Oxovanadium(IV) Chloride Complexes with Purine and Adenine*

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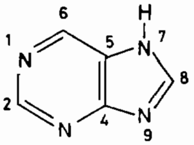
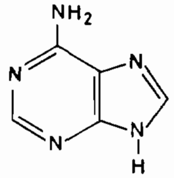
A recent paper by Katsaros, dealing with oxovanadium(IV) complexes with various nucleotides [2], prompts us to report the results of our synthetic and characterization studies of $VOCl_2$ complexes with purine (puH; I) and adenine (adH; II). These studies were conducted within the framework of a systematic synthetic investigation, aimed at the isolation of well-defined solid complexes of puH, adH and guanine with 3d [3, 4], lanthanide, actinide [5] and main group [6] metal halides. It should be mentioned here that, in addition to the polymeric oxovanadium(IV) nucleotide complexes reported by Katsaros [2], the following studies have dealt with the complexation of VO^{2+} with nucleic acid constituents: Association of VO^{2+} with commercial preparations of DNA [7]; complexes of VO^{2+} with uridine [8]; and coupling of ATP with the VO_2^+ + H_2O_2 redox system [9].



(I)



(II)

Experimentally, the new complexes were prepared by a procedure similar to that employed for the syntheses of purine and adenine complexes with

TABLE I. Pertinent IR and Solid-state (Nujol mull) Electronic Spectral Data for $VO(LH)Cl_2$ Complexes.[a]

	puH	$VO(puH)Cl_2$	adH	$VO(adH)Cl_2$	Band assignment
IR data, cm^{-1}	2725s,b	2670m,b	2690w, 2600w	2710w, 2615w	ν_{NH}
			1675vs	1670s	NH_2 sym in-pl. def.
	1613vs	1600s	1600vvs	1647vs, 1600vs	A′ pym 8a
	1568s	1550vvs	1565m,sh	1559s	A′ pym 8b
	1499w	1500m	1510w	1503m	A′ im R_1
	1421s	1440m,sh	1419ms	1410m, 1398m	A′ im R_3
	1398vs	1401m, 1397m,sh	1390w, 1370m	1375m,b	A′ pym 19a
			1252s	1243m	NH_2 as out-pl. def.
		1003ms		1004ms	$\nu_{V=O}$
		436m, 404m		430m, 410m	ν_{V-Cl}
		316 w,b		312w,b	ν_{V-N}
Electronic spectra, nm	188vs, 204vvs, 252vs, 267vs, 293s,sh, 345m,sh	209vvs, 224vvs, 257vs, 285vs, 355s,sh, 430m, 496m, 690mw,vb	185vvs, 208vvs, 260vs,vvb	196vvs, 210vvs, 253s,sh, 275vs,b, 311vs, 431m, 502m, 695mw,vb	

[a] Free puH IR band assignments after Lautié and Novak [10]; free adH IR band assignments based on refs. 10–12; ligand Nujol mull UV spectra are generally in agreement with solution spectra reported by Clark and Tinoco [18].

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*See ref. 1.

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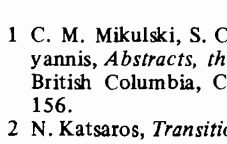
other metal chlorides [5, 6], *viz.*: 0.8 mmol $VOCl_2$ were treated with a mixture of 35 ml ethanol and 15 ml triethyl orthoformate for 2 h at 50–60 °C; then 1.6 mmol puH or adH were added, and the resultant mixture was refluxed for three days. Subsequently, the volume of the supernatant was reduced to about one-half its original volume by heating, and the solid complex was separated by filtration, washed with ethanol–triethyl orthoformate and stored *in vacuo* over P_4O_{10}. Analytical data indicate that, in both cases, adducts of the $VO(LH)Cl_2$ type (L = puH, adH) were formed, *i.e.*: $VO(puH)Cl_2$, grass green, found (calcd.)%: C 22.9(23.3); H 1.3(1.2); N 21.6(21.7); V 19.5(19.75); Cl 27.5(27.5); 10^6 χ_M^{cor} = 1189 cgsu (298 °K); μ_{eff} = 1.69 μB. $VO(adH)Cl_2$, khaki: C 21.7(22.0); H 2.0(1.85); N 25.9(25.7); V 18.8(18.7); Cl 26.2(26.0); 10^6 χ_M^{cor} = 1220 cgsu (298 °K); μ_{eff} = 1.71 μB. Both of the new complexes are insoluble in organic media.

Table I gives pertinent IR and electronic spectral data for the new $VOCl_2$ adducts. Both of these complexes show characteristic ν_{NH} bands, suggestive of the presence of neutral puH or adH ligands [10]. Various vibrational modes of the pyrimidine (pym) and imidazole (im) fragments of the ligands undergo significant shifts and occasional splittings upon adduct formation between puH [10] or adH [10–12] and $VOCl_2$. Ths is interpreted in terms of participation of ligand ring nitrogens in coordination [3–6, 10–12]. On the other hand, the NH_2 deformation modes of free adH are only slightly shifted in the IR spectrum of $VO(adH)Cl_2$; this indicates that the exocyclic N(6) nitrogen of the NH_2 group is not involved in coordination [4–6, 11, 12]. The occurrence of $\nu_{V=O}$ at ~1000 cm^{-1} in the spectra of the two complexes is suggestive of coordination number five for the central V^{4+} ion [13, 14]. Pentacoordinated configurations are also supported by the appearance of ν_{V-Cl} at 436–404 and ν_{V-N} at 316–312 cm^{-1} [5, 14–17].

The UV spectral bands ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions) of free puH or adH [18] show similar types of shifts and splittings upon $VOCl_2$ adduct formation, to those previously reported for 3d metal chloride or perchlorate (M = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) complexes with the same ligands [3, 4, 19, 20]. The d–d transition maxima of the VO^{2+} new complexes (430–431, 496–502 and 690–695 nm) are consistent with coordination number five [14]. Actually, in the d–d transition spectra of oxovanadium(IV) compounds, the V=O bond dominates the energy level diagram, so that clearcut distinction between penta- and hexa-coordinated species cannot be made [14, 21, 22]. Finally, the magnetic moments of the new complexes (1.69–1.71 μB) are very near the spin-only value of 1.73 μ_B expected for magnetically dilute VO^{2+} compounds. Similar μ_{eff} values were reported for polymeric VO^{2+} complexes with a variety of nucleotides by Katsaros [2].

The latter complexes were considered as involving nucleotide bridging ligands, coordinating through one ring nitrogen to a V^{4+} ion and through a phosphate oxygen to an adjacent V^{4+} ion [2]. The complexes under study are also apparently polymeric, in view of their general insolubility in organic media. Since the ligands of interest do not contain ribose or phosphate potential O-ligand sites, as is the case with their nucleotide derivatives, bridging can occur by participation of more than one ring nitrogens in coordination. The tendency of purines to act as bidentate bridging ligands is well established [23]; 3d metal complexes (primarily Cu^{2+}) with multiple purine bridges are generally characterized by clearly subnormal magnetic moments even at room temperature [23–26], while linear chain-like polymeric complexes with single purine bridges between adjacent 3d metal ions (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) exhibit normal ambient temperature magnetic moments, showing evidence in favor of magnetic exchange interactions only at lower temperatures (below about 110 °K) [19]. In view of the preceding discussion, the new $VO(LH)Cl_2$ complexes (LH = puH, adH) are also most likely to involve single LH bridges and linear chain-like polymeric structures; coordination number five is attained by the presence of two terminal chloro and one oxo ligand per V^{4+} ion, as shown in (III). As far as the likely binding sites of puH or adH are concerned, the recent crystal structure elucidation of $[Cu(puH)(OH_2)_4]SO_4 \cdot 2H_2O$, which is of a similar structural type to (III) in that it is a linear, chain-like, single-bridged polymer, revealed that bridging puH coordinates through the two imidazole nitrogens, *i.e.*, N(7) and N(9), to adjacent Cu^{2+} ions [27]. Hence, it is most probable that puH and adH are also N(7), N(9)-bonded in the new $VOCl_2$ adducts.



(III)

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