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Manganese(II), Iron(II) and Nickel(II) Chloride Complexes with Monodeprotonated Anionic Guanine

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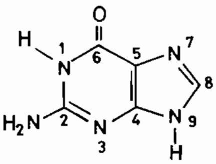
Abstract

Upon refluxing 2:1 mixtures of guanine (guH) and $MnCl_2$, $FeCl_2$ or $NiCl_2$ in a 7:3 (v/v) mixture of ethanol and triethyl orthoformate for 1–2 weeks, partial substitution of gu^- for Cl^- groups occurs, and solid complexes of the $M(gu)Cl\cdot 2ROH$ ($R = C_2H_5$ for M = Mn; R = H for M = Fe, Ni) type are obtained. The new complexes are pentacoordinated and appear to be linear chainlike polymeric species, involving a single-bridged $\left(M-gu\right)_n$ backbone. Coordination number five is attained by the presence of one terminal chloro and two terminal ROH ligands per metal ion. Most probable binding sites of bidentate bridging gu^- are the N(7) and N(9) imidazole ring nitrogens. IR evidence rules out the possibility of coordination of gu^- through any of the exocyclic potential ligand sites (O(6) oxygen or N(2) nitrogen) [1].

Introduction

During interaction of guanine (guH; I) with divalent 3d metal chlorides (M = Mn, Fe, Co, Ni, Cu, Zn) in refluxing ethanol–triethyl orthoformate (teof), in some cases distorted tetrahedral adducts of the $M(guH)Cl_2$ type (M = Co, Cu, Zn) are formed within 2–3 days, as already reported [2], whilst in other cases (M = Mn, Fe, Ni) the corresponding adducts, which are presumably initially formed [3], remain apparently in solution and are eventually (in 1–2 weeks) replaced by precipitates of complexes involving substitution of one monodeprotonated anionic guanine (gu^-) ligand for one Cl^- group per metal ion [1, 2]. The preparation and characterization of the latter complexes are dealt with in the present paper. Similar trends had been previously observed during the preparation of a variety of guanine complexes with metal chlorides [4–7] and perchlorates [8, 9], by similar synthetic procedures, in these laboratories. Thus, among metal chlorides, $VOCl_2$, $CrCl_3$ and $FeCl_3$ yield simple adducts with guH [7], $AlCl_3$ [4], VCl_3 [6], $ThCl_4$ and UCl_4 [5] form gu^- complexes, and $DyCl_3$ affords a mixed-ligand (neutral guH–anionic gu^-) complex of the $Dy(guH)_2(gu)Cl_2$ type [5]. Regarding 3d metal perchlorates, adducts of guH were obtained for $M = Cr^{3+}$, Fe^{3+}, Ni^{2+}, Zn^{2+}, gu^- complexes for $M = Mn^{2+}$, Fe^{2+} and a mixed-ligand (guH–gu^-) complex for $M = Co^{2+}$ [8]. Interactions of $Cu(ClO_4)_2$ with guH under varying synthetic conditions established that, depending on the ligand to Cu^{2+} molar ratio employed and the duration of the refluxive step, a guH adduct or a complex of the $Cu(gu)_2\cdot H_2O$ type can be isolated [9]. As pointed out previously, various factors may affect the precipitation of guH adducts *vs.* that of gu^- complexes; among these, the ligand to salt molar ratio employed, the duration of the refluxive step and the relative solubility (dependent of the degree of polymerization) and stability of the adduct initially formed in refluxing ethanol–teof appear to be most important. The isolation of a neutral ligand adduct or an anionic ligand complex, by using our preparative method, does by no means suggest that a gu^- complex or a guH adduct, respectively, can not be obtained by somewhat changing the conditions of the synthetic procedure [2–9].



I

Experimental

The preparative method employed was as follows: 0.8 mmol metal(II) chloride hydrate and 1.6 mmol

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TABLE I. Analyses of gu^- Complexes with 3d Metal Chlorides.

Complex	Color	C%		H%		N%		Metal%		Cl%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Mn(gu)Cl\cdot 2EtOH$	Cream white	32.50	32.66	4.85	5.04	21.05	20.77	16.52	16.47	10.66	11.03
$Fe(gu)Cl\cdot 2H_2O$	Brownish yellow	21.65	21.80	2.91	3.22	25.24	25.43	20.13	19.87	12.78	12.71
$Ni(gu)Cl\cdot 2H_2O$	Light yellow	21.42	21.11	2.88	2.76	24.98	25.15	20.94	21.10	12.65	12.39

TABLE II. Infrared Spectra of guH and the 3d Metal Chloride Complexes with gu^- (cm^{-1}).

guH[a]	M = Mn	M = Fe	M = Ni	Band assignment
	3400s,sh	3435s,sh	3420s,sh	$\nu_{OH}(ROH)$[b]
3330s, 3290s,sh 3160s	3340vs, 3295vs, 3170vs	3340vs, 3300vs,sh, 3170vs	3320vs, 3290vs,sh, 3160vs	ν_{NH_2}
3000s, 2900s, 2850s, 2700s	2990s, 2895s, 2845s, 2680s,b	3000s, 2910s, 2840s, 2700s,b	3005vs, 2895vs, 2840vs, 2680s,b	ν_{NH}
1705s	1700vs	1702vs	1699vs	$\nu_{C=O}$
1680s	1673vs,b	1677vs	1670vs,b	δ_{NH_2}, scissoring
1635s,sh, 1575m,b	1640svs, 1599s,sh, 1571s,sh	1641svs, 1612s, 1573s,sh	1635svs,b, 1607,sh 1580s,sh	$\nu_{C=C} + \nu_{C=N} + \delta_{OH}$
1563m	1560s, 1543m	1559ms, 1542ms	1566ms, 1540m,sh	δ_{NH}
1477m, 1464m, 1418m, 1375m	1472ms, 1459ms, 1410mw, 1366s	1471m, 1460m, 1411w, 1370s	1469m, 1461m, 1411w, 1365s	Ring vibrations
1263m	1256ms	1259m	1253m	ν_{C-N}
1209m, 1169m	1205mw,b, 1166mw	1207w, 1169w	1202w,b, 1163w	Ring vibrations
1107m	1107w	1111w	1110w	δ_{NH_2}, rocking
1042w	1030w,b	1038w,b	1040w,b	
930w	939mw	940w	936w	Ring vibration
880m, 851m, 781m, 730w	867m, 837m, 780m,sh, 763m, 750mw,sh	868w, 840w, 790m, 769m, 753mw,sh	862w, 839mw, 766m, 747mw,sh	$\delta_{NH} + \delta_{CH}$
705m, 689m	690w, 674w	690w, 677w	690w, 679w	Ring vibrations
640m	635w,b	633w,b	630w,b	δ_{NH_2}, wagging
608m, 570m, 544w, 515w, 506w, 440w	589m, 560w, 540w, 522w, 498vw, 482w, 454w,sh	591w, 562w, 546w, 525w, 478w,vb, 450w, sh	588w, 562w, 541w, 520w, 485w,b	ν_{Ligand} at 610–400 cm^{-1}
	401w	433w,b	459w,b	$\nu_{M-O}(ROH)$[b]
370w, 345w,b	380mw, 328mw	386mw, 332w	381w, 333w,b	ν_{Ligand} at 400–300 cm^{-1}
	285w, 258w	291w, 261w	301w, 276w	ν_{M-Cl}
	252w, 237w	258w, 240w	267w, 251mw	ν_{M-N}

[a] Free guH band assignments after Shirotake and Sakaguchi [39]; [b] R = H, C_2H_5.

guH were admixed and added to 50 ml of a 7:3 (v/v) mixture of ethanol–teof. The resultant mixture was refluxed for a period of 1–2 weeks, depending on the rate of accumulation of sufficient quantities of the solid complex for characterization. Following the refluxive step, the supernatant liquid was reduced in volume by about 50% (heating under reduced pressure), and the solid complexes were separated by filtration, washed on the filter with ethanol–teof and stored *in vacuo* over P_4O_{10}. The new complexes are of the $M(gu)Cl\cdot 2H_2O$ (M = Fe, Ni) and $Mn(gu)Cl\cdot 2EtOH$ types (Table I). They were obtained in relatively low yields (25–40% of the theoretical), and are either insoluble or very sparingly soluble in organic media. IR spectra (Table II) were recorded on KBr pellets and on Nujol and hexachloro-1,3-butadiene mulls between NaCl windows (4000–500 cm^{-1}) and on Nujol mulls between high-

TABLE III. Solid-State (Nujol Mull) Electronic Spectra and Magnetic Properties (298 K) of gu$^-$ Complexes with 3d Metal Chlorides.

Complex	λ_{max} (nm)^{a,b}	$10^6\ \chi_M^{cor}$ (cgsu)	μ_{eff} (μ_B)
Mn(gu)Cl·2EtOH	204vvs, 221vvs, 255vvs,b, 284vvs,b, 311vs,sh, 322vs,sh, 305s,b 382s,b, 444m,sh, (935w,b, 1320w,b)	13,855	5.77
Fe(gu)Cl·2H_2O	204vvs, 225vvs, 253vvs,b, 280vvs,b, 308vs,sh, 324vs, 353s,b 437ms,sh, 702mw,b, 780mw,b, 890w,b, (921w,b), 965w,b, (1335w,b), 1370w,sh	0,871	5.11
Ni(gu)Cl·2H_2O	201vvs, 220vvs, 251vvs, 281vvs,b, 309vs,sh, 320vs, 355s,b, 445s, 540ms, 637ms, (920w,b), 1130w,b, (1310w,sh), 1350w,b, 1960mw,b	4462	3.27

[a] Solid-state (Nujol mull) UV spectrum of guH (nm): 202vvs, 245vs, 276vs,b, 330ms,sh. Aqueous solution spectrum of gu$^-$ (pH 10.7–11.0), λ_{max} (nm) (log ϵ): 243 (3.78–3.93), 273 (3.87–4.00) [55, 56]; [b] Most prominent near-IR bands of free guH, attributable to vibrational overtones and combination modes of the ligand [59], nm: 920w,b, 1310w,b. These bands appear slightly shifted in the spectra of the complexes and are given in parentheses in the Table.

density polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements at 298 K (Table III) were obtained by methods previously described [10].

Discussion

Background on Guanine Metal Complexes

Free guH is protonated at N(1) and N(9) in the solid state [11], but studies in solution established that a tautomeric equilibrium exists between neutral guH protonated at N(9) or at N(7) [12]. Regarding ionic guanine species, monodeprotonation of the neutral base occurs at N(1), leaving only N(9) protonated [12], while proton addition occurs at N(7), leaving only the N(3) site unprotonated in the guH_2^+ cation [13, 14]. The protonation site(s) of purine ligands are of importance, because the preferred binding site when such a ligand acts as unidentate is the imidazole nitrogen which is protonated in the free base; it is also noteworthy that purines show a greater tendency to use imidazole rather than pyrimidine nitrogens as binding sites [15]. N(9) acts indeed as the binding site of guH_2^+ in its complexes with Cu^{2+} [16, 17] and Zn^{2+} [18] chlorides. Although several metal complexes with guH or gu$^-$ were reported [2, 4–9, 19–25], no crystal structure determinations are available. It is, however, most likely that both these ligands use N(9) as their binding site when functioning as terminal unidentate [16–18]. Bridging bidentate guH or gu$^-$ would be expected to bind through N(3), N(9) [15, 26–28] or N(7), N(9) [29–31] (the (N(1), N(9) combination is the least likely). Use of N(7) as the second binding site of bidentate guanine ligands is more probable, since 9-substituted guanine derivatives use N(7) as their preferred binding site [32–35], while the presence of the NH_2 substituent at C(2) may be introducing sufficient steric hindrance as to prevent coordination of this ligand through N(3) [2, 5–9, 31]. As regards the possibility of coordination of guanine and derivatives through the exocyclic O(6) oxygen or N(2) nitrogen, although spectroscopic evidence in favor of participation of the carbonyl oxygen in binding to the metal ion or in H-bonding was reported in certain cases [6, 36–38], no substantiation of such evidence by crystal structure determinations has appeared in the literature thus far.

In the light of the preceding information, these laboratories have previously proposed structural types involving bidentate bridging N(7), N(9)-bonded guH or gu$^-$ for several apparently linear chainlike single-bridged polymeric metal complexes with these ligands [2, 4, 5, 7–9]. In addition to the reasons favoring use of N(7) and N(9) as the likely binding sites of bidentate bridging guanine discussed above, it should be mentioned that the crystal structure determination of a purine (puH) complex of the $[Cu(puH)(OH_2)_4]SO_4\cdot 2H_2O$ type revealed that this compound is a linear polymeric species, involving single bridges of bidentate N(7), N(9)-bonded puH between adjacent Cu^{2+} ions [29]. The overall properties of the new complexes herein reported are also in favor of similar polymeric configurations, as indicated by our characterization work, which is discussed below.

Infrared Evidence

The IR spectrum of free guH recorded previously in these laboratories [8] (Table II) agrees well with other published IR data for this compound [39–41]. The ν_{NH} bands of free guH appear also in the spectra of the new complexes with the monodeprotonated gu$^-$ ligand, which still contains one protonated ring nitrogen site [12]. The $\nu_{C=O}$ and NH_2 absorptions of the ligand are relatively insensitive to complex formation with Mn^{2+}, Fe^{2+}, or Ni^{2+} chloride. Actually, in all the complexes of guanine prepared by these laboratories, these bands were insensitive to complex formation [2, 4, 5, 7–9], with the sole exception of $V(gu)Cl_2 \cdot 2EtOH$, which exhibited a substantial $\nu_{C=O}$ shift to lower wavenumbers [6]; the latter shift was attributed to either participation of the O(6) oxygen in direct binding to V^{3+} or involvement of the C=O group in H-bonding to an ethanol ligand hydrogen [6]. For the new complexes reported, it is obvious that neither of the exocyclic gu^- potential ligand sites (O(6) oxygen or N(2) nitrogen) participates in binding to M^{2+} [2, 4, 5, 7–9, 39, 42, 43]. Coordination of gu^- through ring nitrogens is suggested by more significant shifts and occasional splittings of the $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrational modes of the ligand in the spectra of the metal complexes [2, 4, 5, 7–9, 39, 42, 43], as well as the presence of bands with ν_{M-N} character in the lower frequency IR region. The presence of ethanol or water ligands in the new complexes, indicated by the analytical data (Table I), is substantiated by the identification of the characteristic ν_{OH} band of these ligands at 3435–3400 cm^{-1} [44, 45]. Tentative ν_{M-O}, ν_{M-Cl} and ν_{M-N} band assignments, based on previous studies of 3d metal(II) complexes with nucleobases [2, 46, 47], aqua [48, 49], ethanol [50] and chloro [2, 46, 47, 51, 52] ligands, favor coordination number five for the central M^{2+} ions [2, 46–52]. The location of the ν_{M-Cl} bands at 301–258 cm^{-1} is compatible with exclusively terminal chloro ligands in these pentacoordinated species [46, 47, 51–54].

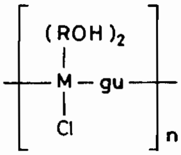
Electronic Spectra and Magnetic Properties

The main $\pi \rightarrow \pi^*$ transition bands of the ligand, occurring at 243 and 273 nm in anionic gu^- [55, 56], appear shifted to lower energies in the spectra of the new complexes, which also exhibit the $n \rightarrow \pi^*$ transition at 308–311 nm [2, 8, 9, 57] (Table III); the latter absorption is masked in the spectrum of guanine. Strong metal-to-ligand charge-transfer absorption [58], originating in the UV and trailing off into the visible region, is observed in the spectra of the new complexes. Near-IR bands with maxima at 920 and 1310 nm in the spectrum of guH and attributable to vibrational overtones and combination modes of this molecule [59], are observed also in the spectra of the complexes. The d–d transition spectra of the Fe^{2+} and Ni^{2+} complexes are characterized by multiple maxima at 702–1370 and 445–1960 nm, respectively. These features are in support of the pentacoordinated configurations (either trigonal bipyramidal or square pyramidal) [46, 47, 60, 61] suggested by the far-IR evidence.

The ambient temperature magnetic moments of the Fe^{2+} and Ni^{2+} complexes are normal for high-spin $3d^6$ or $3d^8$ compounds, while that of the Mn^{2+} complex is on the low side of normal values for high-spin $3d^5$ species [62]. It was previously established that linear chainlike polymeric complexes of the $[M(puH)_2(OH_2)_3](ClO_4)_2$ (M = Co, Ni, Cu) type with single purine bridges between adjacent metal ions have normal magnetic moments at room temperature, while at lower temperatures (below 120 K) they show evidence in favor of magnetic exchange interactions [63]. Hence, the normal or near-normal room temperature μ_{eff} values for the new complexes can by no means be considered as providing evidence against polymeric configurations.

Conclusion

In view of the preceding discussion, combined with the poor solubility of the new complexes in organic media, the pronounced tendency of purine derivatives to act as bridging ligands [15] and the stoichiometry of the complexes, which involve four potential ligands per metal ion but are pentacoordinated, the linear chainlike polymeric structural type II (M = Mn, Fe, Ni; R = H or C_2H_5), which includes terminal chloro and ROH ligands and bidentate bridging gu^-, is considered as most likely for



$$\left[-\overset{(ROH)_2}{\underset{Cl}{M}}-gu- \right]_n$$

II

these compounds. As already discussed (*vide supra*), gu^- is most probably bonded through the N(7) and N(9) imidazole nitrogens to adjacent M^{2+} ions. Prior to concluding, it should be pointed out that by employing our synthetic procedure in the preparation of 3d metal(II) chloride complexes with guanine or adenine (adH), we have obtained neutral ligand adducts only with LH = guH and M = Co, Cu, Zn [2], while in all other cases (LH = guH, M = Mn, Fe, Ni; and LH = adH, M = Mn, Fe, Co, Ni, Cu, Zn [47]) products of partial substitution of monodeprotonated anionic L^- for Cl^- groups were isolated. In view of the fact that other research groups have reportedly isolated adH adducts with several 3d metal(II) chlorides and bromides, by procedures involving refluxing ligand and metal salt mixtures in ethanol [59, 64], we are currently engaged in synthetic work aimed at the preparation of guH adducts with Mn^{2+}, Fe^{2+} and Ni^{2+} chlorides and adH adducts with the whole series of 3d metal(II) chlorides. Our plans include investigation of the feasibility of obtaining these adducts from our standard refluxive step medium (7:3 (v/v) ethanol–teof), by varying the ligand to metal ion molar ratio employed and the duration of the refluxive step [2–9, 65]; other media for the performance of the refluxive step will be also investigated.

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