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Cobalt(II), Copper(II) and Zinc(II) Chloride Complexes Involving both Neutral and Monoanionic Guanine Ligands

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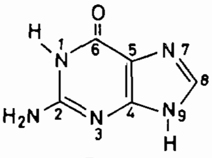
In recent publications we reported on the refluxing of 2:1 molar mixtures of guanine (guH; *I*) and divalent 3d metal chlorides in ethanol–triethyl orthoformate (teof). $M(guH)Cl_2$ adducts are precipitated in 2–3 days when M = Co, Cu or Zn [1]; when M = Mn, Fe or Ni, solid $M(gu)Cl\cdot2ROH$ (R = C_2H_5 or H) complexes with anionic gu^- are formed after 1–2 weeks [2]. Further research aimed at the preparation of the corresponding Co^{2+}, Cu^{2+} and Zn^{2+} complexes with gu^- and Mn^{2+}, Fe^{2+} and Ni^{2+} chloride adducts with guH was subsequently undertaken. We were able to isolate M(guH)guCl (M = Co, Cu, Zn) complexes, which are herein reported, by increasing the molar ratio of guH to metal ion while maintaining the same synthetic conditions [1, 2]: *i.e.*, 0.8 mmol hydrated metal chloride and 2.4 mmol guH (ligand to M^{2+} ratio of 3:1) were admixed and added to 50 ml of a 7:3 (v/v) mixture of ethanol–teof and the resultant mixture was refluxed. Under these conditions, the previously reported $M(guH)Cl_2$ (M = Co, Cu, Zn) adducts, .which were precipitated in substantial yields when the guH to metal ratio was 2:1 [1], started forming at low yields after 3–4 days of refluxing. Upon continuation of the reflux step, these solids were redissolved and eventually replaced by precipitates of the corresponding M(guH)guCl complexes after 1–2 weeks of refluxing. The complexes were separated by filtration, washed with ethanol–teof, and stored *in vacuo* over anhydrous $CaSO_4$. *Anal.* Found (calc.)%; M = Co (blue–gray): C, 30.57(30.36); H, 2.31(2.29); N, 35.20(35.40); Co, 15.12(14.90); Cl, 8.74(8.96). M = Cu (drab-green): C, 29.75(30.01); H, 2.38(2.27); N, 35.31(34.99); Cu, 16.06(15.88); Cl, 8.65(8.86). M = Zn (white): C, 29.61(29.87); H, 2.11(2.26); N, 35.22(34.84); Zn, 16.47(16.26); Cl, 9.09(8.82). As was the case with the $M(guH)Cl_2$ adducts (M = Co, Cu, Zn) [1] and the $M(gu)Cl\cdot2ROH$ complexes (M = Mn, Fe, Ni) [2], the new complexes reported are only slightly soluble in organic media.



I

Table I gives IR and solid-state electronic spectral data and magnetic moments at 298 K for the new complexes. The IR and electronic spectra of these complexes are generally similar to those of the corresponding $M(guH)Cl_2$ adducts [1]. However, in view of the presence of both guH and gu^- ligands in the new complexes, several IR bands of free guH [3] (*i.e.*, ν_{NH}, $\nu_{C=O}$, $\nu_{C=C}$ + $\nu_{C=N}$, δ_{NH_2} and $\nu_{M-Ligand}$ bands) are substantially broader in their spectra relative to the corresponding absorptions in the $M(guH)Cl_2$ adducts [1]. In addition, in one case (M = Co) $\nu_{C=O}$ is split into a doublet, while the higher frequency ν_{M-N} band occurs as a doublet in two cases (M = Co, Cu) and is quite broad in the third (M = Zn). The $\pi \rightarrow \pi^*$ transitions of the ligand [4–7], which are shifted toward lower energies upon complex formation, are also significantly broader in the spectra of the new complexes than in those of the corresponding $guH{-}MCl_2$ 1:1 adducts [1]. The preceding features are consistent with the simultaneous presence of guH and gu^- ligands in the new complexes; in fact, similar IR and UV band broadening was previously observed in the spectra of analogous mixed ligand complexes, such as $Co(guH)guClO_4\cdot EtOH\cdot2H_2O$ [7] and $Dy(guH)_2guCl_2$ [8].

The $\nu_{C=O}$ and δ_{NH_2} absorptions of guH are relatively insensitive to M(guH)guCl complex formation; therefore it can be concluded that neither of the exocyclic potential ligating sites (O(6) oxygen and N(2) nitrogen) of this ligand is involved in coordination [1–3, 6–8]. In contrast, the $\nu_{C=C}$ + $\nu_{C=N}$ bands of the ligand exhibit larger shifts or splittings in the spectra of the new complexes, as would be expected for species containing guanine coordinated through ring nitrogens [1–3, 6–8]. The location of the ν_{M-Cl} [1, 9–11] and ν_{M-N} [1, 12–14] bands is compatible with coordination number four and the exclusive presence of terminal chloro ligands. In addition to the $\pi \rightarrow \pi^*$ transition bands of the ligand (245, 276 nm), which were discussed above, the spectra of the new complexes exhibit the $n \rightarrow \pi^*$ transition at 308–312 nm [1, 15] and near-IR bands of guH, which are vibrational in origin [13] at *ca.* 920 and 1310 nm. The d–d spectrum of the Co^{2+} complex is consistent with a distorted tetrahedral configuration, *viz.*: $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ 567, 622, 645, 668, 701; $\rightarrow {}^4T_{1g}(F)$ 1410, 1595, 1635, 1860; $\rightarrow {}^4T_{2g}$ 2050 nm [12–14, 16]. Comparison to the spectrum of $Co(guH)Cl_2$, which shows a four-compo-

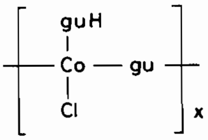
TABLE I. Pertinent Infrared Spectral Data, Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of M(guH)guCl Complexes.

	guH[a,b,c]	M = Co	M = Cu	M = Zn
IR spectra (cm^{-1})				
ν_{NH}	3000s, 2900s, 2850s, 2700s,b	3030s,b, 2895s,b, 2840s,b, 2700s,b	3040s,b, 2905s,b, 2860s,b, 2695s,b	3000s,b, 2900s,b, 2850s,b, 2690s,b
$\nu_{C=O}$	1705s	1701vs, 1696vs,sh	1702vs,b	1697vs,b
δ_{NH_2} scissoring	1680s	1671vs,b	1670vs,b	1673vs,b
$\nu_{C=C} + \nu_{C=N}$	1635s,sh, 1575m,b	1642s, 1604s, 1561ms,b	1640svs, 1611s, 1560ms,b	1633s, 1599s, 1562ms,b
δ_{NH_2} rocking	1107m	1111m,b	1112m,b	1105m,b
ν_{M-Cl}		352w, 321w	333w, 312w	320w, 307w,sh
ν_{M-N}		292w, 287w,sh, 149w,b	295w, 290w,sh, 254w,b	282w,b, 234w,b
Electronic spectra (nm)	202vvs, 245vs, 276vs,b, 330ms,sh, (920w,b, 1310w,vb)	201vs, 225vs,b, 256vvs,vb, 284vvs,vb, 308vvs,sh, 317 vvs, 341vvs, 567s,b, 622s,b, 645ms, 668ms, 701ms,sh (920mw,b, 1330mw,b), 1410mw, b, 1595mw,b, 1635mw,b, 1860mw,b, 2050mw,b	200vvs, 227vvs,b, 251vs,b, 281vs,b, 310vs, 325vs, 350vs, 737ms,vb, 812ms, vb, (915m,b, 1350mw,b)	200vvs, 223vvs,sh, 255vs,vb, 286vs,vb 312vs, 346s,sh, (930mw,b, 1330w,b)
Magnetic properties				
$10^6 \chi_M^{cor}$, (cgsu)		8662	1411	diamagnetic
μ_{eff}, μB		4.56	1.84	

[a] Free guH IR band assignments from ref. 3. [b] Aqueous solution UV spectra of guanine: 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) [4, 5]. [c] The near-IR bands in parentheses, appearing at 920, 1310 nm in free guH, are due to vibrational overtones and combination modes originating from guanine [13].

nent ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and a three-component ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition band [1], suggests that the cobalt coordination in Co(guH)guCl deviates further from T_d symmetry than in Co(guH)Cl_2 [16]. The d–d band maxima of the new Cu^{2+} complex (737, 812 nm) are also in favor of a severely distorted tetrahedral, rather than square-planar, configuration [1, 12–14, 17]. The magnetic moments of the two new paramagnetic complexes are normal for high-spin tetrahedral Co^{2+} and for Cu^{2+} compounds [18]. The new Zn^{2+} complex is most likely isomorphous to its Co^{2+} analog [12–14].

In view of the evidence discussed above, all three new complexes appear to have distorted tetrahedral configurations. Their probable structural type is **II**, which involves a linear chainlike polymeric $-[-M-\text{guanine}-]_{\overline{x}}$ backbone and two terminal (one guanine, one chloro) ligands per metal ion. This structure is analogous to those established for M(mad)Cl_2 adducts (mad = 9-methyladenine) for M = Co [19] or Zn [20] and to those proposed for the M(guH)Cl_2 complexes [1], as far as the presence of the linear polymeric $-[-M-\text{nucleobase}-]_{\overline{x}}$ backbone and two terminal ligands per metal ion is concerned. The terminal guanine ligand would certainly coordinate through the N(9) imidazole nitrogen [1, 2, 6–8, 21, 22], while the bridging bidentate guanine would most likely be N(7), N(9)-bonded to two adjacent metal ions [6–8, 22, 23]. It should be mentioned here that the fact that the new Co^{2+} and Cu^{2+} complexes exhibit normal room temperature magnetic moments does not contradict the proposed polymeric structure **II**. In fact, several linear polynuclear 3d metal complexes ($M = Co^{2+}, Ni^{2+}, Cu^{2+}$) with single bridging diazine, diazole and related ligands (including purines) have been found to exhibit normal ambient temperature magnetic moments, but show evidence in favor of magnetic exchange interactions at lower temperatures [24–26].



$$\left[- \overset{\text{guH}}{\underset{\text{Cl}}{\text{Co}}} - \text{gu} - \right]_x$$

II

In conclusion, the present work in combination with our earlier synthetic study [1] demonstrates that small variations in our synthetic method can influence the precipitation of adducts of neutral guH or complexes of anionic gu^-. Although in the present case we isolated mixed neutral–anionic guanine complexes, in previous work we obtained a guH adduct with $Cu(ClO_4)_2$ and the $Cu(gu)_2 \cdot H_2O$ complex [6] or, with adenine (adH), the $Co(adH)_2(ClO_4)_2 \cdot 3EtOH$ adduct and the $Co(ad)ClO_4 \cdot EtOH \cdot 2H_2O$ complex [27], by employing small variations in our synthetic method. We are now involved in attempts to synthesize MCl_2 adducts with guH for M = Mn, Fe, Ni [2] and with adH for M = Mn, Fe, Co, Ni, Cu, Zn. So far, reactions of adH with MCl_2 under our synthetic conditions have led exclusively to the isolation of complexes involving anionic ad^- ligands [28].

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