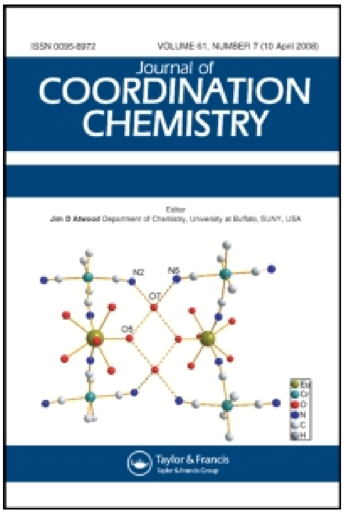

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Theophylline Adducts with cobalt(II), Nickel(II) and Iron(III) Halides

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To cite this Article Mikulski, Chester M. , Grossman, Scott , Bayne, Monica L. , Gaul, Michele , Kanach, Dorothy , Udell, Kimberly and Karayannis, Nicholas M.(1990) 'Theophylline Adducts with cobalt(II), Nickel(II) and Iron(III) Halides', Journal of Coordination Chemistry, 22: 3, 175 — 182
To link to this Article: DOI: 10.1080/00958979009408213
URL: http://dx.doi.org/10.1080/00958979009408213

J. Coord. Chem. 1990, Vol. 22, pp. 175–182
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THEOPHYLLINE ADDUCTS WITH COBALT(II), NICKEL(II) AND IRON(III) HALIDES†

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(Received March 28, 1990)

Theophylline (L) adducts with Co(II) and Ni(II) chlorides, bromides and iodides and Fe(III) chloride and bromide were prepared by boiling under reflux 2:1 molar mixtures of L and hydrated metal salt in triethyl orthoformate–ethyl acetate. The new solid complexes obtained are adducts of the types CoL_2X_2 (X = Cl, Br, I), $NiL_2X_2.H_2O$ (X = Cl, Br), $NiL_2I_2.2H_2O$, and $FeL_2X_3.H_2O$ (X = Cl, Br). On the basis of spectral, magnetic and conductance characterization, these complexes were formulated as being neutral monomeric with terminal N7-bound unidentate L, halo and, wherever applicable, aqua ligands. The Co(II)complexes are distorted tetrahedral species, the Ni(II) chloride and bromide adducts are pentacoordinated and the Ni(II) iodide and the Fe(III) complexes hexacoordinated.

Keywords: Theophylline, first row, complexes, synthesis

INTRODUCTION

The metal complexes of theophylline (1,3-dimethylxanthine; tpH; L; I) have been the subject of extensive studies in recent years.[2–9] The weakly acidic proton of neutral tpH is bound to N7 in the solid,[10,11] while protonation at N9 can occur under relatively acidic conditions.[12,13] Crystal structure determinations of numerous complexes established that terminal unidentate tpH or tp^- preferably binds through the N7 imidazole nitrogen to the metal ion.[12,14–21] Binding of tpH through N9 can occur[12] only when the metal complexes are prepared under sufficiently acidic conditions to preclude ionization at N7[15] or when N7 is blocked by prior metal coordination.[22,23] A number of complexes prepared from acidic media were found to involve N9-bound tpH.[24,25] Regarding bidentate theophylline, it has been shown to act as an O6,N7-bound chelating agent[6,26,27] or a N7,N9-bound bridging ligand,[23] while quite recently the presence of terdentate bridging tpH, binding *via* O6, N7 and N9, was established for a trimethylplatinum–theophylline cyclic hexamer.[9]

Previous work in these laboratories has dealt with the syntheses and characterization of 3d metal perchlorate[2,28] and Zr(IV) oxochloride[29] complexes of tpH. More recently, we synthesized and characterized Co(II) and Ni(II) chloride, bromide and iodide and Fe(III) chloride and bromide complexes with xanthine (xnH), hypo-

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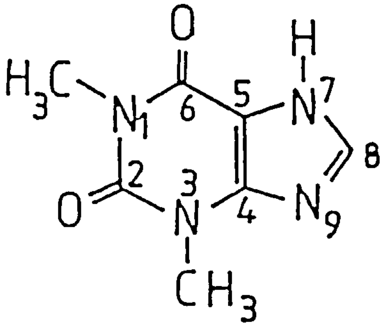
† Presented in part at the 199th ACS Natl. Meetg., see ref 1.

xanthine (hxH),[30–32] theobromine (tbH)[33] and caffeine (caf).[34] The present paper deals with the syntheses and characterization of the corrresponding theophylline complexes with Co(II), Ni(II) and Fe(III) halides.



I

TABLE I

Analytical data for the new complexes.*

Complex	Colour	Yield%	C	H	N	M	X
CoL_2Cl_2	Light blue	34	33.8 (34.3)	3.2 (3.3)	21.6 (21.3)	11.7 (12.0)	14.4 (14.5)
CoL_2Br_2	Light blue	94	28.6 (29.0)	2.6 (2.8)	19.2 (19.4)	10.7 (10.2)	28.2 (27.6)
CoL_2I_2	Light blue	37	25.3 (25.0)	2.2 (2.4)	16.5 (16.7)	9.1 (8.8)	38.3 (37.7)
$NiL_2Cl_2.H_2O$	Yellow-green	25	33.4 (33.1)	3.7 (3.6)	21.8 (22.1)	11.9 (11.6)	14.2 (14.0)
$NiL_2Br_2.H_2O$	Yellow-grey	73	27.9 (28.2)	3.1 (3.0)	19.2 (18.8)	10.3 (9.8)	26.4 (26.8)
$NiL_2I_2.2H_2O$	Mint green	40	24.2 (23.7)	2.8 (2.8)	15.5 (15.8)	7.9 (8.3)	36.3 (35.8)
$FeL_2Cl_3.H_2O$	Off-white	41	30.7 (31.1)	3.7 (3.4)	21.1 (20.7)	10.6 (10.3)	19.9 (19.7)
$FeL_2Br_3.H_2O$	Beige	82	25.5 (25.0)	2.5 (2.7)	16.8 (16.6)	8.7 (8.3)	36.0 (35.6)

*Found % with calc. % in parentheses.

EXPERIMENTAL

The synthetic method employed was as follows. One mmol of hydrated metal halide was dissolved in 25 cm^3 of a 7:3 (v/v) mixture of triethyl orthoformate (teof)-ethyl acetate (ea), and the solution was stirred under reflux for 1 h. Two mmol of tph were mixed with 25 cm^3 of 7:3 teof-ea, and the mixture was warmed to form a slurry, which was added to the stirring, refluxing metal salt 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

TABLE II

Pertinent infrared spectral data, cm^{-1}.

tpH*	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
				3380m,b	3410m,b	3460m,b	3400m,b	3425m,b	ν_{OH}(aqua)
3120s,3060s	3120m,3055m	3120m,3060m	3125m,3065m	3110m,3050m	3115m,3065m	3125m,3050m	3110m,3045m	3115m,3045m	$\nu_{CH}+\nu_{NH}$
2980s,2820s	2990m,2905m	2985m,2915m	2970m,2925m	2980m,2910w	2995m,2920m	2970m,2915m	2970m,2905m	2975m,2910m	
2790ms	2815s,2775s	2825m,2795m	2840m,2790w	2810s,2770m	2825m,2785m	2820s,2790m	2815s,2780s	2820s,2775m	
1713vs	1718vs	1711vs	1700vs	1716vs	1713vs	1710vs	1705vs	1708vs	$\nu_{C=O}$
1668vs,b	1682vs	1673vs	1660vs	1681vs	1676vs	1673vs	1670vs	1677vs	
1613s,sh	1603m,1560s	1606m,1565m	1610m,1571m	1635s,sh	1633s,sh	1625s,sh	1635s,sh	1629s,sh	$\delta_{HOH}+\nu_{C=C}+$
1563m,b	1540sh	1544sh	1541m,1532s	1607m,1562m	1604m,1570m	1606m,1568m	1603m,1560s	1601m,1572s	
				1542sh	1545sh	1540m,1530m	1541m,1533m	1538m,1527m	$\nu_{C=N}+\delta_{NH}$
1478m,sh	1482m,1463w	1500m,1481m	1498m,1483m	1482m,1460w	1485m,1459w	1500m,1483m	1481m,1463m	1485,1461m	Ring vi-
1450vs,1443	1440s,1422w	1460w,1446w	1448w,1440s	1441m,1422w	1444m,1420w	1460w,1444m	1440s,1420m	1442s,1419m	brations+
vs,1427s,sh	1397w,b	1415w,1400w	1410w,1398w	1400w,1377w	1395w,1377w	1418m,1400w	1397w,1376w	1395w,1372w	
1372s,1348m	1378w,1318w	1378w,1352w	1381w,1367w	1350w,1319w	1352w,1325w	1377w,1360w	1358w,1310w	1361w,1314w	
1311m,1279m	1281w,1242w	1320w,1285w	1330m,1313m	1282w,1239w	1280w,1251m	1325w,1284w	1280w,1239w	1283w,1242w	$\nu_{C-N}+\delta_{NH}$
1239m,1218m	1239w,1231w	1240w,1232w	1281w,1252s	1205w,1184m	1227w,1190m	1248m,1222w,	1224w,1182m	1227w,1180m	
1176s,1150m	1180m,1159w	1178m,1157w	1230s,1190m	1150w,1142w	1162w,1143w	1190m,1157w	1150w,1122w	1154w,1123w	
1099m,sh	1140w,1090w	1137w,1095m	1155w,1101m	1115w,1088w	1097w	1124w,1102m	1085w	1088w	
603m,555w,b	610mw,601mw	609mw,601mw	610w,570w	610mw,602w	608mw,575w	611mw,603w	606m,602m	608m,601m	ν_{tpH} at
503m,490w	580w,538w	577w,525w	518mw,507w	570w,522vw	524w,503mw	568w,520vw	575w,522w	580w,524w	610–200 cm^{-1}
446m,420m	502mw,485w	504mw,483w	460w,430mw	502mw,483w	485w,417w	501mw,484w	477w,442w	475w,441w	
390vw, 378m	444w,419w	440w,417w	388vw,376w	419w,390vw	388vw,370w	440w,385vw	421w,390vw	423w,388vw	
292vw	390vw,376w	390vw,373w	333w	375w,330w	332w,292w	374w,333w	373w,240w	376w,330w	
238mw,b	240w,sh	331w		290w,sh	239w,sh	290w		293vw,sh	
				442mw	445mw	417mw	500mw	500mw	ν_{M-O} (aqua)
	355w,328mw	264w,233mw	214mw	303w,277w	215w	142w,b	355m,338m	249m,234mw	ν_{M-X}
							316mw	213w	
	297w,282w	295w,277w	292w,277w	268w,253w	266w,250w	247w,222w	286w,271w	283w,269w	ν_{M-N}
	250w	246w,sh	248w						

*For free tpH band assignments see text.

thoroughly with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. 2:1 adducts of tpH with the metal salts were generally isolated. The Co(II) complexes were anhydrous, the Ni(II) and Fe(III) chloride and bromide adducts were monohydrates, and the Ni(II) iodide complex a dihydrate, as shown by the analytical results in Table I. The new complexes were found to be rather sparingly soluble in organic solvents, showing increased solubility in binary solvent mixtures, as, for instance, nitromethane and acetone. Infrared spectra (Table II) were recorded in KBr discs (4000–500 cm^{-1}) and Nujol mulls between high density polyethylene windows (700–100 cm^{-1}), using Perkin-Elmer 621 and 181 spectrophotometers. Solid-state (Nujol mull) electronic spectra, ambient temperature (300°K) magnetic susceptibility and conductance (on 10^{-3} *M* solutions of the adducts in 1:1 (v/v) nitromethane–acetone at 25°C) measurements (Table III) were obtained by using apparatus and techniques described elsewhere.[35]

TABLE III

Solid-state (Nujol mull) electronic spectral data, magnetic properties (300°K) and molar conductivities of the new tpH complexes.*

M	X	λmax, nm	$10^6\chi_M^{cor}$, cgsu	μeff, μB	ΛM,$\Omega^{-1}cm^2mol^{-1}$
Co	Cl	202vvs,224vs,242vs,sh,272vs,281vs, 300s,sh,352s,sh,544m,614s,653s, 705ms,1360mw,1630w,1890mw,2120mw	8731	4.60	21
Co	Br	204vvs,226vs,241vs,269vs,283vs,b, 297s,sh,354s,sh,551m,617s,660s, 717ms,1385mw,1635w,1880mw,2140mw	8622	4.57	22
Co	I	200vvs,227vs,240vs,279vs,b,298s,sh, 350s,sh,552m,622s,663s,724ms,1400w, 1650w,1920mw,2180mw	8569	4.55	27
Ni	Cl	200vvs,228vs,246vs,277vs,vb,303s, 349s,sh,438s,542ms,644ms,920w,b, 1125w,b,1350w,b,1950mw,b	4544	3.32	18
Ni	Br	201vvs,226vs,243vs,268vs,285vs,sh, 301s,sh,352s,sh,446s,550ms,652ms, 915w,b,1140w,b,1345w,b,1920mw,b	4481	3.29	19
Ni	I	200vvs,227vs,243vs,280vs,b,300s,sh, 355s,sh,457ms,659mw,730mw,833w, 1038w,1270w,b	3956	3.09	29
Fe	Cl	203vvs,226vs,243vs,267vs,285vs,sh, 298s,sh,350s,sh,445m,sh,545mw,b	15,037	6.03	7
Fe	Br	203vvs,228vs,247vs,270vs,283vs,sh, 302s,sh,349s,sh,450m,sh,540mw,b	15,162	6.06	11

*UV spectrum of free tpH (Nujol mull), nm: 223vs, 276vs, 300vs,sh.[2] Aqueous solution spectrum[65] (pH 6–7): 270 nm (log ε 4.02m cm^{-1}). Conductance measurements were performed on 10^{-3} *M* solutions of the adducts in 1:1 (v/v) nitromethane–acetone at 25°C.

RESULTS AND DISCUSSION

The new metal complexes are generally adducts of neutral tpH, involving 2:1 L to metal ion molar ratios, as already mentioned. The metal chloride and iodide adducts were isolated in significantly lower yields (Table I) relative to the corresponding tbH complexes, which were generally obtained in yields ranging between 62–76% (X = Cl, Br or I).[33] However, the new metal bromide adducts of tpH were isolated in high yields (73–94%). Similar trends were previously observed during the syntheses of tpH[2] and tbH[36] adducts with 3d metal perchlorates, *i.e.*, tpH adduct yields in the 30–98% and tbH adduct yields in the 59–100% range. As regards the function of teof as a dehydrating agent,[37] it proved effective only in the case of Co(II) halide adduct preparation, whilst in the cases of Ni(II) and Fe(III) halides it did not prevent the formation of hydrated complexes. As far as theophylline complexes with compounds of the elements under study previously reported are concerned, they include $Co(tp)_2.3H_2O$, prepared by reaction of tpH and $Co(NO_3)_2$ in aqueous $NH_4OH + NH_4Cl$,[3] the Co(III) complex *trans*- or *cis*-$\{Co(en)_2(tp)Cl\}Cl$ (en = ethylenediamine),[14] and the perchlorate adducts $Co(tpH)_2(ClO_4)_2$, $M(tpH)_2(ClO_4)_2.2H_2O$ (M = Co, Ni), $Fe(tpH)_2(ClO_4)_2.H_2O$ and $Fe(tpH)_2(ClO_4)_3.2H_2O$. Mostly studied theophylline metal complexes are those with Cu(II),[2,3,15,16,18,19,26–28,38] Hg(II)[7,12,21,23,39] and Pt(II) or (IV).[5,9,17,22,24] Complexes with Mn(II),[2,40] Zn(II), Cd(II),[3,20,38] Ti(III),[6] Cr(III),[2] Pd(II),[8] Ag(I),[3,40] Au(III),[4] Mg(II),[41] Rh(II),[25] Rh, Ir, Mo and W carbonyls[42] and oxoZr(IV)[29] were studied to a lesser extent.

IR band assignments for free tpH (Table II) were based on our previous work,[2,29] and other IR studies of tpH and its complexes,[3,4,8,12,38,40,42,43] as well as complete assignments for xnH[44,45] and partial assignments for tbH and for caf.[28,33,34,46–48] Amongst the ligand bands in the $\nu_{CH} + \nu_{NH}$ region, those at 3120 and 2820 cm^{-1} involve ν_{C8-H} contribution, while the remaining three bands probably correspond to pure ν_{NH} absorptions.[2,43–48] These bands remain virtually unchanged in the spectra of the new neutral tpH adducts. The two $\nu_{C=O}$ bands of the free ligand are relatively insensitive to complex formation, while the $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrational modes at 1613–1099 cm^{-1} undergo more significant shifts and occasional splittings in the spectra of the adducts. These features favour tpH coordination *via* a ring nitrogen and rule out the participation of C=O oxygens in coordinative bonding interactions with metal ions.[2,28,29,32–36,44,45,49] The hydrated new complexes exhibit the ν_{OH} and δ_{HOH} vibrational modes of the coordinated aqua ligands at 3460–3380 and 1635–1625 cm^{-1}, respectively.[50] Tentative ν_{M-O} (aqua), ν_{M-X} (X = Cl, Br, I) and ν_{M-N} band assignments in the lower frequency IR region show the expected trends of the ν_{M-X} wavenumber decreases in moving from X = Cl to X = Br to X = I,[30–34,51–61] substantiating at the same time the ν_{M-N} band assignments.[2] The metal–ligand bands are generally distinguishable from the tpH bands in this region[62] and favour coordination number four for Co(II),[30,33,51–56,60] five for $NiCl_2$ and $NiBr_2$[30,51–54,57–59] and six for NiI_2 and Fe(III) adducts.[31–34,53–61] The molar conductivities of the new complexes are generally typical for non-electrolytes,[63] while their ambient temperature magnetic moments are normal for high-spin tetrahedral Co(II), penta- or hexacoordinated Ni(II) and hexacoordinated Fe(III) compounds[64] (Table III). The $\pi \rightarrow \pi^*$ transitions of tpH (223, 276 nm)[2,29,65] undergo shifts toward lower energies, as well as occasional splitting upon metal complex formation (Table III). The $n \rightarrow \pi^*$ transition of the ligand[66] appears at 297–303 nm in the spectra of the adducts, which are also characterized by strong metal-to-ligand charge transfer absorption,[67] originating in the UV and trailing off well into the visible region. The d–d transition spectra of the Co(II) complexes are compatible with a pseudotetrahedral configuration,[30,51–53,60,68] *viz:* ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ 544–552, 614–622, 653–663, 705–724; $\rightarrow {}^4T_{1g}(F)$ 1360–1400, 1630–1650, 1880–1920; $\rightarrow {}^4T_{2g}(F)$ 2120–2180 nm. The Ni(II) chloride and bromide adducts exhibit several d–d transition bands at 438–1950 nm, as expected for pentacoordinated compounds of Ni(II).[59,69,70] The spectrum of the Ni(II) iodide complex is characteristic of coordination number six[31,33,57,71], *i.e.*, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 457; $\rightarrow {}^3T_{1g}(F)$, ${}^1E_g(D)$ 659, 730, 833; $\rightarrow {}^3T_{2g}(F)$ 1038, 1270 nm (Dq = 867 cm^{-1}). The weak d-d transition bands of the Fe(III) complexes[72] are masked by the strong charge-transfer absorption in the visible region.

The characterization data generated, combined with the solubility of the new metal complexes in organic media, favour the formulation of these compounds as monomeric neutral species, involving exclusively terminal unidentate ligands. The Co(II) adducts are distorted tetrahedral species of the $\{Co(tpH)_2X_2\}$ type (X = Cl, Br, I), involving CoN_2X_2 chromophores. The Fe(III) complexes are low-symmetry hexacoordinated species of the $\{Fe(tpH)_2X_3(OH_2)\}$ type, (X = Cl, Br) (FeN_2X_3O absorbing species). The Ni(II) chloride and bromide adducts are pentacoordinated (square pyramidal or trigonal bipyramidal) complexes of the $\{Ni(tpH)_2X_2(OH_2)\}$ type, while the nickel iodide complex contains an additional aqua ligand and is hexacoordinated, $\{Ni(tpH)_2I_2(OH_2)_2\}$. The Ni(II) complexes are characterized by NiN_2X_2O (X = Cl, Br) and $NiN_2I_2O_2$ chromophores. The tpH ligands present in the new metal complexes are presumably coordinated through the N7 imidazole nitrogen to the metal ions. As discussed above, N7 is the preferred binding site of terminal unidentate tpH,[12,14–21] while binding *via* N9 occurs only in the case of complexes prepared under acidic conditions.[24,25] Comparison of the adducts herein reported to the corresponding tbH (3,7-dimethylxanthine) adducts[33] indicates that in both cases 2:1 complexes were isolated. The only differences observed concern the degree of hydration of some of them. Thus, the Co(II) and Fe(III) chloride and bromide and Ni(II) iodide complexes of tbH[33] and tpH are isostoicheiometric. However, whereas tbH yielded a monohydrate CoI_2, and dihydrate $NiCl_2$ and $NiBr_2$ adducts,[33] the corresponding tpH complexes isolated are anhydrous in the case of CoI_2 and monohydrates with NiX_2 (X = Cl, Br).

REFERENCES

1. C.M. Mikulski, S. Grossman, M.L. Bayne, M. Gaul and N.M. Karayannis, *Abstr., 199th Am. Chem. Soc. Natl. Meetg.*, Boston, Mass., April 22–27, 1990, No. INOR 182.
2. C.M. Mikulski, M.K. Kurlan, S. Grossman, M.L. Bayne, M. Gaul and N.M. Karayannis, *J. Coord. Chem.*, **15**, 347 (1987), and refs. therein.
3. J.M. Salas Peregrin, E. Colacio Rodriguez, M. Moreno Carretero and J. De D. Lopez Gonzalez, *Ann. Quim., Sect. B*, **80**, 167 (1984).
4. E. Colacio Rodriguez, J.M. Salas Peregrin and M.N. Moreno Carretero, *Monatsh. Chem.*, **117**, 941 (1986).
5. V.F. Ivanov, A.I. Stetsenko, B. Jeżowska-Trzebiatowska, V.G. Duibanova and A.F. Imsyrova, *Koord. Khim.*, **12**, 810 (1986).
6. D. Cozak, A. Mardhy, M.J. Olivier and A.L. Beauchamp, *Inorg. Chem.*, **25**, 2600 (1986).
7. S. Bhatia, N.K. Kaushik and G.S. Sodhi, *J. Chem. Res.*, M, 1519 (1987); K.K. Dahiya, V. Goswami and N.K. Kaushik, *Synth. React. Inorg. Met.-Org. Chem.*, **18**, 769 (1988).
8. G. Pneumatikakis, A. Yannopoulos, J. Markopoulos and C. Angelopoulos, *Inorg. Chim. Acta*, **152**, 101 (1988).
9. J. Lorberth, W. Massa, M. El-Essawi and L. Labib, *Angew. Chem., Intern. Ed. Engl.*, **27**, 1160 (1988).
10. D.J. Sutor, *Acta Cryst.*, **11**, 83 (1958); E. Shefter, *J. Pharm. Sci.*, **58**, 710 (1969).

11. S. Nakao, S. Fujii, T. Sakaki and K.I. Tomita, *Acta Cryst.*, **B33**, 1373 (1977); K. Aoki, T. Ichikawa, Y. Koinuma and Y. Iitaka, *Acta Cryst.*, **B34**, 2333 (1978).
12. A.R. Norris, R. Kumar, E. Buncel and A.L. Beauchamp, *J. Inorg. Biochem.*, **21**, 277 (1984).
13. D. Lichtenberg, F. Bergmann and Z. Neiman, *J. Chem. Soc., C*, 1676 (1971).
14. T.J. Kistenmacher, *Acta Cryst.*, **B31**, 85 (1975); T.J. Kistenmacher and D.J. Szalda, *Acta Cryst.*, **B31**, 90 (1975).
15. T.J. Kistenmacher, D.J. Szalda and L.G. Marzilli, *Inorg. Chem.*, **14**, 1686 (1975); D.J. Szalda, T.J. Kistenmacher and L.G. Marzilli, *Inorg. Chem.*, **15**, 2783 (1976).
16. T. Sorrell, L.G. Marzilli and T.J. Kistenmacher, *J. Am. Chem. Soc.*, **98**, 2181 (1976).
17. B.L. Kindberg, E.H. Griffith, E.L. Amma and E.R. Jones, Jr., *Cryst. Struct. Commun.*, **5**, 533 (1976).
18. M. Biagini Cingi, A.M. Manotti Lanfredi, A. Tiripicchio and M. Tiripicchio Camellini, *Trans. Met. Chem.*, **4**, 221 (1979).
19. M. Biagini Cingi, A.M. Manotti Lanfredi and A. Tiripicchio, *Acta Cryst.*, **C39**, 1523 (1983).
20. M.J. Gardner, F.X. Smith and E. Shefter, *J. Pharm. Sci.*, **72**, 348 (1983).
21. A.R. Norris, R. Kumar, E. Buncel and A.L. Beauchamp, *Can. J. Chem.*, **63**, 2575 (1985).
22. N.H. Agnew, T.G. Appleton, J.R. Hall, G.F. Kilmister and I.J. McMahon, *Chem. Comm.*, 324 (1979).
23. K. Caldwell, G.B. Deacon, B.M. Gatehouse, S.C. Lee and A.J. Canty, *Acta Cryst.*, **C40**, 1533 (1984).
24. E.H. Griffith and E.L. Amma, *Chem. Comm.*, 322 (1979).
25. K. Aoki and H. Yamazaki, *Chem. Comm.*, 186 (1980).
26. T.J. Kistenmacher, D.J. Szalda, M. Rossi, C.C. Chiang and L.G. Marzilli, *Inorg. Chem.*, **17**, 2582 (1978).
27. D.J. Szalda, T.J. Kistenmacher and L.G. Marzilli, *J. Am. Chem. Soc.*, **98**, 8371 (1976).
28. C.M. Mikulski, T.B. Tran, L. Mattucci and N.M. Karayannis, *Inorg. Chim. Acta*, **78**, 269 (1983).
29. C.M. Mikulski, S. Grossman and N.M. Karayannis, *J. Less-Common Met.*, **136**, 41 (1987).
30. C.M. Mikulski, S. Grossman, M.L. Bayne, M. Gaul, D.L. Staley, A. Renn and N.M. Karayannis, *Inorg. Chim. Acta*, **161**, 29 (1989).
31. C.M. Mikulski, M. Gaul, M.L. Bayne, S. Grossman, A. Renn, D.L. Staley and N.M. Karayannis, *Trans. Met. Chem.*, **14**, 336 (1989).
32. C.M. Mikulski, M.L. Bayne, S. Grossman, M. Gaul, A. Renn, D.L. Staley and N.M. Karayannis, *J. Coord. Chem.*, **20**, 185 (1989).
33. C.M. Mikulski, S. Grossman, M.L. Bayne, M. Gaul, D. Kanach, K. Udell and N.M. Karayannis, *Inorg. Chim. Acta*, **173**, 31 (1990).
34. C.M. Mikulski, M. Gaul, D.L. Staley and N.M. Karayannis, *Trans. Met. Chem.*, **14**, 159 (1989).
35. N.M. Karayannis, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta*, **3**, 415 (1969); C.M. Mikulski, J. Fleming, D. Fleming and N.M. Karayannis, *Inorg. Chim. Acta*, **144**, 9 (1988).
36. C.M. Mikulski, M.K. Kurlan, M.L. Bayne, M. Gaul and N.M. Karayannis, *J. Coord. Chem.*, **17**, 267 (1988).
37. P.W.N.M. van Leeuwen and W.L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, **3**, 145 (1967).
38. W.J. Birdsall, *Inorg. Chim. Acta*, **99**, 59 (1985), and refs. therein: M. Melník, *Polyhedron*, **1**, 143 (1982).
39. A.R. Norris, S.E. Taylor, E. Buncel, F. Bélanger-Gariépy and A. L. Beauchamp *Inorg. Chim. Acta*, **92**, 271 (1984).
40. D. Crăciunescu and A. Fruma, *Inorg. Chim. Acta*, **4**, 287 (1970).
41. R.H. Barry, H. Rubin, J.B. Johnson and J.H. Lazarus, *J. Pharm. Sci.*, **70**, 204 (1981).
42. W. Beck and N. Kottmair, *Ber.*, **109**, 970 (1976).
43. E.R. Blout and M. Fields, *J. Am. Chem. Soc.*, **72**, 479 (1950).
44. F. Allaire and A.L. Beauchamp, *Can. J. Chem.*, **62**, 2249 (1984).
45. C.M. Mikulski, M.K. Kurlan, M.L. Bayne, M. Gaul and N.M. Karayannis, *Inorg. Chim. Acta*, **123**, 27 (1986).
46. D. Cook and Z.R. Regnier, *Can. J. Chem.*, **45**, 2895, 2899 (1967); **46**, 3055 (1968).
47. S. Goenechea, *Mikrochim. Acta*, 276 (1972).
48. J. De Taeye and T. Zeegers-Huyskens, *Spectrosc. Lett.*, **19**, 299 (1986).
49. S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull.*, **26**, 2941 (1978).
50. I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).
51. T. Beringhelli, M. Freni, F. Morazzoni, P. Romiti and R. Servida, *Spectrochim. Acta*, **37A**, 763 (1981).
52. N.B. Behrens, D.M.L. Goodgame and Z. Warnke, *Inorg. Chim. Acta*, **31**, 257 (1978).
53. M.A. Guichelaar and J. Reedijk, *Rec. Trav. Chim. Pays-Bas*, **97**, 295 (1978).
54. J.R. Ferraro, J. Zipper and W. Wozniak, *Appl. Spectrosc.*, **23**, 160 (1969); J.R. Ferraro, W. Wozniak and G. Roch, *Ric. Sci.*, **38**, 433 (1968).
55. R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, **4**, 350 (1965); *Spectrochim. Acta*, **22**, 1081 (1966).
56. M. Goldstein, F.B. Taylor and W.D. Unsworth, *J. Chem. Soc., Dalton Trans.*, 418 (1972); M. Goldstein, *J. Inorg. Nucl. Chem.*, **37**, 567 (1975).

57. A.N. Speca, C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski and N.M. Karayannis, *Inorg. Chim. Acta*, **46**, 235 (1980).
58. C.M. Mikulski, S. Cocco, N. DeFranco, T. Moore and N.M. Karayannis, *Inorg. Chim. Acta*, **106**, 89 (1985).
59. C.M. Mikulski, L. Mattucci, L. Weiss and N.M. Karayannis, *Inorg. Chim. Acta*, **107**, 147 (1985).
60. C.M. Mikulski, L. Mattucci, L. Weiss and N.M. Karayannis, *Inorg. Chim. Acta*, **107**, 81 (1985); **108**, L35 (1985).
61. C.M. Mikulski, S. Cocco, N. DeFranco and N.M. Karayannis, *Inorg. Chim. Acta*, **80**, L23 (1983); C.M. Mikulski, L. Mattucci, L. Weiss and N.M. Karayannis, *Inorg. Chim. Acta*, **92**, 275 (1984).
62. C.P. Beetz, Jr. and G. Ascarelli, *Spectrochim. Acta*, **36A**, 299 (1980).
63. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
64. B.N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).
65. W. Pfleiderer and G. Nübel, *Justus Liebigs Ann. Chem.*, **647**, 155 (1961).
66. L.B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc.*, **87**, 11 (1965); L.B. Clark *J. Am. Chem. Soc.*, **99**, 3934 (1977).
67. A.B.P. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 1235 (1962); 3156, 5042 (1963); 1187, 4761 (1964).
68. P.C. Tellinghuisen, W.T. Robinson and C.J. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1289 (1985).
69. M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41, 1150 (1966); **6**, 445 (1967).
70. M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, **5**, 45 (1966).
71. W. Byers, A.B.P. Lever and R.V. Parish, *Inorg. Chem.*, **7**, 1835 (1968).
72. H. Schläfer, *Z. Phys. Chem., N.F.*, **4**, 116 (1955); M. Dvir and W. Low, *Phys. Rev.*, **119**, 1587 (1960).