Vanadium(III) Chloride Complex with Anionic Guanine*

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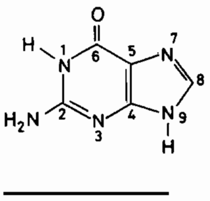
Reaction of purine (puH) or adenine (adH) with VCl_3 in a mixture of ethanol and triethyl orthoformate (teof) results in the formation of a complex of the $V(LH)L_2Cl \cdot EtOH$ (LH = puH or adH; L = pu^- or ad^-) type, as established by recent work in these laboratories [2]. Following our studies on purine and adenine complexes with various metal chlorides [2–10], we recently expanded our research in the field to include the corresponding complexes formed by interaction of guanine (guH; I) with metal chlorides at the reflux temperature of the ethanol–teof reaction medium [1, 10–12]. So far, our studies have shown that, in some cases ($M = Al^{3+}$ [10], Th^{4+}, U^{4+} [5, 11], VO^{2+} and Fe^{3+} [6, 7, 12]), purine, adenine and guanine yield complexes of the same type with the chlorides of each of the preceding metal ions. However, whereas purine and adenine form $Cr_3L_5Cl_4 \cdot 2H_2O$ complexes (L = pu^-, ad^-) upon reaction with $CrCl_3$ [8], guanine yields the $Cr(guH)_2Cl_3$ adduct, under similar synthetic conditions [12]. On the other hand, upon interaction with 3d metal(II) chlorides (M = Mn, Fe, Co, Ni, Cu, Zn), purine yields simple adducts [3], whilst both adenine [4] and guanine [1] form in some cases adducts and in other cases complexes with anionic ad^- or gu^-. Finally, with $DyCl_3$ all three of these nucleobases form mixed neutral-anionic ligand complexes of the $Dy(LH)LCl_2 \cdot H_2O$ (LH = puH, adH) [5] or $Dy(guH)_2(gu)Cl_2$ [11] types. The present letter reports on the synthesis and characterization of the complex produced by reaction of guH with VCl_3.



(I)

This complex is of the $V(gu)Cl_2 \cdot 2EtOH$ type [1], *i.e.*, substantially different from the $V(LH)L_2Cl \cdot EtOH$ species produced during the analogous synthetic work of V^{3+} complexes with purine and adenine [2].

Experimentally, 0.8 mmol VCl_3 were dissolved in 50 ml of a 7:3 (v/v) mixture of dry, degassed ethanol–teof, and 2.4 mmol guH were subsequently added, while all operations were being carried out in a dry nitrogen atmosphere. The resultant mixture was refluxed for 4 days, and then the dark greenish solid $V(gu)Cl_2 \cdot 2EtOH$ complex formed in low yield (*ca.* 20% of the theoretical) was separated by filtration, washed with ethanol–teof (N_2 atmosphere) and stored *in vacuo* over anhydrous $CaCl_2$. The new complex is stable in a dry N_2 atmosphere, but rapidly decomposes when exposed to moist air; it is insoluble in all common organic solvents, and has a magnetic moment of 2.72 μB at 298 K ($10^6 \chi_M^{cor} = 3019$ cgs units).

Infrared and solid-state (Nujol mull) electronic spectral data are given in Table I. The IR spectrum of the new complex seems somewhat unusual when compared to the spectra of other guanine complexes with metal chlorides [10–13] or perchlorates [14, 15]. In the spectra of all these complexes the $\nu_{C=O}$ and δ_{NH_2}, scissoring ligand bands [13] are significantly more intense than the $\nu_{C=C} + \nu_{C=N}$ absorptions at 1640–1550 cm^{-1} [10–15]. In contrast, the spectrum of the new complex is characterized by relatively weak bands in the $\nu_{C=O}$ and the δ_{NH_2}, scissoring regions, and strong to very strong maxima at 1638–1570 cm^{-1}. This may be taken as indicative of $\nu_{C=O}$ or δ_{NH_2} splitting with components of at least one of these modes occurring below 1640 cm^{-1}. Since the ν_{NH_2} and the other δ_{NH_2} absorptions of the ligand [13] do not appear to be significantly shifted (although δ_{NH_2}, wagging appears as a doublet) in the spectrum of the V^{3+} complex, it follows that $\nu_{C=O}$ splitting is most likely. This can be interpreted in terms of either direct participation of the C=O oxygen in coordination [16] or indirect metal–carbonyl group interaction *via* H-bonding of C=O to a coordinated ethanol ligand [17]. The spectrum of the new complex shows some additional differences from the spectra of other guanine metal complexes (*e.g.*, the very strong band at 1412, strong absorptions at 1320 and 1311, and two bands at 1040 and 1000 cm^{-1}) [10–15]; however, some of the additional bands in the spectrum of the new V^{3+} complex probably involve contributions from δ_{CH} absorptions of coordinated ethanol [18]. The ν_{OH} mode of coordinated ethanol appears at 3390 cm^{-1} [19]; while ν_{NH} bands are also present in the spectrum of the complex, since gu^- still contains one proto-

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*Ref. 1.

0020-1693/84/$3.00

TABLE I. Spectral Data for guH and $V(gu)Cl_2 \cdot 2EtOH$.

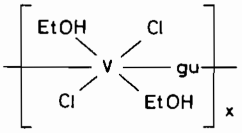
	guH	$V(gu)Cl_2 \cdot 2EtOH$	Band Assignment
IR data, cm^{-1} [a,b]			
		3390s,b	ν_{OH}(EtOH)
	3330s, 3290s,sh, 3160s	3335s,b, 3295s,b, 3160s	ν_{NH_2}
	3000s, 2900s, 2850s, 2700s	3040s, 2980s, 2890s,sh, 2790ms,vb	ν_{NH}
	1705s	1700mw,b	$\nu_{C=O}$
	1680s	1680mw,b	δ_{NH_2}, scissoring
	1635s,sh, 1575m,b	1638s, 1612vs, 1595vs, 1570s,sh	$\nu_{C=C} + \nu_{C=N}$
	1563m	1560m, 1540m,b	δ_{NH}
	1477m, 1464m, 1418m, 1375m	1475s,sh, 1465s, 1412vs, 1370m,b	Ring vibrations
		1320s, 1311s,sh	Ring vibrations
	1263m	1260m	ν_{C-N}
	1209m, 1169m	1227s, 1212s, 1187ms	Ring vibrations
	1107m	1088ms	δ_{NH_2}, rocking
	1042w	1040w,b, 1000m	
	930w	970s, 918m	Ring vibrations
	880m, 851m, 781m, 730w	880m, 845w, 781ms, 740w	$\delta_{NH} + \delta_{CH}$
	640m	660w, 629m	δ_{NH_2}, wagging
		467w, 400m	ν_{V-O} (EtOH)
		377w, 349w	ν_{V-Cl}
		310m,b, 297m,sh	ν_{V-N}
Electronic spectra, λ_{max}, nm [c,d]			
	202vvs, 245vs, 267vs,b, 330m,sh, (920w, 1310w)	200vs, 212vs, 250vvs,b, 277vvs,b, 288vvs, 306vs,sh, 338vvs,b, 375s,sh, 445m,sh, 520m,b, 580m,b, 720m,b, (930w,b, 1300w,b)	

[a] IR spectral band assignments for guH after Shirotake and Sakaguchi [13]. [b] Significant overlap of gu^- and δ_{CH} ethanol [18] absorptions presumably occurs at 1500–1000 cm^{-1}. [c] Aqueous solution electronic spectrum of gu^- (at pH 10.7–11.0): λ_{max} 243, 273 nm; log ϵ = 3.78–4.00 [25, 26]. [d] Near-IR bands, shown in parentheses, are presumably due to vibrational overtones and combination modes originating from the guanine molecule [14, 32].

nated ring nitrogen [20]. Tentative $\nu_{V-ligand}$ band assignments are compatible with coordination number six [2, 14, 21–24]. It is noteworthy that all three types of $\nu_{V-ligand}$ modes appear as doublets, *i.e.*, ν_{V-O} at 467, 400 [2, 14, 21], ν_{V-Cl} at 377, 349 [22, 23] and ν_{V-N} at 310, 297 [2, 14, 24] cm^{-1}. The location of the ν_{V-Cl} band suggests that the chloro ligands are exclusively terminal.

The UV spectrum of guanine shows shifts of the two main $\pi \rightarrow \pi^*$ transitions (243, 273 nm in gu^- [25, 26]) towards lower energies, and a splitting of the 273 nm band into two components (277, 288 nm) upon V^{3+} complex formation. The $\pi \rightarrow \pi^*$ transition, which is masked in the spectrum of guanine [25–27], occurs as a shoulder at 306 nm in the spectrum of the complex. Strong V^{3+}-to-ligand charge-transfer absorption [28], originating in the UV and trailing off into the visible region is also observed. As a result of this the ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ transition (expected at 250–325 nm [29–31]) is masked. The rest of the d–d transitions, which appear split, are assigned as follows, nm: ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ 375, 445; $\rightarrow {}^3T_{2g}(F)$ 520, 580; $\rightarrow {}^1E_g$, ${}^1T_{2g}(D)$ 720; approximate Dq = 1930 cm^{-1}; B = 503 cm^{-1} (β = 0.58) [29]. It is of interest to note that the d–d spectrum of the new complex, which is characterized by a $VN_2O_2Cl_2$ chromophore (*vide infra*), is very similar to those of the previously reported purine and adenine V^{3+} complexes, which involved VN_4OCl absorbing species [2]. Finally, the near-IR bands of guanine (920, 1310 nm), which are apparently due to vibrational overtones and combination modes of this molecule [14, 32], appear slightly shifted in the spectrum of the new complex.

As regards the likely structural type of the new complex, its poor solubility and somewhat low [29] room temperature magnetic moment, combined with the pronounced tendency of purines to function as bidentate bridging ligands [33] and the fact that only five ligands correspond to each V^{3+} ion in the presumably hexacoordinated complex, favor a linear chainlike polymeric structure of type II, with single gu$^-$ bridges between adjacent V^{3+} ions [10–12, 14, 15, 24, 33–35]. *Prima facie*, the N(9) imidazole nitrogen would be anticipated to act as one of the binding sites of bidentate bridging gu$^-$ [36–38], with N(7) as the likely second binding site. In fact, we have previously proposed the presence of N(7), N(9)-bonded bidentate guanine for a variety of apparently polymeric single-bridged metal complexes with this ligand [10–12, 14, 15], in view of the recently elucidated crystal structure of $[Cu(puH)(OH_2)_4]SO_4 \cdot 2H_2O$, which is a linear chainlike single-bridged polymer with N(7), N(9)-bonded bidentate puH ligands [34]. Nevertheless, in view of the IR spectrum of the new V^{3+} complex (*vide supra*), O(6) may be also considered as a potential binding site. If the C=O oxygen of gu$^-$ indeed participates in direct bonding to the metal ion [16, 39, 40], rather than being involved in hydrogen bonding with coordinated ethanol [17], use of O(6), N(7) ('guanine clip') instead of O(6), N(9) as the two binding sites would be more likely [16, 39, 40]. Since alternative possibilities exist as far as the binding sites of gu$^-$ in the new complex are concerned, only a crystal structure determination would unambiguously settle this question.



(II)

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