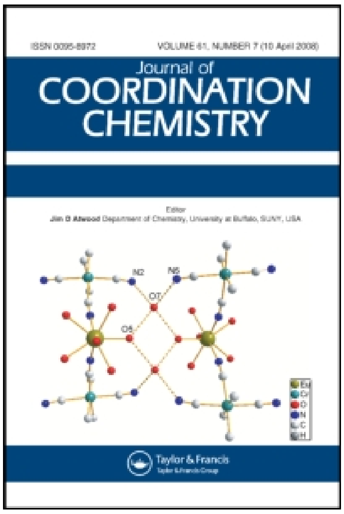

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HYPOXANTHINE COMPLEXES WITH FIRST ROW TRANSITION METAL PERCHLORATES

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HYPOXANTHINE COMPLEXES WITH FIRST ROW TRANSITION METAL PERCHLORATES[+]

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Complexes of hypoxanthine (hxH) with 3d metal perchlorates were synthesized by refluxing mixtures of ligand and metal salt in ethyl acetate–triethyl orthoformate. In all cases investigated, partial substitution of one anionic hx^- for one ClO_4^- group occurred. The solid complexes isolated contain also two or three neutral hxH ligands per metal ion, *viz* $M(hx)(hxH)_3(ClO_4)_2$ (M = Cr, Fe), $M(hx)(hxH)_3ClO_4 \cdot H_2O$ (M = Mn, Cu, Zn), $Co(hx)(hxH)_3ClO_4$ and $M(hx)(hxH)_2ClO_4 \cdot H_2O$ (M = Fe, Ni). The new complexes appear to be generally polymeric species characterized by a single-bridged $\mathrm{+M{-}hx+}_x$ backbone, in which bidentate hx^- probably binds *via* N3 and N7 to adjacent metal ions. The neutral hxH ligands are terminal N7-bound. The Co(II) complex is pentacoordinated with three terminal hxH ligands and ionic ClO_4^-. The rest of the complexes are hexacoordinated, containing two or three terminal hxH ligands and the following additional ligands; $M = Fe^{2+}, Ni^{2+}$: $-OClO_3$, aqua; $M = Cr^{3+}, Fe^{3+}$: $-OClO_3$ (also ionic ClO_4^-); $M = Mn^{2+}, Cu^{2+}, Zn^{2+}$: aqua (ClO_4^- is ionic).

Keywords: hypoxanthine, complex, synthesis, perchlorato ligand, polymers

INTRODUCTION

Hypoxanthine (hxH; 6-oxopurine; **I**), a constituent of inosine in RNA,[2] is a ligand of significant biological interest, both as such and as a simpler analogue of guanine (guH; 2-amino-6-oxopurine).[3] HxH and xanthine (xnH; 2,6-dioxopurine) are intermediates in the reduction of nucleic acids to uric acid in man, catalyzed by the Mo- and Fe-containing enzyme xanthine oxidase. Mo(VI) complexes with xnH or hxH apparently contribute to the mechanism of action of this enzyme.[4] In view of this, the coordination chemistry of hxH and xnH acquires medical interest in connection with disease resulting from disturbances in purine metabolism, such as xanthinuria and gout.[5] Weiss *et al.*[6] isolated the first metal complexes with hxH and determined that the stability constants of Cu(II) complexes with various purines decrease along the series adenine (adH) > purine (puH) > hxH > 7-methyl-hypoxanthine > 9-methyl-hypoxanthine > xnH.[7] The crystal structure determination of the dimeric complex $[Cu_2(hxH)_4Cl_2]Cl_2 \cdot 6H_2O$ revealed the presence of quadruple bridges of N3,N9-bound hxH between the two Cu^{2+} ions.[8] $Cu(hxH)SO_4 \cdot 2H_2O$ was also recently found to contain bidentate bridging N3,N9-bound hxH.[9] Other recent crystal structure determinations by Dubler *et al.*, within the framework of their studies on metal

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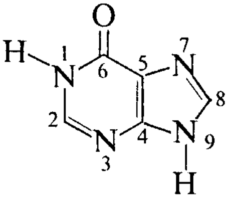
[+] Presented in part at the XXV ICCC; see ref. 1. * Author for correspondence.

complexes with hxH, xnH and uric acid,[10] established a new type of binding for bidentate bridging hxH in the square pyramidal polymeric species $Cu(hxH)SO_4 \cdot H_2O$; this compound is characterized by infinite $\{Cu-hxH\}_x$ chains, involving N3,N7-bound hxH protonated at N1 and N9, and terminal $-OSO_3$ and aqua ligands.[11] Terminal N7-bound hxH is present in $Co(hxH)SO_4 \cdot 5H_2O$,[11] $Ni(hxH)SO_4 \cdot 5H_2O$[12] and $Ru(hxH)(NH_3)_5Cl_3 \cdot 3H_2O$.[13] Previous work in these laboratories on the metal complexes of various purines, including xnH[14,15] and hxH, has resulted in the isolation and characterization of a few hypoxanthine complexes, namely Pd(hx)(hxH)Cl, $Pt(hx)(hxH)Cl_3$,[16] $ZrO(hx)(hxH)_2Cl \cdot H_2O$[17] and $Cu(hx)ClO_4 \cdot 4EtOH$.[14] The latter Cu^{2+} complex was precipitated by refluxing mixtures of hxH and $Cu(ClO_4)_2$ in ethanol–triethyl orthoformate (teof).[14] More recently, we attempted the syntheses of hxH complexes with other 3d metal perchlorates ($M = Cr^{3+}$, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}) from EtOH–teof 7:3 (v/v), but either obtained precipitates in very low yields or failed to produce any solid precipitate. We subsequently developed an improved synthetic method using ethyl acetate (ea)–teof as the interaction medium.[18] By employing this method, which has been successful in producing metal perchlorate complexes with xnH,[15] theophylline (tpH)[19] and theobromine (tbH)[20] in high yields, we were also able to prepare new 3d metal perchlorate complexes with hypoxanthine in 60–100% yields. These complexes are dealt with in the present paper.



hxH

I

EXPERIMENTAL

The synthetic procedure was similar to that previously used for the preparation of metal perchlorate complexes with other substituted purines,[15,19,20] *i.e.*, 1.25 mmol of hydrated metal perchlorate was dissolved in a mixture of 35 cm^3 of ea and 15 cm^3 of teof, 2.5 (for M^{2+}) or 3.75 (for M^{3+}) mmol hxH were added, and the resultant mixture was refluxed for 6 h or until no further significant change in appearance was noted. After cooling to room temperature, 15–20 cm^3 anhydrous diethyl ether was added to the mixture and the volume was then reduced at low heat to *ca* 20 cm^3. The precipitated solid was separated by filtration, washed with 30 cm^3 diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. As was the case with the corresponding xnH complexes,[15] the new hxH complexes involve high ligand to metal ion ratios (4:1 or 3:1), being of the following types (analytical data given in Table I): $M(hx)(hxH)_3(ClO_4)_2$ (M = Cr, Fe), $M(hx)(hxH)_3ClO_4 \cdot H_2O$ (M = Mn, Cu, Zn), $M(hx)(hxH)_2ClO_4 \cdot H_2O$ (M = Fe, Ni) and $Co(hx)(hxH)_3ClO_4$. It is noteworthy that in all cases investigated, substitution of one anionic hx^- ligand for one ClO_4^- group

TABLE I
Analytical data for the new hypoxanthine metal complexes.[a]

Complex	Colour	Yield%	C%	H%	N%	M%	Cl%
$Cr(hx)(hxH)_3(ClO_4)_2$	Lavender-grey	100	30.73	2.23	28.26	6.12	8.55
			(30.24)	(1.90)	(28.21)	(6.55)	(8.93)
$Mn(hx)(hxH)_3ClO_4{\cdot}H_2O$	Tan	61	33.81	2.57	30.98	7.75	5.18
			(33.56)	(2.39)	(31.31)	(7.67)	(4.95)
$Fe(hx)(hxH)_2ClO_4{\cdot}H_2O$	Mustard yellow	71	30.77	2.08	29.21	9.40	5.96
			(31.03)	(2.26)	(28.95)	(9.62)	(6.11)
$Fe(hx)(hxH)_3(ClO_4)_2$	Cocoa brown	100	29.76	2.03	27.82	6.64	9.15
			(30.10)	(1.89)	(28.08)	(7.00)	(8.88)
$Co(hx)(hxH)_3ClO_4$	Purple[b]	81	34.47	2.38	32.22	8.42	5.18
			(34.23)	(2.15)	(31.93)	(8.40)	(5.05)
$Ni(hx)(hxH)_2ClO_4{\cdot}H_2O$	Light green	100	31.14	2.27	29.11	9.78	6.24
			(30.88)	(2.25)	(28.80)	(10.06)	(6.08)
$Cu(hx)(hxH)_3ClO_4{\cdot}H_2O$	Blue-green	95	33.08	2.45	31.09	8.84	4.60
			(33.16)	(2.37)	(30.93)	(8.77)	(4.89)
$Zn(hx)(hxH)_3ClO_4{\cdot}H_2O$	White	66	32.69	2.50	30.43	8.63	4.73
			(33.08)	(2.36)	(30.86)	(9.00)	(4.88)

[a] Found % with Calc. % in parentheses. [b] Moisture-sensitive tacky solid. The rest of the new complexes were obtained as free-flowing powders, stable in the presence of atmospheric moisture.

occurred. The new complexes are generally insoluble in organic media. IR spectra of hxH and the new 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 683 spectrophotometer. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements (300° K) (Table III) were obtained by methods described elsewhere.[21]

RESULTS AND DISCUSSION

Infrared Evidence

IR spectral data for the hxH free base[22,23] and several of its metal complexes[11,14,16,17,24–26] have appeared in the literature. Band assignments for free hxH were made on the basis of some of our previous studies[16,17], in combination with the corresponding assignments for inosine 5′-monophosphate,[27] xnH[28] and guH.[29] The new metal complexes invariably exhibit the $\nu_{CH} + \nu_{NH}$ bands of the free ligand virtually unchanged (Table II), as expected, since both hxH and hx$^-$ contain protonated ring nitrogens. The $\nu_{C=O}$ mode of free hxH undergoes small shifts toward higher wavenumbers upon 3d metal perchlorate complex formation indicating that the C=O oxygen of the ligand is not involved in coordinative bonding interactions with the metal ions.[11,14,16,17,24–29] On the other hand, several of the $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrations of free hxH appear significantly shifted and occasionally split in the spectra of the new complexes. This is suggestive of coordination of the ligands

TABLE II

Relevant IR spectral data for the new hypoxanthine metal complexes (cm^{-1}).

hxH[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
		3380m,b	3400m,b			3410m,b	3390m,b	3380m,b	ν_{OH}(aqua)
3140m,3050m 2960s,2920s 2870s	3130m,3045m 2980ms,2940 ms,2870m,b	3130m,3050m 2975ms,2930 ms,2880m,b	3135m,3040m 2970ms,2925 ms,2875m,b	3130m,3035m 2970ms,2935 ms,2865m,b	3135m,3035m 2980ms,2940 ms,2875m,b	3135m,3040m 2970m,2935 ms,2875m,b	3140m,3045m 2960m,2935 ms,2870m,b	3135m,3040m 2960m,2940m 2880m,b	$\nu_{CH} + \nu_{NH}$
1665vs	1674vs	1667vs	1669vs	1672vs	1669vs	1667vs	1670vs	1670vs	$\nu_{C=O}$
1605w,1579m	1622m,1584m 1550mw,b	1638ms,sh, 1618m,sh, 1578m,1560m	1640ms,sh, 1620m,1600m 1580m,1555m	1620m,1581m 1555mw,b	1618m,1576m 1547mw,b	1635ms,sh, 1622m,1600m 1580m,1577m	1637ms,sh, 1616m,sh 1582s,1565m	1635ms,sh, 1620m,sh 1580s,1568w	$\delta_{H\ O\text{-}H} + \nu_{C=C}$ $\nu_{C=N} + \delta_{NH}$
1510w,1455s 1419m,1377m 1360m,1341m 1268m,1205m 1141m,1123m	1511w,1470w 1423m,1400w 1370w,1352w 1278w,1250 vw,1219ms 1149s,sh	1515w,1466m 1459w,1420m 1390w,1362m 1347m,1270m 1250w,1210s 1192m,1140m, sh,1125s,sh	1512w,1465w, b,1418w, 1397w,1368w 1349w,1270w 1211ms, 1135ms	1510w,1472 w,b,1420m 1395w,1367w 1349w,1273w 1214mw, 1144s,sh	1509w,1470 w,b,1424m 1396w,1370w 1346w,1271m 1250w,1213s 1142m,sh 1126s,sh	1517w,1465w 1450w,1420w 1395mw,1372 w,1335w 1270vw,b 1205m 1130ms,sh	1510w,1469 mw,1422m 1407w,1365m 1346m,1272w 1208s,1151m 1138ms	1507w,1468 mw,1420m 1406w,1367m 1349m,1271w 1211s,1150m 1136ms	Ring vibrations + ν_{C-N} + δ_{NH}
	1140vs,1105 vs,1086vs	1093vvs,b	1094vvs, 1076vvs	1137vs,1102 vvs,1077vvs	1090vvs,b	1097vvs, 1082vvs	1095vvs,b	1098vvs,b	$\nu_3(ClO_4)$
955m,895w, sh,880m, 779w,630m, sh,580m,sh	1038w,969w 940vw,896mw 850vw,795vw 572w,567w	1040w,sh 962s,904s 890s,850w 789m,690w,b 640mw,564m	1039w,sh 961w,900w 890mw,855vw 788w,690w 610m,564mw	1040w,sh 963w,938vw 902w,889w 854w,790w 692w,607m 567w,560w	1035w,sh 962ms,942vw 908w,890w 855vw,790w 691w,646m, sh,566m	1040w,sh 960w,900mw 881mw,850vw 785w,685w,b 606w,sh 560w	1035w,sh 970s,945vw 902ms,890s 850vw,788m 690w,644mw 606mw,568ms	1030w,sh 962m,950vw 905m,890s 852vw,790m 692w,642mw 610m,565m,b	Ring vibrations + γ_{NH} + δ_{CH}
	916mw	920vvw	931mw	922mw	930vvw	930mw	923vvw	925vvw	$\nu_1(ClO_4)$
	648m,632m 626m	620ms	644m,620m	641m,629m 620m	623ms	642m,619m	621s	626ms	$\nu_4(ClO_4)$
545m,520m 450w,sh 387w,362w 345w,b,241w 231w,211w	530w,450vw 372w,350w 307vw,240w, b,214w	522w,470vw 455vw,368m 340m,300w 213w	523w,445vw 367w,340w 325w,211w	522w,452vw 367w,342w 304vw,240w b,215w	524w,470vw 453vw,370m 349m,303w 237w,b 212w	522w,448vw 369w,342w 321w,213w	520w,470vw 445vw,371ms 352m,304w 215w	525w,467vw 450vw,369w 343w,302vw 217w	ν_{Ligand}(560–200 cm^{-1})
	475w		470w,b	472w,b		470w,b			$\nu_2(ClO_4)$
		408mw	411mw			420mw	423mw	404mw	$\nu_{M\text{-}O}$(aqua)
	337w		303w	333w		306w			$\nu_{M\text{-}O}(OClO_3)$
	287w	245w,233w	246w,231w	284w	273w,252w	253w,237w	257w,240w	241w,227w	$\nu_{M\text{-}N}$

[a] Free hxH band assignments based on refs. 16, 17 and 27–29.

TABLE III

Solid-state (Nujol mull) electronic spectra and magnetic susceptibilities (330°K) of the new hypoxanthine metal complexes.

Complex	λ_{max}, nm[a]	μ_{eff}, B.M.
$Cr(hx)(hxH)_3(ClO_4)_2$	200vvs, 233vs,sh, 255vs, 267vs, 309s,sh, 330s, 433ms, 455ms, 535m,b, 573m, 610m	3.81
$Mn(hx)(hxH)_3ClO_4 \cdot H_2O$	198vvs, 229vs,sh, 254vs, 266vs, 312s,sh, 334s, 454m,vb	5.94
$Fe(hx)(hxH)_2ClO_4 \cdot H_2O$	199vvs, 236vs,sh, 258vs, 268vs, 309s,sh, 332s, 440ms,b, 730mw,b, 915mw,b	5.14
$Fe(hx)(hxH)_3(ClO_4)_2$	202vvs, 231vs,sh, 253vs, 266vs, 307s,sh, 329s, 440m,sh, 552mw,b	6.08
$Co(hx)(hxH)_3ClO_4$	201vvs, 234vs,sh, 252vs, 264vs, 309s,sh, 332s, 437ms, 464ms, 500ms, 535ms, 582ms, 617m, 771m,b, 890w,b, 1010w,b, 1900vw,b	4.56
$Ni(hx)(hxH)_2ClO_4 \cdot H_2O$	202vvs, 233vs,sh, 257vs, 265vs, 308s,sh, 334s, 432ms,sh, 450ms, 600mw, 640mw, 728w, 960w, 1020w,b	3.11
$Cu(hx)(hxH)_3ClO_4 \cdot H_2O$	197vvs, 232vs,sh, 256vs, 263vs, 311s,sh, 552s, 590ms,b, 765m,vb	1.92
$Zn(hx)(hxH)_3ClO_4 \cdot H_2O$	200vvs, 230s,sh, 259vs, 271vs, 310s,sh, 337s	Diamagnetic

[a] UV spectrum of free hx (Nujol mull), nm: 200vvs, 247vs, 280vs,sh, 340s,sh.[14,16,17] Aqueous solution spectra of hxH and hx^-,[40] nm (log ε); hxH (pH 5–7): 249 (4.02); hx^- (pH 10–11): 258 (4.05).

through ring nitrogens.[11,14,16,17,24-29] The ν_{OH} and δ_{HOH} modes of the aqua ligands appear at 3410–3380 and 1640–1635 cm^{-1}, respectively, in the spectra of the monohydrate metal complexes.[30] The ClO_4^- group is ionic in four of the M^{2+} complexes (M = Mn, Co, Cu, Zn), as shown by the single ν_3 and ν_4 and IR-inactive ν_1 and $\nu_2(ClO_4)$[31,32] bands. In the remaining M^{2+} complexes (M = Fe, Ni), ν_3 and ν_4 are split into doublets and ν_1 and $\nu_2(ClO_4)$ are IR-active, indicating the exclusive presence of terminal unidentate $-OClO_3$ ligands.[31,32] The spectra of the two M^{3+} complexes (M = Cr, Fe) are characterized by triply split ν_3 and ν_4 (ClO_4) bands (and IR-active ν_1, ν_2). This is interpreted in terms of the simultaneous presence of $-OClO_3$ ligands and ionic ClO_4^-.[31,32] Tentative $\nu_{M\text{-}Ligand}$ band assignments, based on previous studies of 3d metal complexes with various purines,[14,15,19,20,33,34] perchlorato[14,15,19,20,33,35] and aqua[14,15,30,33,34] ligands, favour coordination number five for $M = Co^{2+}$ [14,19,20,34] and six for the rest of the new complexes.[14,15,19,20,30,33-35]

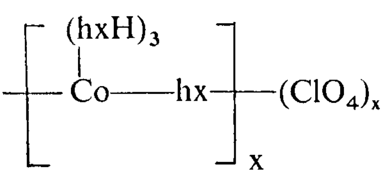
Electronic Spectra and Magnetic Moments

The ambient temperature magnetic moments of the new complexes are generally normal for high-spin $3d^3$–$3d^8$ compounds or the $3d^9$ configuration (Table III).[36] The μ_{eff} value for the Co^{2+} complex (4.56 B.M.) is within the range of values corresponding to pentacoordinated cobaltous compounds.[37] The normal room temperature magnetic moments observed do not exclude linear chainlike polymeric structures with single hx^- bridging ligands between adjacent metal ions (*vide infra*) for the new complexes. In fact, a number of $[M(puH)_2(OH_2)_3](ClO_4)_2$ linear polymeric complexes (M = Co, Ni, Cu), characterized by a $+M\text{–}puH+_x$ backbone, were found to exhibit normal ambient temperature magnetic moments and evidence favouring magnetic exchange interactions only at temperatures below 110° K.[33] Moreover, analogous magnetic behaviour was reported for several single-bridged Cu^{2+} polymeric complexes with a variety of diazine or diazole bridging ligands (Cu–Cu separations > 6.5 Å).[38,39]

The $\pi \rightarrow \pi^*$ transition bands of hxH at 247–249 and hx^- at 258 nm[40] appear shifted toward lower energies (*i.e.*, at 252–259 and 263–271 nm, respectively) in the spectra of the new complexes,[14-17] which also show the $n \rightarrow \pi^*$ transition of the ligand at 307–312 nm[41] (Table III). The paramagnetic complexes exhibit strong metal-to-ligand charge-transfer absorption originating in the UV and trailing off into the visible region.[42] The d–d transition spectrum of the Co^{2+} complex is characterized by several maxima at 437–1900 nm and is typical of pentacoordinated high-spin cobaltous compounds.[19,20,34,43,44] The d–d spectra of the Cr^{3+}, Fe^{2+}, Ni^{2+} and Cu^{2+} complexes are suggestive of low symmetry hexacoordinated configurations, *viz*, nm: $M = Cr^{3+}$ ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 433, 455; $\rightarrow {}^4T_{2g}(F)$ 535, 573, 610 (Dq = 1746 cm^{-1}); Fe^{2+} ${}^5T_{2g} \rightarrow {}^5E_g$ 730, 915 (Dq = 1216 cm^{-1}); Ni^{2+} ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 432, 450; $\rightarrow {}^3T_{1g}(F)$ 600, 648, 728; $\rightarrow {}^1E_g(D)$ 960; $\rightarrow {}^3T_{2g}(F)$ 1020 (Dq = 980 cm^{-1}); Cu^{2+} ${}^2E_g \rightarrow {}^2T_{2g}$ 552, 590, 765.[14,15,19,20,33,34,44] The approximate Dq values calculated for the Cr^{3+}, Fe^{2+} and Ni^{2+} complexes are compatible with CrN_5O and MN_4O_2 (M = Fe, Ni) chromophores.[14,33] The Co^{2+} and Cu^{2+} complexes presumably involve CoN_5 and CuN_5O absorbing species, respectively (*vide infra*).

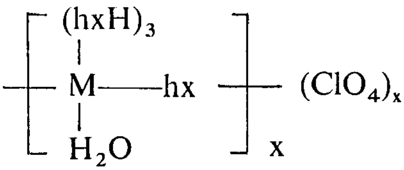
Likely Structures and Hypoxanthine Binding Sites

The overall evidence presented, combined with the insolubility of the new complexes in organic media and the pronounced tendency of purines to function as bidentate bridging ligands,[2,11,14,15,33,34] favours linear chainlike single-bridged polymeric structures with a $-\!\!\left[M{-}hx\right]\!\!-_x$ backbone and terminal unidentate hxH and, wherever applicable, $-OClO_3$ and aqua ligands. Structural types analogous to those proposed for the complexes of xnH with 3d metal perchlorates, which also involved 3:1 or 4:1 xanthine to metal molar ratios,[15] are most probable for the complexes herein reported. The new Co^{2+} complex is most probably of type **II**, with bridging hx^-, three terminal hxH ligands, and ionic ClO_4^-. Coordination number five is supported by the spectral and magnetic evidence, as well as the highly hygroscopic nature of this compound (Table I), which is due to its tendency to form the hexacoordinated monohydrate.[19] The remaining new complexes contain *O*-ligands in addition to the *N*-bound hypoxanthine ligands. Probable structural types are **III** for $M = Mn^{2+}$, Cu^{2+}, Zn^{2+} with one aqua ligand and ionic ClO_4^-, **IV** for $M = Fe^{2+}$, Ni^{2+} with aqua and perchlorato ligands, and **V** for $M = Cr^{3+}$, Fe^{3+} with both ionic and coordinated perchlorate.



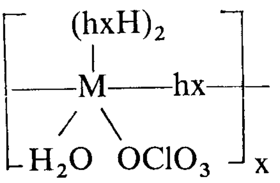
$$-\!\!\left[\overset{\overset{(hxH)_3}{|}}{Co}-hx\right]\!\!-_x(ClO_4)_x$$

II



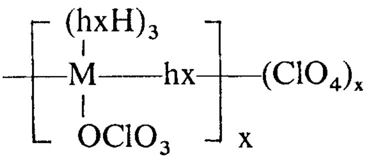
$$-\!\!\left[\underset{\underset{H_2O}{|}}{\overset{\overset{(hxH)_3}{|}}{M}}-hx\right]\!\!-_x(ClO_4)_x$$

III



$$-\!\!\left[\underset{H_2O\ \ OClO_3}{\overset{\overset{(hxH)_2}{|}}{M}}-hx\right]\!\!-_x$$

IV



$$-\!\!\left[\underset{\underset{OClO_3}{|}}{\overset{\overset{(hxH)_3}{|}}{M}}-hx\right]\!\!-_x(ClO_4)_x$$

V

The ring nitrogens that are protonated in free neutral hxH are N1,N7 or N1,N9[40,45,46] (the latter tautomer is shown in **I**). IR evidence appearing to favour the N1,N7-diprotonated tautomer has been presented,[40] and is further supported by the reported crystal structures of Co^{2+},[11] Ni^{2+} [12] and Ru^{3+} [13] adducts with N7-bound hxH (terminal unidentate purines usually bind to metal ions *via* the imidazole nitrogen which is protonated in the free base[2]). It should be mentioned, however, that the existence of linkage isomers of the $[Ru(hxH)(NH_3)_5]Cl_3{\cdot}xH_2O$ complex with either N7- or N9-bound hxH has been demonstrated[13,47] and may be commensurate with a tautomeric equilibrium whereby N7 or N9 acts as acceptor of the most acidic proton of hxH. Furthermore, complexes with N7- ($M = Cd^{2+}$)[48] or N9- ($M = Zn^{2+}$, Hg^{2+})[49,50] bound terminal 8-azahypoxanthine were also reported.

Nevertheless, the fact that the crystal structures available for 3d metal complexes (M = Co^{2+}, Ni^{2+}) with terminal hxH show this ligand binding *via* N7,[11,12] clearly favours N7-bound hxH for the new complexes. As regards the binding sites of bridging bidentate hx^- in these complexes, the N3,N7 combination is most likely. In fact, bridging hxH is, as already mentioned, N3,N7-bound in the single-bridged $Cu(hxH)SO_4 \cdot H_2O$ linear polynuclear complex,[11] which contains a backbone analogous to that proposed for the new complexes. It is also probable that the $Cu(hx)ClO_4 \cdot 4EtOH$ complex we reported earlier[14] involves N3,N7-bound bridging hx^- ligand. It should be noted that the only other type of binding established for bidentate bridging hypoxanthine is *via* N3,N9, which appears to apply in complexes with multiple ligand bridges between adjacent metal ions, as, for instance, $[ClCu(hxH)_4CuCl]Cl_2 \cdot 6H_2O$.[8]

Finally, it is worth noticing that, whereas hxH metal complexes prepared from aqueous media involve relatively low ligand to metal ion molar ratios (1:1 or 2:1) [6–9, 11–13,25,26], the corresponding complexes obtained from the non-aqueous ea–teof medium are characterized by 3:1 or 4:1 hypoxanthine to metal ion ratios. 3:1 or 4:1 complexes of xnH with 3d metal perchlorates were also isolated from ea–teof.[15] On the other hand, $Cu(ClO_4)_2$ yielded $Cu(xn)_2 \cdot 2EtOH$ and $Cu(hx)ClO_4 \cdot 4EtOH$ from EtOH–teof,[14] but xnH formed 3:1 or 4:1 complexes with other 3d metal perchlorates from the latter medium.[15] With other purines, 2:1 or 1:1 complexes with the same metal perchlorates were obtained in these laboratories either from EtOH–teof (puH,[33] adH,[51] guH[52]) or ea–teof (tpH,[19] tbH[20]) with the sole exception of a 3:1 adenine complex with ferric perchlorate.[51] Thus it appears that among the biologically most imporant purines only hxH and xnH have the tendency to yield 3d metal perchlorate complexes with relatively high ligand to metal molar ratios from non-aqueous media and especially ea–teof.

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