

Transition Metal Chemistry of Oxime Containing Ligands: Part III—Complexes of Fe(II), Co(II) & Ni(II) with Pyridine-2-aldoxime & 6-Methylpyridine-2-aldoxime

M. MOHAN*, S. G. MITAL, H. C. KHERA & A. K. SRIVASTAVA

Department of Chemistry, N.R.E.C. College, Khurja 203131

Received 17 June 1976; revised 19 December 1976; accepted 4 April 1977

Complexes of the type $[M(L)_2X_2]$ ($M = \text{Fe(II)}$ or Co(II) ; $L = \text{pyridine-2-aldoxime (HPOX)}$ or $6\text{-methylpyridine-2-aldoxime (HMPX)}$; and $X = \text{Cl, Br, I}$ or NCS) and $[\text{Ni}(L)_2X_2]$ ($L = \text{HPOX}$ or HMPX ; and $X = \text{NO}_3$ or NCS) have been prepared and characterized on the basis of IR and electronic spectral, magnetic moment and X-ray powder diffraction data. X-ray and electronic spectral data indicate that all the complexes have *trans*-pseudo-octahedral microsymmetry around the metal ion. The magnetic susceptibilities for Fe(II) and Ni(II) complexes are independent of temperature (80-300°K), whereas Co(II) complexes show a slight temperature dependence of magnetic moment. Mössbauer spectra also indicate pseudo-octahedral geometry for Fe(II) complexes.

A NUMBER of transition metal complexes of pyridine-2-aldoxime (HPOX) and 6-methylpyridine-2-aldoxime (HMPX) have been reported in literature¹⁻¹⁰. In continuation of our earlier work on Cu(II) and Ni(II) complexes of HPOX and HMPX^{11,12}, we report here the results of our investigation on the isolation and characterization of Fe(II), Co(II) and Ni(II) complexes of HPOX and HMPX.

Materials and Methods

Fe(II), Co(II) and Ni(II) salts, ammonium thiocyanate (all reagent grade), pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime (K & K Laboratories) were used without further purification.

Preparation of the complexes: FeL_2X_2 ($L = \text{HPOX}$ or HMPX , and $X = \text{Cl, Br}$ or I)—A solution of ferrous halide (0.004 mole) in 70 ml of deoxygenated absolute ethanol was prepared and kept under a stream of N_2 gas. A solution of the ligand (0.008 mole) in 90 ml of absolute ethanol was prepared by heating while bubbling a rapid stream of N_2 through the solution. The solution of ferrous halide was then added very slowly under a stream of N_2 to the solution of the ligand. A red colour formed immediately, and a precipitate formed within minutes. The mixture was allowed to stand for 30 min under N_2 , then heated to boiling and filtered hot via suction through a sintered glass under N_2 . The precipitate was dried *in vacuo*.

$\text{FeL}_2(\text{NCS})_2$ ($L = \text{HPOX}$ or HMPX)—An ethanolic solution of ferrous thiocyanate (0.002 mole), prepared from ferrous chloride tetrahydrate and NH_4SCN , was filtered into a solution of the ligand (0.005 mole) in hot ethanol (20 ml) and 2,2'-dimethoxypropane (20 ml). The mixture was gently boiled under N_2 gas for 30 min. The solid product was collected by filtration in an atmosphere of N_2 and washed with anhydrous ethanol and ether.

*To whom all correspondence should be addressed.

CoL_2X_2 ($L = \text{HPOX}$ or HMPX , and $X = \text{Cl, Br}$ or I)—Anhydrous cobalt(II) halide (0.01 mole) was dissolved in a minimum quantity of ethanol and the ligand (0.02 mole) dissolved in ethanol was added. On cooling the solution in refrigerator, a pink crystalline solid was obtained. The complex was filtered and washed with a small amount of ethanol and ether.

$\text{CoL}_2(\text{NCS})_2$ ($L = \text{HPOX}$ or HMPX)—Cobalt chloride hexahydrate (0.01 mole) was dissolved in water (20 ml) and the ligand (0.02 mole) dissolved in a minimum quantity of hot ethanol was added. On adding excess solid NH_4SCN a pink precipitate was obtained immediately. The solid was filtered and washed well with water to remove any excess of thiocyanate and then with a small quantity of anhydrous ethanol and diethylether.

$\text{NiL}_2(\text{NO}_3)_2$ ($L = \text{HPOX}$ or HMPX)— $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.006 mole) was dissolved in a mixture of 25 ml of ethanol and 25 ml of 2,2'-dimethoxypropane and solution refluxed for several hours. The ligand (0.014 mole) was dissolved in 25 ml of 1:1 ethanol-2,2'-dimethoxypropane, refluxed and added dropwise with continuous stirring to the hot metal salt solution. Crystallization occurred almost immediately. A dark green solid was collected by filtration, washed with anhydrous ether and dried *in vacuo* over P_2O_5 .

$\text{NiL}_2(\text{NCS})_2$ ($L = \text{HPOX}$ or HMPX)—A suspension of $\text{NiL}_2(\text{NO}_3)_2$ (0.01 mole) in absolute ethanol was treated with solid NH_4SCN (0.02 mole). The green solid turned dark blue on shaking the mixture. The product was filtered and washed with ethanol and dried *in vacuo* over P_2O_5 .

Physical measurements—Infrared spectra were recorded in mull on Perkin-Elmer infracord, model 180 (4000-400 cm^{-1}) and Beckman IR-12 (400-200 cm^{-1}) instruments. Diffuse reflectance spectra at room temperature and liquid nitrogen temperature were recorded on a Cary spectrophotometer model

14 equipped with a diffuse reflectance accessory using magnesium oxide as the reference. Magnetic measurements were obtained at various temperatures (80-300°K) on a standard Gouy balance. The tube was calibrated with Co[Hg(NCS)₄] as the standard.

X-ray powder photographs were obtained using a Philips (Hungary) X-ray generator, nickel filtered copper radiation and a Debye-Scherrer camera.

A conventional constant acceleration Mössbauer spectrometer was used to obtain the Mössbauer spectral data with an accuracy of ± 0.01 mm/sec.

C, H and N analyses were obtained from the microanalytical laboratory of IIT, Kanpur. Metals were analysed by standard techniques¹³ after decomposition of the complexes with aqua regia. Halide analyses were carried out by potentiometric titration with AgNO₃, after decomposition of the complexes by sodium fusion. The analytical data are presented in Table 1.

Results and Discussion

The X-ray powder diffraction patterns for present compounds and [Fe(py)₄(NCS)₂] suggest that all the compounds are isomorphous. Therefore, in analogy with the known structure¹⁴ of [Fe(py)₄(NCS)₂] the present complexes may also have *trans*-octahedral geometry.

The IR spectra of oximes normally show ν OH around 3250 cm⁻¹. This band is replaced by multiple bands between 3194 and 2791 cm⁻¹ in HPOX and HMPX, the strongest of which lies at ~ 2791 cm⁻¹. This implies much stronger hydrogen bonding in HPOX and HMPX than in other oximes. The ν C=N in HPOX and HMPX occurs around 1520 cm⁻¹ and is in the range observed by Krause *et al.*³ for oximes. The ring stretching frequencies, ring breathing mode, ν N-O, out-of-plane C-H deformation, skeletal modes and out-of-plane deformation bands appear in the regions 1620-1425, ~ 1000 ,

~ 950 , ~ 800 , ~ 740 and ~ 400 cm⁻¹ respectively in HPOX and HMPX ligands.

All the present complexes show bands in the regions 3250-3015, 1635-1630 and 1074-1040 cm⁻¹ which can be assigned to ν OH, ν C=N and ν N-O frequencies respectively. These data show that oxime proton is not removed on complex formation.

The complexes of the general formula [M(L)₂X₂] {M = Fe(II), or Co(II); L = HPOX or HMPX; and X = Cl, Br I or NCS} and [Ni(L)₂X₂] (L = HPOX or HMPX, and X = NO₃ or NCS) exhibit the four ring stretching frequencies in the following ranges: band-I, 1618-1612; band-II, 1578-1574; band-III, 1490-1477; and band-IV, 1440-1426 cm⁻¹. Band-I shows a significant increase in frequency from the free ligand value of ~ 1570 cm⁻¹, an indication of the coordination of pyridine to the metal atom¹⁵. The ring breathing mode observed at ~ 996 cm⁻¹ in the free ligands disappears in the complexes and is replaced by a band at 1005-1020 cm⁻¹. This shift is also indicative of pyridine coordination¹⁶.

Two strong bands are observed in the spectra of free ligands at 798 and 741 cm⁻¹ which may be assigned to ν (C-H) and ν (C-C) respectively¹⁷. The 741 cm⁻¹ band splits into two components lying at 718 and 752 cm⁻¹. This splitting is also an indication of pyridine to metal coordination¹⁸. The band observed at 798 cm⁻¹ in the free ligands is observed as a single band lying between 780 and 824 cm⁻¹ in the complexes.

In the spectra of [M(L)₂(Cl)₂] {M = Fe(II) or Co(II); and L = HPOX or HMPX} complexes, two bands are observed at 240 and 270 cm⁻¹ which may be assigned to ν M-Cl and ν M-N modes, respectively. The band at 270 cm⁻¹ cannot be assigned to ν M-Cl, since it is rather too high in energy and a band of similar energy appears in the spectra of all the remaining complexes also [including Ni(II) complexes]. However, the ν M-Br and ν M-I bands appear below

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Compounds*	Found (calc.), %				
	C	H	N	Metal	X†
Fe(C ₆ H ₆ N ₂ O) ₂ (Cl) ₂	38.94 (38.84)	3.27 (3.23)	15.08 (15.10)	15.14 (15.08)	19.17 (19.14)
Fe(C ₆ H ₆ N ₂ O) ₂ (Br) ₂	31.34 (31.31)	2.57 (2.60)	12.19 (12.17)	12.65 (12.15)	34.82 (34.78)
Fe(C ₆ H ₆ N ₂ O) ₂ (I) ₂	26.14 (26.00)	2.12 (2.16)	10.15 (10.11)	11.24 (10.09)	45.96 (45.85)
Fe(C ₆ H ₆ N ₂ O) ₂ (NCS) ₂	34.69 (34.63)	2.98 (2.88)	13.97 (13.47)	14.10 (13.45)	28.20 (27.90)
Fe(C ₇ H ₈ N ₂ O) ₂ (Cl) ₂	42.22 (42.11)	4.18 (4.01)	14.19 (14.04)	14.18 (14.02)	17.92 (17.80)
Fe(C ₇ H ₈ N ₂ O) ₂ (Br) ₂	34.50 (34.43)	3.23 (3.28)	11.51 (11.48)	11.82 (11.46)	32.86 (32.79)
Fe(C ₇ H ₈ N ₂ O) ₂ (I) ₂	29.10 (28.87)	2.82 (2.74)	9.74 (9.62)	9.90 (9.60)	43.72 (43.64)
Fe(C ₇ H ₈ N ₂ O) ₂ (NCS) ₂	37.99 (37.84)	3.72 (3.68)	12.70 (12.62)	12.90 (12.59)	26.52 (26.13)
Co(C ₆ H ₆ N ₂ O) ₂ (Cl) ₂	40.00 (38.50)	3.28 (3.20)	15.10 (14.97)	15.99 (15.78)	19.20 (18.99)
Co(C ₆ H ₆ N ₂ O) ₂ (Br) ₂	31.19 (31.11)	2.62 (2.59)	12.30 (12.10)	12.95 (12.75)	34.60 (34.55)
Co(C ₆ H ₆ N ₂ O) ₂ (I) ₂	26.10 (25.85)	2.17 (2.15)	10.20 (10.06)	10.71 (10.59)	45.70 (45.59)
Co(C ₆ H ₆ N ₂ O) ₂ (NCS) ₂	34.41 (34.48)	2.90 (2.86)	13.42 (13.37)	14.28 (14.08)	27.80 (27.69)
Co(C ₇ H ₈ N ₂ O) ₂ (Cl) ₂	41.84 (41.79)	4.20 (3.98)	14.12 (13.93)	14.91 (14.68)	17.85 (17.66)
Co(C ₇ H ₈ N ₂ O) ₂ (Br) ₂	34.42 (34.22)	3.36 (3.25)	11.42 (11.40)	12.14 (12.01)	32.70 (32.58)
Co(C ₇ H ₈ N ₂ O) ₂ (I) ₂	28.86 (28.72)	2.81 (2.73)	9.68 (9.57)	11.02 (10.09)	43.50 (43.41)
Co(C ₇ H ₈ N ₂ O) ₂ (NCS) ₂	37.70 (37.58)	3.70 (3.58)	12.66 (12.53)	13.97 (13.20)	26.20 (25.95)
Ni(C ₆ H ₆ N ₂ O) ₂ (NO ₃) ₂	33.86 (33.75)	2.90 (2.81)	13.90 (13.76)	19.90 (19.69)	—
Ni(C ₆ H ₆ N ₂ O) ₂ (NO ₃) ₂	37.12 (36.94)	3.62 (3.51)	18.52 (18.47)	13.30 (12.90)	—
Ni(C ₆ H ₆ N ₂ O) ₂ (NCS) ₂	34.62 (34.40)	2.92 (2.86)	13.50 (13.38)	14.44 (14.02)	27.86 (27.71)
Ni(C ₇ H ₈ N ₂ O) ₂ (NCS) ₂	37.79 (37.61)	3.69 (3.58)	12.76 (12.58)	13.39 (13.14)	26.12 (25.97)

*C₆H₆N₂O = pyridine-2-aldoxime, C₇H₈N₂O = 6-methylpyridine-2-aldoxime.

†X = Cl, Br, I, NO₃ or NCS.

200 cm^{-1} outside the range of the instrument used in the present study.

IR data indicate that both the nitrate groups in $[\text{Ni}(\text{L})_2(\text{NO}_3)_2]$ are coordinated. Assignments of ν_1 at 1310, ν_2 at 1038 and ν_3 at 825 cm^{-1} agree well with the published values for coordinated nitrate groups^{19,20}. The very strong bands at 740 and 1510 cm^{-1} can be assigned to the ν_3 and ν_4 modes respectively. IR bands usually associated with ionic nitrate groups (D_{3h} symmetry) were absent in the spectra of all the complexes studied.

The occurrence of a strong band ($\nu\text{C}\equiv\text{N}$) around 2045 cm^{-1} in $[\text{M}(\text{L})_2(\text{NCS})_2]$ {M = Fe(II), Co(II) or Ni(II); and L = HPOX or HMPX} indicates the presence of N-bonded thiocyanate group²¹⁻²⁵. The occurrence of a band around 882 cm^{-1} which may be assigned to $\nu\text{C-S}$ further corroborates the presence of an N-bonded thiocyanate group²⁵.

The magnetic moments for Fe(II), Co(II) and Ni(II) complexes have been measured as a function of temperature (80-300°K) (Table 2). The magnetic

moments of Fe(II) and Ni(II) complexes are essentially independent of temperature between 107° and 298°K. The magnitude and temperature independence of the moments are in accord with tetragonally distorted octahedral, high spin structures²⁶⁻²⁸. Co(II) complexes show a slight temperature dependence of magnetic moments, the Curie-Weiss law is obeyed and the values of θ are relatively small²⁹.

The electronic absorption spectra of Fe(II) complexes of the type $[\text{Fe}(\text{L})_2\text{X}_2]$ (X = Cl, Br, I or NCS) are similar to one another. For Fe(II) complexes in the O_h field, a single electronic spectral band corresponding to the transition ${}^5T_{2g} \rightarrow {}^5E_g$ is expected and is usually observed around 9 kK³⁰. If the field is lowered to D_4 symmetry, state ${}^5T_{2g}$ is split into the states 5E_g and ${}^5B_{2g}$ while the state 5E_g splits into ${}^5A_{1g}$ and ${}^5B_{1g}$ states.

The reflectance spectra of the present Fe(II) complexes exhibit broad partially resolved bands at 9 and 12 kK at room temperature and 9.2 and 12.3 kK at liquid nitrogen temperature. On the basis of a D_{4h} symmetry, we assign the 9 kK band to the transition ${}^5B_{2g} \rightarrow {}^5A_{1g}$ and the 12 kK band to the transition ${}^5B_{2g} \rightarrow {}^5B_{1g}$. The small increase in the energies of the electronic transitions at liquid nitrogen temperature is most likely a result of increase in the ligand field strength with decreasing temperature which arises from a slight contraction of the unit cell volume at low temperature. The spectra of the Fe(II) complexes show a very strong and broad band at 18 kK also, which may be assigned as a charge-transfer band arising from metal to ligand ($t_{2g} \rightarrow \pi^*$) charge-transfer.

The room temperature Mössbauer chemical isomer shift, δ , relative to iron foil is found to lie in the range 0.96-1.05 mm/sec for several octahedral high spin, Fe(II) complexes containing nitrogen donor atoms³¹⁻³³. We have studied the Mössbauer spectra of the $[\text{Fe}(\text{L})_2\text{X}_2]$ complexes at several temperatures and the spectral parameters are given in Table 3 which confirm pseudo-octahedral nature of these complexes when compared to the Mössbauer data of compounds of known structures³³.

TABLE 2 — MAGNETIC SUSCEPTIBILITIES OF THE COMPLEXES

Compound	Temperature (°K)	μ_{eff} (BM)
Fe(HPOX) ₂ Cl ₂	297.5-83.0	5.29-5.27
Fe(HPOX) ₂ Br ₂	298.0-83.0	5.56-5.56
Fe(HPOX) ₂ I ₂	295.0-101.5	5.59-5.57
Fe(HPOX) ₂ (NCS) ₂	297.5-103.5	5.40-5.38
Fe(HMPX) ₂ Cl ₂	292.5-104.5	5.32-5.32
Fe(HMPX) ₂ Br ₂	290.5-102.5	5.54-5.54
Fe(HMPX) ₂ I ₂	294.5-103.5	5.60-5.58
Fe(HMPX) ₂ (NCS) ₂	290.5-102.5	5.38-5.37
Co(HPOX) ₂ Cl ₂	298.0-103.5	4.60-4.54
Co(HPOX) ₂ Br ₂	296.5-103.0	4.58-4.48
Co(HPOX) ₂ I ₂	292.5-103.0	4.65-4.56
Co(HPOX) ₂ (NCS) ₂	291.5-101.5	4.62-4.54
Co(HMPX) ₂ Cl ₂	297.5-101.5	4.59-4.50
Co(HMPX) ₂ Br ₂	299.5-105.0	4.56-4.50
Co(HMPX) ₂ I ₂	300.0-104.5	4.67-4.58
Co(HMPX) ₂ (NCS) ₂	295.5-104.0	4.60-4.52
Ni(HPOX) ₂ (NO ₃) ₂	298.5-104.5	3.28-3.25
Ni(HPOX) ₂ (NCS) ₂	297.5-104.0	3.30-3.27
Ni(HMPX) ₂ (NO ₃) ₂	299.5-104.5	3.29-3.24
Ni(HMPX) ₂ (NCS) ₂	292.5-101.5	3.30-3.25

TABLE 3 — MÖSSBAUER SPECTRAL PARAMETERS

Compound	T (°K)	δ^* (mm/sec)	ΔE_Q (mm/sec)	$\Gamma_{1\uparrow}$ (mm/sec)	$\Gamma_{2\uparrow}$ (mm/sec)
Fe(HPOX) ₂ (Cl) ₂	78	1.16	2.00	0.26	0.26
	RT	1.06	1.54	0.25	0.24
Fe(HPOX) ₂ (Br) ₂	78	1.14	2.00	0.25	0.26
	RT	1.05	1.54	0.25	0.24
Fe(HPOX) ₂ (I) ₂	78	1.12	1.96	0.26	0.25
	RT	0.99	1.50	0.25	0.24
Fe(HPOX) ₂ (NCS) ₂	78	1.15	2.00	0.25	0.25
	RT	0.98	1.49	0.25	0.24
Fe(HMPX) ₂ (Cl) ₂	78	1.15	1.99	0.26	0.26
	RT	1.04	1.53	0.26	0.25
Fe(HMPX) ₂ (Br) ₂	78	1.12	1.99	0.25	0.25
	RT	1.02	1.50	0.25	0.24
Fe(HMPX) ₂ (I) ₂	78	1.10	1.96	0.26	0.26
	RT	1.00	1.49	0.26	0.25
Fe(HMPX) ₂ (NCS) ₂	78	1.14	1.96	0.25	0.24
	RT	0.98	1.49	0.25	0.25

*Relative to natural iron foil.

†Full width at half-maximum for low-velocity line Γ_1 and high-velocity line Γ_2 .

TABLE 4 — CRYSTAL FIELD PARAMETERS (CM⁻¹) OF Ni(II) COMPLEXES

Compound	B	D _{qxy}	D _{qz}	D _x	D _t	Δ ₁	Δ ₃
Ni(HPOX) ₂ (NO ₃) ₂	824.6	1174	644	533.5	290.1	150	3584.5
Ni(HPOX) ₂ (NCS) ₂	808.2	1150	600	634.5	314.7	330	4111.8
Ni(HMPX) ₂ (NO ₃) ₂	821.2	1173	672	523.1	286.2	138	3523.4
Ni(HMPX) ₂ (NCS) ₂	815.2	1149	592	636.6	318.7	316	4139.9

The electronic spectra of [Co(L)₂X₂] (X = Cl, Br, I or NCS) are similar to one another. The reflectance spectra of Co(II) complexes consist of a broad band centred at 9.6 kK with a weak shoulder at 8.5 kK and a set of four closely spaced and more intense bands at 18.6, 19.4, 20.1 and 21.1 kK. Spin-allowed transitions for Co(II) in C_h field are ⁴T_g(F) → ⁴T_{2g}(F)(ν₁), ⁴T_{1g}(F) → ⁴A_{2g}(F)(ν₂) and ⁴T_{1g}(F) → ⁴T_{1g}(P)(ν₃). The ν₂ transition is a two-electron transition and is normally not observed³⁴. Thus the low-energy band is assigned to the ν₁ transition and the bands at 19.4 and 20.1 kK are assigned as the components of ν₃ band. The structured nature of ν₃ is not uncommon in the spectra of Co(II) complexes and is considered to arise either from spin-forbidden transitions to doublet terms or from low-symmetry ligand field components³⁵. The latter factor is of particular significance in the present case in view of the highly distorted octahedral coordination geometry. The bands observed at 8.5, 18.6 and 21.1 kK, which on cooling to liquid nitrogen temperature intensify without changing in position, can be assigned to the transitions ⁴T_{1g}(F) → ²E_g(H), ⁴T_{1g}(F) → ⁴T_{2g}, ²T_{1g}, and ⁴T_{1g}(F) → ²T_{1g}(H) respectively.

The reflectance spectra of Ni(II) complexes, [Ni(L)₂X₂] (X = NO₃ or NCS), exhibit features associated with the spectrum of [Ni(py)₂(NCS)₂] complex which has been shown to possess the nickel atom in distorted octahedral environment³⁶. Therefore, the bands observed at 9.0, 11.7, 14.9, 16.8, 25.8 and 26.7 kK in the present complexes may be assigned to the transitions ³B_{1g} → ³E_g, ³B_{1g} → ³B_{2g}, ³B_{1g} → ³A_{2g}, ³B_{1g} → ³E_g, ³B_{1g} → ³A_{2g} and ³B_{1g} → ³E_g. The ligand field parameters, calculated using the methods described by Lever³⁶, are presented in Table 4 which confirm the *pseudo*-octahedral (D_{4h}) coordination for these complexes.

Acknowledgement

We are thankful to Dr P. C. Gupta and Dr A. S. Bhatnagar for providing necessary facilities and encouragement. Financial support to S.G.M. and H.C.K. by the UGC, New Delhi, is gratefully acknowledged.

References

1. KRAUSE, R. A. & BUSCH, D. H., *J. Am. chem. Soc.*, **82** (1960), 4830.
2. KRAUSE, R. A., JICHA, D. C. & BUSCH, D. H., *J. Am. chem. Soc.*, **83** (1961), 528.
3. KRAUSE, R. A., COLTHUP, N. B. & BUSCH, D. H., *J. phys. Chem.*, **65** (1961), 2216.
4. KRAUSE, R. A., GUY, C. & HOOKER, M. L., *Inorg. Chem.*, **5** (1966), 1825.
5. HANANIA, G. J. H. & IRVINE, D. H., *J. chem. Soc.*, (1962), 2745.
6. LIU, C. H. & LIU, C. F., *J. Am. chem. Soc.*, **83** (1961), 4167.
7. LIU, C. F. & LIU, C. H., *J. Am. chem. Soc.*, **83** (1961), 4169.
8. GREEN, R. W. & SVASTI, M. C. K., *Aust. J. Chem.*, **16** (1963), 356.
9. HOLMES, F., LEES, G., UNDERHILL, A. E. & POWELL, D., *J. chem. Soc.*, (A) (1971), 333.
10. HOLMES, F., LEES, G. & UNDERHILL, A. E., *J. chem. Soc.*, (A) (1971), 999.
11. MOHAN, M., KHERA, H. C., MITTAL, S. G. & SRIVASTAVA, A. K., *Curr. Sci.*, **46** (1977), 211.
12. MOHAN, M., KHERA, H. C., MITTAL, S. G. & SRIVASTAVA, A. K., *Acta chim.*, (in press).
13. JOULS, R. A. & KATRITZKY, A. R., *J. chem. Soc.*, (1958), 3610.
14. SOTOFTE, I. & RASMUSSEN, S. E., *Acta chem. scand.*, **21** (1967), 2028.
15. FIGGINS, P. E. & BUSCH, D. H., *J. phys. Chem.*, **65** (1961), 2236.
16. SINHA, S. P., *Spectrochim. Acta*, **20** (1964), 879.
17. GREEN, J. H. S., KYNASTON, W. & PAISLEY, H. M., *Spectrochim. Acta*, **19** (1963), 549.
18. GILL, N. S. & KINGDON, H. J., *Aust. J. Chem.*, **19** (1966), 2197.
19. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (Wiley-Interscience, New York), 1963, 69.
20. BULLOCK, J. I., *J. inorg. nucl. Chem.*, **29** (1967), 2257.
21. MITCHELL, P. C. H. & WILLIAMS, R. I. P., *J. chem. Soc.*, (1960), 1912.
22. COTTON, F. A., GOODGAME, D. M. L., GOODGAME, M. & HAQS, T. E., *Inorg. Chem.*, **1** (1962), 595.
23. TURCO, A. & PECILE, C., *Nature*, **191** (1961), 66.
24. LEWIS, J., NYHOLM, R. S. & SMITH, P. W., *J. chem. Soc.*, (1961), 4590.
25. BURMETSTER, J. L., *Coord. chem. Rev.*, **1** (1966), 205; **3** (1968), 225.
26. FIGGIS, B. N., LEWIS, J., MABBS, F. E. & WEBB, G. A., *J. chem. Soc.*, (A) (1967), 442.
27. LEVER, A. B. P., *Inorg. Chem.*, **4** (1965), 763.
28. CLARK, R. J. H. & NATILE, G., *Inorg. chim. Acta*, **4** (1970), 533.
29. CARLIN, R. L., *Transition Metal Chem.*, **1** (1965), 1.
30. LEVER, A. B. P., *Inorganic electronic spectroscopy* (Elsevier, New York), 1968, 299.
31. GOLDING, R. M., MOK, K. F. & DUNCAN, J. F., *Inorg. Chem.*, **5** (1966), 774.
32. TOMINAGA, T., MORIMOTO, T., TADEDA, M. & SAITO, N., *Inorg. nucl. Chem. Lett.*, **2** (1966), 193.
33. BURBRIDGE, C. D., GOODGAME, D. M. L. & GOODGAME, M., *J. chem. Soc.*, (A) (1967), 349.
34. FERGUSON, J., *Progr. inorg. Chem.*, **12** (1970), 159.
35. LEVER, A. B. P. & OGDEN, D., *J. chem. Soc.*, (A) (1967), 2041.
36. LEVER, A. B. P., *Coord. chem. Rev.*, **3** (1968), 119.