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Ligating Properties of Model Bioheterocyclics.
Part VI. Synthesis, Characterization and Structures of Iron(III) Complexes with 3,6-Disubstituted-2,7-dihydro-1,4,5-thiadiazepines

S. S. SANDHU, S. S. TANDON*, T. S. LOBANA and D. S. BEDI

Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India

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Abstract

Iron(III) halides on reaction with 3,6-disubstituted-2,7-dihydro-1,4,5-thiadiazepine derivatives (L) form complexes of the general formula $FeL_2X_3 \cdot nH_2O$ (X = Cl,.Br, n = 1.5, 4, 5; L = L-1, L-2, L-3 and L-4 for substituent R in *para* position of Ar group as H, CH_3, Cl and OCH_3 respectively). These complexes were characterized by elemental analysis, IR, far-IR, ESR, electronic, ^1H NMR and Mössbauer spectra, magnetic moments, molar conductance, t.g.a and d.t.a data. The data support octahedral structures for the cations $[FeX_2L_4]^+$, with L acting as an unidentate ligand (via coordination through nitrogen atom) and tetrahedral structure for the anions, $[FeX_4]^-$. All the complexes are paramagnetic, having μ_{eff} values in the range 5.84–6.15 B.M. at room temperature. Thermal studies and IR spectra show the presence of uncoordinated water.

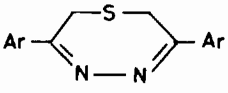
Introduction

Thiadiazepine rings constitute an analogue of diazepines present in many analgesic and sedative drugs [1–5]. An investigation of interaction of such heterocyclic systems with biologically important metal ions is essential for an understanding of their role in living systems [6–9]. There is an abundant evidence that the metal complexes of ligands possessing biological activity are more active than the free ligands. Coordination chemistry of thiadiazepines with Co(II), Cu(II), Zn(II), Cd(II), Pd(II) and Pt(II) has already been studied [10–12]. Since the coordination chemistry of iron(III) with nitrogen and/or sulphur containing ligands is fascinating due to its biological implications [13], it was intended to study the coordination behaviour of 1,4,5-thiadiazepines with iron(III) in the solid state. In this paper the complexes of substituted 1,4,5-thiadiazepine with iron(III) halides are reported. The complexes have been characterized through elemental analyses, IR, far-IR, UV and Visible, Mössbauer and ESR spectra, magnetic moments, conductance, t.g.a and d.t.a data.

Experimental

Materials

Anhydrous iron(III) chloride of BDH grade was used. Iron(III) bromide was prepared by reacting iron(III) chloride repeatedly with hydrobromic acid (60%) at controlled temperature. 3,6-Diaryl-2,7-dihydro-1,4,5-thiadiazepine derivatives (L) were prepared by a method reported earlier [14]. These are denoted as L-1, L-2, L-3 and L-4 containing respectively substituent R in *para* position of phenyl as H, CH_3, Cl and OCH_3. Solvents used were of AR/BDH grade and were dried by reported methods.



L

(L-1, Ar = Ph, L-2, Ar = $C_6H_4CH_3$; L-3, Ar = C_6H_4Cl, L-4, Ar = $C_6H_4OCH_3$)

Preparation of the Complexes

The complexes were prepared by the general procedure described below. Even with the use of 1:1 metal to ligand ratio, the complexes of 1:2 metal to ligand stoichiometry are formed.

A solution of the 3,6-diaryl-2,7-dihydro-1,4,5-thiadiazepine (L) (0.002 mol) in dry benzene (30 ml) was added to a solution of iron(III) chloride/bromide (0.001 mol) in absolute ethanol (15 ml). The reaction mixture was refluxed on a water bath until a permanent change from a brown colour was observed (10–18 h). The reaction mixture was reduced to one–tenth of its volume under reduced pressure. On treating with petroleum ether (40–

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical Data and Decomposition Temperatures of the Complexes.

S. No.	Complex[a]	Elemental Analysis: Found (Calcd)					Dec. temp. (°C)
		C%	H%	M%	N%	S%	
1	$[Fe(L\text{-}1)_4Cl_2][FeCl_4]$	50.07	4.94	6.82		8.88	110–18
		(50.10)	(4.70)	(7.31)		(8.35)	
2	$[Fe(L\text{-}2)_4Cl_2][FeCl_4]$	53.01	5.71	7.29		7.83	98–103
		(52.54)	(5.35)	(6.80)		(7.78)	
3	$[Fe(L\text{-}3)_4Cl_2][FeCl_4]$	40.87	3.04	5.92	5.46		90–96
		(41.64)	(3.69)	(6.07)	(6.07)		
4	$[Fe(L\text{-}4)_4Cl_2][FeCl_4]$	47.11	4.85	5.99		7.54	semi solid
		(47.78)	(5.09)	(6.19)		(7.08)	
5	$[Fe(L\text{-}1)_4Br_2][FeBr_4]$	44.95	3.44	6.45	6.28		110–15
		(44.94)	(3.63)	(6.53)	(6.65)		
6	$[Fe(L\text{-}2)_4Br_2][FeBr_4]$	43.81	4.22	5.62		6.24	87–95
		(44.38)	(4.79)	(5.74)		(6.57)	
7	$[Fe(L\text{-}3)_4Br_2][FeBr_4]$	36.16	3.30	4.80		6.76	85–90
		(36.38)	(3.22)	(5.30)		(6.06)	
8	$[Fe(L\text{-}4)_4Br_2][FeBr_4]$	40.92	4.37	6.00	5.08	5.73	110–15
		(41.63)	(4.43)	(5.39)	(5.40)	(6.16)	

[a] The numbers of water molecules in the respective complexes per iron are 4,4,5,5,1.5,5,5,5.

60 °C), an oily reddish brown product separated out. It was washed with a minimum amount of absolute alcohol, dry benzene and finally with dry petroleum ether (40–60 °C). The oily material was kept in a sulphuric acid desiccator for 4–8 days, when a solid was obtained except in the case of the complex of ligand L-4 with iron(III) chloride, which remained semi-solid even after 15 days. These complexes were highly hygroscopic and were stored under anhydrous conditions.

Analytical and Other Spectral Data

The elemental analyses for carbon, hydrogen, nitrogen and sulphur were carried out by the Microanalytical Service, University College of Sciences, Calcutta. Iron was estimated both gravimetrically and spectrophotometrically (Table I). The spectral and magnetic moment measurements were carried out in the same way as reported earlier [10–11]. Mössbauer spectra of iron(III) chloride complexes were recorded on Mössbauer spectrometer MBS-35, ECIL along with MCA-38/ECIL, India using $^{57}Co/Rh$ as a Mössbauer source. The Mössbauer spectrometer was calibrated with sodium nitroprusside as a reference compound. All spectra were taken at room temperature (30 ± 2 °C) using approximately 10 mg/cm^2 of the natural iron for measurements. The x-band (9.39 GHz) ESR spectra of the solid complexes were recorded with JEOL instrument at the University of Hyderabad, Hyderabad.

Results and Discussion

3,6-Diaryl-2,7-dihydro-1,4,5-thiadiazepines (L-1 to L-4) on reaction with iron(III) halides form reddish-brown complexes of composition, $FeX_3L_2 \cdot nH_2O$ (X = Cl, Br; n = 1.5, 4, 5) (Table I), which are hygroscopic. The thiadiazepine ring of the ligands is retained in these complexes contrary to its cleavage in palladium(II) and platinum(II) complexes [12], because on hydrolysis these complexes liberate free ligands. The complexes are insoluble in CCl_4, C_6H_6 and $PhNO_2$, but are sufficiently soluble in $CHCl_3$, CH_3OH, C_2H_5OH and $(CH_3)_2SO$. The complexes decompose into a black mass in the temperature range 85–115 °C (Table I).

The IR spectra of the complexes and the free ligands are almost identical in the range 5000–650 cm^{-1}. This poses a difficulty in deciding whether the ligands are acting as bidentate via coordination through nitrogen and sulphur, or mono-dentate via either of these. The absence of the expected shift in the stretching frequency of ν(C=N) after coordination through nitrogen might be due to the conjugation of $\rangle$C=N group with phenyl groups on both sides. The assignment to ν(C–S) mode in the IR spectra of the complexes could not be made due to a large number of bands in this region. In the ^1H NMR spectra of the complexes, the aromatic hydrogens and the hydrogen atoms of the two methylene groups flanking sulphur form broad complex multiplets centred at δ 7.55–7.59 and δ 3.55–3.60, respectively, (broadening is due to the paramagnetic effect of iron(III)) (Table II) [14, 15]. There is downfield shift ($\Delta\delta$ 1.01–1.05) in the positions of aromatic hydrogens as compared to those in the free ligand (δ 6.54). The downfield shift in the positions of methylene protons is not significant ($\Delta\delta$ 0.14–0.19, free ligand, CH_2, 3.41). This amply

TABLE II. Electronic Spectra and ^{1}H NMR Data for the Complexes.

S. No.	Complex	Electronic spectra^a					^{1}H NMR data δ (value)
		d–d bands (cm^{-1})	Transition due to	Charge-transfer bands (cm^{-1})	Mixed bands (cm^{-1})	Ligand bands	
1	$[\mathrm{Fe(L\text{-}1)_4Cl_2}][\mathrm{FeCl_4}]$	12034 sh 14658 b	$^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_2(G)$	26247 m	32225 w	40817 s	7.55(m, 10H, ArH) 3.55(m, 4H, CH_2)
2	$[\mathrm{Fe(L\text{-}2)_4Cl_2}][\mathrm{FeCl_4}]$	12034 sh, 12723 sh, 14662 w, 15626 w	-do-	26247 m	32258 m 34483 w	39216 s	
3	$[\mathrm{Fe(L\text{-}3)_3Cl_2}][\mathrm{FeCl_4}]$	12122 sh 16162 w 17889 bw 19345 wb	$^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_2$ $^6A_1 \rightarrow {}^4T_2$	23809 m 26386 m 27778 m	32258 m 35587 w 34725 w	38216 s	
4	$[\mathrm{Fe(L\text{-}4)_4Cl_2}][\mathrm{FeCl_4}]$		T			38422 s^b	
5	$[\mathrm{Fe(L\text{-}1)_4Br_2}][\mathrm{FeBr_4}]$	10153 sh 14706 m 21053 bw	$^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_2(G)$ $^6A_1 \rightarrow {}^4T_2(D)$	29070 m	33670 vs	40817 s	7.59(m, 10H, ArH) 3.60(m, 4H, CH_2)
6	$[\mathrm{Fe(L\text{-}2)_4Br_2}][\mathrm{FeBr_4}]$	10965 sh 13158 w 14185 w 17442 w	$^6A_1 \rightarrow {}^4T_2(G)$ $^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_2(G)$ $^6A_1 \rightarrow {}^4T_2(D)$	26316 m	32895 m 35715 m	39683 s	
7	$[\mathrm{Fe(L\text{-}3)_4Br_2}][\mathrm{FeBr_4}]$	10870 w 12985 w 14280 w 17385 w	$^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_2(G)$ $^6A_1 \rightarrow {}^4T_2(D)$	27750 m	34842 vs	39540 s	
8	$[\mathrm{Fe(L\text{-}4)_4Br_2}][\mathrm{FeBr_4}]$	11628 sh 13514 sh 15625 b 17242 m	$^6A_1 \rightarrow {}^4T_1(G)$ $^6A_1 \rightarrow {}^4T_2(G)$ $^6A_1 \rightarrow {}^4T_2(G)$ $^6A_1 \rightarrow {}^4T_2(D)$	26316 m	35715 vs	41667	

[a] Solid state electronic spectra (Mgo). [b] Solution phase electronic spectrum (absolute alcohol).

TABLE III. Molar Conductance, Magnetic Moments, ESR and Far-IR Data of the Complexes.[a,b]

S. No.	Complex	Λ ohm^{-1}cm^2 mole^{-1} ^{c}	μ_{eff} (B.M.)	g-values	ν(Fe–X) (cm^{-1})	ν(Fe–N) (cm^{-1})
1	$[\mathrm{Fe(L\text{-}1)_4Cl_2}][\mathrm{FeCl_4}]$	52.4	5.84	2.026	368s	252sh, 235m
2	$[\mathrm{Fe(L\text{-}2)_4Cl_2}][\mathrm{FeCl_4}]$	59.4	5.99	2.011	380, 310w	
3	$[\mathrm{Fe(L\text{-}3)_4Cl_2}][\mathrm{FeCl_4}]$	55.9	5.97	2.019	357s	250w, 230m
4	$[\mathrm{Fe(L\text{-}4)_4Cl_2}][\mathrm{FeCl_4}]$	62.9			383s, 288w	255vw,235w
5	$[\mathrm{Fe(L\text{-}1)_4Br_2}][\mathrm{FeBr_4}]$	80.4	6.08		290w, 275s 220w	250m
6	$[\mathrm{Fe(L\text{-}2)_4Br_2}][\mathrm{FeBr_4}]$	73.4	6.15			
7	$[\mathrm{Fe(L\text{-}3)_4Br_2}][\mathrm{FeBr_4}]$	66.4	6.09		285s, 217w	245m
8	$[\mathrm{Fe(L\text{-}4)_4Br_2}][\mathrm{FeBr_4}]$	52.4	5.96			

[a] S = strong, sh = shoulder, w = weak, m = medium, b = broad. [b] μ_{eff} per iron ion. [c] Determined on the basis of molecular formula $FeL_2X_3 \cdot nH_2O$.

demonstrates that coordination through nitrogen is certain as phenyl groups are in the vicinity of nitrogen atoms.

Coordination through sulphur is further ruled out on the basis of far-IR and ESR spectral studies (Table III) which support the structures $[FeX_2L_4]$-$[FeX_4]\cdot nH_2O$, a phenomenon frequently observed in the iron(III) halide complexes with phosphine oxides and other ligands [16]. The chloride complexes show strong ν(Fe–Cl) bands in the range

357–382 cm^{-1} and these are characteristic ν_3 bands of $[FeCl_4]^-$ moiety [16]. Other bands attributable to $[FeCl_4]^-$ are either Raman-active or fall below 200 cm^{-1}. Similarly, the bromide complexes show strong ν_3 bands in the range 275–290 cm^{-1}, characteristic of $[FeBr_4]^-$ moiety. The ν_{as}(Fe–Cl) bands due to octahedral $[FeCl_2L_4]^+$ cation are very weak and appear in the range 288–310 cm^{-1}. The ν_{as}(Fe–Br) bands due to $[FeBr_2L_4]^+$ occur as weak bands in the range 217–220 cm^{-1} [16]. Tentative assignment to ν(Fe–N) bands has been made in the range 230–255 cm^{-1} [17]. The ESR spectra of the chloride complexes show g_{eff} values in the range 2.011–2.026 and these also strongly support tetrahedral moiety $[FeCl_4]^-$. The bands due to $[FeCl_2L_4]^+$ cation being weak have probably escaped detection. Alternatively, this may be attributed to exchange interaction as noted in systems like $[FeCl_2(Me_2SO)_4][FeCl_4]$ having a g-value of 2.0 [18]. The bands due to adsorbed water appear in the range 3250–3350 cm^{-1} and 1645–1670 cm^{-1} for ν(OH) and δ(HOH), respectively [19, 20]. The molar conductance values (Table I) are not compatible with the structures $[FeL_4X_2][FeX_4]\cdot nH_2O$ arrived at from solid state studies, indicating that there is considerable ionization of the complexes in solution phase.

The magnetic moment value (μ_{eff} 5.84–6.15 BM per iron ion) lie in the range generally reported for high spin iron(III) complexes (Table III) [21–27]. These data further indicate that the complexes are monomeric, as in the case of polymeric complexes either ferromagnetic or antiferromagnetic interactions between adjacently placed iron(III) ions might result in an increase or decrease respectively from the normal magnetic moment value. The solid-state electronic spectra of iron(III) complexes exhibit bands in the ranges (i) 10153–17889 cm^{-1} (ii) 26247–29070 cm^{-1}, (iii) 32225–35715 cm^{-1} and (iv) 38462–41667 cm^{-1}. The peaks in the region 10153–17889 cm^{-1} have been attributed to spin-forbidden d–d transitions from $^6A_{1g}$ to $^4T_1(G)$ or $^4A_1(G)$ or $^4E(G)$ or $^4T_2(D)$ characteristic of high-spin iron(III) $[FeX_4]^-$ ion (Table II) [28–33]. The intense bands in the region 26247–29070 cm^{-1} are ligand-to-metal charge transfer transitions [23, 26]. The bands in the region 32225–35715 cm^{-1} might be due to the combination of the internal ligand transitions with charge transfer transitions, as the intensity of these bands in the complexes is far more greater than that in the free ligand. The d–d bands for the cations $[FeX_2L_4]^+$ expected in the range 21000–35000 cm^{-1} have been obscured by the intense change transfer bands. The very strong bands in the region 33462–41667 cm^{-1} are due to the internal ligand transition ($\pi \rightarrow \pi^*$), which is identical with that in the free ligand.

Mössbauer spectral data of three iron(III) chloride complexes show a well-resolved asymmetric

TABLE IV. Mössbauer, t.g.a and d.t.a Data for Iron(III) Complexes with 1,4,5-Thiadiazepines.

S. No.	Complex	Mössbauer data		TGA^a Loss % at (°C)	Assignment	DTA^b peak temp. (°C)	Assignment
		I.S. (δ mm/sec)	Q.S. (Δmm/sec)				
1	$[Fe(L\text{-}1)_3Cl_2][FeCl_4]$	0.572 ± 0.03	0.632 ± 0.03	2.1(120) 87.5(800)	$2H_2O$ L-1 + Cl_3	120endo 160–390 (340)endo 410exo	Melting/loss of H_2O Decomp.
2	$[Fe(L\text{-}2)_4Cl_2][FeCl_4]$	0.407 ± 0.03	0.389 ± 0.03	2.2(120) 88.9(760)	$2H_2O$ L-2 + Cl_3	125endo 170–390 endo 420exo	Melting/loss of H_2O Decomp.
3	$[Fe(L\text{-}3)_4Cl_2][FeCl_4]$	0.619 ± 0.03	0.672 ± 0.03				
5	$[Fe(L\text{-}1)_4Br_2][FeBr_4]$			2.5(120) 86.8(720)	$2H_2O$ L-1 + Br_2	120endo 190–360endo 370–430 (380)exo	Melting/loss of H_2O Decomp.
6	$[Fe(L\text{-}2)_4Br_2][FeBr_4]$			3.5(120) 89.80(800)	$4H_2O$ L-2 + Br_3	110endo 250–380endo 390–450 (410)exo	Melting/loss of H_2O Decomp.

[a] The number of water molecules indicated by t.g.a is less than that shown by analytical data. This may be attributed to the fact that while recording t.g.a. precautions were taken to avoid their contact with the moisture due to their highly hygroscopic nature.

[b] DTA: Endo: endothermic effect, Exo: exothermic effect, Decomp. = decomposition.

quadruply-split doublet at room temperature (303 ± 2 K) (Table IV). The isomer shifts relative to sodium nitroprusside lie in the range δ 0.407 to 0.619 mm s^{-1} and are well within the range expected for high-spin iron(III) complexes [34–37]. The asymmetry in the peaks is attributed to merging of the absorption peak of $[FeCl_4]^-$ with one peak of the quadruply-split doublet of octahedral $[FeCl_2L_4]^+$ cations. Hence Mössbauer spectral data also support the octahedral structure for the cation and tetrahedral structure for the anion. The quadrupole splittings (0.389–0.672 mms) are diagnostic of high spin iron(III) with octahedral stereochemistry [36]. The quadrupole splitting constant of complexes **1** and **3** have almost twice the values observed in complex 2, which clearly shows that the stereochemistry of the former two is *trans* while that of the latter is *cis* [38]. Low values for δ in case of the complex $[FeCl_2(L\text{-}2)_4]^+$ might be attributed to the effect of CH_3 substituent in the phenyl group. The +ve inductive effect of the CH_3 group would enhance the donor property of nitrogen atoms, which in turn would transfer a greater s-electron density on the iron(III) ion, resulting in the negative shift in the values of isomer shift. Iron(III) bromide complexes did not show Mössbauer absorption, probably due to heavy atom absorption (bromine).

The presence of water in these complexes is supported by IR and t.g.a studies. In the t.g.a the loss in weight sets in at *ca.* 80 and up to *ca.* 120 ℃, the weight loss corresponds to nH_2O (Table IV). In d.t.a at a temperature of 110–125 ℃ a very weak endothermic effect is recorded, which might be assigned either to the melting of the complexes, or to the loss of uncoordinated or lattice water held loosely in the complexes. The d.t.a curves of these complexes show one broad strong endothermic peak in the temperature range 160–390 ℃ and an exothermic peak at 370–450 ℃. These peaks have been assigned tentatively to the slow decomposition of the complexes with loss of sulphur, nitrogen and other gases during the decomposition of the ligands. In t.g.a the loss in weight occurs continuously and no stable intermediate species could be obtained, precluding the exact assignment to the endo- or exo-thermic peaks in d.t.a data.

Conclusion

The complexes possess unidentate ligands via coordination through one nitrogen atom and have the formulation $[FeX_2L_4][FeX_4]\cdot nH_2O$. The cations $[FeX_2L_4]^+$ have octahedral structures while the anions $[FeX_4]^-$ are tetrahedral. The unidentate behaviour of these ligands is in sharp contrast to the bidentate coordination reported earlier involving Zn(II), Cd(II), Pd(II) and Pt(II) ions [10–12]. The difference is probably caused by the higher valent state of iron(III), which being a hard Lewis acid is not favouring interaction with soft sulphur. Consequently the cations $[FeX_2L_4]^+$ contain (FeN_4) chromophores with a *cis* or a *trans* configuration.

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References

1 F. D. Pope and A. C. Noble, *Adv. Heterocycl. Chem., 8,* 21 (1967).
2 S. J. Childress and S. I. Gluckman, *J. Pharm. Sci., 53,* 577 (1964).
3 L. H. Sternbach and E. Reeder, *J. Org. Chem., 26,* 4936 (1961).
4 S. C. Bell, T. S. Sulkowski, C. Goachman and S. J. Childress, *J. Org. Chem., 27,* 562 (1962).
5 S. C. Bell and S. J. Childress, *J. Org. Chem., 27,* 1691 (1962).
6 S. S. Sandhu, S. S. Tandon and H. Singh, *J. Chem. Sci. (GNDU), 2,* 1 (1977); *Chem. Abstr., 89,* 901889 (1978).
7 C. Preti and G. Tosi, *J. Inorg. Nucl. Chem., 41,* 263 (1979).
8 A. Mosset, J. P. Tuckagues, J. J. Bonnet, R. Naran and P. Sharrock, *Inorg. Chem., 19,* 290 (1980).
9 C. Preti and G. Tosi, *J. Coord. Chem., 6,* 81 (1976).
10 S. S. Sandhu, S. S. Tandon and H. Singh, *J. Inorg. Nucl. Chem., 41,* 1239 (1979).
11 S. S. Sandhu, S. S. Tandon and H. Singh, *J. Inorg. Nucl. Chem., 40,* 1967 (1979).
12 S, S. Sandhu, S. S. Tandon and H. Singh, *Inorg. Chim. Acta, 34,* 81 (1979).
13 M. N. Hughes, 'Bio-Inorganic Chemistry', Wiley, London, 1974, p. 283.
14 S. S. Sandhu, S. S. Tandon and H. Singh, *Indian J. Chem., 19B,* 1023 (1980);
(a) D. R. Eaton and W. D. Phillips, *Adv. Magn. Reson., 1,* 103 (1963);
(b) D. R. Eaton, *J. Am. Chem. Soc., 87,* 3097 (1965).
15 N. S. Angerman and R. S. Tordan, *Inorg. Chem., 8,* 2579 (1969).
16 S. A. Cotton, *Coord. Chem. Rev., 8,* 185 (1972).
17 J. R. Ferraro and K. C. Davis, *Inorg. Chim. Acta, 3,* 685 (1969).
18 S. A. Cotton and J. F. Gibson, *J. Chem. Soc.,* 1690 (1971).
19 C. Fregni, C. Preti, G. Tosi and G. Verani, *J. Inorg. Nucl. Chem., 37,* 1837 (1975).
20 A. N. Speca, N. M. Karayannis and L. L. Pytlewski, *Inorg. Chim. Acta, 9,* 87 (1974).
21 B. F. Hoskins and C. D. Pannan, *Inorg. Nucl. Chem. Lett., 11,* 409 (1975).
22 P. G. Simpson, A. Vincigerra and J. V. Quagliano, *Inorg. Chem., 2,* 282 (1963).
23 S. K. Madan and M. E. Bull, *J. Inorg. Nucl. Chem., 26,* 221 (1964).
24 W. M. Reiff and W. A. Baker, *Inorg. Chem., 9,* 570 (1970).

25 S. W. Maccann, F. V. Wells, J. P. Collman, H. H. Wickman and T. N. Sorrell, *Inorg. Chem., 19,* 621 (1980).

26 M. C. Jain, R. K. Sharma and P. C. Jain, *J. Inorg. Nucl. Chem., 42,* 1229 (1980).

27 K. S. Patel and A. A. Adimado, *J. Inorg. Nucl. Chem., 42,* 1241 (1980).

28 J. A. Walmsley and S. Y. Tyree, *Inorg. Chem., 2,* 312 (1965).

29 F. A. Cotton and E. Bannister, *J. Chem. Soc.,* 1878 (1960).

30 R. Bemhi, *Indian J. Chem., 15A,* 316 (1977).

31 A. R. Ginsberg and M. B. Robin, *Inorg. Chem., 2,* 817 (1963).

32 H. Yamatera and A. Kato, *Bull. Chem. Soc. Jpn., 41,* 2220 (1981).

33 C. Jorgansen, *Discuss. Faraday Soc., 26,* 110 (1958).

34 W. M. Reiff, W. A. Baker (Jr.) and N. E. Brickson, *J. Am. Chem. Soc., 90,* 4794 (1968).

35 N. N. Greenwood and T. C. Gibb, 'Mössbaur Spectroscopy', Chapman and Hall, London, 1971.

36 S. L. Kessel and D. N. Hendrickson, *Inorg. Chem., 19,* 1883 (1980).

37 S. L. Kessel, R. M. Emberson, P. G. Rebrunner and D. N. Hendrickson, *Inorg. Chem., 19,* 1170 (1980).

38 'Mössbauer Spectroscopy and its Applications', International Atomic Energy Agency, Vienna, 1972, p. 287.