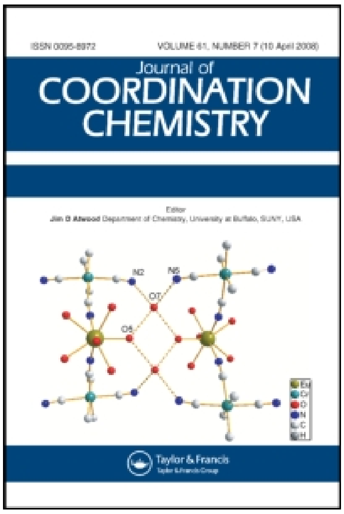

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THEOPHYLLINE ADDUCTS WITH 3d METAL PERCHLORATES†

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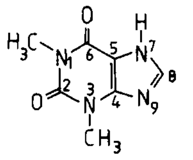
2:1 adducts of theophylline (tpH) with 3d metal perchlorates were prepared by refluxing mixtures of ligand and metal salt in ethyl acetate-triethyl orthoformate. The new complexes appear to be generally monomeric, involving terminal N7-bonded tpH ligands. Mn^{2+}, Co^{2+} and Zn^{2+} perchlorates afforded water-free adducts of the types $[M(tpH)_2(OClO_3)(=O_2ClO_2)]$, (M = Mn, Co) and $[Zn(tpH)_2(OClO_3)_2]$. The former two complexes are pentacoordinated with one unidentate $-OClO_3$ and one bidentate chelating $= O_2ClO_2$ ligand, while the Zn^{2+} complex is analogous to the previously reported Cu^{2+} complex, *i.e.*, tetrahedral with two unidentate $-OClO_3$ ligands. The Co^{2+} complex is moisture-sensitive, being converted to the dihydrate $[Co(tpH)_2(OClO_3)_2(OH_2)_2]$ immediately upon exposure to the atmosphere. The rest of the new complexes were isolated in the form of hydrates and are of the types: $[Ni(tpH)_2(OClO_3)_2(OH_2)_2]$ hexacoordinated with exclusively coordinated $-OClO_3$, $l[Fe(tpH)_2)_2(OClO_3)(OH_2)]ClO_4$, distorted tetrahedral, and $[M(tpH)_2(OClO_3)_2]_2]ClO_4$ (M = Cr, Fe), hexacoordinated, involving both terminal $-OClO_3$ ligands and ionic ClO_4^-.

INTRODUCTION

Amongst substituted xanthines, theophylline (tpH; 1,3-dimethylxanthine; I) has been studied to the largest extent as a model of guanine (guH)-metal ion interactions.[2,3] The weakly acidic proton of neutral tpH is bound to N7 in the solid,[4,5] while protonation at N9 can occur under relatively acidic conditions.[6,7] Numerous metal complexes with theophylline have been reported.[6,8–36] Determination of the formation constants of Cu^{2+} complexes with substituted purines resulted in the following series of decreasing



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values: adenine (adH) > purine (puH) > hypoxanthine (hxH) > xanthine (xnH) $\geqslant$ tpH.[35] Crystal structure determinations of several metal complexes with terminal tpH or tp^-, prepared from neutral or basic solutions, establish the general trend of theophylline preferably binding through the N7 imidazole nitrogen.[6,11–13,21,24,25,30,32] Use of the somewhat sterically hindered (owing to the presence of

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[†] Presented in part at the 189th National Meeting, Am. Chem. Soc., see ref. 1.

the methyl substituent at N3) N9 site for binding of theophylline to metal ions occurs[6] only when the metal complexes are prepared under sufficiently acidic conditions to preclude ionization at N7[14] or when N7 is blocked by prior metal coordination.[20,34] Two complexes prepared from acidic media were found to involve N9-bonded terminal tpH,[22,23], while the presence of N7,N9-bonded bridging tp^- was invoked in order to rationalize the formation of a trimeric Pt^{4+} complex.[20] The presence of strong Hg-N7 (2.08 A) and weaker Hg-N9 (2.91 A) bonds in a Hg^{2+} complex with tp^- was recently established.[34] Bridging of tp^- through N7, N9 was also postulated for $[(CH_3Hg)_2tp]NO_3$,[6] whose interaction with excess CH_3HgNO_3, under conditions leading to C2 substitution in *N*-methylimidazole[37] and C8 substitution in xanthosine[38] and inosine,[39] did not result in C8 substitution.[6] In this respect, theophylline resembles unsubstituted imidazole, which also does not demonstrate carbon-methylmercury bond formation under similar conditions.[6] Finally, the presence of chelating O6, N7-bonded tp^-, involving weak Cu-O6 interaction (bond lengths 2.919-3.340 A), was established for a number of Cu^{2+} complexes with this ligand.[14,15]

As regards the involvement of these laboratories in studies of theophylline metal complexes, the $[Cu(tpH)_2(OClO_3)_2]$ tetrahedral adduct was prepared in early work from ethanol-triethyl orthoformate (teof) and has been characterized.[28] Subsequent synthetic work aimed at the isolation of theophylline complexes with other 3d metal perchlorates ($M^{n+} = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}$) from ethanol-teof resulted in failure to produce solid complexes. At that time a new synthetic method involving use of ethyl acetate (ea)-teof as the interaction medium for the syntheses of metal perchlorate complexes with purines was developed.[40] This method proved to be significantly better, in that it is much more rapid and leads to substantially higher yields than the procedure involving use of ethanol-teof in the cases of ligands that afford solid metal perchlorate complexes from the latter medium, *e.g.*, xnH.[40–43] By employing ea-teof as the interaction medium we were able to isolate solid or semi-solid adducts of tpH with the whole series of 3d metal perchlorates in good yields,[1] and a number of these adducts ($M = Mn^{2+}, Ni^{2+}, Zn^{2+}$) were discussed in a preliminary communication.[29] It should be noted that use of ea-teof resulted also in the precipitation of the $[Cu(tpH)_2(OClO_3)_2]$ adduct in the form of a crystalline powder in 90% yield,[29] while when the same compound was prepared from ethanol-teof, it was initially isolated in the form of a viscous semi-solid, which eventually solidified to a hard glassy green solid upon desiccation.[28] The present paper deals with the preparation of metal(III) (Cr, Fe) and metal(II) (Mn, Fe, Co, Ni, Zn) perchlorate adducts with tpH and their characterization by means of spectral, magnetic and conductance studies.

EXPERIMENTAL

The following synthetic method was employed[1,29]: 1.25 mmol hydrated metal perchlorate is dissolved in a mixture of 35 cm^3 ea and 15 cm^3 teof, 2.5 (for M^{2+}) or 3.75 (for M^{3+}) mmol tpH are added, and the resultant mixture is refluxed for 6 h or until no further significant change in appearance is noted. The mixture is then allowed to cool to ambient temperature, 15–20 cm^3 anhydrous diethyl ether added and the volume is subsequently reduced at low heat to *ca* 20 cm^3. The residue is separated by filtration, washed with 30 cm^3 diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. The new metal complexes are generally adducts involving 2:1 tpH to metal ion molar ratios, of the following types (analytical results are given in Table I): $M(tpH)_2(ClO_4)_3 \cdot 2H_2O$ (M = Cr, Fe), $M(tpH)_2(ClO_4)_2$ (M = Mn, Co, Zn), $Fe(tpH)_2(ClO_4)_2 \cdot H_2O$ and $Ni(tpH)_2(ClO_4)_2 \cdot 2H_2O$. The Fe^{2+} and Fe^{3+} complexes were isolated in the form of tacky semi-solids, which would not solidify completely upon desiccation, whilst the rest of the new complexes were obtained as crystalline free-flowing powders. The purple

TABLE I
Analytical Data for tpH Adducts with Metal Perchlorates.[a]

Complex	Colour	Yield %	C%	H%	N%	M%	Cl%
$Cr(tpH)_2(ClO_4)_3 \cdot 2H_2O$	Khaki	97.6	22.78 (22.52)	2.81 (2.70)	15.06 (15.01)	6.76 (6.96)	14.50 (14.24)
$Mn(tpH)_2(ClO_4)_2$	White	47.2	27.51 (27.38)	2.55 (2.63)	18.48 (18.24)	8.65 (8.95)	11.09 (11.54)
$Fe(tpH)_2(ClO_4)_2 \cdot H_2O$	Brown	59.3	26.82 (26.56)	2.82 (2.87)	18.03 (17.70)	8.97 (8.82)	11.46 (11.20)
$Fe(tpH)_2(ClO_4)_3 \cdot 2H_2O$	Brown	29.6	22.87 (22.40)	2.38 (2.69)	15.30 (14.93)	7.57 (7.82)	14.44 (14.17)
$Co(tpH)_2(ClO_4)_2$	Purple	80.4	27.23 (27.20)	2.52 (2.61)	18.35 (18.13)	9.70 (9.53)	11.39 (11.47)
$Co(tpH)_2(ClO_4)_2 \cdot 2H_2O$	Orange	b	25.46 (25.70)	3.21 (3.08)	17.17 (17.13)	8.82 (9.01)	11.00 (10.84)
$Ni(tpH)_2(ClO_4)_2 \cdot 2H_2O$	Light green	74.6	25.75 (25.71)	3.15 (3.08)	17.44 (17.13)	9.09 (8.98)	10.62 (10.84)
$Zn(tpH)_2(ClO_4)_2$	Cream white	65.8	27.18 (26.92)	2.59 (2.58)	18.23 (17.94)	10.20 (10.47)	11.22 (11.35)

[a]Found%, with Calc.% in parentheses. [b]The hydrated Co^{2+} complex was obtained by exposing the anhydrous analogue to atmospheric moisture (see Experimental Section).

Co^{2+} complex is extremely moisture-sensitive, being immediately converted to the orange-coloured $Co(tpH)_2(ClO_4)_2 \cdot 2H_2O$ species upon exposure to the atmosphere. The latter product was also studied. The rest of the new complexes do not appear to be as moisture-sensitive as the anhydrous Co^{2+} complex. All the complexes exhibit limited solubility in organic solvents, and especially in various binary solvent mixtures. Their molar conductivities were measured in 10^{-3} M solutions in nitromethane-acetone (1:1 v/v).

The IR spectra of tpH and the new complexes (Table II) were recorded in KBr discs (4000-500 cm^{-1}) and in Nujol mulls between NaCl (4000-500 cm^{-1}) and high density polyethylene (700-200 cm^{-1}) windows, in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility (298 K) and conductance measurements (Table III) were obtained by methods described elsewhere.[44]

RESULTS AND DISCUSSION

IR and Conductance Data

Complete or partial IR spectral data for tpH have appeared in several publications.[6,9,16–19,28,29,33,45] Band assignments in Table II were based on these previous works, as well as complete assignments for xnH[43,46] and partial assignments for theobromine (tbH; 3,7-dimethylxanthine)[28,47,48] and caffeine (caf; 1,3,7-trimethylxanthine).[28,48–50] The spectra of the new metal complexes are quite interesting as far as the differences observed in the fundamental vibrational modes of the perchlorate groups are concerned.[51,52] In fact, the Cr^{3+}, Fe^{2+} and Fe^{3+} complexes exhibit triply split ν_3 and ν_4 (ClO_4) bands, while the strongest and broadest $\nu_3(ClO_4)$ absorption (1100-1090 cm^{-1}) has the characteristic shape of the single band observed in compounds involving exclusively ionic ClO_4^-; hence, the spectra of these three

TABLE II

Relevant Infrared Spectral Data for tpH Complexes with Metal Perchlorates (cm^{-1})

tpH[a]	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{2+}	M = Fe^{3+}	M = Co^{2+} [b]	M = Co^{2+} [c]	M = Ni^{2+}	M = Zn^{2+}	Band assignment
	3410s, b		3380s, b	3440s, b		3410s, b	3420s, b		ν_{OH}(aqua)
3120s, 3060s 2980s, 2820s 2790ms, 2720 m, 2625ms	3120s, 3060s 3000s, 2820 ms, 2780s 2710m, 2630m	3120s, 3055s 2980s, 2820s 2780s, 2715 ms, 2605ms	3130s, 3075s 2990s, 2825s 2790s, 2710 ms, 2615ms	3120s, 3050s 2980s, 2825s 2790m, 2710 m, b, 2615m	3130s, 3072s 2980s, 2825s 2795s, 2710m 2620m b	3135s, 3080s 2990s, 2830s 2795s, 2714m 2615m, b	3125s, 3070s 3000s, 2825s 2785s, 2720m 2610m, b	3120s, 3070s 2995s, 2830s 2795m, 2715m 2630m, b	$\nu_{CH} + \nu_{NH}$
1713vs	1710vs	1714vs	1711vs	1707vs	1715vs	1702vs	1705vs	1706vs, b	$\nu_{C6=O}$
1668vs, b	1670vs	1672vs, b	1663vs	1665vs	1670vs, b	1681vs, b	1680vs, b	1662vs	$\nu_{C2=O}$
1613s, sh. 1563ms, b	1637ms, 1615 ms, 1589m, 1560m, 1540ms	1610m, 1579m 1560s, 1543m	1638ms, 1614ms, 1593m, 1562m, 1545m	1635ms, 1612ms, 1590m, 1560m, 1540m	1611s, 1580m, 1558s, 1541m	1633s, 1620s 1607s, 1595s 1562m, 1546m	1630s, 1618s, 1609s, 1597s 1560m, 1550m	1617m, 1563m 1558m, 1538m	$\nu_{C=C} + \nu_{C=N} + \delta_{HOH}$
1478m, sh, 1450vs, 1443vs, 1427s, sh 1372s, 1348m 1311m, 1279m 1239m, 1218m 1176s, 1150m 1099m, sh	1480m, 1460m 1448m, 1420m 1409mw, 1365mw 1352mw, 1330mw 1292mw, 1240mw 1233mw, 1222m 1200mw, 1170mw	1491ms, 1481s 1472ms, 1444s 1428ms, 1398w, b, 1376w, 1337vw, 1311mw, 1282mw, 1239m, 1223 mw, 1187s	1483m, 1461m, 1449m, 1418mw, 1350mw, 1330mw, 1295mw, 1242mw, 1230mw, 1220m, 1198mw, 1165m	1480m, 1463m 1450ms, 1442ms, 1420m, 1410mw, 1370mw, b, 1357mw 1312m, 1283m 1240m, 1229m, 1187m, 1150ms	1493s, 1480s 1470s, 1445s 1430ms, 1400w, b, 1309mw 1284mw, 1240m 1225mw, 1190s	1495m, 1461m 1450m, b, 1410m, 1378m 1353m, 1313m 1306m, 1278m, b, 1256w, 1240m, b, 1220mw, 1183mw, 1150ms	1490m, 1458m, 1448m, 1406m 1377m, 1355w, 1310m, 1304m 1276w, b, 1259w, 1242m, b, 1218mw, 1183mw,	1490m, 1460m 1442ms, 1423m, 1408mw, 1388mw, 1370mw, b, 1326w 1311w, 1285w 1249w, 1220w 1187w	Ring vibrations + $\nu_{C-N} + \delta_{CH_2}$[d]
	1139s, 1100s, b, 1075s, b	1128m, 1099m 1079m, 1068m 1046m	1134s, 1097s b, 1078s	1130s, 1090s, b, 1070s, sh	1137s, 1102s 1081s, 1069s 1047m	1135s, b, 1075vs	1150ms 1130s, b, 1079vs	1106s, 1077s	$\nu_3(ClO_4)$
1038m, 960s 913s	1040mw, 970w 900w	976s, 967ms 945w	1040m, 981m 967m, 906w	1035mw, 978m 969m, 911w	979s, 965ms 947w	1028w, 980w 970mw, 911w	1030w, 981w, 969mw, 910w	1030w, 981w 915vw, sh	Ring vibrations
	930w	924m, 916w	931w	925mw	935w, 921w	927w	924w	926w	$\nu_1(ClO_4)$
835ms, 780m 752s, 730s, 653w	885mw, 860mw 852w, 780w 759mw, 749mw 730mw, 680w	880w, 843m, b 780mw, 760m 740s, 720vw 660w	885mw, 861mw 846mw, 782w 760mw, 741m 684vw, 667vw	890w, 858w, sh 841mw, 782w 769mw, 740m 680vw, 668vw	875w, 844m, b 779mw, 758m 742s, 720vw 665w	887w, 869mw 858mw, 840mw 819w, 790w, 771mw, 742m 680mw	890w, 870mw 860mw, 842mw 820w, 789w 768mw, 739mw 679mw	888vw, 865vw 853vw, 843vw 791w, 786vw 769w, 761w 740mw, 678mw	Ring vibrations[d] + $\delta_{NH} + \delta_{CH}$
	628w, 621w 610mw	655w, 626w 619w, 604m 599m	632m, 624m 617m	629m, 620m 608m	650w, 638w 629m, 620m 611ms	633ms, 622ms	629ms, 621ms	621mw, 609mw	$\nu_4(ClO_4)$
603m, 555w, b 503m, 490w 503m, 490w 446m, 420m 390vw, 378m 305vw, 292vw	600w, 575w 509w, 492vw 509w, 492vw 451mw, 419w 370w, 300vw 240vw, b	560vw, 504ms 442m, 419m 442m, 419m 393vw, 374m 356w, 300vw 290vw	600w, 573vw 510w, 490vw 510w, 490vw 420w, 378w 356vw, 300vw 290vw, 237vw	601mw, 570vw 512w, 489vw 512w, 489vw 445mw, 419mw 395w, 373w 302vw, 241mw	565vw, 505ms 440m, 419m 440m, 419m 397vs, 375mw 358w, 300vw 290vw, 237vw	604w, 568vw 539vw, 505w 490vw, 454w 422mw, 373vw 340vw, 299vw 285vw, 241vw	503w, 565vw 535vw, 504w 488vw, 452w 420mw, 375vw 340vw, 300vw 283vw, 240vw	599w, 570vw 408w, 483w 445w, 420w 380w, 298vw 240vw, sh	ν_{tpH}(610–200 cm^{-1})[d]
	475vw, b	480vw, vb	475vw, b	465vw, b	485w, 473w	470vw, sh	470vw sh	469vw	$\nu_2(ClO_4)$
	505mw		449mw	504mw		399w	402w		ν_{M-O}(aqua)
	335vw, b	321vw	338vw	329vw, b	330vw	311vw	313vw	327vw	ν_{M-O}(perchlorato)
	275vw, b	261vw, 241vw	283vw, 259vw	272vw, b	273vw, 250vw	258vw, 229vw	259vw, 231w	279vw, 252w	ν_{M-N}

[a] Free tpH band assignments based on refs. 6, 9, 16–19, 28, 29, 33, 45–50. [b] Anhydrous purple Co^{2+} complex. [c] Hydrated orange Co^{2+} complex. [d] Some of the absorptions in these regions are masked by ν_{ClO_4} or $\nu_{M\text{-}Ligand}$ bands.

complexes are interpreted in terms of the simultaneous presence of ionic ClO_4^- and unidentate coordinated $-OClO_3$ ligands.[51,52] The Ni^{2+}, Zn^{2+} and the hydrated Co^{2+} complexes exhibit doublets in the ν_3 and $\nu_4(ClO_4)$ regions, and are presumably similar to $[Cu(tpH)_2(OClO_3)_2]$,[28,29] as far as the exclusive presence of unidentate coordinated $-OClO_3$ is concerned.[51,52] However, the Mn^{2+} and anhydrous Co^{2+} complexes show quintuply split ν_3 and $\nu_4(ClO_4)$ bands, which were previously[29] attributed to the simultaneous presence of unidentate $-OClO_3$ and bidentate chelating $=O_2ClO_2$ ligands.[51,52] Actually, the Mn^{2+} and anhydrous Co^{2+} complexes exhibit doublets or complexes, as would be expected for compounds containing coordinated perchlorato ligands.[51,52] Actually, the Mn^{2+} and an hydrous Co^{2+} complexes exhibit doublets or very broad maxima in the ν_1 and $\nu_2(ClO_4)$ regions. A single ν_{OH} band at 3420–3380 and a single δ_{HOH} absorption at 1638–1630 cm^{-1} indicate that exclusively coordinated water is present in the new hydrated metal complexes.[53]

As regards the tpH IR bands, all the new adducts exhibit the $\nu_{CH} + \nu_{NH}$ bands of the ligand practically unchanged (3130–2600 cm^{-1} region), since they comprise neutral tpH. Among these bands, those at 3120 and 2820 cm^{-1} involve ν_{C8-H} contribution,[28,46–50] whilst the rest (3060, 2980 and bands at 2790–2620 cm^{-1}) are most probably purely ν_{NH} absorptions.[45–50] The $\nu_{C=O}$ bands of free tpH are generally insensitive to 3d metal perchlorate adduct formation, so that it can be concluded that the new complexes do not involve tpH binding through one of the C=O oxygens.[6,9,16–19,28,29,41–43,46,54] Coordination of tpH through a ring nitrogen is suggested by the more significant shifts and splittings of various $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrational modes at 1620–1150 cm^{-1}.[6,9,16–19,28,29,41–43,46,54] Tentative $\nu_{M\text{-ligand}}$ band assignments (Table II), based on previous studies of tetra-, penta- and hexa-coordinated 3d metal complexes with various purines,[19,28,41,43,55–58] aqua[19,41,43,55–60] and perchlorato[28,41,43,56,57,60,61] ligands, are in favour of the following coordination numbers: four for the Fe^{2+} and Zn^{2+},[19,28,55,57,60] five for the Mn^{2+} and anydrous Co^{2+} [41,55,57,58] and six for the Cr^{3+}, Fe^{3+}, Ni^{2+} and hydrated Co^{2+} [41,43,55–61] complexes. The spectrum of free tpH at 600–200 cm^{-1} recorded during our study agrees with published data[19]; the free ligand bands below 500 cm^{-1} are mostly due to out-of-plane ring vibrations.[62]

The molar conductivities of the Cr^{3+}, Fe^{2+} and Fe^{3+} complexes (Table III) are within the range of values corresponding to 1:1 electrolytes,[63] and indicate that among the perchlorate groups present in these compounds only one is ionic. The remaining M^{2+} complexes involve exclusively coordinated perchlorate in the solid state, on the basis of the IR evidence (*vide supra*). In nitromethane-acetone solutions they show Λ_M values corresponding practically to non-electrolytes (Mn^{2+} and anhydrous Co^{2+} complexes) or intermediate between non- and 1:1-electrolytes (Zn^{2+}, Ni^{2+} and hydrated Co^{2+} complexes).[63] In the latter cases, partial displacement of $-OClO_3$ by solvent ($(CH_3)_2C=O$ or CH_3NO_2) ligands presumably occurs in solution, as was also the case with $[Cu(tpH)_2(OClO_3)_2]$.[28]

Electronic Spectra and Magnetic Moments

The magnetic moments of the new paramagnetic metal complexes (Table III) are generally normal for high-spin $3d^3$-$3d^8$ compounds or the $3d^9$ configuration.[64] In addition, the μ_{eff} values of the two Co^{2+} perchlorate adducts are consistent with the far-IR evidence, *i.e.*, indicative of coordination number five for the anhydrous (4.52 BM)[65] and six for the hydrated (4.84 BM)[64] cobaltous complexes. The UV spectrum of tpH (Nujol mull[28] and aqueous solution[66] spectra previously reported; Table III) generally undergoes shifts of the $\pi \rightarrow \pi^*$ transition bands (223, 276 nm) toward lower energies, as well as splittings of the same bands, upon 3d metal perchlorate adduct formation. The $n \rightarrow \pi^*$ transition of free tpH is observed at 300 nm in the Nujol mull spectrum[28,67] and appears at 298–304 nm in the spectra of the new complexes. The new

TABLE III

Solid-state (Nujol mull) Electronic Spectra, Magnetic Susceptibilities (298 K) and Molar Conductivities of tpH Adducts with Metal Perchlorates

Complex	λ_{max}, nm[a]	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, μB	Λ_M, Ω^{-1} cm^2 mol^{-1} [b]
$Cr(tpH)_2(ClO_4)_3 \cdot 2H_2O$	204vvs, 225vs, 240vs, sh, 279vs, b, 299s, sh, 355s, sh, 435ms, 460ms, 581m, 602m, 653mw, b	5921	3.77	86
$Mn(tpH)_2(ClO_4)_2$	200vvs, 226vs, 214vs, 282vs, b, 298vs, sh, 351s, sh, 420m, b	15008	6.01	12
$Fe(tpH)_2(ClO_4)_2 \cdot H_2O$	200vvs, 227vs, 243vs, 268vs, 279vs, b, 304s, sh, 352s, sh, 560mw, b, 828w, b, 952w, b	10,215	4.96	74
$Fe(tpH)_2(ClO_4)_3 \cdot 2H_2O$	201vvs, 228vs, 245vs, 280vs, vb, 298vs, sh, 351s, sh, 445s, sh, 540w, sh	15,633	6.13	82
$Co(tpH)_2(ClO_4)_2$	202vvs, 227vs, 242vs, sh, 269vs, 286vs, b, 302s, sh, 350s, sh, 463 ms, 522ms, 554ms, 630m, 768m, b, 870w, b, 1000w, b, 1910vw, b	8503	4.52	9
$Co(tpH)_2(ClO_4)_2 \cdot 2H_2O$	201vvs, 226vs, 239vs, 245vs, sh, 272vs, 287vs, 300s, sh, 353s, sh, 471ms, 525ms, 551ms, 960mw, b, 1185mw, b	9735	4.84	27
$Ni(tpH)_2(ClO_4)_2 \cdot 2H_2O$	200vvs, 225vs, 232vs, sh, 246vs, 273vs, 284vs, 301s, sh, 353s, sh, 431ms, 640m, b, 717m, sh, 993w, b, 1171w, b	4111	3.14	31
$Zn(tpH)_2(ClO_4)_2$	200vvs, 222vs, 241vs, 288vs, vb, 303s, sh, 347s, sh	Diamagnetic		28

[a] Nujol mull UV spectrum of tpH, nm: 223vvs, 276vs, 300vs, sh. Aqueous solution spectrum (pH 6–7): 270 nm (logα 4.02).[66]

[b] Conductance measurements were performed at 25C on 10^{-3}M solutions of the complexes in 1:1 (v/v) nitromethane-acetone.

paramagnetic metal complexes exhibit strong metal-to-ligand charge-transfer absorptions, originating in the UV and trailing off into the visible region.[68] The d–d transition spectra of the Cr^{3+}, Ni^{2+} and hydrated Co^{2+} complexes are consistent with low symmetry hexacoordinated configurations,[69] *vis*, nm: M = Cr^{3+} $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 435, 460; $^4T_{2g}(F)$ 581, 602, 653 (approximate Dq = 1634 cm^{-1}); Ni^{2+} $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 431; $\rightarrow {}^3T_{1g}(F)$ 640, 717; $\rightarrow {}^3T_{2g}(F)$ 993, 1171 (approximate Dq = 923 cm^{-1}); Co^{2+} $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 471; $\rightarrow {}^4A_{2g}(F)$ 525, 551; $\rightarrow {}^4T_{2g}(F)$ 960, 1185. The approximate Dq values calculated for the Cr^{3+} and Ni^{2+} complexes for pure O_h symmetry are compatible with MN_2O_4 chromophores.[56,57,70] The d–d spectrum of the anhydrous Co^{2+} complex is characteristic of pentacoordinated compounds of this metal ion (multiple maxima at 463–1910, including bands at 760–870 and 1910 nm).[69,71] Finally, the spectrum of the Fe^{2+} adduct, with maxima at 560, 828 and 952 nm, is consistent with distorted tetrahedral symmetry.[60,72,73]

The overall evidence presented indicates that the new adducts of tpH with 3d metal perchlorates are monomeric species. The inner coordination sphere of the central metal ions is occupied by two terminal unidentate tpH ligands, which are presumably bound by the N7 iidazole nitrogen of this ligand.[6,11–13,21,24,25,30–32] The coordination is completed by two, three or four oxygen ligands from perchlorato and, in the hydrated species, water molecules, depending on whether the coordination number is four, five or six, respectively. Among M^{2+} perchlorates, only the Zn^{2+} salt produced a tetrahedral adduct analogous to the corresponding Cu^{2+} complex,[28] *i.e.*, $[Zn(tpH)_2(OClO_3)_2]$. The Fe^{2+} complex is also tetrahedral, but involves one water in place of one of the perchlorato ligands and one ionic ClO_4^- group, *viz.* $[Fe(tpH)_2(OClO_3)(OH_2)]ClO_4$. The Mn^{2+} and anhydrous Co^{2+} complexes contain four ligands, but are pentacoordinated with one of the perchlorato ligands functioning as a chelating bidentate: $[M(tpH)_2(OClO_3)(=O_2ClO_2)]$ (M = Mn, Co). It is somewhat surprising that in the environment of the same four ligands, Co^{2+} in the preceding complex is pentacoordinated, while the corresponding Zn^{2+} complex is tetrahedral; in fact, Co^{2+} and Zn^{2+} tend to produce isomorphous complexes, as, for instance, the tetrahedral 1:1 adducts of their chlorides with 9-methyladenine.[74,75] The rest of the new complexes are dihydrates, involving coordination of two of each of the following three ligands: tpH, $-OClO_3$ and water. The M^{3+} complexes contain also one ionic ClO_4^-, *i.e.*, $[M(tpH)_2(OClO_3)_2(OH_2)_2]ClO_4$ (M = Cr, Fe), while the M^{2+} complexes are neutral of the $[M(tpH)_2(OClO_3)_2(OH_2)_2]$ (M = Co, Ni) type.

REFERENCES

1. C.M. Mikulski, M.K. Kurlan, S. Grossman and N.M. Karayannis, *Abstr., 189th Natl. Meetg., Am. Chem. Soc., Miami Beach, Florida,* April 28–May 3, 1985; No. INOR 117.
2. D.J. Hodgson, *Progr. Inorg. Chem.,* **23,** 211 (1977).
3. L.G. Marzilli, T.J. Kistenmacher and C.H. Chang, *J. Am. Chem. Soc.,* **95,** 7507 (1973).
4. D.J. Sutor, *Acta Cryst.,* **11,** 83 (1958); E. Shefter, *J. Pharm. Sci.,* **58,** 710 (1969).
5. 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).
6. A.R. Norris, R. Kumar, E. Buncel and A.L. Beauchamp, *J. Inorg. Biochem.,* **21,** 277 (1984).
7. D. Lichtenberg, F. Bergmann and Z. Neiman, *J. Chem. Soc., C,* 1676 (1971).
8. R. Weiss and H. Venner, Hoppe Seyler's *Z. Physiol. Chem.,* **340,** 138 (1965); **345,** 122 (1966).
9. D. Crăciunescu and A. Fruma, *Inorg. Chim. Acta.,* **4,** 287 (1970).
10. D. Crăciunescu and I. Mihalcea, *Rev. Real Acad. Cienc. Ex. Fis. Nat. Madrid.,* **64,** 1039 (1970).
11. T.J. Kistenmacher, *Acta Cryst.,* **B31,** 85 (1975); T.J. Kistenmacher and D.J. Szalda, *Acta Cryst.,* **B31,** 90 (1975).
12. 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).
13. T. Sorrell, L.G. Marzilli and T.J. Kistenmacher, *J. Am. Chem. Soc.,* **98,** 2181 (1976).
14. T.J. Kistenmacher, D.J. Szalda, M. Rossi, C.C. Chiang and L.G. Marzilli, *Inorg. Chem.,* **17,** 2582 (1978).

15. D.J. Szalda, T.J. Kistenmacher and L.G. Marzilli, *J. Am. Chem. Soc.*, **98,** 8371 (1976).
16. W. Beck and N. Kottmair, *Chem. Ber.*, **109,** 970 (1976).
17. M.S. Zitzman, R.R. Krebs and W.J. Birdsall, *J. Inorg. Nucl. Chem.*, **40,** 571 (1978); W.J. Birdsall, M.S. Zitzman, *J. Inorg. Nucl. Chem.*, **41,** 116 (1979).
18. S.D. Rothenberger, M.S. Zitzman and W.J. Birdsall, *J. Inorg. Nucl. Chem.*, **43,** 1673 (1981); B.J. Acken, D.A. Cole and W.J. Birdsall, *Synth. React. Inorg. Met.-Org. Chem.*, **13,** 659 (1983).
19. W.J. Birdsall, *Inorg. Chim. Acta.*, **99,** 59 (1985).
20. N.H. Agnew, T.G. Appleton, J.R. Hall, G.F. Kilmister and I.J. McMahon, *Chem. Commun.*, 324 (1979).
21. B.L. Kindberg, E.H. Griffith, E.L. Amma and E.R. Jones, Jr., *Cryst. Struct. Commun.*, **5,** 533 (1976).
22. E.H. Griffith and E.L. Amma, *Chem. Commun.*, 322 (1979).
23. K. Aoki and H. Yamazaki, *Chem. Commun.*, 186 (1980).
24. M. Biagini Cingi, A.M. Manotti Lanfredi, I.A. Tiripicchio and M. Tiripicchio Camellini, *Trans. Met. Chem.*, **4,** 221 (1979).
25. M. Biagini Cingi, A.M. Manotti Lanfredi and A. Tiripicchio, *Acta. Cryst.*, **C39,** 1523 (1983).
26. R.H. Barry, H. Rubin, J.B. Johnson and J.H. Lazarus, *J. Pharm. Sci.*, **70,** 204 (1981).
27. M. Melnik, *Polyhedron.*, **1,** 143 (1982).
28. C.M. Mikulski, T.B. Tran, L. Mattucci and N.M. Karayannis, *Inorg. Chim. Acta.*, **78,** 269 (1983).
29. C.M. Mikulski, M.K. Kurlan, S. Grossman, M. Bayne and N.M. Karayannis, *Inorg. Chim. Acta.*, **108,** L7 (1985).
30. M.J. Gardner, F.X. Smith and E. Shefter, *J. Pharm. Sci.*, **72,** 348 (1983).
31. A.R. Norris, S.E. Taylor, E. Buncel, F. Belanger-Gariépy and A.L. Beauchamp, *Inorg. Chim. Acta.*, **92,** 271 (1984).
32. A.R. Norris, R. Kumar, E. Buncel and A.L. Beauchamp, *Can. J. Chem.*, **63,** 2575 (1985).
33. E. Colacio Rodriguez, J.M. Salas Peregrin and M.A. Romero Molina, *Rev. Chim. Miner.*, **21,** 123 (1984).
34. K. Caldwell, G.B. Deacon, B.M. Gatehouse, S.C. Lee and A.J. Canty, *Acta Cryst.*, **C40,** 1533 (1984).
35. H. Reinert and R. Weiss, *Hoppe Seyler's Z. Physiol. Chem.*, **350,** 1310 (1969).
36. N.N. Basargin, Dzh.N. Askerov, I.K. Guseinov and Sh.U. Islamov, *Zh. Neorg. Khim.*, **27,** 311 (1982); P. Umapathy, R.A. Harnesswala and C.S. Dorai, *Polyhedron.* **4,** 1595 (1985).
37. A.R. Norris, E. Buncel and S.E. Taylor, *J. Inorg. Biochem.*, **16,** 279 (1982).
38. E. Buncel, B.K. Hunter, R. Kumar and A.R. Norris, *J. Inorg. Biochem.*, **20,** 171 (1984).
39. E. Buncel, A.R. Norris, W.J. Racz and S.E. Taylor, *Inorg. Chem.*, **20,** 98 (1981); S.E. Taylor, E. Buncel and A.R. Norris, *J. Inorg. Biochem.*, **15,** 131 (1981); E. Buncel, A.R. Norris, S.E. Taylor and W.J. Racz, *Can. J. Chem.*, **60,** 3033 (1982).
40. C.M. Mikulski,M.K. Kurlan, C.J. Lee, M. Bayne, M. Gaul and N.M. Karayannis, *Inorg. Chim. Acta,* **108,** L15 (1985).
41. C.M. Mikulski, T.B. Tran, L. Mattucci and N.M. Karayannis, *Inorg. Chim. Acta,* **78,** 211 (1983).
42. C.M. Mikulski, M.K. Kurlan and N.M. Karayannis, *Inorg. Chim. Acta,* **106,** L25 (1985).
43. C.M. Mikulski, M.K. Kurlan, M. Bayne, M. Gaul and N.M. Karayannis, *Inorg. Chim. Acta,* **123,** 27 (1986).
44.. 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).
45. E.R. Blout and M. Fields, *J. Am. Chem. Soc.*, **72,** 479 (1950).
46. F. Allaire and A.L. Beauchamp, *Can. J. Chem.*, **62,** 2249 (1984).
47. D. Cook and Z.R. Regnier, *Can. J. Chem.*, **45,** 2899 (1967).
48. D. Cook and Z.R. Regnier, *Can. J. Chem.*, **46,** 3055 (1968).
49. D. Cook and Z.R. Regnier, *Can. J. Chem.*, **45,** 2895 (1967).
50. S. Goenechea, *Mikrochim. Acta.* 276 (1972).
51. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961); B.J. Hathaway, D.G. Holah and M. Hudson, *J. Chem. Soc.*, 4586 (1963).
52. A.E. Wickenden and R.A. Krause, *Inorg. Chem.*, **4,** 404 (1965); 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).
53. I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta,* **20,** 429 (1964).
54. S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull.*, **26,** 2941, (1978).
55. C.M. Mikulski, L. Mattucci, L. Weiss and N. Karayannis, *Inorg. Chim. Acta,* **107,** 81, 147 (1985); **108,** L35 (1985).
56. C.M. Mikulski, L. Mattucci, Y. Smith, T.B. Tran and N.M. Karayannis, *Inorg. Chim. Acta,* **80,** 127 (1983).
57. A.N. Speca, C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski and N.M. Karayannis, *Inorg. Chem.*, **19,** 3491 (1980); *Inorg. Chim. Acta,* **46,** 235 (1980); *J. Inorg. Nucl. Chem.*, **43,** 2771 (1981).
58. C.M. Mikulski, S. Cocco, N. DeFranco, T. Moore and N.M. Karayannis, *Inorg. Chim. Acta,* **106,** 89 (1985).
59. A.N. Speca, L.S. Gelfand, L.L. Pytlewski, C. Owens and N.M. Karayannis, *Inorg. Chem.*, **15,** 1493 (1976); L.S Gelfand, L.L. Pytlewski, D.L. Cosgrove, C.M. Mikulski, A.N. Speca and N.M. Karayannis, *Inorg. Chim. Acta,* **32,** 59 (1979).

60. N.M. Karayannis and C.M. Mikulski, *Inorg. Nucl. Chem. Lett.*, **17**, 261 (1981).
61. J.R. Ferraro and A. Walker, *J. Chem. Phys.*, **42**, 1273, 1278 (1965).
62. C.P. Beetz, Jr., and G. Ascarelli, *Spectrochim. Acta*, **A36**, 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. L. Sacconi, *J. Chem. Soc., A*, 248 (1970).
66. W. Pfleiderer and G. Nübel, *Justus Liebigs Ann. Chem.*, **647**, 155 (1961).
67. L.B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc.*, **87**, 11 (1965).
68. A.B.P. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 1235 (1962); 3156, 5042 (1963); 1187, 4761 (1964)
69. W. Byers, A.B.P. Lever and R.V. Parish, *Inorg. Chem.*, **7**, 1835 (1968).
70. M.A. Guichelaar and J. Reedijk, *Rec. Trav. Chim. Pays-Bas*, **97**, 295 (1978).
71. I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, **14**, 1639 (1975).
72. D.H. Gerlach and R.H. Holm, *Inorg. Chem.*, **8**, 2292 (1969).
73. C.M. Mikulski, R. Minutella, N. DeFranco, G. Borges, Jr., and N.M. Karayannis, *Inorg. Chim. Acta*, **123**, 105 (1986).
74. P. deMeester, D.M.L. Goodgame A.C. Skapski and Z. Warnke, *Biochim. Biophys. Acta*, **324**, 301 (1973).
75. M.J. McCall and M.R. Taylor, *Acta Cryst.*, **B32**, 1687 (1976).