 2330vw, b, 1760vw, 1625vw, b, 1555vw, 1438vs, sh, 1355s, sh, 1310w, b, 1240w, 1228m, 1170vw, 1147m, 1088w, 1050m–w, 958m, 922w, 911w, 889m, 820vw, 781vs, 721m, 620m	314s(c), 290s(c), 283s(c), 256s(l), 229s(l)	585s, 562 m, 540w, 500w, 400vw, b, 350vw, b, 330vw, sh, 307sh, 270w, 248m, 215w, 208w
$FeL_2(ClO_4)_2 \cdot 4H_2O$	3530s, vb,[c] 3200–3100w, vb, 2640w, sh, 2530w, b, 2340vw, b, 1750w, sh, 1626m,[c] 1551w, 1438s, sh, 1358s, sh, 1310w, b, 1235w, sh, 1150s, sh, 1082vvs, vb[d], 928w, b, 780m, sh, 715m, sh, 620s[d]	390w, b(a), 241s(l)	590m, 550m–s, b[c], 380w, 370w, 305w, 275s, 266m–w, 220m–s
$CoL_3(ClO_4)_2 \cdot 3H_2O$	3490vs, vb[c], 3170sh, 3100sh, 2680w, sh, 2520vw, sh, 2260vw, vb, 1770vw, sh, 1620m[c], 1555w, sh, 1441s, sh, 1355m, sh, 1305w, vb, 1232w, sh, 1152s, sh, 1070vs, vb,[d] 920vw, sh, 780m, sh, 720m, sh, 620s[d]	392w(a), 239m(l)	598m, sh, 550m–s, b,[c] 410w, 380w, 360w, b, 343w, 329vw, 320w, 262m, 223m–w, sh
$NiL_4(ClO_4)_2 \cdot 2H_2O$	3500s, vb,[c] 3160w, sh, 3095vw, 2690vw, sh, 2600vw, sh, 2555vw, sh, 2300vw, vvb, 1740vw, 1622m,[c] 1552w, 1442s, sh, 1348m, sh, 1310vvw, b, 1224m, sh, 1160s, sh, 1068vs, vb[d], 940vw, sh, 890vvw, sh, 790vw, sh, 720m, sh, 628s[d]	394w(a), 242w–m(l)	599w, b, 552m–w,[c] 540w, 490w, b, 410vw, b, 370vw, 312w, 280m, 263w, 220w–m
$CuL_3(ClO_4)_2 \cdot H_2O$	3420s, vvb[c], 3200–3100w, vb, 2680w, sh, 2605vw, sh, 2520vw, b, 2330vw, b, 1750vw, 1628w,[c] 1550vw, 1428s, sh, 1355m, sh, 1315w, b, 1240vw, sh, 1170m, sh, 1075m–s, vb,[d] 950w, 915 vw, 895vw, 850vw, sh, 775m, sh, 720m, 628s[d]	405w, b(a), 241w–m(l)	580w, sh, 540m, b[c], 480w, b, 450w, b, 390w, 380w, 362w, b, 340w, b, 315w, 272w, 260w, 220w

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

[a] (c): chloro; (l) isoxazole; (a) aquo, ligands. [b] Spectrum obtained on neat (liquid) isoxazole. [c] Coordinated water: ν_{OH} at 3530–3420 cm^{-1}; δ_{H-O-H} at 1628–1622 cm^{-1}; OH_2 wag, at 552–540 cm^{-1} [28,29]. [d] Ionic (T_d) ClO_4: ν_3 at 1082–1068 cm^{-1}; ν_4 at 628–620 cm^{-1} [25–27].

complexes (2, 3, or 4; *cf.* Table I) may be attributed to competition between isoxazole and aquo ligands for the central metal ion. Similar tendencies, leading to the formation of mixed heterocyclic ligand–aquo cationic 3*d* metal complexes, have been encountered by this laboratory during the syntheses of tetrahydrofuran[22] and dioxane[23] complexes with divalent 3*d* metal perchlorates.

Infrared and Conductance Data

The molar conductivity values for the new metal perchlorate complexes (Table I) are typical of those of 1:2 electrolytes[24]. Thus, at least in nitromethane solution, these compounds appear to involve exclusively ionic perchlorate. The metal chloride complexes exhibit Λ_M values intermediate between those corresponding to non- and 1:1-electrolytes[24].

TABLE III. Solid State (Nujol Mull) Electronic Spectra of Isoxazole Metal Complexes.

Compound	λ_{max}, nm
Isoxazole = L	211vs[a]
NiL_2Cl_2	212vs, 216vs, sh, 253s, sh, 400m, 671m, b, 718m, sh, 1070m–w, vb
$CuLCl_2$	217s, sh, 247s, 435s, sh, 782s, vvb
$FeL_2(ClO_4)_2 \cdot 4H_2O$	212vs, 217vs, sh, 282vs, 318s, sh, 641m–s, vb, 976m, vb
$CoL_3(ClO_4)_2 \cdot 3H_2O$	214vs, 500s, 576s, 1060m, vb
$NiL_4(ClO_4)_2 \cdot 2H_2O$	212vs, 257s, sh, 288s, sh, 397m–s, 553m, b, 623m, b, 1000m–w, vb
$CuL_3(ClO_4)_2 \cdot H_2O$	213vs, 218vs, sh, 268s, 303s, sh, 671m–s, sh, 741m–s, 835m–s, sh

[a] Spectrum obtained on neat (liquid) isoxazole. Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

The perchlorate groups are also exclusively ionic in the solid metal perchlorate complexes, as suggested by the ir evidence (Table II). In fact, the ν_3 mode of ionic (T_d) perchlorate occurs as a very strong, single, broad band, with a relatively sharp maximum at 1082–1068 cm^{-1}, while the ν_4 mode appears as a strong, sharp absorption at *ca.* 620 cm^{-1}; no indication of activation of the ir-inactive (in T_d ClO_4^-) ν_1 (∼930 cm^{-1}) and ν_2 (∼460 cm^{-1}) ClO_4 modes is present in the spectra of these complexes[25–27]. The metal perchlorate complexes also contain coordinated aquo ligands, which cannot be removed even after prolonged vacuum desiccation. Their spectra exhibit the characteristic ν_{OH} (3530–3420 cm^{-1}), δ_{H-O-H} (1630–1620 cm^{-1})[28], and the OH_2 wag at 552–540 cm^{-1} [28,29]; the bands due to the rocking mode of coordinated water were not identified, probably owing to overlaps with ligand absorptions (750–640 cm^{-1})[29].

Among the fundamental vibrational modes of the ligand[16,17,30], the ring vibrations (ring stretching modes at 1653, 1564, 1432 and 1366 cm^{-1} and bending modes at 1129, 843 (in-plane) and 632, 593 (out-of-plane) cm^{-1}, after Califano *et al.* [16]) appear to generally undergo more pronounced shifts and/or splittings than the vibrations corresponding to CH stretching and bending modes, upon metal complex formation. This ought to be expected, since the potential electron pair donor atoms (O- and N-) are members of the ring. The above spectral changes are better observed in the spectra of the metal chloride complexes, which are devoid of interfering absorptions from the perchlorate and aquo groups (Table II).

In the lower frequency ir spectrum, bands attributable to metal–ligand vibrations occur. Tentative assignments are given in Table II. In the metal perchlorate complexes, ν_{M-O} (aquo) is assigned to bands in the 405–390 cm^{-1} region[29]. The metal–isoxazole stretching modes appear to be associated with the absorptions at 242–239 cm^{-1}. The frequencies of these bands are in favor of coordination of isoxazole through nitrogen rather than oxygen[1–4, 11–13]. The metal chloride complexes exhibit richer spectra in the 320–200 cm^{-1} region. The following assignments were made (cm^{-1}): Ni complex: ν_{M-Cl} (terminal 290; bridging 220)[31,32]; ν_{Ni-O} (isoxazole) 281; ν_{Ni-N} (isoxazole) terminal 240, bridging 233[1–4]; Cu complex: ν_{Cu-Cl} (terminal) 314, 290, 256[1–3, 31, 32]; ν_{Cu-O} (isoxazole) 283; ν_{Cu-N} (isoxazole) 229[1–4]. On the basis of the above assignments, which are substantiated by the electronic spectral evidence (*vide infra*), the metal perchlorate complexes appear to contain exclusively terminal, N-bonded isoxazole, whereas the metal chloride complexes involve bridging, O,N-bonded isoxazole and terminal Cl groups, in the case of the $CuCl_2$ complex, and both terminal and bridging isoxazole and Cl groups, in the case of the $NiCl_2$ complex.

Electronic Spectra and Magnetic Moments

The magnetic moments of the new complexes (Table I) are generally typical of high-spin compounds of the metal ions under study[33]. With regard to the metal chloride complexes, which are bi- or poly-nuclear, it should be pointed out that, as far as Ni(II) is concerned, many polynuclear high-spin $NiCl_2$ complexes with aromatic amines[32], oxazole derivatives[1–3], aromatic amine N-oxides[34], *etc.* have been reported. Nevertheless, bi- or poly-nuclear $CuLX_2$ (X = halogen) L-bridged complexes with similar ligands exhibit, in most cases, subnormal room temperature magnetic moments[1,3,35,36]. However, benzoxazole and 2-methylbenzoxazole 1 : 1 complexes with $CuCl_2$ are magnetically normal (μ_{eff} = 2.03–2.04 BM), whereas the corresponding $CuBr_2$ complexes are diamagnetic[1,3]. In all these cases, the presence of bridging, substituted oxazole, O,N-ligands has been postulated from the spectral evidence[1,3]. Hence, it is not surprising that the new $CuCl_2$ complex is magnetically normal, despite the fact that it contains bridging isoxazole ligands (*vide supra*).

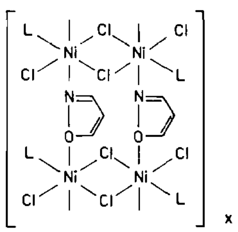
The electronic spectra (Table III) of the Fe(II), Co(II) and Ni(II) complexes are suggestive of low-symmetry hexacoordinated configurations[1–4, 11, 37]. Thus, the $^5T_{2g} \rightarrow {}^5E_g$ transition in the ferrous complex appears as a split band at 641 and 976 nm[37]. In the Co(II) complex the *d–d* bands are assigned as follows: $^4T_{1g}(F) \rightarrow {}^4A_{2g}$, $^4T_{1g}(P)$ at 500 and 576 nm; and $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ at 1060 nm. The Ni(II) complexes exhibit the following *d–d* transitions: $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ at 397–400 nm; $^3A_{2g} \rightarrow {}^3T_{1g}$, ^1E_g at 623–718 nm; and $^3A_{2g} \rightarrow {}^3T_{2g}$ at 1000–1070 nm. The two Cu(II) complexes, on the other hand, appear to be tetracoordinated, with a distorted square planar configuration. In fact, the location of the $^2E_g \rightarrow {}^2T_{2g}$ transition, which is either split or very broad[37], is in support of tetra-rather than hexa-coordinated structures, on the basis of previously reported spectra of square planar and octahedral Cu(II) complexes with similar ligands (oxazoles, pyrazole)[1–3, 11–13].

The uv band of isoxazole occurs at 211 nm[38, 39], and is due to a $\pi \rightarrow \pi^*$ transition. In the spectra of the new metal complexes this maximum is only slightly shifted towards lower energies, but the ligand band becomes generally broader and exhibits new absorption maxima at 215–320 nm. These absorptions are apparently due to the ligand[1–3], as well as charge-transfer (metal-to-ligand)[3, 40]. With the exception of the ferrous complex, the uv spectra of the new complexes are characterized by very strong to strong absorptions at 200–305 nm, becoming weak to very weak above 320 nm. No overlaps between the charge-transfer and the *d–d* bands are, therefore, observed. In the case of the Fe(II) complex, the charge-transfer trails well into the visible. The occurrence of lower in energy charge-transfer bands in Fe(II) complexes in comparison to those in Co(II), Ni(II) or Cu(II) complexes with the same ligand is quite common (*e.g.*, 2,2′-bipyridine[41], its mono-N-oxide[9], picolinate N-oxide[42]).

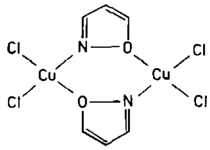
Conclusion

On the basis of the overall evidence available (analytical, spectral, magnetic and conductance data), the new metal perchlorate complexes are formulated as (L = isoxazole) $[FeL_2(OH_2)_4](ClO_4)_2$, $[CoL_3(OH_2)_3](ClO_4)_2$, $[NiL_4(OH_2)_2](ClO_4)_2$ and $[CuL_3(OH_2)](ClO_4)_2$. These compounds involve coordinated aquo and monodentate, N-bonded, isoxazole ligands and exclusively ionic perchlorate. The Fe(II), Co(II) and Ni(II) complexes are hexacoordinated, involving FeN_2O_4, CoN_3O_3 and NiN_4O_2 moieties, and the Cu(II) complex is tetra-coordinated with a CuN_3O moiety. From the available evidence it appears that isoxazole as a nitrogen ligand is about as strong as pyrazole (Dq towards octahedral Ni(II) 1065 cm^{-1})[11] and substantially stronger than the aquo ligand (Dq towards octahedral Ni(II) 860 cm^{-1})[43]. In fact, the Dq value obtained from the electronic spectrum of the mixed ligand (isoxazole–aquo) Ni(II) perchlorate complex (if a pure O_h symmetry is assumed) is 1000 cm^{-1}.

The $NiCl_2$ complex is hexacoordinated, polynuclear and contains both terminal and bridging chloro and



(V)



(VI)

isoxazole (N- and O,N-bonded) ligands. Structure (V) is considered as likely for this complex[8, 44]. The tetracoordinated $CuCl_2$ complex is probably binuclear with terminal chloro and bridging, O,N-bonded, isoxazole ligands. A structure resembling those reported for the corresponding aromatic amine N-oxide complexes is most probable in this case (structure (VI)).

It should be noted at this point that quite recently two other groups have also been involved in work on transition metal complexes of isoxazole and substituted isoxazoles[45, 46]. Details of their work are not available at present.

References

1 E.J. Duff and M.N. Hughes, *J. Chem. Soc. A*, 2144 (1968); 477 (1969).

2 E.J. Duff, M.N. Hughes and K.J. Rutt, *J. Chem. Soc. A*, 2126 (1969).

3 E.J. Duff, *J. Inorg. Nucl. Chem.*, *32*, 3103 (1970).

4 W.J. Eilbeck, F. Holmes and A.E. Underhill, *J. Chem. Soc. A*, 757 (1967).

5 P.P. Singh and A.K. Srivastava, *J. Inorg. Nucl. Chem.*, *36*, 928 (1974).

6 R. Rivest and A. Weisz, *Can. J. Chem.*, *49*, 1750 (1971).

7 A.N. Speca, N.M. Karayannis and L.L. Pytlewski, *Inorg. Chim. Acta*, *6*, 639 (1972); A.N. Speca, L.L. Pytlewski and N.M. Karayannis, *J. Inorg. Nucl. Chem.*, *34*, 3671 (1972); A.N. Speca, R. Mink, N.M. Karayannis, L.L. Pytlewski and C. Owens, *J. Inorg. Nucl. Chem.*, *35*, 1833 (1973).

8 A.N. Speca, L.L. Pytlewski and N.M. Karayannis, *Inorg. Nucl. Chem. Lett.*, *9*, 365 (1973); *J. Inorg. Nucl. Chem.*, *35*, 4029 (1973); A.N. Speca, N.M. Karayannis and L.L. Pytlewski, *J. Inorg. Nucl. Chem.*, *35*, 3113 (1973).

9 A.N. Speca, N.M. Karayannis, L.L. Pytlewski, L.J. Winters and D. Kandasamy, *Inorg. Chem.*, *12*, 1221 (1973); A.N. Speca, N.M. Karayannis and L.L. Pytlewski, *Inorg. Chim. Acta*, *9*, 87 (1974); A.N. Speca, L.L. Pytlewski and N.M. Karayannis, *J. Inorg. Nucl. Chem.*, *36*, 1227 (1974).

10 N.N. Daugherty and J.H. Swisher, *Inorg. Chem.*, *7*, 1651 (1968).

11 J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, *88*, 1451 (1969); *89*, 605 (1970); *90*, 117 (1971); *91*, 1373 (1972).

12 J. Reedijk, J.C.A. Windhorst, N.H.M. van Ham and W.L. Groeneveld, *Recl. Trav. Chim. Pays-Bas, 90,* 234 (1971).

13 J. Reedijk and D.W. Engelfriet, *Recl. Trav. Chim. Pays-Bas, 91,* 883 (1972).

14 C.W. Reimann, A.D. Mighell and F.A. Mauer, *Acta Crystallogr., 23,* 135 (1967); A.D. Mighell, C.W. Reimann and A. Santoro, *Acta Crystallogr., B25,* 595 (1969); C.W. Reimann, A. Santoro and A.D. Mighell, *Acta Crystallogr., B26,* 521 (1970).

15 S.N. Poddar, *Sci. Cult. Calcutta, 35,* 28 (1969).

16 S. Califano, F. Piacenti and G. Speroni, *Spectrochim. Acta, 15,* 86 (1959).

17 A.R. Katritzky and A.J. Boulton, *Spectrochim. Acta, 17,* 238 (1961).

18 P.W.N.M. van Leeuwen and W.L. Groeneveld, *Inorg. Nucl. Chem. Lett., 3,* 145 (1967).

19 N.M. Karayannis, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta, 3,* 415 (1969); N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta, 8,* 91 (1974).

20 A. Quilico and G. Palazzo, *Proc. XI Intern. Congr. Pure and Applied Chem. (London), 2,* 253 (1947); G.S. D'Alcontres and G. Mollica, *Atti accad, nazl. Lincei, Rend. Classe sci. fis., mat. e nat., 10,* 52 (1951); G. Gaudiano, A. Quilico and A. Ricca, *Atti accad. nazl. Lincei, Rend. Classe sci. fis., mat. e nat., 21,* 253 (1956).

21 T.V. Protopopova and A.P. Skoldinov, *Zhur. Obshch. Khim., 26,* 3355 (1956); V.T. Klimko, T.V. Protopopova, N.V. Smirnova and A.P. Skoldinov, *Zhur. Obshch. Khim., 32,* 2961 (1962).

22 N.M. Karayannis, E.E. Bradshaw, J. Wysoczanski, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta, 4,* 272 (1970).

23 N.M. Karayannis, C.M. Mikulski, A.N. Speca, L.L. Pytlewski and M.M. Labes, *Inorg. Chem., 11,* 2330 (1972).

24 W.J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).

25 B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.,* 3091 (1961); A.E. Wickenden and R.A. Krause, *Inorg. Chem., 4,* 404 (1965).

26 S.F. Pavkovic and D.W. Meek, *Inorg. Chem., 4,* 1091 (1965); M.E. Farago, J.M. James and V.C.G. Trew, *J. Chem. Soc. A,* 820 (1967).

27 D.M.L. Goodgame, M. Goodgame and P.J. Hayward, *J. Chem. Soc. A,* 1352 (1970).

28 I. Gamo, *Bull. Chem. Soc. Japan, 34,* 760 (1961).

29 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 20,* 429 (1964); J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc., 78,* 3963 (1956).

30 E. Borello, *Gazz. Chim. Ital., 89,* 1437 (1959).

31 R.J.H. Clark, *Spectrochim. Acta, 21,* 955 (1965); R.J.H. Clark and C.S. Williams, *Inorg. Chem., 4,* 350 (1965).

32 D.M.L. Goodgame, M. Goodgame and M.J. Weeks, *J. Chem. Soc.,* 5194 (1964); D.M.L. Goodgame, M. Goodgame, P.J. Hayward and G.W. Rayner-Canham, *Inorg. Chem., 7,* 2447 (1968).

33 B.N. Figgis and J. Lewis, *Progr. Inorg. Chem., 6,* 37 (1964).

34 N.M. Karayannis, C.M. Paleos, L.L. Pytlewski and M.M. Labes, *Inorg. Chem., 8,* 2559 (1969); D.H. Brown, D. Kenyon and D.W.A. Sharp, *J. Chem. Soc. A,* 1474 (1969).

35 N.M. Karayannis, L.L. Pytlewski and C.M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973); W.H. Watson, *Inorg. Chem., 8,* 1879 (1969); and references therein.

36 E.J. Halbert, C.M. Harris, E. Sinn and G.J. Sutton, *Aust. J. Chem., 26,* 951 (1973).

37 A.B.P. Lever, *Coord. Chem. Rev., 3,* 119 (1968); W. Byers, A.B.P. Lever and R.V. Parish, *Inorg. Chem., 7,* 1835 (1968).

38 P. Pino, G. Speroni and V. Fuga, *Gazz. Chim. Ital., 84,* 759 (1954).

39 A.K. Murthy, K.S.R.K.M. Rao and N.V.S. Rao, *Aust. J. Chem., 21,* 2315 (1968).

40 See, *e.g.,* A.B.P. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc.,* 1235 (1962); 3156, 5042 (1963); 4761 (1964).

41 P. Krumholz, *J. Am. Chem. Soc., 75,* 2163 (1953); J. Hidaka and B.E. Douglas, *Inorg. Chem., 3,* 1180 (1964).

42 A.B.P. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc.,* 5262 (1962); W. Byers, B. Fa-Chun Chov, A.B.P. Lever and R.V. Parish, *J. Am. Chem. Soc., 91,* 1329 (1969).

43 V. Imhof and R.S. Drago, *Inorg. Chem., 4,* 427 (1965).

44 J.R. Ferraro, C. Cristallini and G. Roch, *Ric. Sci., 37,* 435 (1967); J.R. Ferraro, W. Wozniak and G. Roch, *Ric. Sci., 38,* 433 (1968); J.R. Ferraro, J. Zipper and W. Wozniak, *Appl. Spectroscopy, 23,* 160 (1969).

45 G. Ponticelli and C. Preti, *XVI ICCC, Dublin, Ireland,* August 19–24, 1974; paper No. 2.23b; G. Ponticelli, private communication.

46 P.H. van der Voort and W.L. Driessen, *XVI ICCC, Dublin, Ireland,* August 19–24, 1974; review paper on Wed. August 21st.