Xanthine Complexes with 3d Metal Perchlorates

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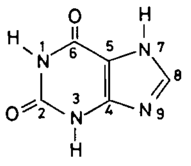
Abstract

Complexes of xanthine (xnH) with 3d metal perchlorates were prepared by refluxing mixtures of ligand and metal salt in ethyl acetate–triethyl orthoformate. In all cases, partial substitution of anionic xn^- for ClO_4^- groups occurs, and the solid complexes isolated also contain invariably two neutral xnH ligands per metal ion, *viz.* $Cr(xn)_2(xnH)_2ClO_4$, $Fe(xn)_2(xnH)_2ClO_4 \cdot H_2O$, $M(xn)(xnH)_2ClO_4 \cdot H_2O$ (M = Fe, Co, Ni) and $M(xn)(xnH)_2ClO_4 \cdot 2H_2O$ (M = Mn, Zn). The new complexes are generally hexacoordinated and appear to be linear chainlike polymeric species characterized by a $\text{-}(M\text{–}xn)\text{-}_n$ single-bridged backbone. Four terminal ligands per metal ion, including two xnH groups in all cases, complete its inner coordination sphere; the remaining two terminal ligands differ from complex to complex as follows: $M = Cr^{3+}$ xn^-, $-OClO_3$; Fe^{3+} xn^-, H_2O; Fe^{2+}, Co^{2+}, Ni^{2+}–$OClO_3$, H_2O; Mn^{2+}, Zn^{2+} two aqua ligands. Probable binding sites of bidentate bridging xn^- and unidentate terminal xnH and xn^- are discussed.

Introduction

Earlier work in these laboratories has resulted in the preparation of $Cu(xn)_2 \cdot 2EtOH$ [1], as well as a series of complexes of xanthine (xnH, I) with other 3d metal ions (Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}) [2, 3]. All the preceding complexes were prepared by refluxing mixtures of ligand and 3d metal perchlorate in a 7 3 (v/v) mixture of ethanol and triethyl orthoformate (teof) [1–3]. $Cu(xn)_2 \cdot 2EtOH$ was obtained in good yield (53.1% of the theoretical), by refluxing a 2·1 mixture of xnH and $Cu(ClO_4)_2$ in ethanol–teof for a week [1]. However, the corresponding reactions of xnH with other 3d metal perchlorates in the same medium (at 2·1 for M^{2+} or 3.1 for M^{3+} ligand to metal ion molar ratios) [2, 3], generally resulted in poor yields (less than 10–15%) even when the duration of the refluxive step was extended to 1–2 months. The complexes obtained under these conditions involved relatively high xanthine to metal ion ratios in most cases, as already reported [2, 3]. More recently, attempts at synthesizing theophylline (tpH; 1,3-dimethylxanthine) complexes with 3d metal perchlorates from ethanol–teof failed to produce solid products in all but one cases [4], the sole exception being $Cu(tpH)_2(ClO_4)_2$, which was precipitated by treating the reaction mixture with acetone after discontinuing the refluxive step [5]. Later, we succeeded in preparing solid tpH complexes with the whole series of 3d metal perchlorates in good yields, by employing a 7:3 (v/v) mixture of ethyl acetate–teof as the interaction medium [4], and we felt that this improved and substantially more rapid synthetic method would give better results when applied to the preparation of xnH complexes with metal perchlorates. Accordingly, synthetic work in this direction was undertaken, and solid metal complexes were easily prepared in yields exceeding 60% in all cases The present paper deals with the preparation and characterization of these complexes.



I

Neutral xnH involves three acidic protons, two of which are attached to the N(1) and N(3) pyrimidine nitrogens, while the third is attached to the N(7) imidazole nitrogen [6–10]. Monodeprotonated xn^- seems to contain the two protons at N(1) and N(3), on the basis of NMR and UV studies [8]. The crystal structure determination of bis(dimethylglyoximato) (xanthinato) (tri-n-butylphosphine) Co(III) revealed that xn^- is also protonated at N(1), N(3) and coordinates through the N(9) imidazole nitrogen to Co^{3+} [11], but in $Na(xn) \cdot 4H_2O$, the two

TABLE I. Analytical Data for Xanthine Complexes with 3d Metal Perchlorates

Complex	Color	Yield%	C%		H%		N%		Metal%		Cl%	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cr(xn)_2(xnH)_2ClO_4$	Drab green	100.0	31.70	31.89	1.86	1.61	29.57	29.33	6.86	7.07	4.68	4.45
$Mn(xn)(xnH)_2ClO_4\cdot2H_2O$	White	65.4	27.90	28.17	2.34	2.52	26.03	25.90	8.51	8.75	5.49	5.54
$Fe(xn)(xnH)_2ClO_4\cdot H_2O$	Rust	71.6	28.66	29.11	2.08	2.16	26.74	26.89	8.88	8.53	5.64	5.38
$Fe(xn)_2(xnH)_2ClO_4\cdot H_2O$	Mustard	86.2	30.81	31.11	2.07	2.23	28.74	28.51	7.16	6.71	4.55	4.27
$Co(xn)(xnH)_2ClO_4\cdot H_2O$	Lilac	75.7	28.52	28.67	2.08	2.09	26.61	26.34	9.33	9.21	5.61	5.73
$Ni(xn)(xnH)_2ClO_4\cdot H_2O$	Pale green	76.2	28.53	28.12	2.08	2.21	26.62	26.42	9.30	9.17	5.61	5.46
$Zn(xn)(xnH)_2ClO_4\cdot2H_2O$	Off white	62.5	27.45	27.19	2.30	2.47	25.62	25.95	9.96	10.34	5.40	5.23

protons of xn^- ara attached to N(1) and N(9) [12]. It appears that the most acidic proton of xn^- is involved in a tautomeric equilibrium, whereby N(3), N(7), and even N(9), could act as acceptors [13]. In the xn^{2-} dianion only N(1) is protonated and in μ-(xanthinato)tris(methylmercury(II)) nitrate xn^{2-} acts as tridentate bridging N(3), N(7), N(9)-bonded [13]; whereas the xn^{3-} trianion functions as tetradentate bridging N(1), N(3), N(7), N(9)-bonded in μ-(xanthinato)tetrakis(methylmercury(II)) nitrate [13]. In addition to the preceding metal complexes [11–13], the preparations of a number of Co^{2+}, Ni^{2+} and Cu^{2+} complexes with unsubstituted xnH or xn^- have been reported [1, 14–17]. In metal complexes of xanthosine and its 5′-monophosphate, N(7) is apparently the preferred binding site [18–22]. Infrared evidence in favor of coordination of various monomethylxanthines through one of the carbonyl oxygens (O(2) or O(6)), in addition to a ring nitrogen, was recently presented for a number of Pd^{2+} and Pt^{2+} complexes [23, 24]. Finally, several complexes with di- and tri-methylxanthines, including the 1,3,8- [25] and 1,3,9- [24, 29] trimethyl-derivatives, as well as tpH, theorbromine (tbH; 3,7-dimethylxanthine) and caffeine (caf; 1,3,7-trimethylxanthine) (several references on complexes with the latter three ligands were provided in previous papers [4, 5]), have been prepared and studied.

Experimental

The synthetic method employed for the preparation of tpH complexes [4] was used, *viz.*: 1.25 mmol hydrated metal perchlorate is dissolved in a mixture of 35 ml ethyl acetate and 15 ml teof, 2.5 (for M^{2+}) or 3.75 (for M^{3+}) mmol xnH are added, and the resultant mixture is refluxed for 6 h or until no further significant change in appearance is noted. After cooling to ambient temperature, 15–20 ml anhydrous diethyl ether are added to the mixture and the volume is then reduced at low heat to *ca.* 20 ml. The solid residue is separated by filtration, washed with 30 ml diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. The new complexes involve relatively high ligand to metal ion ratios (4:1 for the M^{3+} and 3:1 for the M^{2+} complexes), as was also the case for most of the xanthine complexes previously isolated from ethanol–teof [2, 3]. Analytical data (Table I) indicate that the new complexes are of the $Cr(xn)_2(xnH)_2ClO_4$, $Fe(xn)_2(xnH)_2ClO_4\cdot H_2O$, $M(xn)(xnH)_2ClO_4\cdot H_2O$ (M = Fe, Co, Ni) and $M(xn)(xnH)_2ClO_4\cdot2H_2O$ (M = Mn, Zn) types. Only Fe^{3+} produced the same complex from both ethyl acetate–teof and ethanol–teof [2, 3]. Use of the latter medium had resulted in the formation of the monohydrate of the anhydrous Cr^{3+} complex herein reported, EtOH adducts of the $M(xn)(xnH)_2ClO_4$ species (M = Co, Ni, Zn), and the perchlorate-free $Fe(xn)_2$ and $Mn(xn)_2(xnH)_2$ complexes [2, 3]. The synthetic procedure used in the present work led to substitution of either two (for M^{3+}) or one (for M^{2+}) ClO^{4-} by xn^- groups, leaving in all cases one perchlorate group per metal ion in the solid complex. The new complexes are either insoluble or very sparingly soluble in organic media.

The IR spectra of the ligand and the new complexes (Table II) were recorded on KBr discs (4000–500 cm^{-1}) and on 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 and ambient temperature (298 K) magnetic susceptibility measurements (Table III) were obtained by using apparatus and techniques previously described [27].

Discussion

Infrared Evidence

IR [1, 13, 28] and far-IR [29] spectra of xnH have been published. For the assignments of the IR bands of the ligand, the recent works of Allaire and Beauchamp [13], Lusty *et al.* [24], Beetz and Ascarelli [29], as well as the corresponding band assignments for guanine [30], were used (Table II). Formation of the new metal complexes does not

TABLE II. Infrared Spectra of Xanthine Complexes with 3d Metal Perchlorates (cm^{-1})

xnH[a]	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{2+}	M = Fe^{3+}	M = Co^{2+}	M = Ni^{2+}	M = Zn^{2+}	Band assignment
		3410m,b	3390m,b	3400m,b	3390m,b	3370m,b	3400m,b	$\nu_{OH}(H_2O)$
3132w	3140m	3130m	3125m	3130m	3140m	3125m	3135m	ν_{C8-H}
3006s,2881s, 2828m,2795m, 2670mw,2590mw	3010ms,2885m, 2825m,2780m, 2675w,2595w	3000ms,2870m, 2822m,2790m, 2685w,2580w	2995ms,2865m, 2818m,2785m, 2680w,2580w	3005ms,2880m, 2820m,2800m, 2670w,2570w	3000ms,2880m, 2820m,2780m, 2675w,2580w	3000ms,2875m, 2815m,2795m, 2660w,2580w	2995ms,2875m, 2820m,2800m, 2670w,2585w	ν_{NH}
1702vs,1667vs	1709vs,1669vs	1700vs,1665vs	1704vs,1658vs	1697vs,1665vs	1700vs,1660vs	1705vs,1668vs	1702vs,1663vs	$\nu_{C6=O} + \nu_{C2=O}$
		1632m,sh	1633m,sh	1635m,sh	1630m,sh	1635m,sh	1628m,sh	δ_{H-O-O}
1569m,1539m, 1530w,sh	1583,1575m, 1563m,1550m,b, 1530w	1568m,1559m, 1542m,1525w	1570m,1561m, 1554m,1537w	1562m,vb, 1545m,1525w	1580m,1569m, 1560m,1530w	1567m,1559m, 1540m,1526w	1572m,1560m, 1548m,1534w	$\nu_{C=C} + \nu_{C=N} +$ δ_{NH}
1462ms,1449ms, 1437m,1415ms, 1390w,1336m, 1328m,1255w, 1234vw,1206w, 1199m,1161w, 1153w,1117w	1463m,1441w, 1424m,1382w, 1340m,1331mw, 1262w,1233vw, 1209m,1202m, 1162m,1155ms, 1112s	1473m,1454m, 1437w,1417m, 1375w, 1331ms, 1327ms,1257w, 1226w,1201ms, 1198ms,1158ms, 1150ms,1118ms	1461m,1453m, 1440w,1420m, 1365w,1335m, 1331w,1256w, 1220vw,1202m, 1198m,1156m, 1150ms,1115vs	1462m,1454m, 1437w,1419m, 1365w,1332m, 1326w,1259w, 1225vw,1204m, 1200m,1160m, 1150ms	1460m,1450m, 1438w,1419m, 1362w,1335m, 1330w,1258w, 1221vw,1202m, 1199m,1155m, 1150ms,1115s	1460m,1453m, 1435w,1418m, 1359w,1332m, 1326m,1255w, 1230w,1203m, 1196m,1158m, 1148ms,1110vs	1458m,1449m, 1439w,1418m, 1365w,1336m, 1330m,1259w, 1225vw,1204m, 1197m,1160m, 1150ms,1117ms	Ring vibrations + $\nu_{C-N} + \delta_{NH}$
	1130s,1090s	1090ms,b	1127vs,1080vs	1095vs,b	1120s,1090vs	1122vs,1078vs	1095ms,b	$\nu_3(ClO_4)$
1032w,953w	1038w,962w	1030w,958w	1035w,957w	1033w,959w	1035w,957w	1030w,955w	1030w,956w	Ring vibrations
	923w		931w		932w	930w		$\nu_1(ClO_4)$
895w,b,854m, 763m,720m, 630vw,sh,615w	900mw,855m, 767mw,724mw, 630w,sh	890m,851m, 763m,720m, 630w,sh	885w,850m, 763w,720w, 630w,sh	890w,850m, 762w,720w, 630w,sh	885w,850m, 763w,720w, 630w,sh	890w,848m, 761m,719m, 630w,sh	892w,851m, 761m,720m, 630w,sh	Ring vibrations + $\gamma_{NH} + \delta_{CH}$
	626m,612m	617m	625ms,614ms	618m	622m,611m	621m,612m	616m	$\nu_4(ClO_4)$
520w,507w,sh, 495w,430w, 371w,355w, 345w,sh,320vw, 232vw,208w	542m,503m, 431w,b,372w, 353w,320w, 209vw,b	538m,497m, 423w,365w, 348m,323w, 210vw,b	537m,498m, 425w,414w, 368w,348m, 337w,322w, 210vw,b	539m,498m, 423w,b,370w, 349w,341w, 326w,210w,vb	540m,500m, 426w,419w, 369w,350w, 338w,322w, 211vw,b	540m,497m, 424w,b,367w, 348mw,326w, 213vw,b	539m,500m, 430w,421w, 370w,350m, 341w,322w, 206vw,b	Ring vibrations
	470m,b		465m,b		470m,b	465m,b		$\nu_2(ClO_4)$
		385w	391w	479m,sh	396w	403w	382w	$\nu_{M-O}(H_2O)$
	345w,sh		304w		311w	314w		$\nu_{M-O}(OClO_3)$
	284w,b	240w,219w	247w,220w	277w,b	252w,226w	258w,229w	233w,229w	ν_{M-N}

[a] Free xnH band assignments based on refs. 13, 24, 29 and 30.

TABLE III. Solid-state Electronic Spectra and Magnetic Properties (298 K) of Xanthine Complexes with 3d Metal Perchlorates

M^{n+}	λ_{max}, (nm)[a]	$10^6\chi_M^{cor}$ (cgsu)	μ_{eff} (μB)
Cr^{3+}	<200vvs,229vvs,sh,256vvs,282vvs,b,307vs,sh,322s,sh,397s,424s,568ms,b,697w,sh	6147	3.84
Mn^{2+}	202vvs,236vvs,sh,260vs,277vs,311vs,sh,324s,sh,422m,b	13933	5.79
Fe^{2+}	<200vvs,228vvs,sh,255vs,b,283vs,b,306vs,sh,327s,sh,427m,sh,722m,b,915m,b	9706	4.83
Fe^{3+}	<200vvs,231vs,sh,257vs,279vs,291vs,305s,sh,330s,sh,423m,535m,b	14649	5.93
Co^{2+}	<200vvs,232vs,sh,255vs,278vs,294vs,307s,sh,329s,sh,455ms,505m,521m,1090w,vvb	9879	4.87
Ni^{2+}	201vvs,233vs,sh,258vs,284vs,b,310vs,sh,323s,sh,382s,417s,617m,b,675m,b,705mw,sh, 947w,b,1025w,vb	3536	2.92
Zn^{2+}	<200vvs,229vs,sh,258vs,285vs,b,309s,sh,330s,sh,380m,b	Diamagnetic	

[a] Solid-state UV spectrum of xnH; nm: <200vvs,225vs,sh,270vs,b (all solid-state spectra obtained on Nujol mulls [27]). Aqueous solution spectra of xnH and xn^- show the $\pi \rightarrow \pi^*$ transition maxima as follows: λ_{max} (nm) (log ϵ): xnH (pH 5.0–7.0): 225 (3.49), 266–267 (3.90–4.03); xn^- (pH 10.0–11.0): 240–241 (3.91–3.95), 276–277 (3.92–3.97) [7, 40].

affect the ν_{CH} and ν_{NH} ligand bands at 3132–2590 cm^{-1} to any significant extent, since both xnH and xn^- are present. Coordination of xanthine through any of the C=O oxygens is ruled out by the relative insensitivity of the $\nu_{C(6)=O}$ and $\nu_{C(2)=O}$ bands of xnH at 1702, 1667 cm^{-1}, respectively [13], to complex formation [1, 13, 21–25, 30]. On the other hand, the $\nu_{C=C} + \nu_{C=N}$ ligand bands at 1569–1530 cm^{-1} [13, 24, 30] undergo more significant shifts as well as splittings in the spectra of the complexes, which are indicative of participation of ring nitrogens of xanthine in coordination [1, 30–32]. The spectra of the metal complexes are characterized by ν_{OH} and δ_{H-O-H} absorptions of coordinated water at 3410–3370 and 1635–1628 cm^{-1}, respectively [33], with the exception of the Cr^{3+} complex, which does not show water bands. The perchlorate group is ionic in the Mn^{2+}, Fe^{3+} and Zn^{2+} complexes, as manifested by the single nature of the ν_3 and $\nu_4(ClO_4)$ bands [34, 35]. On the other hand, both ν_3 and ν_4 are split into two components and ν_1 and $\nu_2(ClO_4)$ are clearly IR-active in the spectra of the Cr^{3+}, Fe^{2+}, Co^{2+} and Ni^{2+} complexes. These features are suggestive of the exclusive presence of unidentate $-OClO_3$ ligands in these compounds [34, 35]. In the 520–200 cm^{-1} region, free xnH exhibits several absorptions, which are mainly due to out-of-plane ring vibrations [29]. Metal–ligand stretching modes are generally easily distinguishable in the same region and were tentatively assigned as ν_{M-O}(aqua), $\nu_{M-O}(-OClO_3)$ [32, 33, 36–38] and ν_{M-N} [31, 32, 39] modes. All these ν_{M-L} assignments are compatible with coordination number six for the central metal ions [1, 31–33, 36–39].

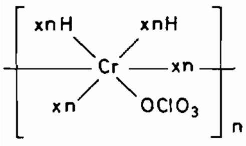
Electronic Spectra and Magnetic Moments

The solid-state UV spectrum of xnH is in good agreement with the published solution spectra of xnH and xn^- [7, 40] (Table III). Complex formation results in a general trend of occurrence of the $\pi \rightarrow \pi^*$ transitions of both xnH and xn^- toward lower energies. Thus, all new complexes show two maxima at 228–236 and 255–260 nm, corresponding, respectively, to the xnH band at 225 and that of xn^- at 240–241 nm [7, 40]. In contrast, $Cu(xn)_2 \cdot 2EtOH$ exhibits a single band at 255 nm [1], as would be expected for a complex with exclusively anionic xn^-. As regards the lower energy $\pi \rightarrow \pi^*$ transitions of xnH and xn^- (266–267 and 276–277 nm), some complexes show them also as doublets at 277–279 and 291–294, while other complexes show a single broader maximum at 282–285 nm. The $n \rightarrow \pi^*$ transition of xanthine is observed at 305–311 nm in the spectra of the new complexes [1, 41]. The spectra of the paramagnetic metal ion complexes are also characterized by strong metal-to-ligand charge-transfer absorption originating in the UV and trailing off into the visible region [42]. This charge-transfer absorption is not, however, as intense and does not extend as far in the visible as was the case with previously studied purine [31], adenine [32] or guanine [39] complexes with 3d metal perchlorates. The d–d transition spectra of the new complexes are generally typical of low-symmetry hexacoordinated configurations [31, 32, 39, 43], *viz.*, nm: $M = Cr^{3+}$: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 397, 424; $\rightarrow {}^4T_{2g}(F)$ 568 (with a weak shoulder at 697); Fe^{2+}: $^5T_{2g} \rightarrow {}^5E_g$ 722, 915; Co^{2+}: $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 455; $\rightarrow {}^4A_{2g}(F)$ 505, 521; $\rightarrow {}^4T_{2g}(F)$ 1090; Ni^{2+}: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 382, 417; $\rightarrow {}^3T_{1g}(F)$, $^1E_g(D)$ 617, 675, 705; $\rightarrow {}^3T_{2g}(F)$ 947, 1025. Approximate calculations of spectrochemical parameters (for pure O_h symmetry), cm^{-1}: $M = Cr^{3+}$, Dq = 1761; Fe^{2+}, Dq = 1222; Co^{2+}, Dq = 1053, B = 942; Ni^{2+}, Dq = 1014. The calculated Dq values are compatible with the presence of CrN_5O and MN_4O_2 (M = Fe, Co, Ni) absorbing species in these compounds [31, 32, 39, 44–46] (*vide infra*).

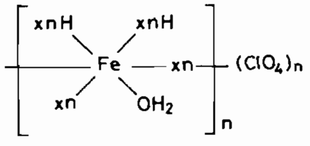
The ambient temperature magnetic moments of the Cr^{3+} and Fe^{3+} complexes are normal for high-spin compounds of these metal ions [47]. Among the M^{2+} complexes, those with Mn^{2+} and Fe^{2+} exhibit slightly low μ_{eff} values (5.79 and 4.83 μB, respectively), while the moments of the Co^{2+} and Ni^{2+} complexes are within the range of values corresponding to high-spin hexacoordinated $3d^7$ and $3d^8$ compounds [47].

Likely Structures and Binding Sites

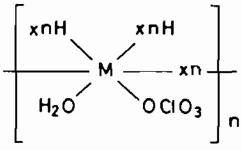
The new complexes seem to be polymeric species, in view of their poor solubility in organic media and the pronounced tendency of purines to act as bridging ligands [48]. The normal or near-normal room temperature magnetic moments of the new complexes are against structural types with multiple xanthine bridges between adjacent metal ions, but are consistent with linear chainlike single-bridged polymeric structures with a $\left(M{-}xanthine \right)_n$ backbone [31, 32, 39]. In fact, a number of $[M(puH)_2(OH_2)_3](ClO_4)_2$ polymeric complexes (M = Co, Ni, Cu; puH = purine), characterized as linear with single puH bridges between adjacent metal ions, were found to show normal room temperature magnetic moments and evidence favoring magnetic exchange interactions only at lower temperatures (below 110 K) [31]. Furthermore, several Cu^{2+} complexes with single bridges of diazine or diazole ligands were also shown to exhibit analogous magnetic behavior [49, 50]. Hence, on the basis of the overall evidence presented, the most likely structural types for the new complexes are **II** for $M = Cr^{3+}$, **III** for $M = Fe^{3+}$, **IV** for $M = Fe^{2+}$, Co^{2+}, Ni^{2+}, and **V** for $M = Mn^{2+}$, Zn^{2+}.



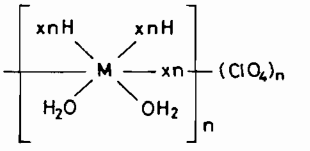
II



III



IV



V

The common feature of structures **II** and **III** is that they involve one bidentate bridging xn^-, one terminal xn^- and two terminal xnH ligands per metal ion, while that of structures **IV** and **V** is the presence of one bidentate bridging xn^-, two terminal xnH and one terminal aqua ligand per metal ion. The difference between structure **II** or **IV** and **III** or **V**, respectively, is that in the former the sixth ligand is $-OClO_3$, whilst in the latter the perchlorate is ionic and an aqua ligand occupies the sixth position in the coordination sphere of the metal ion.

In a previous communication, we discussed the possibility that some of the xanthine groups in metal complexes with high ligand to metal ion ratios, instead of being coordinated to the metal, might be H-bonded to aqua (or ethanol) ligands [3], as is the case with the caffeine molecules in the $[Mg(OH)_6]Br_2 \cdot 2caf$ and $[Mn(OH_2)_6]I \cdot I_3 \cdot 2caf$ complexes [51]. Such a possibility seems highly unlikely, at least for the metal complexes herein reported. In fact, the overall evidence presented strongly suggests that the new complexes, including the anhydrous Cr^{3+} compound, are characterized by closely resembling structures. The Cr^{3+} complex does not, of course, contain aqua ligands that could form H-bonds with uncoordinated xanthine molecules, while the formation of H-bonds between coordinated and uncoordinated xanthine groups (N–H···O bonds) would result in significant $\nu_{C=O}$ shifts to lower wavenumbers [22, 52, 53]. The IR spectrum of the Cr^{3+} complex shows the two $\nu_{C=O}$ bands at 1709, 1669 cm^{-1} (*i.e.*, both shifted slightly towards higher wavenumbers, relative to free xnH) and the next maximum in the $\nu_{C=C} + \nu_{C=N}$ region (1583 cm^{-1}), so that there is no indication whatever of any negative $\nu_{C=O}$ frequency shifts.

As regards the likely binding sites of the xanthine ligands present in the new complexes, terminal unidentate neutral xnH would be expected to coordinate through N(7). In fact, neutral purines have the tendency to use the imidazole nitrogen which is protonated in their free base form as their preferred binding site [48]. Furthermore, theophylline, which is also protonated at N(7) [54], reportedly binds through this site in several metal complexes with terminal unidentate neutral tpH [55–57] or anionic tp^- [58–61] ligands. This would seem to imply that both xnH and xn^- would bind through N(7) when acting as unidentate. The situation is nevertheless complicated by the fact that the only crystal structure available of a metal complex with anionic xn^- reveals that this ligand is N(9)-bonded [11], although coordination through this site may have been promoted by H-bonding between the hydrogen of xn^- at N(3) and oxygen atoms of the dimethylglyoxime ligands present in this particular Co^{3+} complex [13], and the fact that even tpH was found to bind through N(9) in metal complexes prepared under acidic conditions [62, 63]. Hence, in view of the preceding discussion and the lack of crystal structure determinations of metal complexes with xnH, it is not possible to unambiguously propose the N(7) over the N(9) nitrogen as the binding site of unidentate xnH or xn^-. As far as the two binding sites of bridging bidentate xn^- are concerned, the N(7), N(9)-combination would appear as the most probable for single-bridged complexes of types **II** through **V** [64]. Possible alternatives are the N(1), N(7)- and N(3), N(9)-combinations. The former can be ruled out, since N(1) seems to be the least likely ring nitrogen of xanthine to become involved in coordination, as indicated by the fact that even tridentate bridging xn^{2-} is N(3), N(7), N(9)-bonded in its tris(methylmercury(II)) complexes [13]. However, the N(3), N(9)-combination can not be completely excluded, although the presence of the oxygen substituent at C(2) may render coordination of xn^- through N(3), N(9) less favorable than that through N(7), N(9), due to steric hindrance [1, 65].

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