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Adducts of Guanine with Chromium(III), Iron(III) and Oxovanadium(IV) Chlorides

CHESTER M. MIKULSKI, LINDA MATTUCCI, LYNNE WEISS

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

and NICHOLAS M. KARAYANNIS

Amoco Chemicals Corporation, P.O. Box 400, Naperville, Ill. 60566, U.S.A.

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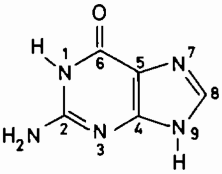
*The preparation of well-defined adducts of the $M(guH)_2Cl_3$ (M = Cr, Fe) and $VO(guH)Cl_2$ types (guH = neutral guanine), by refluxing ligand and metal chloride mixtures in ethanol–triethyl orthoformate, is reported. Characterization studies suggest that the new complexes are probably linear chain-like polymeric species, involving single bridges of bidentate guH ligands between adjacent metal ions. Bidentate bridging guH is most probably coordinated through the N(7) and N(9) imidazole nitrogens. The chloro ligands present in the adducts are exclusively terminal. Infrared evidence rules out the possibility of coordination of guanine through either of its exocyclic potential binding sites (*i.e., *C=O oxygen and NH_2 nitrogen) [1].*

Introduction

Following synthetic and characterization studies of metal chloride complexes of purine (puH) and adenine (adH) [2–10], we recently extended our research to the preparation of the corresponding metal chloride complexes with guanine (guH; **I**) [1, 10]. In many cases studied, partial substitution of anionic gu^- for Cl^- ligands occurred under our synthetic conditions, leading to such complexes as $Al(gu)Cl_2 \cdot 2H_2O$ [10], $Dy(guH)_2(gu)Cl_2$, $M(gu)_2Cl_2$ (M = Th, U) [11] and $V(gu)Cl_2 \cdot 2EtOH$ [1]. Reactions of guH with 3d metal(II) chlorides (M = Mn, Fe, Co, Ni, Cu, Zn) led in some cases to neutral guH adducts and in other cases to anionic gu^- complexes [1], as will be described in a forthcoming publication. Finally, with $CrCl_3$, $FeCl_3$ and $VOCl_2$, guH was found to yield well-defined adducts of the $M(guH)_2Cl_3$ (M = Cr, Fe) and $VO(guH)Cl_2$ types. The preparation and characterization of the latter adducts are the subject of the present paper. It is of interest to note at this point that puH and adH also afforded $Fe(LH)_2Cl_3$ [5] and $VO(LH)Cl_2$ [4], under similar synthetic conditions. However, both these ligands reacted with $CrCl_3$ to yield polynuclear complexes with anionic pu^- or ad^-, of the $Cr_3L_5Cl_4 \cdot 2H_2O$ type [7].



(**1**)

Experimental

A synthetic procedure similar to that employed for the isolation of the corresponding purine and adenine complexes [4, 5, 7] was followed, *viz.*: 0.8 mmol of the metal chloride are dissolved in a mixture of 35 ml absolute ethanol and 15 ml triethyl orthoformate (teof), and the resultant solution is stirred for 1–2 h at 40–50 °C. Then, 2.4 (M = Cr^{3+}, Fe^{3+}) or 1.6 (M = VO^{2+}) mmol guH are added, and the mixture is refluxed for 72 h. Upon completion of the refluxive step, the volume of the supernatant is reduced to about one-half its original volume, by mild heating under reduced pressure, and the solid complex is then separated by filtration, washed with ethanol–teof, and stored *in vacuo* over P_4O_{10}. Analytical data (found(calcd.)%) were as follows: $Cr(guH)_2Cl_3$ (green): C 25.81(26.09); H 2.02(2.19); N 30.76(30.42); Cr 11.55(11.29); Cl 22.76(23.10); $Fe(guH)_2Cl_3$ (brownish): C 26.13(25.87); H 2.31(2.18); N 29.92(30.57); Fe 12.37(12.03); Cl 22.62(22.91); $VO(guH)Cl_2$ (green): C 21.04(20.78); H 1.90(1.74); N 23.88(24.23); V 17.70(17.63); Cl 24.21(24.54). The Cr^{3+} and Fe^{3+} complexes are very sparingly soluble in organic media, whilst $VO(guH)Cl_2$ is completely insoluble in all common organic solvents.

Characterization of the complexes was based on spectral and magnetic studies. Infrared spectra (Table I) were recorded on KBr pellets (4000–500 cm^{-1}) and on Nujol mulls between high-density

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TABLE I. Infrared Spectra of Guanine Complexes with 3d Metal Chlorides (cm^{-1}).

guH[a]	M = Cr^{3+}	M = Fe^{3+}	M = VO^{2+}	Band assignment
3330s, 3290s,sh, 3160s	3340s, 3300s,sh, 3150s	3350s, 3295s,sh, 3150s	3335s, 3285s, 3165s	ν_{NH_2}
3000s, 2900s, 2850s, 2700s	3000s, 2890s, 2840s, 2710s,b	3000s, 2900s, 2850s,b, 2690s,b	2995s, 2905s, 2840s, 2690s,b	ν_{NH}
1705s	1698vs	1712vs	1706vs	$\nu_{C=O}$
1680s	1675vvs	1680vvs	1670vvs	δ_{NH_2}, scissoring
1635s,sh, 1575m,b	1640vs, 1610vs, 1565s	1640vs, 1605vs, 1560s	1635vs, 1602vs, 1570s	$\nu_{C=C} + \nu_{C=N}$
1563m	1549s, 1528m,sh	1545s, 1525m,sh	1552s, 1530m,sh	δ_{NH}
1477m, 1464m, 1418m, 1375m	1470s, 1455s, 1411w, 1369vs	1475s, 1460s, 1412mw, 1367vs	1472s, 1462s, 1414w, 1371vs	Ring vibrations
1263m	1257m	1259m	1259m	ν_{C-N}
1209m, 1169m	1205w, 1168w	1210w, 1168w	1204w, 1168mw	Ring vibrations
1107m	1111w	1112w	1110mw	δ_{NH_2}, rocking
1042w	1030m	1040w,b	1040mw	
			1010mw	$\nu_{V=O}$
930w	925w	940mw	939mw	Ring vibration
880m, 851m, 781m, 730w	865w, 837w, 767w, 730vw	870w, 841w, 777w,b, 735vw	867m, 838m, 766m, 735vw	$\delta_{NH} + \delta_{CH}$
640m	635w,b	637w,b	632w,b	δ_{NH_2}, wagging
608m, 570m, 544m, 515w, 506w, 440w, 370w, 345w,b	590w, 570w, 540w, b, 465w,b, 440w, sh, 380w	592w, 575w, 540vw, 455w,sh, 440w,vb, 395w, 370w	595w, 570w, 545w, b, 470w,b, 445w, sh	ν_{Ligand} at 610–300 cm^{-1}
	355w, 337w, 321w	348w, 327w, 315w	433w, 409w	ν_{M-Cl}
	292w	286w	315w	ν_{M-N}

[a] guH band assignments after Shirotake and Sakaguchi [15].

polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra and ambient temperature (298 K) magnetic susceptibility measurements (Table II) were obtained by methods previously described [12].

Discussion

Several adducts of guH with 3d metal perchlorates have been synthesized and characterized by these laboratories [13, 14]. The infrared spectra of the new complexes are generally similar to those of the adducts of 3d metal perchlorates with neutral guH [13, 14], as far as the response of various vibrational modes of free guH to metal complex formation is concerned. Thus, bands attributable to the exocyclic potential ligand sites of guanine, *i.e.*, the amino group nitrogen at C(2) and the carbonyl oxygen at C(6) [15–17], are apparently insensitive to complexation (Table I), as was also the case with the 3d metal perchlorate complexes [13, 14]. This is taken as indicative of non-participation of either N(2) or O(6) in coordination [10, 13–15, 18, 19]. In contrast, several $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrational modes of free guH show significant shifts and occasional splittings upon adduct formation with Cr^{3+}, Fe^{3+} or VO^{2+} chloride. This suggests that one or more ring nitrogens are functioning as the binding sites of the guH ligands [2, 4–8, 10, 13–15, 18, 19]. The occurrence of $\nu_{V=O}$ at 1010 cm^{-1} in the spectrum of the $VOCl_2$ adduct is consistent with previously reported data on oxovanadium(IV) complexes with nucleobases [4] and derivatives [20], and favors coordination number five for the central V^{4+} ion [21, 22].

Coordination number five for $VO(guH)Cl_2$ is also suggested by the occurrence of the tentatively assigned ν_{V-Cl} at 433, 409 and ν_{V-N} at 315 cm^{-1} [4, 8, 22–25]. The location of the ν_{V-Cl} bands is consistent with the exclusive presence of terminal chloro ligands in this complex [4, 23]. Likewise, the appearance of three ν_{M-Cl} (M = Cr, Fe) absorptions at 355–315 cm^{-1} in the spectra of the $CrCl_3$ and $FeCl_3$ adducts is in favor of exclusively terminal Cl ligands and hexacoordinated configurations [5, 7, 23, 26]. In fact, similar ν_{Fe-Cl} spectral bands were reported for the purine and adenine analogs of the new ferric complex [5], whilst in the case of the $Cr_3L_5Cl_4 \cdot 2H_2O$ complexes with pu^- and ad^-, which seem to contain exclusively bridging chloro groups, the ν_{Cr-Cl} bands were observed at 322–299 cm^{-1} [7]. Coordination number six for the Cr^{3+} and Fe^{3+} adducts is also favored by the occurrence of the ν_{M-N} band at 292–286 cm^{-1} [5, 7, 13, 14, 27].

The UV spectral bands of free guH ($\pi \rightarrow \pi^*$ transitions at 245 and 276 nm, with the $n \rightarrow \pi^*$ transition

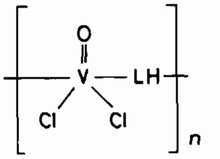
TABLE II. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of guanine adducts with 3d Metal Chlorides.

Complex	λ_{max}, nm[a,b]	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μB
$Cr(guH)_2Cl_3$	203vs,sh, 222vs,sh, 251vs,sh, 275vs, 282vs,sh, 309vs,sh, 342vs,b, 475ms, 493ms, 565ms, 588ms,b, 640m,b, 935w,b, 1290w,b	5674	3.69
$Fe(guH)_2Cl_3$	207vvs, 252vs,b, 279vs, 310s,sh, 349s,sh, 425m,b, 545mw,b 680w,b, 950w,vb, 1280w,vb	14,771	5.96
$VO(guH)Cl_2$	202vvs, 218vvs,sh, 251vs,sh, 274vs,b, 288vs,b, 306s,sh, 349s,sh, 433m, 500m, 697mw,vb, 895w,vb, 1325w,vb	1162	1.67

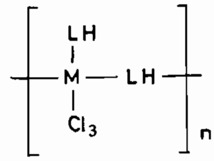
[a] Nujol mull UV spectrum of free guH, nm: 202vvs, 245vs, 276vs,b, 330m,sh [13, 14]. Aqueous solution spectrum of guH from the literature [28, 29], nm (logϵ): 245–246 (4.01–4.04), 274–275 (3.89–3.92). [b] The Nujol mull near-IR spectrum of free guH is characterized by continuous absorption at 900–1500 nm, with most prominent maxima at 920 and 1310 nm. These bands, which are presumably due to vibrational overtones and combination modes originating from guH [35], appear shifted in the spectra of the three new complexes.

masked) [13, 14, 28, 29] undergo significant changes upon 3d metal chloride adduct formation (Table II). The general trend observed is shifting of the $\pi \rightarrow \pi^*$ transition bands to lower energies (in some cases the 276 nm band of free guH appears as a doublet at 274–275 and 282–288 nm). The $n \rightarrow \pi^*$ transition, which would be expected to occur at 290–300 nm in free guH [30], appears at 306–310 nm in the spectra of the new complexes [13, 14]. Strong metal-to-ligand charge-transfer absorption [31], originating in the UV and trailing off into the visible region, is present in the spectra of the complexes. This is especially conspicuous in the spectrum of the Fe^{3+} compound, which shows medium-to-weak absorption at 400–700 nm. The d–d transition bands of the $CrCl_3$ adduct, which are clearly split ($^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 473, 493; $\rightarrow {}^4T_{2g}(F)$ 565, 588, 640 nm), are suggestive of a low-symmetry hexacoordinated structure [32]. The approximate Dq value of 1673 cm^{-1} is compatible with a CrN_3Cl_3 chromophore [7]. The d–d transition bands in the spectrum of the $VOCl_2$ adduct (433, 500, 697 nm) are consistent with [22], but not necessarily diagnostic [22, 33, 34] of coordination number five. The new complexes show near-IR maxima at 895–950 and 1280–1325 nm. Absorptions of this type have been invariably present in the guanine metal complexes we have prepared so far [11, 13, 14], and presumably arise from shifts of the free guH absorptions in these regions, which are attributable to vibrational overtones and combination modes of the guanine molecule [35].

The ambient temperature magnetic moments of the new complexes are normal for high-spin compounds of the metal ions of interest [36], with only that of the Cr^{3+} complex being on the low side of the range of normal values. On the other hand, the three new complexes are either insoluble or very sparingly soluble in organic media and, therefore, likely to be bi- or poly-nuclear. Furthermore, the fact that the pentacoordinated VO^{2+} complex contains only four ligands per V^{4+} ion, and the hexacoordinated Cr^{3+} and Fe^{3+} adducts involve only five ligands per metal ion, is also in favor of bi- or poly-nuclear configurations, which by, the way, are not necessarily in conflict with the magnetic evidence available. In fact, linear, chainlike, single-bridged purine complexes of the $[M(puH)_2(OH_2)_3](ClO_4)_2$ type (M = Co, Ni, Cu) reportedly exhibit normal ambient temperature magnetic moments, showing evidence of magnetic exchange interactions only at temperatures below about 110 K [37]. Hence, polymeric structural types, involving single guH bridges between adjacent metal ions, are most probable for the new complexes. For the $VOCl_2$ adduct, a structure similar to that proposed for the puH and adH analogs [4] would be most probable (**II**: LH = guH), while in the case of the Cr^{3+} and Fe^{3+} complexes, structural type **III**, analogous to that proposed for the $FeCl_3$ adducts with puH and adH [5], is considered as most likely.



(II)



(III)

As regards the binding sites of guH in the new adducts, it is generally recognized that terminal unidentate purines tend to coordinate through the imidazole nitrogen which is protonated in the free base [38]. Free guH is protonated at N(9) and N(1) [39]. This information, combined with the fact that coordination of unidentate guH_2^+ (guaninium cation) occurs through N(9) in various 3d metal complexes [40–42], leads to the conclusion that the binding site of terminal guH in structure **III** is N(9). With respect to the binding sites of bridging bidentate guH in both structures **II** and **III**, N(9) would again be most likely to be one of these sites [13]. As far as the second binding site is concerned, N(1), N(3) and N(7) would be equally likely candidates. However, as mentioned previously [13], N(7) may be considered as most likely to act as the second binding site, in view of the crystal structure of [Cu(puH)(OH$_2$)$_4$](SO$_4$)·2H$_2$O, which is a linear chain-like polymer with single N(7), N(9)-bonded puH bridges between adjacent Cu^{2+} ions [43], and the fact that coordination of guH through N(1) or N(3) might conceivably be unfavorable, owing to steric interference of these sites with the exocyclic substituents at C(2) and C(6) of guH [44, 45].

Prior to concluding it should be stressed that the fact that not only FeCl$_3$ and VOCl$_2$, but also CrCl$_3$ afforded adducts with guH under our synthetic conditions, should not be necessarily taken as indicating that guH is less prone than puH or adH to react with metal chlorides and form complexes involving partial substitution of anionic gu$^-$ for Cl$^-$ ligands. Although puH and adH yielded adducts with FeCl$_3$ [5] and VOCl$_2$ [4], but Cr$_3$L$_5$Cl$_4$·2H$_2$O complexes upon reaction with CrCl$_3$ (L = pu$^-$, ad$^-$) [7], in other cases different trends were observed, *viz.*: with 3d metal(II) chlorides puH formed strictly adducts [2], while both adH and guH produced some neutral ligand adducts and some anionic ligand complexes [1, 9]. As already pointed out, the factors determining whether a neutral or anionic purine base metal complex will be isolated are the duration of the refluxive step, the metal to ligand ratios employed, and the stability of the initially formed adduct at the reflux temperature and in the presence of ethanol and teof [13, 14, 46]. It is obvious that under more drastic synthetic conditions, the new adducts herein reported would eventually react to form anionic gu$^-$ complexes.

References

1 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Abstracts, the 185th Natl. Meetg., Am. Chem. Soc., Seattle, Washington,* March 20–25, 1983; No. INOR 167.
2 A. N. Speca, C, M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta, 46,* 235 (1980).
3 C. M. Mikulski, S. Cocco, N. DeFranco and N. M. Karayannis, *Abstracts, the 28th IUPAC Congress, Vancouver, B.C., Canada,* Aug. 16–21, 1981; No. IN 156.
4 *Idem, Inorg. Chim. Acta, 78,* L25 (1983).
5 *Idem, Inorg. Chim. Acta, 80,* L23 (1983).
6 *Idem, Inorg. Chim. Acta, 80,* L61 (1983).
7 *Idem, Inorg. Chim. Acta, 80,* L71 (1983).
8 *Idem, Inorg. Chim. Acta, 67,* 61 (1982).
9 C. M. Mikulski, D. F. Delacato, D. Braccia and N. M. Karayannis, *Abstracts, the 186th Natl. Meetg., Am. Chem. Soc., Washington, D.C.,* Aug. 28–Sept. 2, 1983; No. INOR 146.
10 C. M. Mikulski, S. Cocco, L. Mattucci, N. DeFranco, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 67,* 173 (1982).
11 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 92,* 181 (1984).
12 N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3,* 415 (1969); N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *ibid., 8,* 91 (1974).
13 C. M. Mikulski, L. Mattucci, Y. Smith, T. B. Tran and N. M. Karayannis, *Inorg. Chim. Acta, 80,* 127 (1983).
14 C. M. Mikulski, T. B. Tran, L. Mattucci and N. M. Karayannis, *Inorg. Chim. Acta, 78,* 211 (1983).
15 S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull., 26,* 2941 (1978).
16 E. R. Blout and M. Fields, *J. Am. Chem. Soc., 72,* 479 (1950).
17 J.-M. Delabar and M. Majoube, *Spectrochim. Acta, 34A,* 129 (1978).
18 W. Beck and N. Kottmair, *Chem. Ber., 109,* 970 (1976).
19 P. Piperaki, N. Katsaros and D. Katakis, *Inorg. Chim. Acta, 67,* 37 (1982).
20 N. Katsaros, *Trans. Met. Chem., 7,* 72 (1982).
21 R. G. Garvey and R. O. Ragsdale, *Inorg. Chem., 4,* 1604 (1965); *J. Inorg. Nucl. Chem., 29,* 745, 1527 (1967).
22 N. M. Karayannis, L. L. Pytlewski and C. Owens, *J. Inorg. Nucl. Chem., 42,* 675 (1980).
23 R. J. H. Clark, *Spectrochim. Acta, 21,* 955 (1965); R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965).
24 K. Dehnicke, *Chem. Ber., 97,* 3354 (1964); *98,* 290 (1965).
25 G. Schmauss and H. Specker, *Z. anorg. allg. Chem., 364,* 1 (1969).
26 J. Lewis, R. S. Nyholm and G. A. Rodley, *J. Chem. Soc.,* 1483 (1965).
27 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem., 43,* 2771 (1981).
28 S. F. Mason, *J. Chem. Soc.,* 2071 (1954).
29 W. Pfleiderer, *Justus Liebigs Ann. Chem., 647,* 167 (1961).
30 L. B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc., 87,* 11 (1965).
31 A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.,* 1235 (1962); 3156, 5042 (1963); 1187, 4761 (1964).
32 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7,* 1835 (1968).
33 K. L. Baker, D. A. Edwards, G. W. A. Fowles and R. G. Williams, *J. Inorg. Nucl. Chem., 29,* 1881 (1967).
34 J. Selbin, *Chem. Rev., 65,* 153 (1965).
35 M. A. Guichelaar and J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 97,* 295 (1978).
36 B. N. Figgis and J. Lewis, *Progress in Inorg. Chem., 6,* 37 (1964).
37 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chem., 19,* 3491 (1980).
38 D. J. Hodgson, *Progress in Inorg. Chem., 23,* 211 (1977).
39 U. Thewalt, C. E. Bugg and R. E. Marsh, *Acta Cryst., B27,* 2358 (1971).
40 L. Srinivasan and M. R. Taylor, *Chem. Commun.,* 1668 (1970).
41 J. A. Carrabine and M. Sundaralingam, *J. Am. Chem. Soc., 92,* 369 (1970).
42 J. P. Declercq, M. Debbaudt and M. van Meersche, *Bull. Soc. Chim. Belg., 80,* 527 (1971).
43 P. I. Vestues and E. Sletten, *Inorg. Chim. Acta, 52,* 269 (1981).
44 L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, *J. Am. Chem. Soc., 101,* 2765 (1979); A. L. Beauchamp, *J. Cryst. Mol. Struct., 10,* 149 (1980).
45 J. Hubert and A. L. Beauchamp, *Can. J. Chem., 58,* 1439 (1980); *Acta Cryst., B36,* 2613 (1980).
46 C. M. Mikulski, R. DePrince, T. B. Tran, F. J. Iaconianni, L. L. Pytlewski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta, 56,* 163 (1981).