Inorganica Chimica Acta, *173* (1990) 31–35

Cobalt(II), Nickel(II) and Iron(III) Halide Adducts with Theobromine*

CHESTER M. MIKULSKI, SCOTT GROSSMAN, MONICA L. BAYNE, MICHELE GAUL, DOROTHY KANACH, KIMBERLY UDELL

Department of Chemistry and Physics, Beaver College, Glenside, PA 19038 (U.S.A.)

and NICHOLAS M. KARAYANNIS**

Amoco Chemical Company, P.O. Box 3011, Naperville, IL 60566 (U.S.A.)

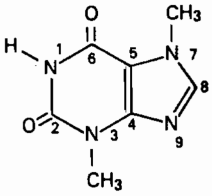
(Received November 13, 1989)

Abstract

Adducts of theobromine (L) with Co(II) and Ni(II) chlorides, bromides and iodides and Fe(III) chlorides and bromides were synthesized by refluxing 2:1 molar mixtures of L and the hydrated metal salt in triethyl orthoformate–ethyl acetate. Solid complexes of the CoL_2X_2 (X = Cl, Br), $CoL_2I_2 \cdot H_2O$, $NiL_2X_2 \cdot 2H_2O$ (X = Cl, Br, I) and $FeL_2X_3 \cdot H_2O$ (X = Cl, Br) types were isolated. Characterization studies suggest that the new adducts are neutral monomeric with terminal unidentate L, halo and, wherever applicable, aqua ligands. The Co(II) complexes are distorted tetrahedral for X = Cl, Br and pentacoordinated for X = I, while the Ni(II) and Fe(III) adducts are hexacoordinated. The pyrimidine N1 and imidazole N9 ring nitrogens were considered as equally likely to act as the binding site of terminal theobromine.

Introduction

Methyl derivatives of xanthine (xnH; 2,6-dioxopurine) are important components of tea, coffee, cocoa and chocolate products and have found medicinal applications as stimulants, diuretics and in heart disease and cancer therapy [2, 3]. Their metal complexes are increasingly attracting attention. Among dimethylxanthines, the metal complexes of theophylline (tpH; 1,3-dimethylxanthine) have been studied rather extensively [4, 5], whilst for those of theobromine (tbH; I; L; 3,7-dimethylxanthine) a relatively limited number of reports have appeared. These include 3d metal perchlorate [6, 7], Cu(II) propionate [8] and a number of 4d and 5d metal chloride [9–11] or carbonyl 12] theobromine complexes. These laboratories have recently reported synthetic and characterization studies of Co(II), Ni(II) and Fe(III) halide complexes with xnH, hypoxanthine (hxH) [13–15] and caffeine (caf; 1,3,7-trimethylxanthine) [16]. We have now extended our earlier work on theobromine metal complexes [6, 7, 10, 11] to include its adducts with Co(II) and Ni(II) chlorides, bromides and iodides and Fe(III) chloride and bromide [1]. These studies are reported in the present paper.



I

Experimental

The synthetic method employed was as follows. One mmol of hydrated metal salt was dissolved in 25 ml of a 7:3 (vol./vol.) mixture of triethyl orthoformate (teof)–ethyl acetate (ea), and the solution was stirred under reflux for 1 h. Two mmol of tbH were mixed with 25 ml of 7:3 teof–ea, and the mixture was warmed to form a slurry, which was added to the stirring, refluxing metal halide solution. The resultant mixture was refluxed for one week. Then, the mixture was allowed to cool to room temperature, the solid complex formed was collected by gravity filtration, washed thoroughly with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. Adducts involving a 2:1 tbH to metal molar ratio were generally obtained. The $CoCl_2$ and $CoBr_2$ adducts are anhydrous, those of CoI_2 and FeX_3 (X = Cl, Br) monohydrates, and the three Ni(II) complexes dihydrates, as shown by the analytical data of Table 1. They are sparingly soluble in organic media, showing increased solubility in binary solvent mixtures such as nitromethane–acetone. Infrared spectra (Table 2) were recorded on KBr discs (4000–500 cm^{-1}) and Nujol mulls between high density polyethylene windows (700–

---

*Presented in part at PACIFICHEM '89, see ref. 1.

**Author to whom correspondence should be addressed.

00201693/90/$3.50

TABLE 1. Analytical data[a]

Complex	Color	Found (calc.) (%)				
		C	H	N	M	X
CoL_2Cl_2	light blue	34.0(34.3)	2.9(3.3)	21.2(21.3)	12.1(12.0)	14.2(14.5)
CoL_2Br_2	light blue	29.0(29.0)	2.9(2.8)	19.6(19.4)	10.4(10.2)	28.0(27.6)
$CoL_2I_2 \cdot H_2O$	green	24.1(24.3)	2.9(2.6)	16.2(16.2)	8.8(8.5)	37.3(36.7)
$NiL_2Cl_2 \cdot 2H_2O$	pale green	32.2(32.0)	3.8(3.8)	21.6(21.3)	11.4(11.2)	13.7(13.5)
$NiL_2Br_2 \cdot 2H_2O$	pale green	27.6(27.4)	3.4(3.3)	17.9(18.2)	9.8(9.6)	25.6(26.0)
$NiL_2I_2 \cdot 2H_2O$	mint green	24.0(23.7)	2.9(2.8)	15.5(15.8)	8.1(8.3)	35.2(35.8)
$FeL_2Cl_3 \cdot H_2O$	off-white	30.8(31.1)	3.5(3.4)	21.0(20.7)	10.7(10.3)	20.1(19.7)
$FeL_2Br_3 \cdot H_2O$	beige	25.3(25.0)	2.9(2.7)	16.2(16.6)	8.5(8.3)	35.1(35.6)

[a]The complexes were obtained in yields ranging between 62 and 76%.

100 cm^{-1}) using Perkin-Elmer 621 and (for the CoI_2, $NiBr_2$ and NiI_2 complexes) 181 spectrophotometers. Solid-state (Nujol mull) electronic spectra, ambient temperature (300 K) magnetic susceptibility and conductance (on 10^{-3} M solutions of the complexes in 1:1 (vol./vol.) nitromethane–acetone at 25 °C) measurements (Table 3) were obtained by methods previously described [17].

Results and Discussion

The new metal complexes are generally adducts of neutral tbH, involving 2:1 L to metal ion ratios, as already mentioned. Among previously reported theobromine complexes, those with 3d metal salts [6–8] and $K\{Pt(tbH)Cl_3\} \cdot H_2O$ [9] are also neutral tbH adducts, $Rh(CO)(tb)(PPh)_3$ contains anionic tb^- [12], and complexes with Pd(II), Pt(IV) [10] and oxozirconium(IV) [11] chlorides involve both neutral tbH and anionic tb^- ligands [10, 11]. It should be noted here that $(tbH)_2I_2O_8$ [18] and theobromine complexes with Brönsted and carboxylic acids [19] and Na benzoate [20] were also studied in the past. As regards the function of teof as a dehydrating agent [21] in the synthetic work herein reported, it proved effective only in the case of the $CoCl_2$ and $CoBr_2$ adduct preparation, while in the remaining cases hydrated complexes were isolated (Table 1).

IR band assignments for free tbH (Table 2) were based on our previous work [6, 7, 10, 11] and other IR studies of free theobromine and its complexes [12, 19, 22], as well as band assignments for xnH [23], tpH [4] and caf [24–26]. Among the ligand bands in the νCH + νNH region, those at 3112 and 2825 cm^{-1} involve νC8–H contribution, while those at 3150 and 3030 cm^{-1} are probably pure νNH absorptions [4, 6, 7, 10, 11, 19, 22–26]. In view of the fact that νC2=O and νC6=O were respectively assigned at 1702 and 1660 in the spectrum of caf [26], and at 1672 and 1702 cm^{-1} in that of xnH [23], their assignment for tbH was not attempted. In the spectra of the new complexes, the νCH + νNH bands of tbH remain virtually unchanged, since these compounds contain neutral tbH, which involves one protonated ring nitrogen. The two νC=O bands of the free ligand are relatively insensitive to complex formation, whilst the νC=C, νC=N and ring vibrational modes at 1600–1120 cm^{-1} undergo more significant shifts and occasional splittings in the spectra of the adducts. These features favor tbH coordination via a ring nitrogen and rule out the participation of C=O oxygens in coordinative bonding interactions with the metal ions [4, 6, 7, 10–12, 23, 26, 27]. The hydrated new adducts exhibit the νOH and δHOH modes of coordinated water at 3450–3390 and 1640–1630 cm^{-1}, respectively [28]. Distinction of νM–ligand bands from the tbH absorptions in the 500–100 cm^{-1} region [29] was generally possible. Tentative assignments for the former modes were based on our recent studies of complexes of xnH and hxH with the same metal halides [13–15], as well as similar assignments for various Co(II), Ni(II) or Fe(III) halide [30–39] and aqua [13, 36–38] complexes. These assignments (Table 2) show the expected trends of νM–X wavenumber decreases in moving from X = Cl to X = Br to X = I [13–15, 30–39], which are also substantiating the νM–N band assignments [14], and favor coordination numbers six for the Ni(II) and Fe(III) complexes [14–16, 31, 33–39], five for the CoI_2 [13, 30–33, 36, 37] and four for the $CoCl_2$ and $CoBr_2$ adducts [13, 30–35, 38].

The molar conductivities of the complexes correspond to non-electrolytes [40], while their room temperature magnetic moments are normal for high-spin tetrahedral or pentacoordinated Co(II) and hexacoordinated Ni(II) or Fe(III) compounds [41, 42]. The $\pi \rightarrow \pi^*$ transition bands of tbH (232, 273 nm) [6, 7, 10, 11, 43] undergo shifts toward lower energies, as well as occasional splittings upon metal halide complex formation (Table 3). The $n \rightarrow \pi^*$ transition occurs at 303–309 nm in the spectra of the complexes [44], which are also charac-

TABLE 2. Pertinent infrared spectral data (cm^{-1})

tbH*	M = Co, X = Cl	M = Co, X = Br	M = Co, X = I	M = Ni, X = Cl	M = Ni, X = Br	M = Ni, X = I	M = Fe, X = Cl	M = Fe, X = Br	Band assignment[a]
			3440m,b	3390m,b	3395m,b	3450m,b	3390m,b	3415m,b	νOH (aqua)
3150m,3112m 3030m,2825m	3162m,3122m 3040m,2827w	3160m,3118m 3025m,2822w	3170m,3111m 3037m,2821w	3167m,3116m 3032m,2824w	3162m,3115m 3031m,2828w	3170m,3124m 3035m,2830w	3165m,3120m 3032m,2822w	3168m,3117m 3043m,2830w	νCH + νNH
1685vs,b 1660vs,b	1692vs 1670vs	1694vs 1668vs	1691vs 1662vs	1686vs 1664vs	1690vs 1665vs	1692vs 1670vs	1685vs 1667vs	1688vs 1670vs	νC=O
1595s,sh 1547m,b	1602m,1591m 1560m,1545m	1592m,1557m 1541m,1520w	1640s,sh 1600m,1589m 1561m,1542m	1635s,sh 1595m,1588m 1555m,1537m	1635s,sh 1595m,1588m 1563m,1541m	1633s,sh 1600m,1592m 1557m,1546m	1640s,sh 1612m,1594m 1560m,1545m	1637s,sh 1610m,1592m 1561m,1544m	δHOH + νC=C + νC=N + δNH
1479w,sh 1449s,1422m 1360s,1335m 1290m,1222m 1152mw,b 1121mw,b	1491m,1470m, 1451m,1440m 1424m,1409m 1390w,1367m 1330w,1290m 1265w,1221s 1204m,1170w 1137m	1495m,1467m 1456m,1425w 1413m,1390w 1370m,1336w 1297w,1262w 1227s,1204w 1177w,1165w 1141m	1488m,1464m 1453m,1422m 1411m,1392w 1366m,1328w 1300w,1267w 1224s,1202w 1180w,1166w 1138m	1481m,1459m 1447m,1430m 1417m,1398w 1370m,1333w 1296w,1260w 1227s,1200w 1183w,1167w 1133m	1486m,1464m 1455m,1426w 1412m,1393w 1369m,1333w 1292m,1262w 1222s,1206m 1179w,1169w 1137m	1487m,1461m 1455m,1427w 1412m,1388w 1366w,1338w 1303w,1275w 1227s,1205m 1172mw 1142ms	1479m,1460m 1451m,1419m 1408m,1392w 1370m,1336w 1297m,1260w 1222s,1203m 1199w,1172w 1138m	1482m,1458m 1457m,1420m 1410m,1395w 1367m,1333w 1300m,1264w 1222s,1207m 1188w,1170w 1142ms	ring vibrations + νC–N + δCH$_3$
598m,552w 525w,505w 489w,435w 402vw,381vw 350vw,310vw 261w,235mw	600w,548vw 510mw,490vw 456mw,420w 390w,370w	595w,552vw 506mw,487vw 452mw,424w 378w,355vw 315w,303w	589w,558w 515w,480vw 418w,sh 380w,359vw 323w,300w,b	602w,555vw 510w,490vw 450w,390w 370w,350vw 313w,265w	597w,552w 508w,485vw 445w,385w 372w,351vw 310w,260w	598w,545vw 512w,495vw 447w,382w 368w,350vw 311w,264w	596w,550vw 486w,sh 452w,390w 300w,261w 244mw,b	602w,557vw 483w,sh 455w,386w 372w,348vw 313w,302w	νtbH at 600–200 cm^{-1}
			440mw	414mw	418mw	420mw	500mw	495mw	νM–O (aqua)
	352w,327mw	263w,236mw	195w,b	256w,245w	181w,b	139w,b	354m,337m 318mw	247m,237mw 219w	νM–X
	296w,281w 248w	292w,276w 248vw	267w,241w	240w,221w	242w,219w	245w,223w	284w,270w	279w,266w	νM–N

[a] For free tbH band assignments see text.

TABLE 3. Solid state (Nujol mull) electronic spectra, magnetic susceptibilities at 300 °K and molar conductivities of the new tbH metal complexes[a]

M	X	λ_{max} (nm)	$10^6 \times \chi_M^{cor}$ (cgsu)	μ_{eff} (μB)	Λ_M (Ω^{-1} cm^2 mol^{-1})
Co	Cl	198vvs, 242vvs, 284vvs, 305vs,sh, 352s, 555ms, 620s, 660s, 705ms, 1390mw, 1640w, 1890mw, 2110mw	8790	4.60	17
Co	Br	199vvs, 244vvs, 281vvs, 303vs,sh, 349s, 548ms, 616s, 652s, 730ms, 1365mw, 1650w, 1920w, 2150mw	8843	4.62	20
Co	I	202vvs, 239vvs, 282vvs, 309vs,sh, 350s, 461s, 550m, 630m, 745mw, 869mw, 995w, 1870mw,b	8245	4.47	26
Ni	Cl	199vvs, 239vvs, 280vvs, 306vs,sh, 351s, 440ms, 642mw, 705mw, 829w, 1026w, 1229w,b	4002	3.11	18
Ni	Br	200vvs, 244vvs, 279vvs, 305vs,sh, 347s, 447ms, 650mw, 716mw, 832w, 1026w, 1241w,b	4097	3.14	17
Ni	I	200vvs, 240vvs, 278vvs, 304vs,sh, 352s, 460ms, 656w, 732mw, 834w, 1045w, 1262w,b	3730	3.00	29
Fe	Cl	203vvs, 239vvs, 281vvs, 308vs,sh, 353s, 441m,sh, 530mw,b	14, 182	5.84	8
Fe	Br	204vvs, 242vvs, 278vvs, 307vs,sh, 353s, 447m,sh, 540mw,b	14, 948	6.02	13

[a] UV spectrum of free tbH (Nujol mull) (nm): 200vvs, 232vs, 273vvs, 301s,sh [7]. In aqueous solution at pH 6–7: 271 nm, log ϵ 4.01 [43]. Conductance measurements performed on 10^{-3} M solutions of the adducts in 1:1 (vol./vol.) nitromethane–acetone at 25 °C.

terized by strong metal-to-ligand charge-transfer absorption [45], originating in the UV and trailing off into the visible region. The d–d transition spectra of the Ni(II) complexes are compatible with low-symmetry hexacoordinated configurations [4, 7, 14, 36, 46], i.e. $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 440–460; $\rightarrow {}^3T_{1g}(F)$, $^1E_g(D)$ 642–656, 705–732, 829–834; $\rightarrow {}^3T_{2g}(F)$ 1026–1045, 1229–1262 nm. Approximate *Dq* value calculations (887, 877 and 867 cm^{-1} for X = Cl, Br and I, respectively) are consistent with the presence of $NiN_2O_2X_2$ chromophores [36], and show the expected trend of decrease with X variation from Cl to Br to I [47]. The d–d spectra of the Co(II) chloride and bromide adducts are typical for pseudotetrahedral compounds of this metal ion [13, 30–32, 38, 48], viz. $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ 548–555, 616–620, 652–660, 705–730; $\rightarrow {}^4T_{1g}(F)$ 1365–1390; 1640–1650, 1890–1920; $\rightarrow {}^4T_{2g}(F)$ 2110–2150 nm. The d–d transition spectrum of the CoI_2 complex shows seven maxima at 461–1870 nm, substantially less intense than the absorption bands of the preceding tetrahedral complexes, and compatible with a pentacoordinated configuration [13, 36, 49, 50]. Finally, the weak d–d transitions of the Fe(III) adducts [51] overlap with the stronger charge-transfer absorption in the visible region.

The overall evidence presented, combined with the solubility of the new complexes in organic media, favors the formulation of these compounds as monomeric, neutral species, involving exclusively terminal unidentate ligands. The hexacoordinated adducts are presumably of the $\{Ni(tbH)_2X_2(OH_2)_2\}$ (X = Cl, Br, I) and $\{Fe(tbH)_2X_3(OH_2)\}$ (X = Cl, Br) types, involving $NiN_2O_2X_2$ and FeN_2OX_3 absorbing species, respectively. The Co(II) complexes may be formulated as distorted tetrahedral $\{Co(tbH)_2X_2\}$ (X = Cl, Br) and pentacoordinated $\{Co(tbH)_2I_2(OH_2)\}$, with CoN_2X_2 and CoN_2OI_2 chromophores, respectively. As regards the likely binding site of terminal tbH, the free ligand is protonated at N1 [52, 53], as shown in I. Purines have the tendency to use the ring nitrogen which is protonated in the free base as their primary binding site, but, on the other hand, their imidazole ring nitrogens are more prone than the pyrimidine ring nitrogens to coordinate to metal ions [54]. In view of this, N1 and N9 were considered in the past as about equally likely to act as the binding site of unidentate terminal tbH [6, 8]. The only crystal structure determination of a tbH metal complex available is that of $K\{Pt(tbH)Cl_3\} \cdot H_2O$, in which the ligand is N9-bound to the platinum ion [9]. However, this compound was prepared under acidic conditions [9] and is not necessarily characteristic of the binding tendencies of tbH [7]. In fact, tpH was found to bind via N9 only in a number of complexes [55, 56], prepared under sufficiently acidic conditions to preclude ionization at N7 [57], while in most of its metal complexes this ligand binds via N7 [4, 5, 58–60], which is the protonation site of free tpH. Hence it is not possible at this point to distinguish between the imidazole N9 and the pyrimidine N1 ring nitrogens as the primary binding site of terminal unidentate theobromine [7, 10, 11].

References

1 C. M. Mikulski, S. Grossman, M. L. Bayne, M. Gaul and N. M. Karayannis, *1989 Int. Congress Pacific Basin Socs., PACIFICHEM '89, Honolulu, HI, U.S.A., Dec. 17–22, 1989*, Abstr. No. INOR 63.

2 R. H. Barry, H. Rubin, J. B. Johnson and J. H. Lazarus, *J. Pharm. Sci., 70* (1981) 204.

3 J. E. Byfield, J. Murnane, J. F. Ward, P. Calabro-Jones, M. Lynch and F. Kulhanian, *Br. J. Cancer, 43* (1981) 669.

4 C. M. Mikulski, M. K. Kurlan, S. Grossman, M. L. Bayne, M. Gaul and N. M. Karayannis, *J. Coord. Chem., 15* (1987) 347, and refs. therein.

5 W. J. Birdsall, B. W. Pfennig and J. L. Toto, *Polyhedron, 8* (1986) 1357; D. Cozak, A. Mardhy, M. J. Olivier and A. L. Beauchamp, *Inorg. Chem., 25* (1986) 2600; S. Bhatia, N. K. Kaushik and G. S. Sodhi, *J. Chem. Res. M*, (1987) 1519; J. Lorberth, W. Massa, M. El-Essawi and L. Labib, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1160; G. Pneumatikakis, A. Yannopoulos, J. Markopoulos and C. Angelopoulos, *Inorg. Chim. Acta, 152* (1988) 101.

6 C. M. Mikulski, T. B. Tran, L. Mattucci and N. M. Karayannis, *Inorg. Chim. Acta, 78* (1983) 269.

7 C. M. Mikulski, M. K. Kurlan, M. L. Bayne, M. Gaul and N. M. Karayannis, *J. Coord. Chem., 17* (1988) 267.

8 M. Melník and P. Sharrock, *XXIII ICCC, Boulder, CO, U.S.A., July 29–Aug. 3, 1984*, Abstr. THa-44-7.

9 E. H. Crowston, D. M. L. Goodgame, P. B. Hayman, A. M. Z. Slawin and D. J. Williams, *Inorg. Chim. Acta, 122* (1986) 161.

10 C. M. Mikulski, S. Grossman, C. J. Lee and N. M. Karayannis, *Transition Met. Chem., 12* (1987) 21.

11 C. M. Mikulski, S. Grossman and N. M. Karayannis, *J. Less-Common Met., 136* (1987) 41.

12 W. Beck and N. Kottmair, *Chem. Ber., 109* (1976) 970.

13 C. M. Mikulski, S. Grossman, M. L. Bayne, M. Gaul, D. L. Staley, A. Renn and N. M. Karayannis, *Inorg. Chim. Acta, 161* (1989) 29.

14 C. M. Mikulski, M. Gaul, M. L. Bayne, S. Grossman, A. Renn, D. L. Staley and N. M. Karayannis, *Transition Met. Chem., 14* (1989) 336.

15 C. M. Mikulski, M. L. Bayne, S. Grossman, M. Gaul, A. Renn, D. L. Staley and N. M. Karayannis, *J. Coord. Chem., 20* (1989) 185.

16 C. M. Mikulski, M. Gaul, D. L. Staley and N. M. Karayannis, *Transition Met. Chem., 14* (1989) 159.

17 N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3* (1969) 415; C. M. Mikulski, J. Fleming, D. Fleming and N. M. Karayannis, *Inorg. Chim. Acta, 144*, 9 (1988).

18 F. H. Herbstein and M. Kapon, *Phil. Trans. R. Soc. London, Ser. A, 291* (1979) 14.

19 D. Cook and Z. R. Regnier, *Can. J. Chem., 45* (1967) 2899; *46* (1968) 3055.

20 J. Nishijo and I. Yonetani, *J. Pharm. Sci., 71* (1982) 354.

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

22 E. R. Blout and M. Fields, *J. Am. Chem. Soc., 72* (1950) 479.

23 F. Allaire and A. L. Beauchamp, *Can. J. Chem., 62* (1984) 2249.

24 D. Cook and Z. R. Regnier, *Can. J. Chem., 45* (1967) 2895.

25 S. Goenechea, *Mikrochim. Acta*, (1972) 276.

26 J. De Taeye and T. Zeegers-Huyskens, *Spectrosc. Lett., 19* (1986) 299.

27 S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull., 26* (1978) 2941.

28 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 20* (1964) 429.

29 C. P. Beetz, Jr. and G. Ascarelli, *Spectrochim. Acta, Part A, 36* (1980) 299.

30 T. Beringhelli, M. Freni, F. Morazzoni, P. Romiti and R. Servida, *Spectrochim. Acta, Part A, 37* (1981) 763.

31 M. A. Guichelaar and J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 97* (1978) 295.

32 N. B. Behrens, D. M. L. Goodgame and Z. Warnke, *Inorg. Chim. Acta, 31* (1978) 257.

33 J. R. Ferraro, J. Zipper and W. Wozniak, *Appl. Spectrosc., 23* (1969) 160; J. R. Ferraro, W. Wozniak and G. Roch, *Ric. Sci., 38* (1968) 433.

34 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4* (1965) 350; *Spectrochim. Acta, 22* (1966) 1081.

35 M. Goldstein, F. B. Taylor and W. D. Unsworth, *J. Chem. Soc., Dalton Trans.*, (1972) 418; M. Goldstein, *J. Inorg. Nucl. Chem., 37* (1975) 567.

36 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta, 46* (1980) 235.

37 C. M. Mikulski, S. Cocco, N. DeFranco, T. Moore and N. M. Karayannis, *Inorg. Chim. Acta, 106* (1985) 89.

38 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 107* (1985) 81, 147; *108* (1985) L35.

39 C. M. Mikulski, S. Cocco, N. DeFranco and N. M. Karayannis, *Inorg. Chim. Acta, 80* (1983) L23; C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 92* (1984) 275.

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

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

42 L. Sacconi, *J. Chem. Soc. A*, (1970) 248.

43 W. Pfleiderer and G. Nübel, *Justus Liebigs Ann. Chem., 647* (1961) 155.

44 L. B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc., 87* (1965) 11; L. B. Clark, *J. Am. Chem. Soc., 99* (1977) 3934.

45 A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1962) 1235; (1963) 3156, 5042; (1964) 1187, 4761.

46 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7* (1968) 1835.

47 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968, pp. 204, 333–349.

48 P. C. Tellinghuisen, W. T. Robinson and C. J. Wilkins, *J. Chem. Soc., Dalton Trans.*, (1985) 1289.

49 I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 14* (1975) 1639.

50 M. Ciampolini and N. Nardi, *Inorg. Chem., 5* (1966) 41, 1150.

51 H. Schläfer, *Z. Phys. Chem., 4* (1955) 116; M. Dvir and W. Low, *Phys. Rev., 119* (1960) 1587.

52 D. Lichtenberg, F. Bergmann and Z. Neiman, *J. Chem. Soc. C*, (1971) 1676.

53 Li-Ming Twanmoh, H. B. Wood, Jr. and J. S. Driscoll, *J. Hetero. Chem., 10* (1973) 187.

54 D. J. Hodgson, *Prog. Inorg. Chem., 23* (1977) 211.

55 E. H. Griffith and E. L. Amma, *Chem. Commun.*, (1979) 322.

56 K. Aoki and H. Yamazaki, *Chem. Commun.*, (1980) 186.

57 A. R. Norris, R. Kumar, E. Buncel and A. L. Beauchamp, *J. Inorg. Biochem., 21* (1984) 277.

58 T. Sorrell, L. G. Marzilli and T. J. Kistenmacher, *J. Am. Chem. Soc., 98* (1976) 2181.

59 M. Biagini Cingi, A. M. Manotti Lanfredi and A. Tiripicchio, *Acta Crystallogr., Sect. C, 39* (1983) 1523.

60 A. R. Norris, S. E. Taylor, E. Buncel, F. Bélanger-Gariépy and A. L. Beauchamp, *Inorg. Chim. Acta, 92* (1984) 271.