

Guanine Complexes with 3d Metal Perchlorates*

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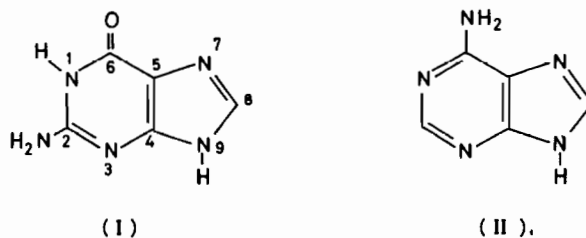
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The metal complexes of guanine (2-amino-6-oxo-purine; guH; I) have not been studied to as large an extent as the corresponding complexes of adenine (6-amino-purine; adH; II) [2]. The main reason for this is that it is much more difficult to isolate crystalline metal complexes with guH than with adH, at least from aqueous solutions [2]. In neutral guH, N(1) and N(9) are both protonated in the solid state [3]. Ionization leads to deprotonation at N(1) for the gu^- monoanion [4], whereas in the guaninium cation (guH_2^+), the addition of proton has been shown to be at N(7), leaving only the N(3) nitrogen unprotonated [5]. Solution studies demonstrated a tautomeric equilibrium between neutral guH protonated at N(9) and at N(7) [4]; the importance of the protonation sites of purine ligands lies in their established tendency to act preferentially as binding sites upon metal complex formation [2]. Regarding reported metal complexes of guanine and derivatives, early studies have dealt with Hg^{2+} [6], Cu^{2+} [7-9] and Ag^+ [10] complexes. Crystal structure determinations of guH_2^+ complexes with Cu^{2+} and Zn^{2+} revealed that this ligand coordinates through the N(9) nitrogen [11, 12]. No crystal structures for metal complexes with either neutral guH or anionic gu^- have been reported thus far, but it has been proposed that, in $[\text{Fe}(\text{guH})(\text{OH})]_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, guH functions as a bidentate chelating agent, coordinating through N(3) and N(9) [13]. 9-substituted guanines tend to coordinate through N(7) [14], whilst with 7,9-disubstituted guanines, N(1) seems to be the preferred ligand site [15]. With respect to the C=O (O(6)) oxygen site of guH, it is usually not involved in coordination to metal ions, but quite often participates to H-bonding with water molecules present in metal complexes [16]. Nevertheless, the possibility of chelation of 8-substituted guanines through N(1), O(6) has been advanced for a number of Cu^{2+} complexes [17]; it should be noted,



in this connection, that participation of O(6) in coordination has been established for a Cu^{2+} complex with theophylline (1,3-dimethyl-2,6-dioxo-purine) (chelation through O(6), N(7)) [18].

These [19-21] and other [22, 23] laboratories were recently successful in isolating well-defined, crystalline transition metal complexes with purine [19, 20], adH [21, 22] and 9-methyladenine [22, 23] from non-aqueous media. Since, in our synthetic studies, we could relatively easily obtain 3d metal chloride or perchlorate complexes with purine or adH, by using a mixture of ethanol and triethyl orthoformate (teof) as the preparation medium [19-21], we became interested in extending our synthetic work to include the corresponding complexes of guanine. The present letter gives a preliminary account of our studies on guanine complexes with 3d metal perchlorates [1].

Experimentally, 0.65 mmol hydrated metal perchlorate was dissolved in a mixture of 35 ml ethanol and 15 ml teof, and warmed to 50-60 °C, for 2 hr, under stirring. Then, 2.5 ml guH were added to the metal salt solution, and the result mixture was refluxed for 2-4 days. Subsequently, the supernatant was concentrated to about one-half its original volume, and the solid complexes were separated by filtration, washed with ethanol-teof and stored *in vacuo* over P_4O_{10} . The stoichiometries of the new complexes (established by means of elemental analyses), yields (% of theoretical) and magnetic moments at 297 K were as follows: $\text{Cr}(\text{guH})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ (gray; yield 31.7%; $\mu_{\text{eff}} = 3.96 \mu_{\text{B}}$); $\text{Mn}(\text{gu})_2 \cdot 3\text{EtOH}$ (white, yield 22.3%; $\mu_{\text{eff}} = 5.92 \mu_{\text{B}}$); $\text{Fe}(\text{guH})(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (brown; yield 53.8%; $\mu_{\text{eff}} = 4.93 \mu_{\text{B}}$); $\text{Fe}(\text{guH})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ (brown; yield 31.8%; $\mu_{\text{eff}} = 6.17 \mu_{\text{B}}$); $\text{Co}(\text{gu})(\text{guH})(\text{ClO}_4) \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ (lavender; yield 38.0%; $\mu_{\text{eff}} = 4.96 \mu_{\text{B}}$); $\text{Ni}(\text{guH})_2(\text{ClO}_4)_2 \cdot 3\text{EtOH}$ (brown; yield 48.1%; $\mu_{\text{eff}} = 3.34 \mu_{\text{B}}$); $\text{Cu}(\text{guH})_2(\text{ClO}_4)_2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ (green; yield 42.7%; $\mu_{\text{eff}} = 2.17 \mu_{\text{B}}$); $\text{Zn}(\text{guH})_2(\text{ClO}_4)_2 \cdot 3\text{EtOH}$ (beige; yield 35.1%; diamagnetic). The new M^{3+} complexes ($\text{M} = \text{Cr}, \text{Fe}$) dissolve in some organic solvents, and behave as 1:3 electrolytes in nitromethane-acetone ($\Lambda_{\text{M}}, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, of 10^{-3} M solutions at 25 °C: $\text{M} = \text{Cr}$ 223; $\text{M} = \text{Fe}$ 211) [24]. However, the new M^{2+} complexes are insoluble in all common organic solvents.

*See Ref. 1.

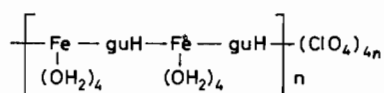
The IR spectra of the new complexes indicate that in none of these compounds does guanine coordinate through the C=O oxygen or the NH₂ (N(2)) nitrogen. In fact, the $\nu_{\text{C=O}}$, δ_{NH_2} (scissoring) and δ_{NH_2} (rocking) modes, which appear at 1705(s), 1680(s) and 1100(sh) cm^{-1} , respectively, in free guH [25], are observed in the following wavenumber regions (cm^{-1}) in the spectra of the complexes: $\nu_{\text{C=O}}$ 1735–1720(s); δ_{NH_2} (scissoring) 1690–1670(a); δ_{NH_2} (rocking) ca. 1100 (w) [25]. On the other hand, various $\nu_{\text{CC}} + \nu_{\text{CN}}$ bands of free guH (e.g., absorptions at 1587(m), 1578(m), 1477(m), 1464(m), 1418(m) cm^{-1} [25]) undergo significant shifts upon metal complex formation (occurring at 1610–1595(s), 1455–1438(mw) and 1410–1390(mw) cm^{-1}). This is taken as indicative of coordination of guanine through imidazole and/or pyrimidine ring nitrogens [19–21, 25]. The ν_{OH} mode of coordinated water or ethanol appears as a relatively sharp, medium intensity absorption at 3500–3300 cm^{-1} [26]; ν_{OH} doublets are observed in the spectra of the complexes involving both aqua and ethanol ligands ($\text{M} = \text{Co}^{2+}, \text{Cu}^{2+}$). Amongst the perchlorate-containing complexes (i.e., all but one ($\text{M} = \text{Mn}^{2+}$) of the new complexes), those with M^{2+} ions ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) involve exclusively ionic ClO_4^- , as manifested by the single character of the ν_3 (ca. 1080 cm^{-1}) and ν_4 (ca. 620 cm^{-1}) fundamental vibrations of this group [27, 28]. Whereas in the case of the Cr^{3+} and Fe^{3+} complexes, both ν_3 and ν_4 (ClO_4^-) are triply split (1110, 1080 and 1050, and 645, 625 and 620 cm^{-1} , respectively), and ν_1 and ν_2 (ClO_4^-) are IR-active, occurring at 920 and 480 cm^{-1} , respectively; these data are interpreted in terms of the presence of both ionic ClO_4^- and unidentate coordinated $-\text{OClO}_3$ in these complexes [27, 28]. The fact that both the Cr^{3+} and Fe^{3+} complexes behave as 1:3 electrolytes in nitromethane–acetone (*vide supra*) is obviously due to displacement of coordinated $-\text{OClO}_3$ by solvent molecules in solution.

The d–d transition spectral data available (solid-state (Nujol mull) spectral measurements) are generally in favor of low-symmetry hexacoordinated configurations [19–23, 29], viz. (nm): $\text{M} = \text{Cr}^{3+}$: ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ 437 ms; $\rightarrow {}^4\text{T}_{2g}(\text{F})$ 564 m, 604m, 657m ($\text{Dq} = 1644 \text{ cm}^{-1}$); $\text{M} = \text{Fe}^{2+}$: ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ 890m, 1100m ($\text{Dq} = 1005 \text{ cm}^{-1}$); $\text{M} = \text{Co}^{2+}$: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ 449 ms; $\rightarrow {}^4\text{A}_{2g}(\text{F})$ 503m, 517m; $\rightarrow {}^4\text{T}_{2g}(\text{F})$ 1135w, sh ($\text{Dq} = 1048 \text{ cm}^{-1}$; $\text{B} = 968 \text{ cm}^{-1}$); $\text{M} = \text{Ni}^{2+}$: ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ 440ms,b; $\rightarrow {}^3\text{T}_{1g}(\text{F})$ 640m, 697m; $\rightarrow {}^3\text{T}_{2g}(\text{F})$ 971m,sh, 1120w,b ($\text{Dq} = 957 \text{ cm}^{-1}$); $\text{M} = \text{Cu}^{2+}$: ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ 570ms, 785ms (with shoulders at 550 and 652 nm). The calculated approximate Dq values, given above in parentheses, are consistent with MN_3O_3 ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}$) or MN_2O_4 ($\text{M} = \text{Cr}^{3+}, \text{Fe}^{2+}$) (*vide infra*) absorbing species [19–23, 30, 31]; as regards the spectrum of the Cu^{2+} complex, the presence of two main d–d

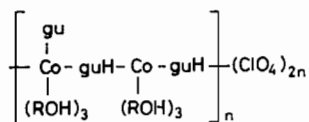
maxima at 570 and 785 nm is compatible with coordination number six [22, 32].

Finally, the ambient temperature magnetic moments of the new complexes are normal for high-spin $3d^3$, $3d^5$, $3d^7$ and $3d^8$ compounds or the $3d^9$ configuration [33]; only in the case of Fe^{2+} ($3d^6$), the observed μ_{eff} of 4.93 μB may be slightly low for high-spin hexacoordinated ferrous compounds. It should be noted here that the normal μ_{eff} values reported do not necessarily rule out the presence of bridging guanine ligands in some of the new complexes. In fact, during previous studies of purine (puH) complexes with 3d metal perchlorates, normal ambient temperature magnetic moments were observed, but subsequent magnetic studies at 300–80 K revealed the effects of spin-spin coupling interactions, attributable to linear polymeric structures, involving single $-\text{M}-\text{puH}-\text{M}-\text{puH}-$ bridging sequences [20].

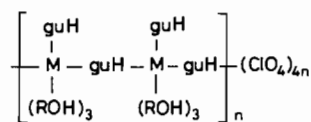
The overall evidence available at this point favours monomeric configurations for the two M^{3+} complexes which dissolve in some organic media, and polymeric structures for the M^{2+} complexes, which are generally insoluble in organic solvents. The Cr^{3+} and Fe^{3+} complexes are most probably of the $\text{M}(\text{guH})_2(\text{OH}_2)_2(\text{OClO}_3)_2(\text{ClO}_4)$ type, with terminal unidentate guH ligands. For the M^{2+} complexes, structures involving a linear, single-bridged polymeric backbone ($-\text{M}-\text{guanine}-\text{M}-\text{guanine}-$ sequences), similar to that postulated for the purine analogs [20], with guanine functioning as bidentate, are considered as most likely [19–21]. With $\text{M} = \text{Fe}^{2+}$, coordination number six is attained by the presence of four terminal aqua ligands per Fe^{2+} ion, i.e.,



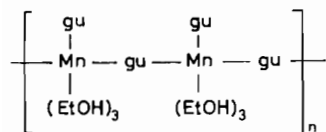
For $\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$, a similar type of structure, differing only in that each metal ion is surrounded by one terminal unidentate guanine and three terminal ROH ($\text{R} = \text{H}, \text{C}_2\text{H}_5$ or, in the case of mixed aqua–ethanol complexes, both) ligands, is most probable, viz.



and



($\text{M} = \text{Ni}, \text{Cu}, \text{Zn}$). Finally, $\text{Mn}(\text{gu})_2 \cdot 3\text{EtOH}$ would be also expected to be of the same polymeric type, i.e.,



Terminal unidentate guanine should be coordinating through the N(9) nitrogen [2, 7–13], while with bridging bidentate guanine, N(9) would certainly be one of the binding sites and N(1), N(3) and N(7) would be equally likely to function as the second binding site [2, 13–15, 19–21, 34–37].

Prior to concluding, it should be mentioned that, whereas Cr^{3+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} and Zn^{2+} perchlorates formed, under our synthetic conditions, simple adducts with guH, in the case of $\text{Co}(\text{ClO}_4)_2$ one ClO_4 group was substituted by one gu^- ligand, whilst $\text{Mn}(\text{ClO}_4)_2$ reacted fully with the purinic base, affording $\text{Mn}(\text{gu})_2$. In view of these differences in behavior, we have recently extended our synthetic studies in attempts to establish the synthetic conditions that will favor substitution rather than addition reactions for each of the metal ions under study. So far we were able to produce $\text{Cu}(\text{gu})_2$ by following our standard synthetic procedure, with the following differences; the molar ratio of guH to $\text{Cu}(\text{ClO}_4)_2$ was decreased to 2:1 and the period of refluxing was extended to more than one week. Results of this ongoing synthetic work will be reported in the future.

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