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Guanine Complexes with First Row Transition Metal Perchlorates*

CHESTER M. MIKULSKI, LINDA MATTUCCI, YALE SMITH, THU BA TRAN

Department of Chemistry and Physics, Beaver College, Glenside, Pa. 19038, U.S.A.

and NICHOLAS M. KARAYANNIS

Amoco Chemicals Corporation, Naperville, Ill. 60566, U.S.A.

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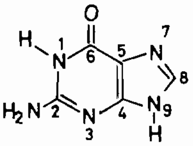
Complexes of guanine (LH) with 3d metal perchlorates were prepared by refluxing a mixture of ligand and metal salt (4:1 molar ratio) in ethanol–triethyl orthoformate. This synthetic procedure led to the formation of some adducts of the neutral ligand (LH), some complexes with anionic L^-, and one complex involving both LH and L^- ($M = Co^{2+}$). Ir evidence indicates that neither of the exocyclic potential ligand sites (N(2) nitrogen and O(6) oxygen) of guanine is involved in coordination. Among the new complexes, the hexacoordinated $[M(LH)_2(EtOH)_2(OClO_3)_2](ClO_4)$ ($M = Cr^{3+}$, Fe^{3+}) are apparently monomeric, with terminal unidentate LH, coordinating through the N(9) imidazole ring nitrogen. For the M^{2+} complexes isolated, namely $[MnL_2(EtOH)_3]_n$, $[FeL(OH_2)_4]_n(ClO_4)_n$, $[CoL(LH)(EtOH)(OH_2)_2]_n(ClO_4)_n$, $[Ni(LH)_2(EtOH)_3]_n(ClO_4)_{2n}$ and $[Zn(LH)_2(EtOH)_3]_n(ClO_4)_{2n}\cdot 2nEtOH$, linear chain-like hexacoordinated polymeric structures, involving single bridges of bidentate guanine ligands (–M–guanine–M–guanine– sequences), binding through N(9) and, most probably, N(7) to adjacent M^{2+} ions, are proposed; in most cases ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}), a second guanine ligand acts as terminal, unidentate, N(9) nitrogen-bonded.

Introduction

Early studies of guanine (2-amino-6-oxo-purine; guH; I) metal complexes have dealt with Hg^{2+} [2], Cu^{2+} [3–6] and Ag^+ [7] complexes. Crystal structure determinations are available for two complexes of the guaninium cation (guH_2^+), *i.e.*, $[Zn(guH_2)Cl_3]$ [8] and $[Cu(guH_2)Cl_3]\cdot 2H_2O$ [9, 10], in both of which this ligand coordinates through the N(9) nitrogen atom to the metal ion [8–10]. Although no crystal structures of metal complexes with either neutral guH or its monodeprotonated anionic derivative (gu^-) have been reported, it was proposed that guH functions as a bidentate chelating agent, coordinating through N(3), N(9), in $[Fe(guH)(OH)]_2(SO_4)_2\cdot 4H_2O$ [11]. Among substituted guanines, 9-substituted derivatives tend to coordinate through N(7) [12], while 7,9-disubstituted guanines use N(1) as the preferred binding site [13]. The exocyclic potential ligand sites of guH (O(6) oxygen and N(2) nitrogen) do not exhibit any great tendency to coordinate to metal ions, but may be involved in H-bonding (*e.g.*, O(6) to water hydrogens or NH_2 hydrogens to chloro ligands) with either coordinated ligands or water of crystallization present in metal complexes [8, 14]. However, the possibility of coordination of guanine derivatives through O(6), in metal complexes with bridging [15] or chelating ('guanine clip') [16, 17] guanines, has been proposed in some cases. It is worth noticing that an analogous ligand, theophylline (1,3-dimethyl-2,6-dioxo-purine), was found to chelate through O(6), N(7) in a Cu^{2+} complex [18].



(I)

Fairly recent studies dealing with guanine metal complexes include gu^- complexes with Mo, Rh and Ir carbonyls and bis(tri-n-butylphosphine)Pd(II) [19], $Cu(guH_2)X_3$ (X = F, Cl, Br) [20], $(guH_2)_4Mo_8O_{26}\cdot 4H_2O$ [21], $Al(gu)Cl_2\cdot 2H_2O$ [22], and a series of complexes with 3*d* metal perchlorates [1, 23]. The latter work, performed by these laboratories, has been briefly reported in preliminary communications [1, 23]; now our studies have been

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*Ref. 1.

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completed, and the syntheses and characterization of two Cu^{2+} complexes formed by interaction between guH and $Cu(ClO_4)_2$ ($Cu(gu)_2 \cdot H_2O$ and $Cu(guH)_2(ClO_4)_2 \cdot EtOH \cdot 2H_2O$) were already reported in a paper dealing with copper(II) complexes of various oxopurines [24]. The present paper reports on the preparation and characterization of the complexes obtained by interaction of guH with Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Zn^{2+} perchlorates in ethanol–triethyl orthoformate (teof).

Experimental

0.65 mmol hydrated metal perchlorate were dissolved in 50 ml of a 7:3 (v/v) mixture of absolute ethanol and teof, and the resultant solution was stirred at 50–60 °C for 2 h. Then, 2.5 mmol guH were added, and the ligand–salt mixture was refluxed for 2–4 days. The volume of the supernatant was subsequently reduced to about one-half by heating, and the solid complexes were separated by filtration, washed with ethanol–teof and stored *in vacuo* over P_4O_{10}. As shown by the analytical data of Table I, adducts of neutral guH were formed in most cases (M = Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}); however, with M = Co^{2+} a mixed neutral guH–anionic gu^- complex was obtained, whilst in the cases of Mn^{2+} and Fe^{2+} complexes containing exclusively anionic gu^- were isolated. The new M^{3+} complexes (M = Cr, Fe) dissolve in some organic solvents, but the M^{2+} complexes are generally insoluble in organic media. It should be noted here that, by employing the above synthetic procedure for M = Cu^{2+}, we have isolated the $Cu(guH)_2(ClO_4)_2 \cdot EtOH \cdot 2H_2O$ adduct [23, 24]; $Cu(gu)_2 \cdot H_2O$ was prepared in a slightly different manner, *i.e.*: guH and $Cu(ClO_4)_2$ hydrate were premixed at a 2:1 molar ratio and added to 50 ml of a 7:3 (v/v) mixture of ethanol and teof, and the resultant mixture was refluxed for 10 days [24].

Characterization of the new complexes was based on spectral, magnetic and conductance studies. Infrared spectra (Table II) 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. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility (298 K) (Table III) and molar conductivity (on 10^{-3} *M* solutions of the M^{3+} complexes in a 1:1 (v/v) mixture of nitromethane/acetone, at 25 °C) measurements were obtained by using apparatus and techniques described elsewhere [25]. The Λ_M values for the solutions of the two soluble complexes (M = Cr^{3+} 214; M = Fe^{3+} 203 Ω^{-1} cm^2 mol^{-1}) indicate that these compounds behave as 1:3 electrolytes [26].

TABLE I. Analytical Data for Guanine Complexes with Metal Perchlorates.

Complex	Color	Yield %[a]	C%		H%		N%		Metal%		Cl%	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Cr(guH)_2(ClO_4)_3 \cdot 2EtOH$	Gray	29.3	22.58	22.31	2.98	3.12	18.81	18.56	6.98	6.69	14.28	13.83
$Mn(gu)_2 \cdot 3EtOH$	White	22.3	38.95	39.22	5.31	5.52	28.39	28.06	11.13	10.74	0.00	0.38
$Fe(gu)(ClO_4) \cdot 4H_2O$	Brown	89.6	15.91	15.60	3.20	3.34	18.55	18.37	14.79	14.50	9.39	9.75
$Fe(guH)_2(ClO_4)_3 \cdot 2EtOH$	Brown	29.4	22.46	22.75	2.96	3.17	18.71	18.60	7.46	7.17	14.21	13.83
$Co(gu)(guH)(ClO_4) \cdot EtOH \cdot 2H_2O$	Lavender	38.0	26.61	26.33	3.54	3.22	25.86	26.08	10.88	11.24	6.54	6.23
$Ni(guH)_2(ClO_4)_2 \cdot 3EtOH$	Brown	48.1	27.53	27.12	4.04	3.90	20.06	19.77	8.41	8.58	10.16	9.82
$Zn(guH)_2(ClO_4)_2 \cdot 5EtOH$	Beige	31.0	30.15	29.93	5.06	4.84	17.58	17.76	8.21	7.87	8.90	8.52

[a] % of theoretical yield, based on the metal present in the system.

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

guH[a]	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{2+}	M = Fe^{3+}	M = Co^{2+}	M = Ni^{2+}	M = Zn^{2+}	Band Assignment
	3460s	3450m,b	3420s	3445m,b	3480sh, 3425s	3470s	3480m[b]	$\nu_{OH}(OH_2, EtOH)$
3330s, 3290s, sh, 3160s	3340s, 3285s, 3160s	3340vs, 3305 vs,sh, 3175vs	3335s, 3290s, sh, 3175s	3350m,b, 3170m,b	3340s, 3300s, 3170s,b	3325s, 3280s, sh, 3170s,b	3350s, 3295s, sh, 3170s	ν_{NH_2}
2850s, 2700s	2850s, 2700s,b	2850vs, 2685vs	2845s, 2690s,b	2855s, 2695ms	2860s, 2700s,b	2855s, 2695s,b	2840s, 2700s,b	ν_{NH}
1705s	1722vs	1710vs	1717vs	1724vs	1707vs	1695vs,sh	1702vs	$\nu_{C=O}$
1680s	1695vs	1675vs,b	1690vs	1698vs	1670vs	1680vs,sh	1685vs	δ_{NH_2}, scissoring
1635s,sh, 1575 m,b	1640vs,sh, 1611vs, 1585vs	1645s,sh, 1610 s, 1575m,sh	1638vs, 1604 vs, 1585vs,b	1640vs, 1608 vs, 1579s	1645s, 1605s, 1580ms,b	1639vs, 1610 vs, 1590s,sh	1640vs,vb, 1585s,sh	$\nu_{C=C} + \nu_{C=N} + \delta_{OH}$
1563m	1552s, 1525ms	1555ms, 1520m	1558vs, 1520ms	1552m, 1520m	1557m, 1515m	1552ms, 1515m	1549m, 1518m	δ_{NH}
1477m, 1464m	1465ms,vb	1470s, 1452s,	1472s, 1444s,	1458m,vb,	1470m, 1452m,	1468m, 1451m,	1466m, 1447m,	Ring vibrations
1418m, 1375m	1410w, 1351ms	1412w, 1368vs	1413m, 1353s	1407m, 1355ms	1490w, 1367ms	1408w, 1370ms	1403w, 1357s	
1263m	1257m,sh	1258m	1255m	1256m,sh	1257m	1252m	1248m	ν_{C-N}
1209m, 1169m	1210w[c]	1206w, 1158m	1211w, 1152ms	1212w[c]	1200w, 1162m	1200w, 1160m	1199w, 1166m	Ring vibrations
1107m	c	1104m	c	c	c	c	c	δ_{NH_2}, rocking
	1135s,sh, 1080vs,b, 1052vs,b		1070vs,b	1130vs,sh, 1085vs,b, 1050vs,b	1075vs,b	1065vs,b	1070vs,b	$\nu_3(ClO_4)$
1042w	c	1045w,sh	c	c	c	c	c	
930w	932m, 925m,b	932mw	930mw	930m, 922m	933w	930vw	930w	Ring vib. + $\nu_1(ClO_4)$
880m, 851m, 781m, 730w	850m, vvb, 765m,vvb	862ms, 837ms, 770m, 740mw	860ms, 832ms, 772m, 743m	865m,sh, 812m, 775w, 750m	905w, 862mw, 839mw, 775m, 755m	902w, 848mw, 827m, 799m,sh, 760ms, 740m,sh	860m, 826m, 770m,sh, 750m	$\delta_{NH} + \delta_{CH}$
705m, 689m	702w, 688w,sh	705w, 688m,b	708w, 692m	701w, 690w,sh	707w, 691w	702w, 688w	698w, 678w	Ring vibrations
640m	c	642m	643m,sh	c	639m,sh	645m,sh	650m,sh	δ_{NH_2}, wagging
	655m, 628m, 619m		624m	650m, 631m, 620m	624ms	622ms	620ms	$\nu_4(ClO_4)$
608m, 570m, 544w, 515w, 506w, 440w	600m,sh, 575m, b, 530mw,b, 445w,sh, 430w	606m, 577m,sh, 550w,b, 455w,b	600m,sh, 570m,sh, 550w,b, 445w,b	598m,sh, 575m, 530w,b, 430w, 408w	597m,sh, 570w,sh, 545w,b, 455w,b	595m, 570m,sh, 520mw,sh, 445w,b	598m, 575m,sh, 545mw,b, 447w,b	ν_{ligand} at 600–400 cm^{-1}
	472w,sh			470w,sh				$\nu_2(ClO_4)$
	461w	381w	401w	453w	418mw, 397w	402w	376w,b[d]	ν_{M-O} (OH_2, EtOH)
370w, 345w,b	370w,b[d]	372w,sh, 335w	375w,b, 333w,b	372w,b[d]	377w,sh, 330w	375w,sh, 330w	[d]332w,b	ν_{ligand} at 400–300 cm^{-1}
	342w			337w				$\nu_{M-O}(OClO_3)$
	287w,vb	237w, 216w	245w, 223w	278w,vb	254w, 227w	257w, 226w	229w, 213w	ν_{M-N}

[a] guH band assignments after Shirotake and Sakaguchi [29]. [b] This maximum appears on top of a very broad absorption, covering the 3600–3400 cm^{-1} region. [c] Bands masked by $\nu(ClO_4)$. [d] Overlap with $\nu_{M-ligand}$ bands.

Discussion

The fact that the synthetic procedure employed in this work resulted in some cases in the isolation of simple adducts of guH with metal perchlorate and in other cases in the formation of metal complexes of gu^-, demonstrates that the conditions of our preparative method are approaching the threshold conditions beyond which partial or complete substitution of ClO_4^- by gu^- is favored. This is also supported by the fact that, when the duration of refluxing was significantly increased during the interaction of guH and $Cu(ClO_4)_2$, $Cu(gu)_2 \cdot H_2O$ was obtained, instead of the $Cu(guH)_2(ClO_4)_2 \cdot EtOH \cdot 2H_2O$ adduct, which was formed when the standard preparative method used during this work was employed [24]. It is noteworthy that during previous synthetic studies of adenine (adH)-metal perchlorate complexation, a number of adH adducts (M = Mn^{2+}, Co^{2+}, Cu^{2+}), ad^- complexes (M = Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) and mixed adH–ad^- (M = Fe^{3+}) complexes were isolated [27]. Further refinement of the synthetic details will undoubtedly result in methods of preparing at will neutral ligand adducts or anionic ligand complexes of purines with 3d metal ions.

Infrared and Conductance Data

The IR spectrum of free guH recorded during this work (Table II) agrees with published IR spectral data for this compound [28–30]. The ν_{NH} bands of guH do not undergo significant changes in the spectra of the metal complexes, regardless of whether neutral guH or anionic gu^- is present; this was anticipated, since even monodeprotonated gu^- still contains one protonated ring nitrogen. The $\nu_{C=O}$ and NH_2 bands of guH are relatively insensitive to *3d* metal complex formation, so that participation of either of the exocyclic potential ligand sites (O(6) oxygen or N(2) nitrogen) in coordination can be ruled out [19, 21–24, 29]. On the other hand, several $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrational modes of guH undergo significant shifts and occasional splittings upon *3d* metal complex formation; these are indicative of participation of ring nitrogens in coordination [5, 19, 21–24, 27, 29].

Regarding the various potential O-ligands present in the complexes (water, ethanol, perchlorate group), the presence of coordinated aqua or ethanol ligands is manifested by relatively sharp ν_{OH} bands at 3500–3400 cm^{-1} [31, 32]; it is worth noticing that the new Co^{2+} complex, which contains both water and ethanol, exhibits a ν_{OH} doublet in this region. The Zn^{2+} complex shows, in addition to the ν_{OH} maximum at 3480 cm^{-1}, a weaker broad absorption covering the 3600–3400 cm^{-1} region; this is apparently due to the simultaneous presence of coordinated [32] and lattice [33] ethanol in this compound. With the exception of $Mn(gu)_2 \cdot 3EtOH$, the new metal complexes contain perchlorate groups. These are obviously strictly ionic in all of the metal(II) complexes, as manifested by the single ν_3 and $\nu_4(ClO_4)$ fundamentals [34, 35]. On the other hand, in the spectra of the Cr^{3+} and Fe^{3+} complexes, ν_3 and $\nu_4(ClO_4)$ are triply split, whilst ν_1 and ν_2-(ClO_4) are IR-active; these features suggest that these compounds involve both ionic ClO_4^- and unidentate coordinated $-OClO_3$ ligands [34, 35]. The molar conductivity data (see Experimental Section) provide no indications as far as the numbers of ClO_4^- ions and $-OClO_3$ ligands present in the solid Cr^{3+} and Fe^{3+} complexes are concerned. In fact, both these compounds behave as 1:3 electrolytes in nitromethane–acetone [26]; this may be interpreted in terms of either displacement of coordinated $-OClO_3$ by solvent molecules in the first coordination sphere of the M^{3+} ion or complete dissociation of the complexes in solution.

Tentative metal–ligand band assignments in the lower frequency IR region were based on previous IR studies of *3d* metal complexes with various purines [27, 36–38], aqua [39, 40], ethanol [41, 42] and perchlorato [43] ligands. These assignments are consistent with the rest of the IR evidence in that the two M^{3+} complexes exhibit ν_{M-O} $(OClO_3)$ bands, all the new complexes show ν_{M-O} (aqua or EtOH) absorptions, while in the spectrum of the Co^{2+} complex two ν_{Co-O} (aqua and EtOH) bands are observed (ν_{Co-O} (aqua) probably corresponds to the band at 418 cm^{-1}, and ν_{Co-O} (EtOH) to that at 397 cm^{-1} [39–42]). The wavenumbers at which the various ν_{M-O} and ν_{M-N} assigned absorptions occur are generally in favour of hexacoordinated configurations for the new complexes [27, 36–43].

Electronic Spectra, Magnetic Moments and Likely Structural Types

The solid-state (Nujol mull) UV spectrum of free guH (Table III) is in agreement with aqueous solution spectra reported in the literature, for both guH and gu^- [44, 45]. The solid-state spectrum of the free ligand shows two $\pi \rightarrow \pi^*$ transition maxima at 245 and 276 nm, while the $n \rightarrow \pi^*$ transition, which is expected to occur at 290–300 nm [46], is masked. The near-IR spectrum of free guH shows a broad absorption at 900–1500 nm, with the most prominent maxima occurring at 920 and 1310 nm; this absorption is presumably due to vibrational overtones and combination modes originating from guH [36]. In the UV spectra of the metal complexes, the $\pi \rightarrow \pi^*$ transition bands of the ligand undergo small shifts to lower energies. These bands appear at slightly higher energies in the gu^- complexes, relative to the guH adducts, as would be expected [44, 45]; although no distinct $\pi \rightarrow \pi^*$ transition

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Susceptibilities (298 K) of Guanine Complexes with Metal Perchlorates.

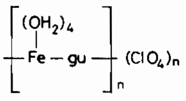
Complex	λ_{max}, nm[a,b]	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μ_B
$Cr(guH)_2(ClO_4)_3 \cdot 2EtOH$	202vvs, 253vs,b, 282vs,sh, 311s,sh, 351s,sh, 437ms, 564m, 604m, 657m	6330	3.90
$Mn(gu)_2 \cdot 3EtOH$	201vvs, 250vs,b, 279vs, 308s,sh, 344s,sh, 385w,sh, 445w,vb	13650	5.73
$Fe(gu)(ClO_4) \cdot 4H_2O$	205vvs, 249vs,b, 278vs, 312s,sh, 347s,sh, 890m, 1100m	9071	4.67
$Fe(guH)_2(ClO_4)_3 \cdot 2EtOH$	205vvs, 251vs,b, 282vs, 309s,sh, 347s,sh, 415m,b, 540mw,b	15572	6.12
$Co(gu)(guH)(ClO_4) \cdot EtOH \cdot 2H_2O$	202vvs, 251vs,b, 280vs,b, 310s,sh, 352s,sh, 449ms, 503m, 517m, 1135w,sh	10231	4.96
$Ni(guH)_2(ClO_4)_2 \cdot 3EtOH$	203vvs, 251vs,b, 283vs, 308s,sh, 345s,sh, 440ms,b, 649m, 697m, 971m,sh, 1120w,b	4653	3.34
$Zn(guH)_2(ClO_4)_2 \cdot 5EtOH$	204vvs, 250vs,b, 280vs, 311s,sh, 350m,sh	Diamagnetic	

[a] Solid-state (Nujol mull) UV spectrum of guH, nm: 202vvs, 245vs, 267vs,b, 330ms,sh. Aqueous solution spectra from the literature, λ_{max}, nm (log ϵ): neutral guH (pH 6.0–6.2): 245–246 (4.01–4.04), 274–275 (3.89–3.92); anionic gu^- (pH 10.7–11.0: 243 (3.78–3.93), 273 (3.87–4.00) [44, 45]. [b] The solid-state spectrum of guH shows the following bands in the near-IR region, nm: 920w,b, 1310w,vb. These bands, which obviously arise from vibrational overtones and combination modes originating from guH [36] are also observed in the spectra of the new complexes at 900–1010 and 1270–1350 nm, and have been omitted from the Table. The *d–d* band at 971 nm in the spectrum of the Ni^{2+} complex appears as a distinct shoulder of the ligand near-IR band at 953 nm.

doublets are observed in the spectrum of the mixed ligand (guH-gu^-) Co^{2+} complex, both $\pi \rightarrow \pi^*$ peaks are considerably broader than the corresponding peaks in the spectra of the rest of the new complexes. The $n \rightarrow \pi^*$ transition of the ligand is detectable in the spectra of all of the complexes, appearing as a shoulder at 308–312 nm, while metal-to-ligand charge-transfer absorption [27, 37, 38, 47], originating in the UV and trailing off well into the visible region, is observed in the spectra of all the paramagnetic new complexes (*e.g.*, maxima at 380–540 nm in the spectra of the Mn^{2+} and Fe^{3+} complexes). The near-IR bands of guH appear slightly shifted in the spectra of all of the new complexes (bands at 900–1010 and 1270–1350 nm).

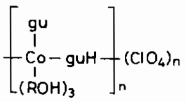
The d–d transition bands in the spectra of the Cr^{3+}, Fe^{2+}, Co^{2+} and Ni^{2+} complexes are compatible with low-symmetry hexacoordinated configurations [23, 27, 36–38, 48]. Band assignments (nm) and approximate Dq calculations (on the basis of pure O_h symmetry): $M = Cr^{3+}$: ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 437; $\rightarrow {}^4T_{2g}(F)$ 564, 604, 657; $Dq = 1644\ cm^{-1}$; $M = Fe^{2+}$: ${}^5T_{2g} \rightarrow {}^5E_g$ 890, 1100; $Dq = 1005\ cm^{-1}$; $M = Co^{2+}$: ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 449; $\rightarrow {}^4A_{2g}(F)$ 503, 517; $\rightarrow {}^4T_{2g}(F)$ 1135; $Dq = 1048\ cm^{-1}$; $B = 968\ cm^{-1}$; $M = Ni^{2+}$: ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 440; $\rightarrow {}^3T_{1g}(F)$ 640, 697; $\rightarrow {}^3T_{2g}(F)$ 971, 1120; $Dq = 957\ cm^{-1}$. The Dq values calculated are generally consistent with the presence of either MN_3O_3 ($M = Co^{2+}, Ni^{2+}$) or MN_2O_4 ($M = Cr^{3+}, Fe^{2+}$) chromophores (*vide infra*) in these complexes [27, 36–38, 49–51].

Before dealing with the ambient temperature magnetic moments of the new complexes, their likely structural types should be discussed on the basis of the overall evidence available. The Cr^{3+} and Fe^{3+} complexes are the only new compounds that are soluble in organic media, and may be considered as monomeric species, involving exclusively terminal unidentate guH, ethanol and $-OClO_3$ ligands (*i.e.*, $[M(guH)_2(EtOH)_2(OClO_3)_2](ClO_4)$; M = Cr, Fe). On the other hand, the new M^{2+} complexes seem to be analogous to a number of previously reported adenine or purine (puH) complexes with 3*d* metal perchlorates, which were considered as linear chainlike polymeric species, involving single bridges of bidentate nucleobase ligands between adjacent metal ions [27, 37]; this type of structure was later substantiated by the crystal structure determination of an analogous complex, namely $[Cu(puH)(OH_2)_4](SO_4) \cdot 2H_2O$, which was found to be a linear chainlike polymer with single bridges of N(7), N(9)-bonded bidentate puH between adjacent Cu^{2+} ions [52]. Thus, the only 1:1 new complex ($M = Fe^{2+}$) can be tentatively formulated as comprising exclusively bidentate bridging gu^- and four terminal aqua ligands per Fe^{2+} ion (II), while the Co^{2+} (III; $R = H, C_2H_5$), Ni^{2+} (IV) and Zn^{2+} (V) complexes would contain both terminal unidentate and bridging bidentate guanine ligands, with coordination number six being attained by the presence of three ethanol or aqua ligands per metal ion. Finally, the Mn^{2+} complex would be also of the same general



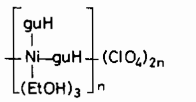
$$\left[\begin{array}{c}(\mathrm{OH_2})_4\\ |\\ -\mathrm{Fe}-\mathrm{gu}-\end{array}\right]_n(\mathrm{ClO_4})_n$$

(II)



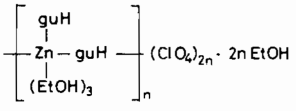
$$\left[\begin{array}{c}\mathrm{gu}\\ |\\ -\mathrm{Co}-\mathrm{guH}-\\ |\\ (\mathrm{ROH})_3\end{array}\right]_n(\mathrm{ClO_4})_n$$

(III)



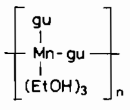
$$\left[\begin{array}{c}\mathrm{guH}\\ |\\ -\mathrm{Ni}-\mathrm{guH}-\\ |\\ (\mathrm{EtOH})_3\end{array}\right]_n(\mathrm{ClO_4})_{2n}$$

(IV)



$$\left[\begin{array}{c}\mathrm{guH}\\ |\\ -\mathrm{Zn}-\mathrm{guH}-\\ |\\ (\mathrm{EtOH})_3\end{array}\right]_n(\mathrm{ClO_4})_{2n}\cdot 2n\,\mathrm{EtOH}$$

(V)



$$\left[\begin{array}{c}\mathrm{gu}\\ |\\ -\mathrm{Mn}-\mathrm{gu}-\\ |\\ (\mathrm{EtOH})_3\end{array}\right]_n$$

(VI)

type, *i.e.*, a linear polymeric species with both terminal unidentate and bridging bidentate gu$^-$ ligands (VI). It should be pointed out here that, although several magnetically subnormal $[\mathrm{CuL_2}]\mathrm{X_2}$ or $[\mathrm{CuL_2}]\cdot n\mathrm{H_2O}$ complexes (L = purine derivative; X = Cl, Br, *etc.*) have been shown to be dimeric with quadruple L bridges between the $\mathrm{Cu^{2+}}$ ions [53–55], no binuclear complexes of this type have been reported for other 3*d* metal ions.

The ambient temperature magnetic moments of the $\mathrm{Cr^{3+}}$ and $\mathrm{Fe^{3+}}$ complexes are normal for high-spin compounds of these metal ions [56], as would be expected for monomeric species. Among the $\mathrm{M^{2+}}$ complexes, those with $\mathrm{Mn^{2+}}$ and $\mathrm{Fe^{2+}}$ exhibit slightly low μ_{eff} values (5.73 and 4.67 μB, respectively), while for M = Co or Ni, the moments are within the normal range for high-spin, hexacoordinated $\mathrm{Co^{2+}}$ or $\mathrm{Ni^{2+}}$ [56]. It should be noted, in this connection, that the corresponding puH complexes ($[\mathrm{M(puH)_2(OH_2)_3}](\mathrm{ClO_4})_2$) with $\mathrm{Co^{2+}}$ and $\mathrm{Ni^{2+}}$ were also found to exhibit normal room temperature magnetic moments, but at lower temperatures (below 110 K) their magnetic behavior was suggestive of antiferromagnetic exchange interactions [37]. It is also noteworthy that the $\mathrm{Mn^{2+}}$ and $\mathrm{Fe^{2+}}$ puH complexes of the preceding type exhibited normal room temperature μ_{eff} values (6.07 and 4.94 μB, respectively) [37]. It is recognized that magnetic studies of the new complexes at low temperatures would be necessary in order to make the proposed structural types II–VI more convincing. Nevertheless, the fact that at least two of the new complexes show slightly subnormal ambient temperature magnetic moments, combined with the magnetic data at 80–300 K available for some of their puH analogs, for which similar linear chainlike single-bridged polymeric structures were proposed (including the $\mathrm{Cu^{2+}}$ complex) [37], the μ_{eff} values at 298 K (2.17 μB) and 201 K (2.04 μB) reported for the apparently analogous $[\mathrm{Cu(guH)_2(EtOH)(OH_2)_2}](\mathrm{ClO_4})_2$ [24], and the established crystal structure of the linear chainlike single-bridged $[\mathrm{Cu(puH)(OH_2)_4}](\mathrm{SO_4})\cdot 2\mathrm{H_2O}$ complex [52], is lending support to our structural assignments. Magnetic studies of the complexes herein reported at 80–300 K are planned for the future.

As regards the likely binding site(s) of the guanine ligands in the new complexes, it is generally recognized that, as far as the binding site of terminal unidentate purines is concerned, the imidazole nitrogen, which is protonated in the free base, is the usual coordination site [57]. In the case of free guH, one imidazole (N(9)) and one pyrimidine (N(1)) nitrogen are protonated [58]; however, studies in solution have shown that a tautomeric equilibrium exists between neutral guH protonated at N(7) or N(9) [59]. With respect to ionic guanine species, monodeprotonation occurs at N(1), leaving only N(9) protonated [59], while proton addition occurs at N(7), leaving only the N(3) site unprotonated in the $\mathrm{guH_2^+}$ cation [6]. It is noted here that, in its $\mathrm{Cu^{2+}}$ and $\mathrm{Zn^{2+}}$ complexes, $\mathrm{guH_2^+}$ coordinates through N(9) [8–10]. In light of the preceding information, terminal unidentate guH (M = $\mathrm{Cr^{3+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Zn^{2+}}$) or gu$^-$ (M = $\mathrm{Mn^{2+}}$, $\mathrm{Co^{2+}}$) would almost certainly use N(9) as its binding site [8–10, 57]. Regarding bridging bidentate guH (M = $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Zn^{2+}}$) or gu$^-$ (M = $\mathrm{Mn^{2+}}$, $\mathrm{Fe^{2+}}$), one of the binding sites would again be N(9) [8–10, 57], but N(1), N(3) and N(7) would be equally likely, *prima facie*, to act as the second binding site [12–14, 27, 37, 38, 52–55, 57, 61, 62]. It is, nevertheless, more likely that N(7) is the second binding site in the new complexes, in view of the recent crystal structure of $[\mathrm{Cu(puH)(OH_2)_4}](\mathrm{SO_4})\cdot 2\mathrm{H_2O}$, which indeed contains single bridges of N(7), N(9)-bonded bidentate puH [52], and the exocyclic substituents at C(2) and C(6) of guH, which could conceivably introduce sufficient steric hindrance as to prevent coordination of this ligand through N(1) or N(3) [61, 62].

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