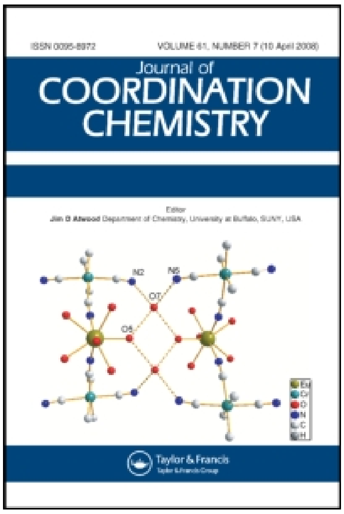

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ADDUCTS OF THEOBROMINE WITH 3d METAL PERCHLORATES

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ADDUCTS OF THEOBROMINE WITH 3d METAL PERCHLORATES*

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Adducts of theobromine (tbH) with 3d metal perchlorates ($M^{n+} = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$) were prepared by refluxing mixtures of the ligand and a metal salt in ethyl acetate-triethyl orthoformate. The new complexes invariably involve 2:1 molar ratios of tbH to metal ion and are apparently monomeric with terminal tbH ligands binding *via* a ring nitrogen (N9 or N1). The Mn^{2+}, Cu^{2+} and Zn^{2+} complexes are distorted tetrahedral, involving two tbH and two unidentate perchlorato ligands in the first coordination sphere of the metal ion. The remaining metal(II) complexes (Fe, Co, Ni) were obtained as monohydrates. These compounds are pentacoordinated of the $[M(tbH)_2(OClO_3)_2(OH_2)]$ type, containing one aqua ligand in addition to the tbH and perchlorato ligands. The Cr^{3+} and Fe^{3+} complexes are low-symmetry hexacoordinated, with two tbH ligands, two unidentate and one bidentate chelating perchlorate ligands.

Keywords: theobromine, complexes, first row, synthesis, perchlorate

INTRODUCTION

The metal complexes of methyl-substituted xanthines, such as caffeine (caf; 1,3,7-trimethyl-), isocaffeine (1,3,9-trimethyl-), theobromine (tbH; 3,7-dimethyl-; **I**) and theophylline (tpH; 1,3-dimethyl-), are attracting increasing attention. The free bases are important components of tea, coffee, cocoa and chocolate products, and have found medicinal applications as stimulants, diuretics and for their cardiovascular effects.[2] They are also relevant to cancer therapy because of their ability to sensitize cells towards the cytotoxic effects of UV radiation, alkylating agents and *cis*-$Pt(NH_3)_2Cl_2$.[3] Metal complexes of tpH have been studied to the largest extent,[4] while the number of research papers on caf metal complexes shows a significant increase recently.[5,6] In contrast, there is a relative paucity of information on complexes of tbH. Earlier work on theobromine complexes has included the crystal structure determination of $(tbH)_2I_2O_8$,[7] spectral investigations of the complexation tbH with sodium benzoate,[8] Brönsted (HCl, HI, $HSbCl_6$, HPF_6, $HAsF_6$) and carboxylic acids[9] and the preparation of $Rh(CO)(PPh_3)_2(tb)$.[10] More recent work includes the preparation and characterization of $Cu(tbH)_2(ClO_4)_2$,[11] $Cu(tbH)(CH_3CH_2COO)_2$,[12] $Pd(tbH)(tb)Cl$[13] and $ZrO(tbH)_2(tb)Cl{\cdot}H_2O$,[14] and the crystal structure determination of $K[Pt(tbH)Cl_3]{\cdot}H_2O$.[15] In the latter complex, which was prepared under acidic conditions, tbH binds through the N9 imidazole

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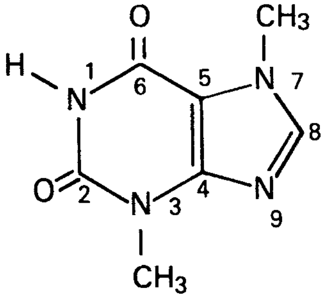
nitrogen to Pt^{2+}.[15] This is not necessarily indicative of a general trend for terminal unidentate tbH. In fact, tpH was found to bind through N9 only in complexes (including $(tpH_2)[Pt(tpH)Cl_3]$),[16,17] prepared under sufficiently acidic conditions to preclude ionization at N7,[18] while in most of its metal complexes tpH binds through N7,[18-20] which is the protonation site of the free neutral ligand. Purines have the tendency to use the ring nitrogen 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.[21] In neutral tbH, the N1 pyrimidine nitrogen is protonated[22,23] as shown in **I**. In view of this, N1 and N9 were considered as about equally likely to act as the binding site of terminal unidentate tbH.[11,12] It should be also noted that the presence of a bridging bidentate tb^- in Pd(tbH)(tb)Cl, binding *via* N1,N9, has been proposed (infinite $\left[\text{Pd–tb}\right]_x$ chains).[13] Binding of bidentate bridging purines *via* N1,N9 has not been so far established; the closest analogy is that of $Cu(hxH)SO_4{\cdot}H_2O$ (hxH = hypoxanthine), the crystal structure determination of which revealed the presence of infinite $\left[\text{Cu–hxH}\right]_x$ chains involving N3,N7-bound hxH.[24]



I

Special interest in these laboratories has attended the syntheses and characterization of 3d metal perchlorate complexes with purines.[4,25-29] Following the preparation of the tetrahedral $[Cu(tbH)_2(OClO_3)_2]$ adduct from ethanol-triethyl orthoformate (teof),[11] we attempted to synthesize tbH adducts with other 3d metal perchlorates from the same medium, but failed to obtain solid products. We later developed an alternative synthetic method, involving the use of ethyl acetate (ea)-teof as the preparation medium.[30] This method proved to be generally more rapid and efficient (higher yields) than that using ethanol-teof,[30] and was successfully employed in the preparation of crystalline tbH adducts with a series of 3d metal perchlorates ($M^{n+} = Cr^{3+}$, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}).[1] The tbH adducts were obtained in 59–100% yields (Table I); regarding the Cu^{2+} adduct, it was obtained in 95% yield from ea-teof, whereas its yield from EtOH-teof was only 73.5%.[11] The present paper deals with the syntheses of the above tbH adducts and their characterization by means of spectral, magnetic and conductance studies.

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

Complex	Colour	Yield %	C %	H %	N %	M %	Cl %
$Cr(tbH)_2(ClO_4)_3$	Olive green	78	23.84 (23.66)	2.08 (2.27)	16.12 (15.77)	7.40 (7.32)	15.20 (14.97)
$Mn(tbH)_2(ClO_4)_2$	Cream white	59	27.67 (27.38)	2.71 (2.63)	18.11 (18.24)	8.86 (8.95)	11.41 (11.54)
$Fe(tbH)_2(ClO_4)_2{\cdot}H_2O$	Mustard yellow	69	26.70 (26.56)	2.94 (2.87)	17.97 (17.70)	8.97 (8.82)	11.58 (11.20)
$Fe(tbH)_2(ClO_4)_3$	Orange brown	91	23.00 (23.53)	2.47 (2.26)	15.34 (15.68)	7.53 (7.82)	14.91 (14.89)
$Co(tbH)_2(ClO_4)_2{\cdot}H_2O$	Lavender	90	26.88 (26.43)	2.67 (2.85)	18.02 (17.61)	9.29 (9.26)	11.33 (11.15)
$Ni(tbH)_2(ClO_4)_2{\cdot}H_2O$	Light green	100	26.50 (26.44)	2.91 (2.85)	17.47 (17.62)	9.45 (9.23)	11.36 (11.15)
$Cu(tbH)_2(ClO_4)_2$[b]	Light yellow	95	27.29 (27.00)	2.63 (2.59)	17.76 (17.99)	10.28 (10.20)	11.60 (11.39)
$Zn(tbH)_2(ClO_4)_2$	White	69	26.79 (26.92)	2.45 (2.58)	17.82 (17.94)	10.58 (10.47)	11.64 (11.85)

[a] Found % with Calc. % in parentheses. [b] Cu^{2+} complex prepared from ea-teof (this work); the same complex was previously prepared from EtOH-teof in 73.4% yield (analysis: C 27.17%; H 2.78%; N 18.15%; Cu 9.97%; Cl 11.47%).[11]

EXPERIMENTAL

The synthetic method employed was identical to that previously used for the preparation of tpH adducts with the same metal perchlorates,[4] *i.e.*: 1.25 mmol of hydrated metal perchlorate is dissolved in a mixture of 35 cm^3 ea and 15 cm^3 teof, 2.5 mmol (for M^{2+}) or 3.75 mmol (for M^{3+}) of tbH 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 room temperature, 15–20 cm^3 anhydrous diethyl ether are added and the volume is subsequently reduced at low heat to about 20 cm^3. The solid residue is separated by filtration, washed with 30 cm^3 diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. The new metal complexes were generally isolated in the form of crystalline free-flowing powders. 2 : 1 tbH to metal ion adducts were formed in all cases, as indicated by analytical results (Table I). The Fe^{2+}, Co^{2+} and Ni^{2+} complexes were isolated as monohydrates, while the remaining complexes are anhydrous 2 : 1 adducts. The complexes exhibit limited solubility in organic media. Their solubility increases when certain binary solvent mixtures, such as nitromethane-acetone, are used.

IR spectra of tbH and its metal complexes (Table II) were recorded in KBr discs (4000–500 cm^{-1}) and Nujol mulls between NaCl (4000–500 cm^{-1}) and high density polyethylene (700–200 cm^{-1}) windows, using a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility (300 K) and conductance measurements (on $10^{-3}M$ solutions of the complexes in 1 : 1 (v/v) nitromethane-acetone at 25°C) (Table III) were obtained by methods previously described.[31]

TABLE II

Relevant Infrared Data for the New tbH Adducts with Metal Perchlorates (cm^{-1}).

tbH[a]	$M = Cr^{3+}$	$M = Mn^{2+}$	$M = Fe^{2+}$	$M = Fe^{3+}$	$M = Co^{2+}$	$M = Ni^{2+}$	$M = Cu^{2+}$	$M = Zn^{2+}$	Band assignment
			3455m,b		3460m,b	3480m,b			ν_{OH}(aqua)
3150m,3112m 3030m,2825m	3174m,3120m 3034m,2834w	3158m,3118m 3023m,2821w	3168m,3114m 3033m,2827w	3165m,3111m 3024m,2820w	3160m,3115m 3035m,2828w	3170m,3118m 3039m,2830w	3166m,3116m 3040m,2828w	3160m,3120m 3028m,2826w	$\nu_{CH} + \nu_{NH}$
1685vs,b 1660vs,b	1694vs 1671vs	1685vs 1662vs	1686vs 1664vs	1690vs 1671vs	1688vs 1665vs	1692vs 1669vs	1690vs,vb	1690vs 1666vs	ν_{C-O}
1595s,sh 1547m,b	1617m,1598m 1568m,1551m 1546m	1590m,1557m 1542m,1520w	1637s,sh 1589m,1558m 1540m	1611m,1592m 1561m,1547m	1640s,sh, 1600m,1590m 1562m,1547m	1635s,sh, 1592m,1560m 1549ms	1600mw,sh 1559mw,sh 1543m	1591m,1562m 1545ms, 1520w	$\delta_{HOH} + \nu_{C-C} +$ $\nu_{C-N} + \delta_{NH}$
1479w,sh 1449s,1422m 1360s,1335m 1290m,1222m 1152mw,b, 1121mw,b	1492m,1471m 1450m,1438m 1426m,1410w 1392w,1371m 1339w,1298m 1262w,1237m 1229s,1210m 1178w,1170w 1141ms	1481m,1460m 1450m,1439m 1421m,1412m 1390w,1365m 1331w,1290m 1257w,1220s 1202m,1170w 1137ms	1480m,1459m 1450m,1419m 1409m,1385w 1363m,1330w 1290m,1255w 1220s,1200w 1169w, 1136ms	1483m,1463m 1454m,1424m 1412m,1390w 1369m,1335w 1295w,1260w 1222s,1202w 1170w, 1140ms	1481m,1463m 1454m,1449m 1422m,1410m 1390w,1369m 1331w,1295m 1224s,1203m 1171mw, 1137ms	1488m,1463m 1458m,1426w 1411m,1395w 1370w,1338w 1298w,1262w 1227s,1208w 1174w, 1141ms	1490w,1454s 1430m,1369s 1361m,1346m 1303w,1275w 1250w,1188w 1140m,sh, 1119m,sh	1483m,1462m 1456m,1422m 1412m,1391w 1368m,1335w 1293w,1259w 1221m,1202w 1170w, 1139ms	Ring vibrations $+ \nu_{C-N} + \delta_{CH_3}$
	1133ms,1119 ms,1108s, 1083s,1066ms	1109ms 1082ms	1100ms 1078ms	1130ms,1118 ms,1100s, 1085s,1060s	1108s 1080s,b	1108s 1087ms	1097s,sh 1062s	1099s 1069s	$\nu_3(ClO_4)$
1050w,1010w 960vw,932vw	1042w,1018w 1000w,977vw	1039w,1020w 995vw,982vw	1038w,1018v.w, 975vw,b	1042w,1020w 990vw,975vw	1045w,1020w 978vw,961vw	1043w,1022w 980vw,962vw	1050m,1012w 982w,955w	1044w,1018w 970vw,b	Ring vibrations
	943w,936w	937w	935w	939w,b	936mw	941w	925w,b	936w	$\nu_1(ClO_4)$
880w,845mw 775vw,750w 735w,712mw 655w,b	891mw,868mw 783w,762mw 749mw,729m 681m,675m 667w,sh	884m,860m 780w,760mw 749mw,729m 679m,666w	882mw,858mw 778vw,759mw 748w,739mw 680m,663mw	886m,863m 780w,760mw 750mw,730mw 690vw,680m 667mw	887mw,859mw 780w,760mw 750mw,730mw 680mw,664w, sh	890w,869w 783w,766w 754w,736w 687m,662w, sh	860w,vb, 802w,775w 753w,728vs, b,666w,sh	888w,862w 780w,761w 750w,730w 681m,657w, sh	Ring vibrations $+ \delta_{NH} + \delta_{CH}$
	644mw,633ms 622m,615m, 607m,sh	627m,617m	629m,614m	645mw,632m 626m,618m 609m	631m,616m	630mw,619m	633m,620m	628m,617m	$\nu_4(ClO_4)$
598m,552w 525w,505w 489w,435w 402vw,381vw 350vw,310vw 261w,235mw	589w,547vw 511m,507m 490vw,456mw 423w,377w 360w,315w 247mw,b	600w,550vw 509m,492w 453mw,420w 390w,370w 350w,238mw	600w,548vw 508mw,488vw 417w,390vw 370w,236mw	597w,550vw 509w,453mw 420w,372w 244mw,b	595w,550vw 510w,487vw 427w,420w 381w,239mw	600w,545vw 510w,490vw 423w,380w 238mw,b	598m,552vw 490vw,b, 440w,412w 375w,240mw	599w,552vw 540w,452w 420w,372w 245mw,b	ν Ligand (600-230 cm^{-1})
	485w,470w	479w	472w	483w,469w	480w	472w,sh	475w,sh	474w,sh	$\nu_2(ClO_4)$
			444m		451m	458m			ν_{M-O}(aqua)
	335w	328w	319w	331w	324w	326w	336w,b	325w	ν_{M-O}(perchlorato)
	277w,b	284w,253mw	263w,249mw	274w,b	271w,255mw	274w,257mw	304w,sh, 275w,b	280w,251mw	ν_{M-N}

TABLE III
Solid-state (Nujol mull) Electronic Spectra, Magnetic Properties (300 K) and Molar Conductivities of tbH Adducts with Metal Perchlorates.[a]

Complex	λ_{max}, nm	$10^6\chi_M^{cor}$ cgsu	μ_{eff},μB	Λ_M,Ω^{-1}cm^{2}mol^{-1}
$Cr(tbH)_2(ClO_4)_3$	197vvs, 244vvs, 270vvs, 302vs,sh, 354s,sh, 436ms, 464ms, 577m,b, 604m, 657m	5932	3.79	11
$Mn(tbH)_2(ClO_4)_2$	199vvs, 245vvs, 280vvs, 304vs,sh, 349s,sh, 460m,b	14,720	5.97	25
$Fe(tbH)_2(ClO_4)_2 \cdot H_2O$	200vvs, 245vvs, 279vvs, 307vs,sh, 360s,sh, 475m,sh, 695mw,b, 827mw,b, 950mw,b, 1420w,b	10,257	4.98	20
$Fe(tbH)_2(ClO_4)_3$	204vvs, 243vs, 250vs, 278vs, 303s, 350s,sh, 442m,sh 545mw,b	15,121	6.05	14
$Co(tbH)_2(ClO_4)_2 \cdot H_2O$	202vvs, 241vvs, 280vvs, 304vs,sh, 355s,sh, 461ms, 520ms, 560ms, 625m, 772m,b, 885w,b, 1010w,b, 1920vw,b	8533	4.54	30
$Ni(tbH)_2(ClO_4)_2 \cdot H_2O$	197vvs, 240vvs, 277vvs, 303vs,sh, 348s,sh, 452ms,sh 487m, 570m, 642mw,b, 755mw,b, 904w,b, 1020w,b, 1300vw, 1820vw,b	4839	3.42	27
$Cu(tbH)_2(ClO_4)_2$	196vvs, 243vvs,sh, 268vvs,b, 276vs,sh, 307vs,sh, 347s,sh, 405ms, 812m,b	1615	1.98	37
$Zn(tbH)_2(ClO_4)_2$	200vvs, 247vvs, 281vs, 305vs,sh, 355ms,sh	Diamagnetic		22

[a] UV spectrum of free tbH (Nujol mull), nm: 200vvs, 232vs, 273vvs, 301s,sh. Reported aqueous solution spectrum at pH 6–7: 271 nm, log ε 4.01.[52] Conductance measurements were performed at 25°C on $10^{-3}M$ solutions of the complexes in a 1 : 1 (v/v) mixture of nitromethane and acetone.

RESULTS AND DISCUSSION

IR and conductance Data

Table II gives relevant IR spectral data for tbH and the new complexes. Band assignments for free tbH were based on reported complete or partial IR spectra of the free base or its metal complexes,[9–11,13,14,32] and band assignments for xanthine,[33] tpH[4] and caf.[34–36] Among the ligand bands in the $\nu_{CH} + \nu_{NH}$ region, those at 3112 and 2825 cm^{-1} involve a $\nu_{C8\text{–}H}$ contribution, while those at 3150 and 3030 cm^{-1} are probably pure ν_{NH} absorptions.[9,11,13,14,32–36] No attempts at distinguishing between $\nu_{C2=O}$ and $\nu_{C6=O}$ were made; these modes were *assigned* to absorptions at 1702 and 1660 cm^{-1}, respectively, in the IR spectrum of caf,[36] while in that of xanthine the same modes were *assigned* to bands at 1672 and 1702 cm^{-1}, respectively.[33] In the spectra of the new complexes, neither the $\nu_{CH} + \nu_{NH}$ nor the $\nu_{C=O}$ bands of the free ligand undergo significant changes. This is consistent with the presence of neutral tbH ligands not involved in binding through a C=O oxygen atom.[4,10,11,13,14,33,37] It should be mentioned at this point that xanthine and its derivatives do not show a tendency to bind through the C=O oxygen. Bonding of this type has been established in only a few cases, as, for instance, for tp^- chelation to

Cu^{2+} *via* O6,N7, involving a strong Cu–N7 and a weak Cu–O6 (bond length 2.9–3.3Å) bond.[38] Coordination of tbH through ring nitrogens in the new complexes is suggested by significant shifts and splittings of the free ligand $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrational modes at 1600–1150 cm^{-1} upon complex formation.[4,10,11,13,14,33,37] The $\nu(ClO_4)$ bands in the spectra of the complexes suggest that these compounds contain exclusively coordinated perchlorato ligands. Thus, both ν_1 and ν_2 (ClO_4) are IR-active, while the ν_3 and ν_4 modes are each split into two components in the M^{2+} and five components in the M^{3+} complexes.[39,40] This is interpreted in terms of the exclusive presence of unidentate $-OClO_3$ ligands in the M^{2+} and both uni- and bidentate perchlorato ligands ($-OClO_3$ and $=O_2ClO_2$) in the M^{3+} complexes.[4,39,40] The presence of exclusively coordinated perchlorate was previously reported for tpH complexes with various 3d M^{2+} perchlorates[4] and an adenine adduct with $Ru(ClO_4)_3$.[41] It should be pointed out that a medium-strong to strong band observed at 1141–1136 cm^{-1} in the spectra of the new complexes is not due to a component of $\nu_3(ClO_4)$, but a tbH ligand vibration. In fact, a medium intensity band at *ca* 1140 cm^{-1} is also observed in the spectra of metal chloride complexes with theobromine, such as Pd(tbH)(tb)Cl and $ZrO(tbH)_2(tb)Cl\cdot H_2O$;[13,14] this ligand band is intensified due to partial overlap with the very strong $\nu_3(ClO_4)$ absorption in the spectra of the complexes herein reported. The ν_{OH} and δ_{HOH} modes of coordinated water appear at 3480–3455 and 1640–1635 cm^{-1}, respectively, in the spectra of the hydrated complexes.[42] Tentative $\nu_{M-Ligand}$ band assignments, based on previous studies of tetra-, penta- and hexa-coordinated complexes of various purines,[4,11,25–30,43,44] aqua[4,27,28,42–44] and perchlorato[4,11,29,45] ligands with 3d metal ions, favour coordination number four for M = Mn^{2+}, Cu^{2+}, Zn^{2+}, five for M = Fe^{2+}, Co^{2+}, Ni^{2+} and six for M = Cr^{3+}, Fe^{3+}. The ligand bands at below 500 cm^{-1} are mostly due to out-of-plane ring vibrations.[46]

The molar conductivity values for the new complexes (Table III) in nitromethane–acetone either correspond to non-electrolytes or are intermediate between values reported for non- and 1 : 1-electrolytes.[47] In the latter case, partial displacement of perchlorato ligands by solvent molecules ($(CH_3)_2C=O$ or CH_3NO_2) presumably occurs in solution. The conductance data support the IR evidence, indicating that the complexes contain exclusively coordinated perchlorate in the solid state.

Electronic Spectra and Magnetic Moments

The ambient temperature magnetic moments of the new complexes (Table III) are generally normal for high-spin $3d^3$–$3d^8$ compounds or the $3d^9$ configuration.[48] In addition, the μ_{eff} values for the Co^{2+} (4.54 µB) and Ni^{2+} (3.42 µB) complexes are within the ranges corresponding to high-spin pentacoordinated compounds of these metal ions.[49–51] The UV spectrum of tbH (Nujol mull[11] and aqueous solution[52] spectra previously reported: Table III) undergoes shifts and splitting of the $\pi \rightarrow \pi^*$ transition bands (232, 273 nm) upon metal complex formation. The observed trend is shifting of these bands toward lower energies. The $n \rightarrow \pi^*$ transition band of the ligand (301 nm)[53] appears at 302–307 nm in the spectra of the complexes. Strong metal-to-ligand charge-transfer absorption, originating in the UV and trailing off into the visible region is observed in the spectra of the new paramagnetic complexes.[54] The d–d spectrum of the Cr^{3+} complex is compatible with a low symmetry hexacoordinated configuration: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 436, 464; $\rightarrow {}^4T_{2g}(F)$ 577, 604, 657 nm.[55] The calculated approximate Dq value is 1632 cm^{-1}, similar to that of

$[Cr(tpH)_2(OClO_3)_2(OH_2)_2]ClO_4$ (1634 cm^{-1}).[4] The d–d spectra of the Fe^{2+}, Co^{2+} and Ni^{2+} complexes are characterized by multiple maxima at 690–1420, 461–1920 and 452–1820 nm, respectively, as expected for pentacoordinated compounds of these metal ions.[55-58] The previously reported Cu^{2+} complex exhibits its main d–d maximum at 812 nm;[11] this spectrum is consistent with a distorted tetrahedral configuration.[44,59-61]

On the basis of the overall evidence discussed, the new complexes appear to be monomeric adducts with exclusively coordinated perchlorate and terminal unidentate tbH ligands, coordinating either *via* the imidazole N9 or the pyrimidine N1 ring nitrogen.[11,12,15] The Mn^{2+} and Zn^{2+} complexes are distorted tetrahedral analogues of the previously reported Cu^{2+} complex. The Fe^{2+}, Co^{2+} and Ni^{2+} adducts involve an aqua ligand in addition to two tbH and two $-OClO_3$ ligands and are pentacoordinated. The Cr^{3+} and Fe^{3+} complexes are low symmetry hexacoordinated species with two terminal tbH, two unidentate and one bidentate perchlorato ligand. The presence of both unidentate and bidentate chelating perchlorato ligands was previously proposed for tpH adducts with Co^{2+} and Mn^{2+} perchlorates.[4] Regarding the types of 2 : 1 adducts between tpH[4,11] or tbH (this work) and 3d metal perchlorates prepared in these laboratories, only those with Cu^{2+} and Zn^{2+} are of the same type (distorted tetrahedral $[ML_2(OClO_3)_2]$). The Mn^{2+} tbH complex is also of the preceding type, but the tpH analogue is pentacoordinated with one $-OClO_3$ and one chelating $=O_2ClO_2$ ligand.[4] The M^{3+} (Cr, Fe) complexes with tbH are water-free and involve both unidentate and bidentate coordinated perchlorate, whilst the corresponding tpH adducts are dihydrates with two $-OClO_3$ and two aqua ligands and one ionic ClO_4^-.[4] Finally, Fe^{2+}, Co^{2+} and Ni^{2+} yielded pentacoordinated monohydrates with tbH. The corresponding[4] tpH Fe^{2+} complex was also a monohydrate, but contained both ionic and coordinated unidentate perchlorate (distorted tetrahedral, *viz*, $[Fe(tpH)_2(OClO_3)(OH_2)]ClO_4$). Co^{2+} formed an anhydrous pentacoordinated adduct, similar to its Mn^{2+} analogue. Ni^{2+} yielded the dihydrate $[Ni(tpH)_2(OClO_3)_2(OH_2)_2]$. A Co^{2+} complex of the latter type was formed upon exposure of the anhydrous $[Co(tpH)_2(OClO_3)(=O_2ClO_2)]$ to atmospheric moisture.[4] It is somewhat surprising that two very similar ligands, such as tbH and tpH, produce structurally different 2 : 1 adducts with many 3d metal perchlorates. This applies not only to differences between anhydrous *vs* hydrated species, but also to complexes of exactly the same stoichiometries (specifically $MnL_2(ClO_4)_2$ and $FeL_2(ClO_4)_2 \cdot H_2O$; L = tbH, tpH).

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