Xanthine, Hypoxanthine and Guanine Copper(II) Complexes*

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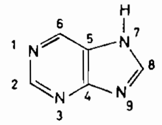
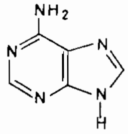
Copper(II) complexes with xanthine (xnH), hypoxanthine (hxH) and guanine (guH), of the types $Cu(xn)_2 \cdot 2C_2H_5OH$, $Cu(hx)(ClO_4) \cdot 4C_2H_5OH$, $Cu(gu)_2 \cdot H_2O$ *and* $Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$, *were prepared from non-aqueous media (ethanol–triethyl orthoformate) and characterized. The* $CuL_2 \cdot xROH$ *complexes* ($L = xn^-$, gu^-; $R = H$, C_2H_5) *show subnormal room temperature magnetic moments (1.57–1.60 μB) and are probably dimeric with four bidentate bridging anionic L groups (similar to fully characterized adenine and hxH analogs). The other two complexes appear to be linear polymers with single bridges of bidentate bridging* hx^- *or guH (–Cu–L–Cu–L– sequences). One of the binding sites of the bidentate bridging substituted purines is the N(9) ring nitrogen; the likelihood of function of N(7) or N(3) as the second binding site is discussed for each case.*

Introduction

These laboratories have developed methods for the preparation of 3d metal complexes with purine free bases from non-aqueous media, and reported, among other works, on the syntheses and characterization of 3d metal perchlorate complexes with purine (puH; I) [2], adenine (adH; II) [3] and guanine (guH; III) [4]. Current research is aimed at studies of the effects of variation of the synthetic conditions on the types of metal complexes isolated during reactions of 3d metal perchlorates with various substituted purines. A variety of preparation media, including reportedly successful solvents or diluents, such as a mixture of ethanol–triethyl orthoformate (teof) [2–4], absolute ethanol [5, 6], ethyl acetate [7], as well as other organic liquids (*e.g.*, alkyl benzoates, ethers, ketones, *etc.*), are being investigated. Regarding the 3d metal ion of choice, screening studies established that Cu^{2+} complexes with purine free bases are the easiest to isolate; this was also obvious from the existing pertinent literature [8]. At this point Cu^{2+} complexes with xanthine (xnH; IV), hypoxanthine (hxH; V) and guanine were prepared from ethanol–teof and characterized. The present paper deals with these complexes and compares the synthetic results obtained during this work to those of previous preparative studies [2–4].



(I)



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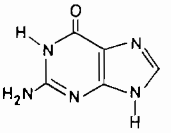

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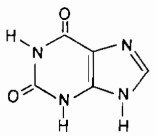

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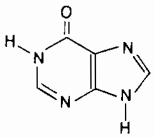

(V)

Experimental

The following standard synthetic procedure was employed for the preparation of the Cu^{2+} complexes: 2.5 mmol of the ligand (xnH, hxH, guH) and 1.25 mmol of hydrated Cu^{2+} perchlorate were mixed together and added to a mixture of 35 ml absolute ethanol and 15 ml teof. The resultant mixture was swirled for 5–10 minutes and subsequently refluxed for a week to 10 days (depending on the ligand), until the reaction was complete. The solid products were then separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. This synthetic method yielded complexes of the monodeprotonated anionic ligands, *i.e.*, $Cu(xn)_2 \cdot 2C_2H_5OH$, $Cu(hx)(ClO_4) \cdot 4C_2H_5OH$ and $Cu(gu)_2 \cdot$

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*Ref. 1.

0020/1693/83/$03.00

TABLE I. Analyses, Yields and Colors of Cu^{2+} Complexes with Substituted Purines.

Complex	Color	Yield %[a]	%C		%H		%N		%Cu		%Cl	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cu(xn)_2 \cdot 2C_2H_5OH$	Pale yellow	53.1	36.72	37.07	4.40	4.46	24.47	24.83	13.88	13.45	0.00	0.15
$Cu(hx)(ClO_4) \cdot 4C_2H_5OH$	Blue gray	54.6	32.36	32.65	5.01	4.84	11.61	11.39	13.17	12.78	7.35	7.59
$Cu(gu)_2 \cdot H_2O$	Greenish	29.3	31.46	31.19	3.17	3.26	36.69	37.03	16.64	16.58	0.00	0.27
$Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$	Green	42.7	22.28	22.08	3.12	2.81	21.66	21.94	9.82	9.54	10.96	10.74

[a] % of theoretical value, based on Cu present.

H_2O (analytical data, yields and colors are shown in Table I). Since the new Cu^{2+} complexes differ from those previously isolated in these laboratories [2–4] in that they contain anionic rather than neutral substituted purine ligands, brief descriptions of the preparative methods that led to the formation of neutral ligand adducts of $Cu(ClO_4)_2$ are given here: $Cu(puH)_2(ClO_4)_2 \cdot 3H_2O$: Precipitated immediately upon mixing ethanol–teof solutions of puH and $Cu(ClO_4)_2$, at a 4:1 ligand to Cu^{2+} molar ratio [2]. $Cu(adH)_2(ClO_4)_2 \cdot C_2H_5OH$: Prepared by refluxing a 2:1 mixture of adH and $Cu(ClO_4)_2$ in ethanol–teof for 2–5 days [3]. $Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$: Prepared by refluxing a 4:1 mixture of guH and $Cu(ClO_4)_2$ in ethanol–teof for 2–5 days [4].

Characterization of the new complexes was effected by means of spectral and magnetic studies. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements (Table II) were obtained by methods described elsewhere [9]. IR spectra (Tables III, IV) were recorded on Nujol and hexachloro-1,3-butadiene mulls between NaCl windows (4000–500 cm^{-1}) and on Nujol mulls between high-density polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. Analytical, spectral and magnetic data are also given for $Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$, whose preparation has been reported briefly in a research letter [9]. The new complexes are either insoluble (hx^- and guH complexes) or very sparingly soluble (xn^- and gu^- complexes) in organic media, so that performance of any characterization studies in solution (electronic spectra, molar conductivities, *etc.*) was precluded.

Discussion

The fact that the synthetic procedure employed during this work led to the formation of Cu^{2+} complexes with monodeprotonated anionic purines rather than adducts of $Cu(ClO_4)_2$ with the corresponding neutral ligands is presumably due to the substantially extended duration of the interaction between ligand and Cu^{2+} salt, relative to the preparative methods we previously used [2–4] (*cf.* experimental section). This is also substantiated by the fact that, in at least one analogous case (LH = adenine N(1)-oxide), the eventual formation of an olive green complex of the $Cu_2(LH)L_2(ClO_4)_2$ type, was preceded by the precipitation of a maroon-colored adduct of LH with $Cu(ClO_4)_2$, which subsequently dissolved in the mother liquor (ethanol–teof) at the reflux temperature [10].

Electronic Spectra and Magnetic Susceptibilities

Solid-state (Nujol mull) UV spectra of the free bases are in agreement with the corresponding

TABLE II. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of Cu^{2+} Complexes with Substituted Purines.

Complex	λ_{max}, nm^{a,b}	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μB
$Cu(xn)_2 \cdot 2C_2H_5OH$	<200vs, 255vs, 279vs, 306s, sh, 328s, sh, 555s, vb	1061	1.60
$Cu(hx)(ClO_4) \cdot 4C_2H_5OH$	196vvs, 231vs, sh, 262vs, b, 310s, sh, 330s, 543s, 577s, sh, 723m, sh, 775m, sh	1427	1.85
$Cu(gu)_2 \cdot H_2O$	203vvs, 247vs, sh, 280vs, 312s, sh, 334s, sh, 548s, vb	1022	1.57
$Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$	203vvs, 252vs, b, 282vs, 313s, sh, 339s, sh, 550m, sh, 570ms, 652m, sh, 785ms	1965	2.17

[a] Solid-state UV spectra of the neutral free bases are generally in agreement with aqueous solution spectra previously reported [11–13], *i.e.*: Solid-state spectra, nm: xnH <200vvs, 225vs, sh, 270vs, b; hxH <200vvs, 247vs, 280vs, sh, 340s, sh; guH 202vvs, 245vs, 276vs, b, 330ms, sh. Aqueous solution spectra, λ_{max}, nm (logε): neutral bases (pH 5.0–7.0): xnH 225(3.49), 266–267 (3.90–4.03); hxH 249(4.02); guH 245–246(4.01–4.04), 274–275(3.89–3.92); corresponding monoanions (pH 10.0–11.0): xn^- 240–241(3.91–3.95), 276–277(3.92–3.97); hx^- 258(4.05); gu^- 243(3.78–3.93), 273(3.87–4.00) [11–13]. [b] Solid-state d–d transition spectra of previously reported Cu^{2+} complexes, nm: $Cu(puH)_2(ClO_4)_2 \cdot 3H_2O$ 556m, sh, 585ms, b, 777m, b [2]; $Cu(adH)_2(ClO_4)_2 \cdot C_2H_5OH$ 540m, vb [3].

aqueous solution spectra [11–13] (see footnote a of Table II, where solution spectra for the xn^-, hx^- and gu^- anions are included). The solid-state spectra of the ligands show in all cases two $\pi \rightarrow \pi^*$ transition maxima, while the $n \rightarrow \pi^*$ transition, which is expected to appear at 290–300 nm [14], is generally masked. The UV spectra of the Cu^{2+} complexes show shifts of the $\pi \rightarrow \pi^*$ transition bands to lower energies, relative to the location of these bands in the spectra of anionic xn^-, hx^- or gu^- or neutral guH [11–13]. The $\pi \rightarrow \pi^*$ transitions in the guH adduct occur at somewhat lower energies than those of the gu^- complex, as would be expected from the spectra of free guH and gu^- [12, 13]. Shifts to lower energies were also observed in complexes of puH and adH with 3d metal perchlorates [2, 3]. The spectra of the new Cu^{2+} complexes show detectable $n \rightarrow \pi^*$ ligand transition maxima at 306–313 nm, while strong metal-to-ligand charge-transfer absorption, originating in the UV and trailing off into the visible region is also observed [2, 3, 15]. The d–d transition maxima in the spectra of the complexes fall in two categories: $Cu(xn)_2 \cdot 2C_2H_5OH$ and $Cu(gu)_2 \cdot H_2O$ exhibit a single, very broad band with its maximum at 548–555 nm (Table II). These spectra are similar to that of $Cu(adH)_2(ClO_4)_2 \cdot C_2H_5OH$ (λ_{max} 540 nm) [3] and compatible with a pentacoordinated configuration involving a CuN_4O chromophore [3, 5]. On the other hand, $Cu(hx)(ClO_4) \cdot 4C_2H_5OH$ and $Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$ show three to four maxima at 543–785 nm. A similar spectrum was reported for the hexacoordinated $Cu(puH)_2(ClO_4)_2 \cdot 3H_2O$ [2] (footnote b, Table II), as well as other hexacoordinated Cu^{2+} analogs [5, 6, 16]; it should be noted here that, whereas the guH complex is characterized by a CuN_3O_3 absorbing species, the new hx^- complex involves a CuN_2O_4 chromophore (*vide infra*).

The ambient temperature magnetic moments of $Cu(xn)_2 \cdot 2C_2H_5OH$ and $Cu(gu)_2 \cdot H_2O$ (1.57–1.60 μB; Table II) are in the same range of values as that of $Cu(adH)_2(ClO_4)_2 \cdot C_2H_5OH$ (1.66 μB) [3], as well as a number of square pyramidal binuclear Cu^{2+} complexes with adH, ad^- and hxH, first reported by Weiss and Venner [17] and later shown by means of crystal structure determinations to involve quadruple bridges of bidentate adenine or hypoxanthine, binding through the N(3) and N(9) ring nitrogens ($X{-}CuL_4{-}Cu{-}X$; L = adH, ad^-, hxH; X = Cl, Br, $OClO_3$, H_2O, NH_3, *etc.*) [18–21]. All these complexes exhibit room temperature magnetic moments between 1.38–1.74 μB [22–26]. Studies of magnetic susceptibility variation with temperature established antiferromagnetic exchange interactions [22–26], with the μ_{eff} values dropping to below 1.00 μB at lower temperatures (ranging between 175 K and 50 K, depending on the complex) [24]. Exchange energies were found to increase in passing from ionic (ad^-) to neutral (adH, hxH) purine ligands or from chloride to aqua axial X ligands [26]. Although no complete studies of the temperature dependence of the paramagnetism of the two complexes under study were performed, it was determined that their magnetic moments at 201 K are 1.26 μB for the xn^- and 1.21 μB for the gu^- complex; these data are in favor of structures similar to that of $[(H_2O)Cu(adH)_4Cu(OH_2)] \cdot nH_2O$ (n = 4 or 6) [20, 22, 24]. It should be noted at this point that, quite recently, Cr^{2+} binuclear complexes with adH, exhibiting antiferromagnetic behavior (*e.g.*, $Cr(adH)_2Br_2 \cdot L$, where L = 2-methoxyethanol: μ_{eff} at 318 K 1.53 μB; at 209 K 1.24 μB; at

TABLE III. Infrared Spectra of Cu^{2+} Complexes with Xanthine and Hypoxanthine (cm^{-1}).

xnH[a]	$Cu(xn)_2 \cdot 2C_2H_5OH$	hxH[a]	$Cu(hx)(ClO_4) \cdot 4C_2H_5OH$	Band assignment
	3350m, b[b]		3440s[b]	ν_{OH}
2800s, 2670s, 2590s	2810s, 2660s, sh, 2575s	2815s, 2710s, 2620s	2790s, 2715s, 2630s, b	ν_{NH}
1700vs, 1660vs	1700vs, 1666vs	1665vs	1671vs, b	$\nu_{C=O} + \delta_{OH}$[c]
1569m	1560m	1605w, 1579m	1600m, 1570mw, sh	$\nu_{C=C} + \nu_{C=N}$
1455ms, 1437s, 1411m, 1332m, 1250w, 1195ms, 1145ms, 1111m	1450m, 1431w, 1410m, 1375m, b, 1331ms, 1249w, 1190ms, 1148m, 1105m	1510w, 1450ms, 1419m, 1360m, 1341m, 1260m, 1205ms, 1141m, 1123ms	1500m, b, 1455m, sh, 1402ms, 1370ms, 1320mw, 1307w, sh, 1250w, 1197s, 1152ms	Ring vibrations + ν_{C-N}
			1080s, b, 1045s, b	$\nu_3(ClO_4)$
1040mw, sh, 1015w, 947w	1052mw, sh, 1025w, 948w	955m	1009mw, 945w, sh	Ring vibrations
			920mw	$\nu_1(ClO_4)$
865w, 841m, 819m, 750m, b, 709m, 630w	860m, sh, 825ms, b, 750m, 710m, 630w	895w, sh, 880m, 779w, 630m, sh	870m, vb, 777m, 718w, 690w, 630w, sh	Ring vibrations + δ_{CH}
			652m, 617m	$\nu_4(ClO_4)$
595m, 520m, 507w, sh, 490m, b, 431w, sh, 382w, 347w, b, 320w, sh, 208w	600m, 560m, sh, 500m, b, 485m, 455mw, b, 390w, 345w, b, 210vw, b	580m, sh, 545m, 520m, 450w, sh, 387w, 362w, 345w, b, 241w, 231w, 211w	585m, 540m, b, 450w, sh, 360w, sh, 340w, 211w, sh	ν_{ligand} (600–200 cm^{-1})
			465w, b	$\nu_2(ClO_4)$
	419mw		395mw	$\nu_{Cu-O}(C_2H_5OH)$
			307w	$\nu_{Cu-O}(OClO_3)$
	305w, sh, 265w, 243w		257w, 238w, b, 220w	ν_{Cu-N}

[a] Free ligand bands, in agreement with previously reported ir spectra [32–35], were assigned on the basis of analogous assignments for guH [36]. [b] In addition to the main ν_{OH} maximum, weaker broad absorption covers the 3600–3300 cm^{-1} region. [c] δ_{OH} is masked by the broad $\nu_{C=O}$ bands.

TABLE IV. Infrared Spectra of Cu^{2+} Complexes with Guanine (cm^{-1}).

guH[a]	$Cu(gu)_2 \cdot H_2O$	$Cu(guH)_2(ClO_4)_2 \cdot C_2H_5OH \cdot 2H_2O$	Band assignment
	3470m, sh	3510m, sh, 3450m, sh	ν_{OH}
3330s, 3290s, sh, 3160s	3340s, 3305s, sh, 3180s	3345s, 3300s, sh, 3170s	ν_{NH_2}
3000s, 2900s, 2850s, 2700s	3000s, vb, 2680ms, vb	3010s, 2920s, 2860s, 2705ms, 2630m, b	ν_{NH}
1705s	1700s	1710s, sh, 1699s	$\nu_{C=O}$
1680s	1670s	1680s, vb	δ_{NH_2}, scissoring
1635s, sh, 1575m, b	1640s, 1605ms, 1585m, b	1641s, 1607s, 1590s, 1580m	$\nu_{C=C} + \nu_{C=N} + \delta_{OH}$
1563m	1560m, 1515m	1555m, 1520w	δ_{NH}
1477m, 1464m, 1418m, 1375m	1470m, 1453m, sh, 1411w, 1367m	1471m, 1456m, sh, 1408w, 1380m	Ring vibrations
1263m	1257m, 1240w, sh	1260mw, b	ν_{C-N}
1209m, 1169m	1205m, b, 1162m	1195m, 1161m	Ring vibrations
1107m	1110m, b	[b]	δ_{NH_2}, rocking
		1090vvs, vb	$\nu_3(ClO_4)$
1042w	1050w, b	[b]	
930w	930w	930w	Ring vibration + $\nu_1(ClO_4)$
880m, 851m, 781m, 730w	861m, 839m, 763m, 740w, sh	865m, 841m, 775m, 735w, sh	$\delta_{NH} + \delta_{CH}$
705m, 689m	710m, 678m	708m, 680m	Ring vibrations
640m	650w, sh	[b]	δ_{NH_2}, wagging
		624vs	$\nu_4(ClO_4)$
608m, 570m, 544w, 515w, 506w, 440w	610w, 595w, 550w, 520w, b, 440m, sh	605w, 565w, vb, 525w, b 440w, sh	ν_{ligand}(610–400 cm^{-1})
	453m	425m, 396m	ν_{Cu-O}(OH_2 or C_2H_5OH)
370w, 345w, b	370w, 333w	370w, 345w	ν_{ligand} (400–300 cm^{-1})
	311w, 261w, 247mw	260w, 245w, 225w, sh	ν_{Cu-N}

[a] Band assignments for guH after Shirotake and Sakaguchi [36]. [b] Bands masked by $\nu(ClO_4)$.

85 K 0.75 μB), and presumably being structurally similar to the quadruply-bridged Cu^{2+} analogs, were reported [27].

$Cu(hx)(ClO_4)\cdot 4C_2H_5OH$ and $Cu(guH)_2(ClO_4)_2\cdot C_2H_5OH\cdot 2H_2O$ show normal room temperature magnetic moments (1.85 and 2.17 μB, respectively), which are reduced to 1.72 and 2.04 μB, respectively, at 201 K. $Cu(puH)_2(ClO_4)_2\cdot 3H_2O$, whose magnetic behavior was studied at 300–80 K, showed decrease of its μ_{eff} from 2.05 (296.5 K) to 1.94 (213.7 K) to 1.78 (88.5 K) μB, and its $1/\chi$ *vs.* T plot was found to deviate in the ferromagnetic direction from Curie-Weiss behavior at temperatures below 110 K [2]. A linear chainlike polymeric structural type, involving single bridges of bidentate puH ligands between adjacent Cu^{2+} ions (–Cu–puH–Cu–puH sequences) was proposed for this complex [2]; this assignment was later supported by the crystal structure determination of an analogous compound ($[Cu(puH)(OH_2)_4](SO_4)\cdot 2H_2O$), which is indeed a linear chainlike polymeric species with single bridges of bidentate N(7), N(9)-bonded puH between adjacent Cu^{2+} ions [28]. Furthermore, evidence demonstrating ferromagnetic exchange has been recently reported for several Cu^{2+} complexes with nucleobase derivatives (cytosine and derivatives, xanthosine, adenosine, inosine, 8-substituted guanosines, adenylic acid [29], caffeine [30]); all of these complexes are single-bridged polymers, with either the nucleobase derivative [29] or other ligands, such as -OH [29] or -Cl [30, 31] acting as the bridging group. On the basis of the above precedents, the complete insolubility of the hx^- and guH complexes in organic media, the decrease of the magnetic moments of these complexes by 0.13 μB as the temperature decreased from 298 K–201 K, and the fact that the composition of the guH complex resembles that of $Cu(puH)_2(ClO_4)_2\cdot 3H_2O$, it is considered as reasonable to propose linear single-bridged polymeric structures for these two complexes.

Infrared Evidence

The IR spectra of the free ligands recorded during this work are in agreement with IR data published in the literature for xnH, hxH (spectra at 5000–600 cm^{-1} [32], far-IR spectra [33], as well as behavior of several IR absorptions during coordination [34, 35]) (Table III) and guH (spectra of free guH [33, 36, 37] and band shifts on complexation [34, 35, 36, 38]) (Table IV). The spectra of the new xn^- and hx^- Cu^{2+} complexes exhibit, in addition to the relatively sharp ν_{OH} band of coordinated ethanol [39], a weaker broad absorption, covering the whole 3600–3300 cm^{-1} region (Table III), which is presumably due to the simultaneous presence of lattice ethanol [3, 40]. The ν_{OH} (water) band in the gu^- complex and the ν_{OH} (water, ethanol) doublet in the guH adduct are relatively sharp (Table IV) and indicative of the presence of exclusively coordinated aqua and ethanol ligands [39, 41]. Regarding the perchlorate groups present in two of the complexes, the doubly split ν_3 and $\nu_4(ClO_4)$ and IR-active ν_1 and $\nu_2(ClO_4)$ modes, as well as the appearance of $\nu_{Cu-O}(OClO_3)$ band in the spectrum of the hx^- complex favor the exclusive presence of coordinated unidentate $-OClO_3$ ligands [3, 42, 43]; whereas, in the case of the guH adduct, ClO_4^- is exclusively ionic, as shown by the single character of ν_3 and $\nu_4(ClO_4)$ [42].

Insofar as the IR bands of the substituted purine ligands are concerned, the group of ν_{NH} bands of neutral xnH, hxH or guH do not show significant changes upon formation of complexes of the xn^-, hx^- or gu^- monoanions, since these anionic species still contain one (hx^-, gu^-) or two (xn^-) protonated ring nitrogens. The relative insensitivity of the $\nu_{C=O}$ and, in the case of guanine, the various NH_2 IR bands to Cu^{2+} complex formation demonstrates that none of these exocyclic potential ligand sites (*i.e.*, O(2), O(6) in xn^-, O(6) in hx^- and N(2), O(6) in gu^- or guH) is coordinated [36]. On the other hand, various $\nu_{C=N}$, $\nu_{C=C}$ and ring vibrations of the ligands undergo significant shifts upon Cu^{2+} complex formation; this is indicative of participation of ring nitrogens in coordination [2, 3, 36]. In the lower frequency IR region, bands attributable to Cu–ligand stretching modes were assigned on the basis of previous studies of Cu^{2+} complexes with purine derivatives [2, 3, 5, 6, 44], perchlorato [3, 45], aqua [2, 3, 46] and ethanol [3, 47] ligands. The location of the various ν_{Cu-O} and ν_{Cu-N} absorptions tentatively assigned favor coordination numbers five for $Cu(xn)_2\cdot 2C_2H_5OH$ and $Cu(gu)_2\cdot H_2O$ [3, 44, 46, 47] and six for $Cu(hx)(ClO_4)\cdot 4C_2H_5OH$ and $Cu(guH)_2(ClO_4)_2\cdot C_2H_5OH\cdot 2H_2O$ [2–5, 44–47].

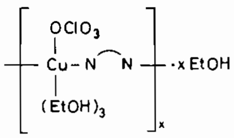
Conclusion

Monodeprotonation of the neutral substituted purines of interest generally results in deprotonation of N(3) in xanthine (leaving N(1) and N(9) protonated) [48] and N(1) in guanine and presumably hypoxanthine (leaving only N(9) protonated) [49]. In their 3d metal (Cu^{2+} or Co^{3+}) complexes, neutral or anionic xanthine or hypoxanthine coordinate through the N(9) nitrogen [21, 50], as well as the N(3) nitrogen when they function as bidentate [21]; in the case of unsubstituted guanine metal complexes, the only crystal structures available are those of the guaninium (guH_2^+) cation complexes $[Zn(guH_2)Cl_3]$ [51] and $[Cu(guH_2)Cl_3]_2\cdot 2H_2O$ [52], in which the ligand is unidentate, binding through the N(9) nitrogen [51, 52]. The structure of $[Zn(guH_2)Cl_3]$ may be taken as indicative of a greater tendency of guanine to coordinate through N(9), relative to adenine, since in the corresponding adH_2^+ complex, this ligand coordinates through N(7) [51].

As already discussed in the preceding sections, the new complexes are of two different types; their most likely structural types are as follows ($N^\frown N$: bidentate bridging xn^-, hx^-, gu^- or guH; N_9: unidentate terminal guH): Binuclear, square pyramidal with quadruple xn^- (VI) or gu^- (VII) bridges for the $CuL_2 \cdot nROH$ complexes; and linear chainlike polymeric hexacoordinated single-bridged structures for the hx^- (VIII) and guH (IX) complexes [2–4]. The xn^- and hx^- complexes are characterized by the presence of both coordinated and lattice ethanol (*vide supra*). One of the binding sites of the bidentate bridging ligands is undoubtedly N(9) [50–52]. It is, nevertheless, difficult to predict the second binding site with any degree of confidence. For the quadruple-bridged structural types VI and VII ($L = xn^-$, gu^-), N(3) would be the most likely second binding site, in view of the established structures of adH, ad^- and hxH analogs [18–21]. However, it is conceivable that the presence of the exocyclic O or NH_2 substituents on C(2) of xn^- or gu^- (respectively), may provide sufficient steric hindrance as to prevent binding through N(3) [53, 54] and force the use of N(7) as the second binding site [28, 53, 54]. In the case of the single-bridged structural types VIII and IX, in view of the recent crystal structure determination of the linear polymeric single-bridged $[Cu(puH)(OH_2)_4](SO_4) \cdot 2H_2O$ [28], N(7) would appear as the most likely second binding site of bridging hx^- or guH.

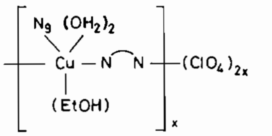
$[(EtOH)Cu(N^\frown N)_4Cu(EtOH)] \cdot 2EtOH$ $[(H_2O)Cu(N^\frown N)_4Cu(OH_2)]$

(VI) (VII)



$$\left[\begin{matrix} OClO_3 \\ | \\ -Cu-N^\frown N- \\ | \\ (EtOH)_3 \end{matrix} \right]_x \cdot xEtOH$$

(VIII)



(IX)

Prior to concluding, some previously reported Cu^{2+} complexes with the ligands of interest are listed: For $[Cu_2(hxH)_4Cl_2]Cl_2 \cdot 6H_2O$ [21] and $[Cu(guH_2)Cl_3]_2 \cdot 2H_2O$ [52] crystal structures are available. Other complexes: $Cu(xnH)_2Cl_2 \cdot 2H_2O$, $Cu(hxH)Cl_2$, $Cu(hxH)_nCl_2 \cdot H_2O$ (n = 1, 2), $Cu(hxH)_2Br_2 \cdot 2H_2O$, $Cu(hxH)Br_2 \cdot 0.5H_2O$, $Cu(guH)Cl_2$, $Cu(guH)_2Cl_2$, $Cu(guH)_2Cl_2 \cdot 3H_2O$, $Cu(xnH)(SO_4) \cdot 3H_2O$, $Cu(hxH)(SO_4) \cdot H_2O$, $Cu(guH)(SO_4) \cdot H_2O$, $Cu(guH)_2(SO_4) \cdot nH_2O$ (n = 1, 3), $Cu(xn)_2(NH_3) \cdot 2H_2O$, $Cu(hx)_2(NH_3)_2 \cdot 2H_2O$ and $Cu(hx)_2(NH_3) \cdot 3H_2O$ [17, 24, 38]. Finally, the stability constants of Cu^{2+} complexes with hypoxanthine and xanthine have been determined and found to be smaller than the corresponding constants for adenine and purine (adenine > purine > hypoxanthine > xanthine) [55].

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