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Vanadium(III) Complexes with Purine and Adenine

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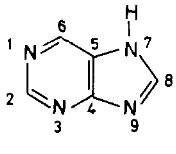
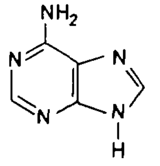
The majority of synthetic and characterization studies of metal complexes with nucleic acid bases, nucleosides and nucleotides have dealt with adducts or complexes of these ligands with metal ions in stable oxidation states [2–5]. Significantly less is known about the corresponding complexes with oxidatively labile metal ions; complexes of this type reported include uracilatobis[*bis*(η^5-methylcyclopentadienyl)Ti(III)] [6], and various Cr^{2+} [7], Ru^{2+} [8], Rh^{2+} [9] and lower-valent Mo, W, Rh and Ir complexes [10]. In so far as vanadium complexes with ligands of these types are concerned, only systems involving exclusively oxovanadium(IV) or (V) cations appear to have been studied [11 – 16]. During the course of our studies of purine (puH; I) and adenine (adH; II) complexes with various metal chlorides [16–18], it was felt that attempts at the isolation and characterization of the complexes formed by refluxing mixtures of VCl_3 with either of these ligands in ethanol-triethyl orthoformate (teof) [16–18] were in order. Vanadium would be certainly maintained in the +3 oxidation state in the presence of puH or adH. In fact, several VCl_3 complexes with aliphatic or aromatic amines are stable in the absence of oxygen and moisture [19, 20], while, as already mentioned, reasonably stable Cr^{2+}–adenine [7] and Ti^{3+}–uracil [6] complexes have been isolated. Accordingly, research in this direction was undertaken, and the V^{3+} complexes synthesized are described in the present letter.



(I)



(II)

Unlike $VOCl_2$ or $FeCl_3$, which form adducts of the $VO(LH)Cl_2$ [16] and $Fe(LH)_2Cl_3$ [18] types (LH = puH, adH) when refluxed in the presence of these ligands in ethanol-teof, VCl_3 reacts with puH or adH to yield mixed anionic-neutral (*i.e.*, L^--LH) nucleobase complexes. During early synthetic studies it was established that ligand and VCl_3 should be used at a 3:1 molar ratio in order to yield well-defined complexes. In addition, the synthetic and subsequent work must be carried out in a dry inert atmosphere, using dry deaerated ethanol and teof; otherwise, the complexes obtained are contaminated with major or minor amounts of VO^{2+} species. The most successful synthetic procedure used was as follows: 0.8 mmol VCl_3 are dissolved in 50 ml of a 7:3 (vol/vol) mixture of dry degassed ethanol-teof, and 2.4 mmol puH or adH are subsequently added (all operations are carried out in a dry nitrogen atmosphere). The resultant mixture is refluxed for 3–4 days, and then the solid complexes formed are separated by filtration, washed with ethanol-teof and stored *in vacuo* over anhydrous $CaCl_2$. In both cases complexes of the $V(LH)L_2Cl\cdot EtOH$ type were isolated. *Analyses: Found (Calcd.) %:* $V(puH)pu_2Cl\cdot EtOH$, drab green: C 41.79(41.60); H 3.10(3.29); N 33.97(34.25); V 10.07(10.38); Cl 7.31(7.22); $V(adH)ad_2Cl\cdot EtOH$, brownish green: C 38.25(38.11); H 3.72(3.57); N 38.93(39.21); V 9.27(9.51); Cl 6.48(6.62). The new complexes are stable in an inert atmosphere, but are rapidly oxidized upon exposure to the atmosphere; they are insoluble or very sparingly soluble in various organic solvents.

Characterization of the complexes was based on IR and solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements at 298 K (Table I). The IR spectra of both complexes exhibit the characteristic ν_{OH} band of coordinated ethanol at 3360–3395 cm^{-1} [21], as well as the ν_{NH} bands of neutral puH or adH at 2700–2600 cm^{-1} [22]. Several IR bands associated with the imidazole (im) or pyrimidine (pym) fragments of the ligands [22–24] exhibit significant shifts and occasional splittings upon V^{3+} complex formation, as would be expected for complexes involving participation of ring nitrogens in coordination [16–18, 22–24]. On the other hand, bands associated with the NH_2 exocyclic substituent of adH are relatively insensitive to V^{3+} complex formation; this indicates that none of the adenine ligands in $V(adH)ad_2Cl\cdot EtOH$ uses the amino group nitrogen for coordination [23–25]. Tentative $\nu_{V\text{-ligand}}$ band assignments are generally in favor of coordination number six. In fact, the occurrence of ν_{V-Cl} at 342–337 cm^{-1} [26] and ν_{V-N} at 296–294 cm^{-1} [18, 25, 27], is consistent with hexacoordinated configurations [18, 25–27]; a similar conclusion can be reached from the wavenumbers of the bands assigned as ν_{V-O}(EtOH) (471–467 cm^{-1}) [27, 28].

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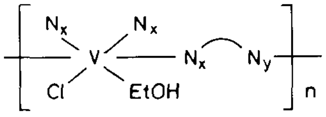
TABLE I. Spectral and Magnetic Data for $V(LH)L_2Cl{\cdot}EtOH$ Complexes.[a]

IR data, cm^{-1}	puH	$V(puH)pu_2Cl{\cdot}EtOH$	adH	$V(adH)ad_2Cl{\cdot}EtOH$	Band Assignment
		3360vs[b]		3395vs[b]	ν_{OH} (EtOH)
	2725s,b	2685s	2690w, 2600w	2700w, 2600w	ν_{NH}
			1675vs	1667vs	NH_2 sym in-pl def
	1613vs	1640s, 1611s	1600vvs,b	1642s, 1599s	A′ pym 8a
	1568s	1567s	1565m,sh	1560m	A′ pym 8b
	1499w	1500m	1510w	1498w	A′ im R_1
	1421s	1435m,sh	1419ms	1401m	A′ im R_3
	1398vs	1407m, 1370m	1390w, 1370m	1375m,b	A′ pym 19a
			1252s	1249w	NH_2 as out-pl def
		471m[c]		467m[c]	ν_{V-O}(EtOH)
		342w,b		337w,b	ν_{V-Cl}
		296w,b		294w,b	ν_{V-N}
Electronic spectra					
λ_{max}, nm					
	188vs, 204 vvs, 252vs, 267vs, 293s, sh, 345m,sh	204vvs, 221vvs, 255vvs, 280vs, 307vs, 351vs,sh, 376s,sh, 442m,sh, 520m,b, 581m,b, 725m,b	185vvs, 208 vvs, 260vs, vvb	207vs,vb, 240vs, sh, 272vvs, 290vs, 310vs, 357vs,sh, 373s,sh, 444m,sh, 519m,b, 580m,b, 721m,b	
Magnetic data					
(298 K)					
$10^6\ \chi_M^{cor}$, cgsu		3460		3120	
μ_{eff}, μ_B		2.88		2.79	

[a] Free puH IR band assignments after Lautié and Novak [22], and corresponding assignments for free adH based on refs. 22–24; ligand Nujol mull UV spectra are in agreement with solution spectra reported by Clark and Tinoco [29]. [b] Sharp band. [c] A second medium to weak band appearing at 385 cm^{-1} in the spectra of both complexes may be due to a splitting of the ν_{V-O} (EtOH) mode.

The UV maxima of free puH or adH ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions) [29] undergo similar shifts and splittings upon V^{3+} complex formation to those previously observed in the spectra of various 3d metal chloride [16–18] or perchlorate [25, 30] complexes with the same ligands. Strong vanadium-to-ligand charge-transfer absorption [31], originating in the UV and trailing off well into the visible region, is also observed in the spectra of the new complexes. The higher energy d–d transition bands overlap with charge-transfer and ligand bands; as a result of this, the $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ band is not detectable (anticipated range of occurrence of this band is 250–325 nm [32–34]), while the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition bands appear as shoulders. Both the latter absorption and the $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ transition are split into two components, *i.e.*, doublets at *ca.* 375, 445 and 520, 580 nm, respectively [32–34]; an approximate Dq of 1930 cm^{-1} and a Racah parameter B of 503 cm^{-1} (β = 0.58) are calculated from these data [32]. The relatively high Dq is consistent with a VN_4OCl chromophore (*vide infra*), while rather low β ratios (0.62–0.65) were previously observed in the spectra of Co^{2+} chloride or bromide complexes with 9-methyladenine [32, 35]. The near-IR band at 721–725 nm in the spectra of the new complexes is presumably due to transitions from $^3T_{1g}(F)$ to the ^1E_g and $^1T_{2g}(D)$ levels [32]. The splittings of the d–d transition bands in the spectra of the complexes are suggestive of low-symmetry hexacoordinated configurations [36]. It should be noted here that the d–d transition spectra of the two complexes are not compatible with coordination number five, which could have been possible, since the first coordination sphere of the V^{3+} ion is occupied by five ligands. In fact, the d–d spectra of pentacoordinated V^{3+} complexes with amines or thioethers exhibit several maxima at 500–2400 nm, including one or two bands at 1300–2400 nm [20]. In contrast, the spectra of the new complexes are characterized by d–d bands at 375–725 nm with no significant absorption at 750–2400 nm, and are, therefore, consistent with coordination number six [32–34]. The ambient temperature magnetic moments of the two complexes are normal for high-spin 3d^2 compounds [32].

The poor solubility of the new complexes, combined with the fact that, although these compounds are surrounded by five ligands, their coordination number is six, is in favor of polymeric configurations. Both purines and chloride ions have the tendency to act as bridging ligands in complexes containing ligands of both these types [2, 37]. Since the Cl ligands present in the new complexes are apparently terminal (occurrence of ν_{V-Cl} at *ca.* 340 cm^{-1} [26]), it is most likely that one of the three nucleobase ligands acts as bidentate bridging, and the complexes are linear chainlike polymers of type III (N_x: terminal unidentate and $N_x\frown N_y$: bridging bidentate purine or adenine). Similar linear chainlike polymeric structures have been previously proposed for several 3d metal complexes with purine and adenine [16–18, 25, 30], and were recently substantiated by the crystal structure determination of [Cu(puH)(OH$_2$)$_4$]SO$_4$·2H$_2$O, which is indeed a single-bridged linear polymer with N(7), N(9)-bonding bidentate bridging puH [38]. Polymeric 3d metal complexes of this type usually exhibit normal room temperature magnetic moments, showing evidence of magnetic exchange interactions only at lower temperatures [30, 39]. The most likely binding sites of the bidentate bridging purine or adenine in structure III would be the N(7) and N(9) imidazole nitrogens [38], while the unidentate terminal adenine ligands in V(adH)ad$_2$Cl·EtOH would be certainly N(9)-bonded (x = 9) [2, 40–42].



As regards the unidentate terminal purine ligands in V(puH)pu$_2$Cl·EtOH, free purine is protonated at N(7) [43], but it is also known that, in solution, the N(7)–H and N(9)–H tautomers of this compound are of comparable energies [44]. Although no crystal structures of metal complexes with terminal puH or pu$^-$ ligands were reported so far, it was found that the purinium cation (puH$_2^+$) coordinates through N(3) in its CuCl$_2$ complex [45] and through N(7) in its ZnCl$_2$ complex [46]; whereas in the corresponding complexes with adH$_2^+$, coordination occurs through N(9) (CuBr$_2$ complex) [47] and N(7) [48], respectively. As mentioned previously [18], these comparisons suggest that unidentate purine is not as prone as unidentate adenine to coordinate through the N(9) nitrogen; thus, N(7) or N(3) would appear as more likely than N(9) to function as the binding site of terminal purine, with N(7) being most probable, since it is also the site of protonation in crystalline free puH [2, 43]. However, no speculations on the preferred binding site of terminal purine would be advisable before the crystal structure of at least one metal complex with such a terminal ligand is elucidated [18].

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