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Guanine Complexes with Dysprosium(III), Thorium(IV) and Uranium(IV) Chlorides

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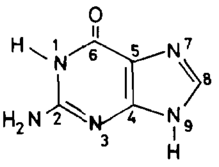
By refluxing mixtures of guanine (guH) and $DyCl_3$, $ThCl_4$ *or* UCl_4 *in ethanol–triethyl orthoformate, solid complexes of the* $Dy(guH)_2(gu)Cl_2$ *and* $M(gu)_2Cl_2$ *(M = Th, U) types were isolated. The insolubility of the new complexes in organic media, combined with the coordination number six suggested by the spectral evidence, favors polymeric configurations. Most likely structures involve a linear, chainlike, single-bridged polymeric backbone* $-(-M-\text{guanine}-)-_x$ *The* Dy^{3+} *complex is probably a linear polymer, also containing terminal unidentate guanine ligands, whilst for* $M = Th^{4+}$, U^{4+} *highly polymeric structures arising from cross-linking between linear polymeric* $-(-M-\text{guanine}-)-_x$ *units seems most likely. IR evidence rules out participation of the O(6) oxygen of guanine in coordination, despite the hard acid character of the metal ions under study. Guanine apparently coordinates exclusively through ring nitrogens in the new metal complexes; N(9) and N(7), N(9) are, respectively, the most likely binding sites of terminal unidentate and bridging bidentate guanine. The chloro ligands present in the complexes seem to be exclusively terminal.*

Introduction

Some complexes of lanthanide and actinide ions with nucleobases [1–3], nucleosides [4] and nucleotides [5–12] were reported in recent years. These hard metal ions are generally expected to show greater affinity toward oxygen rather than nitrogen ligand sites [13]. In fact, lanthanide(III) ions reportedly form uracil [3] and cytidine [4] complexes, in which the ligands coordinate through a C=O oxygen. Whereas in the case of nucleotide complexes with lanthanide(III) or UO_2^{2+} ions, the ligands coordinate through phosphate and ribose oxygens [5–13], although in certain cases some of the nucleobase ring nitrogens appear to be also involved in coordination [12]. These laboratories have recently reported on the preparation and characterization of $Dy(LH)LCl_2 \cdot H_2O$ and ML_2Cl_2 (M = Th, U) complexes (LH = purine (puH) or adenine (adH)) with nucleobases possessing only nitrogen ligand sites [2]. It was of interest to us to prepare the corresponding complexes with guanine (guH; I), and determine whether the C=O oxygen of this ligand would be involved in coordination. In previous studies of guanine metal complexes, we found that this ligand does not coordinate through the O(6) site, not only in 3d metal complexes [14, 15], but also in a complex with the hard Al^{3+} ion [16]. Actually, puH, adH and guH form, upon reaction with $AlCl_3$, complexes of the general type $AlLCl_2 \cdot 2H_2O$, in which the anionic ligand (pu^-, ad^- or gu^-) acts presumably as bridging, coordinating most probably [17] through the N(7) and N(9) imidazole ring nitrogens [16]. Synthetic work aimed at the preparation of solid complexes by reacting guH with $DyCl_3$, $ThCl_4$ and UCl_4 was undertaken, and the results of this study are reported in the present paper.



(I)

Experimental

The synthetic procedure employed was similar to that used for the preparation of purine and adenine analogs [2], *i.e.*: 0.8 mmol of the hydrated metal chloride were dissolved in a mixture of 15 ml triethyl orthoformate (teof) and 35 ml absolute ethanol, and the resultant solution was heated to 50–60 °C for 2 h, under stirring. Then, 1.6 mmol guH were added, and the mixture was refluxed for 5 days. After the refluxive step, the volume of the supernatant was reduced to about one-half its original

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TABLE I. Analytical Data for the New Guanine Metal Complexes.

Complex	Color	C%		H%		N%		Metal%		Cl%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Dy(guH)_2(gu)Cl_2$	Tan	26.27	26.55	2.06	1.92	30.64	30.25	23.70	24.24	10.36	10.11
$Th(gu)_2Cl_2$	Light orange	19.91	20.16	1.34	1.48	23.22	22.97	38.47	38.04	11.76	11.31
$U(gu)_2Cl_2$	Maroon	19.72	19.37	1.32	1.26	22.99	22.63	39.07	38.54	11.64	12.02

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

guH[a]	M = Dy^{3+}	M = Th^{4+}	M = U^{4+}	Band assignment
3330s, 3290s,sh, 3160s	3350s, 3295s, 3165s	3350s, 3285s, 3155s	3340s, 3300s, 3170s	ν_{NH_2}
3000s, 2900s, 2850s, 2700s	3000s, 2910s, 2850s, 2695m, 2660m,b	3005s, 2995s, 2845s, 2670mw,b	3000s, 2900s 2840s, 2680m,b	ν_{NH}
1705s	1703vs	1702vs	1707vs	$\nu_{C=O}$
1680s	1675vs	1670vs	1672vs	δ_{NH_2}, scissoring
1635s,sh, 1575m,b	1610vs,1565s	1605vs, 1570s,b	1598vs, 1570s,sh	$\nu_{C=C} + \nu_{C=N}$
1563m	1550s,sh, 1530ms	1547s, 1528m	1550s, 1525m	δ_{NH}
1477m, 1464m, 1418m, 1375m	1476s, 1457s, 1415m, 1371vs	1470s, 1451s, 1411m, 1367s	1471s, 1459s, 1410m, 1370vs	Ring vibrations
1263m	1261s	1255m	1259s	ν_{C-N}
1209m, 1169m	1211mw, 1170m	1208mw,b, 1166m	1210m, 1169m	Ring vibrations
1107m	1114m	1111mw	1111m	δ_{NH_2}, rocking
1042w	1045w,b	1038w,b	1040w,vb	
930w	940mw	938mw	941mw	Ring vibration
880m, 851m, 781m, 730w	870m, 842m, 771m, 730w,b	867m, 840m, 765m,b, 735w,sh	866m, 839m, 769m, 740w,sh	$\delta_{NH} + \delta_{CH}$
705m, 689m	699w, 680w	693w, 682w	691mw, 679mw	Ring vibrations
640m	638w	635w,b	633w	δ_{NH_2}, wagging
608m, 570m, 544m, 515w, 506w, 440w, 370w, 345w,b	594m, 570w,sh, 545w, b, 465w,b, 440w,b, 381m, 323m	592m, 546w,b 530w,b, 480w,vb, 378m,b, 333w,b	592m, 541m, 530m 488m, 472m,sh, 381m, 330m	ν_{Ligand} at 610–300 cm^{-1}
	315mw,sh	270m	272m	ν_{M-Cl}
	255mw,b	238m,b	241m,b	ν_{M-N}

[a] guH band assignments after Shirotake and Sakaguchi [19].

volume by heating, and the new solid complexes were separated by filtration, washed with ethanol–teof and stored *in vacuo* over P_4O_{10}. As shown by the analytical results (Table I), the new Th^{4+} and U^{4+} complexes are of the same type as their purine and adenine analogs [2], *i.e.*, $M(gu)_2Cl_2$. In the case of Dy^{3+}, however, a complex containing two neutral guH and one anionic gu^- ligands, of the $Dy(guH)_2(gu)Cl_2$ type, was obtained. The corresponding purine and adenine complexes were monohydrates with only one LH ligand ($Dy(LH)LCl_2 \cdot H_2O$) [2]. The new complexes are generally insoluble in organic media. Table II gives IR spectral data for guH and the complexes; the IR spectra were obtained on KBr discs (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 and ambient temperature (298 K) magnetic measurements (Table III) were obtained by methods previously described [18].

Discussion

As was also the case with purine and adenine [2], guanine reacted with lanthanide and actinide chlorides, under our synthetic conditions, to yield complexes involving partial substitution of anionic gu^- for chloro ligands. The insolubility of the new complexes in organic media may be taken as favoring bi- or poly-nuclear configurations, which are also supported by the fact that the coordination number six suggested by the IR spectral evidence (*vide infra*) for the three complexes reported favors

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of the New Guanine Metal Complexes.

Complex	λ_{max}, nm[a]	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μB
$Dy(guH)_2(gu)Cl_2$	204vvs, 250vs,b, 280vs,b, 312s,sh, 352m,sh, 421w,sh	46,902	10.62
$Th(gu)_2Cl_2$	205vvs, 255vs,b, 283vs, 309s,sh, 346s,sh, 415w,vb	Diamagnetic	
$U(gu)_2Cl_2$[b]	203vvs, 222vs,sh, 252vs,sh, 272vs, 290vs,sh, 313vs, sh, 322vvs, 358vs,sh, 375s,sh, 421s,sh, 445ms,b, 475ms,b, 498ms,b, 545m,b, 602m,b, 634m,b, 678m, 726m, 790mw, 870w,b, 915w, 940w, 1085w, 1248w,sh, 1282w,sh, 1395w,vvb	3,227	2.79

[a] Nujol mull spectrum of free guH, nm: 202vvs, 245vs, 276vs,b, 330m,sh [14, 15]. 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) [28, 29]. [b] Free guH exhibits near-IR bands at 920 and 1310 nm [15], which are due to vibrational overtones and combination modes of this molecule [31]. These bands appear in the spectra of the Dy^{3+} and Th^{4+} complexes at 910–935 and 1275–1340 nm. In the spectrum of the U^{4+} complex there is an obvious overlap between the ligand near-IR bands and transition bands of the metal ion at 915–940 and 1245–1400 nm.

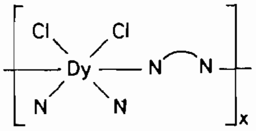
the presence of bridging ligands, since the stoichiometries are $Dy(guH)_2(gu)Cl_2$ and $M(gu)_2Cl_2$.

The IR spectrum of free guH [14, 15, 19–21] is given in Table II, along with band assignments [19], and compared to the spectra of the complexes. The ν_{NH} bands of free guH do not show significant changes upon complex formation, even in the case of the actinide complexes, which contain exclusively anionic gu^-. This is, of course, due to the fact that gu^- still contains one protonated ring nitrogen. The $\nu_{C=O}$ and the various NH_2 bands of guH appear to be insensitive to lanthanide(III) or actinide(IV) complex formation. This indicates that neither of the exocyclic potential ligand sites of guanine (O(6) oxygen and N(2) nitrogen) are involved in coordination [14–16, 19, 22, 23]. Thus, despite the hard acid character of the metal ions under study, the C=O oxygen of guanine does not offer the preferred binding site. On the other hand, several $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrations of guH undergo sizeable shifts upon metal complex formation, so that it is reasonable to assume that the ring nitrogens of this ligand are exclusively used as binding sites in the complexes herein reported [14–16, 19, 22, 23]. The bands tentatively assigned as ν_{M-Cl} and ν_{M-N} in Table II occur in the same frequency regions as those of the hexacoordinated purine and adenine complexes with the same metal chlorides [2]. More specifically, ν_{Dy-Cl} at 315 and ν_{Dy-N} at 255 cm^{-1} favor coordination number six and the exclusive presence of terminal chloro ligands in the Dy^{3+} complex [2, 24, 25]. The same features are also suggested by the occurrence of ν_{M-Cl} (M = Th, U) at 272–270 cm^{-1} [2, 26, 27], while the appearance of the ν_{M-N} mode for the same metal ions at 241–238 cm^{-1} is also consistent with hexacoordinated configurations, as previously discussed [2].

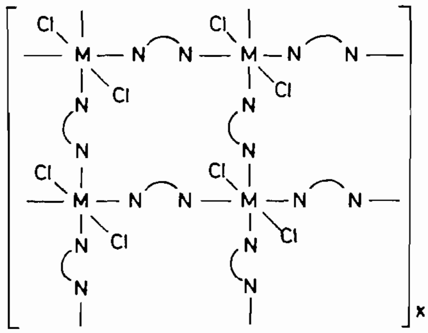
The solid-state (Nujol mull) UV spectrum of free guH (Table III) [14, 15] is in agreement with aqueous solution spectra reported in the literature for both guH and gu^- [28, 29]. The solid-state spectrum of the free ligand shows two $\pi \rightarrow \pi^*$ transition maxima at 245 and 276 nm, while the $n \rightarrow \pi^*$ transition, which would appear at 290–300 nm [30], 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 [15]. This absorption is presumably due to vibrational overtones and combination modes originating from guH [31]. The $\pi \rightarrow \pi^*$ transition bands of the ligand undergo shifts to lower energies and occasional splittings upon formation of the new complexes. It is of interest to note that these bands are significantly broader in the spectrum of the Dy^{3+} complex, which contains both neutral guH and anionic gu^- ligands. The $n \rightarrow \pi^*$ transition of the ligand is observed at 309–313 nm in the spectra of the new complexes. The visible and near-IR spectrum of the U^{4+} complex is characterized by multiple maxima as is typical for compounds of this metal ion [32–34]. As mentioned in Table III, some of the absorptions at 915–940 and 1248–1397 nm in the spectrum of the U^{4+} complex are due to near-IR bands of guH in these regions [31].

The ambient temperature magnetic moments of the Dy^{3+} and U^{4+} complexes (Table III) are in the normal region for Dy(III) or octahedral U(IV) compounds [2, 34–36]. As previously mentioned [2], in the case of Dy^{3+} the 4f electrons are effectively shielded [37], so that no magnetic exchange would be expected in its polymeric complexes. Whereas, in the case of the U^{4+} complex, the presence of single gu^- bridging ligands (*vide infra*) would most probably result in normal room temperature magnetic moments, with evidence favoring magnetic exchange becoming increasingly apparent as the magnetic susceptibility measurement temperature is lowered [2, 38]. Magnetic measurements at 300–80 K are planned for the future for the UL_2Cl_2 (L = pu^-, ad^-, gu^-) complexes.

Regarding the likely structural types of the new complexes, it is obvious that we are dealing with bi- or poly-nuclear species, in view of the insolubility of these compounds in organic media, the compatibility of the low frequency IR spectra with coordination number six, and the fact that only four (M = Th^{4+}, U^{4+}) or five (M = Dy^{3+}) ligands surround each metal ion. The linear chainlike single-bridged polymeric structure II (where N and N⌒N designate terminal unidentate and bridging bidentate guanine, respectively) is considered as the most reasonable for the Dy^{3+} complex. For the Th^{4+} and U^{4+} complexes, a similar structural type to that proposed for their pu^- and ad^- analogs (*i.e.*, III) [2] is most likely. Although this structure is highly polymeric, the fact that it consists of cross-linked linear chainlike single-bridged –M–L–M–L– segments makes it more compatible with the normal ambient temperature magnetic moment of the U^{4+} complex, relative to simpler structures involving double- or multiple-guanine bridges [2, 38, 39]. With respect to the binding site or sites of the guanine ligands in the new complexes, it is generally recognized that terminal unidentate purines tend to coordinate through the imidazole nitrogen, which is protonated in the free base [40]. Free guH is protonated at N(9) and N(1) [41], while monodeprotonation to gu^- occurs by removal of the proton attached to N(1), with only N(9) remaining protonated [42]. It is also known that the guaninium cation (GuH_2^+) uses N(9) as its binding site in complexes with Cu^{2+} and Zn^{2+} halides [43–45]. Hence, terminal unidentate guH or gu^- would almost certainly use N(9) as binding site in the Dy^{3+} complex [14, 15]. As far as bidentate bridging guanine is concerned, use of the N(7) and N(9) imidazole nitrogens as the preferred binding sites is considered as most likely [14–17]. Although participation of the N(1) or N(3) pyrimidine nitrogens instead of N(7) in the coordination of bidentate guanine cannot be ruled out, the exocyclic substituents at C(2) and C(6) might conceivably introduce sufficient steric hindrance [46, 47] as to prevent the binding of this ligand through any of the pyrimidine ring nitrogens [15].



(II)



(III)

Prior to concluding, it should be mentioned that the fact that guanine does not bind through the C=O oxygen to lanthanide or actinide ions, as well as Al^{3+} [16], despite the definitely hard acid character of these metal ions [13, 48, 49], is not too surprising. In fact, participation of the O(6) site of guanine in coordination has been only proposed for a number of cases involving bidentate bridging [50] or chelating [51] O(6), N(7)-bonded and N(9)-substituted guanine derivatives. Nevertheless, unsubstituted guanine seems to preferentially use N(9) as primary binding site, regardless of whether it functions as uni- or bi-dentate [14, 15, 40, 43–45]. Hence, the N(7), N(9) [17] or N(3), N(9) [40] binding site combinations for bidentate guanine would appear more favorable than use of either N(1), N(9) or O(6), N(9) as coordination sites.

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