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Compelxes of Vanadium(V) with 8-Quinolinolate and its Substituted Derivatives

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I.r., u.v., and visible spectra of complexes $[VO(OR)Q_2]$ *(R = H, Et; HQ = 8-quinolinol; R = H, HQ = 5,7-dichloro-8-quinolinol) and* $[V_2O_3Q_4]$ *(HQ = 8-quinolinol) have been measured. Increasing the donor ability of the –OR group has no effect on the* $V\text{-}O_t$ *stretching wavenumbers but shifts the (8-quinolinolate)-to-vanadium charge-transfer transition to higher wavenumbers. The effect of coordination to vanadium(V) on the internal* $(\pi\rightarrow\pi^*)$ *transitions of 8-quinolinolate is discussed. Structures are proposed in which –OR groups are cis to terminal oxide* (O_t)*, and* $-O^-$ *groups of 8-quinolinol are cis to* O_t *and –OR groups. We conclude that bonding to vanadium from oxygen of –OR and 8-quinolinolate includes a significant π-bonding contribution.*

Introduction

Vanadium in oxidation state +5 forms complexes of the species VO^{3+}; VO_2^+, and $VO(OR)^{2+}$ (R = H, alkyl).[1] With vanadium(V), in contrast to, for example, molybdenum(VI) and tungsten(VI),[2] complexes of the dioxo species, VO_2^+, are less common than those of the oxohydroxo species, $VO(OH).^{2+}$ Complexes of oxovanadium(V), like complexes of oxovanadium(IV), have in their infrared spectra a strong band in the region 900 - 1000 cm^{-1} which is assigned to a stretching vibration of a multiple vanadium-oxygen bond.[1] For oxovanadium(IV) complexes the wave number of the V-O stretching vibration varies with the ligand bonded to vanadium and attempts have been made to interpret trends in V-O stretching wavenumbers in terms of donor properties of ligands.[1,3] Less is known of the electronic effects of ligands in oxovanadium(V) complexes and we were interested in determining whether such effects might be revealed in their vibrational and electronic spectra. In this paper we describe our work with the complexes $[VO(OR)Q_2]$ (R = H, Et; HQ = 8-quinolinol), $[VO(OH)(Cl_2Q)_2]$-(Cl_2QH = 5,7-dichloro-8-quinolinol), and $[V_2O_3Q_4]$. Complexes of oxovanadium(V) with 8-quinolinolate are well known.[4] They are strongly coloured and the development of a red colour in the reaction of $[VO(OH)Q_2]$ with alcohols has been used as a test for alcohols.[4c,d,5] Complexes of vanadium(V) with 8-quinolinolate are also of interest because of the activating effect of 8-quinolinolate on the catalysis by vanadium(V) of the oxidation of p-phenetidine with chlorate.[6] While our work was in progress Doadrio and Martinez reported the infrared spectra of a number of complexes of vanadium(V) with 8-quinolinolate and its derivatives.[7]

Experimental Section

Preparations and Analyses. Hydroxooxobis(8-quinolinolato)vanadium(V), $[VO(OH)(C_9H_6NO)_2]$ (I). The compound precipitated from an aqueous solution of ammonium metavanadate and 8-quinolinol at pH 4 - 4.5 and was dried at 130°.[4d] (Found: C, 58.0; H, 3.7; N, 6.8; V 13.7. Calculated for $C_{18}H_{13}N_2O_4V$: C, 58.0; H, 3.5; N, 7.5; V, 13.7%).

Ethoxyoxobis(8-quinolinolato)vanadium(V), $[VO(OEt)(C_9H_6NO)_2]$, (II). The compound was prepared by heating under reflux a solution of the hydroxo-complex (I) in ethanol.[4d] (Found: C, 57.3; H, 4.1; N, 6.9; V, 12.7. Calculated for $C_{20}H_{17}N_2O_4V$: C, 60.0; H, 4.3; N, 7.0; V, 12.7%).

μ-Oxobis[oxobis(8-quinolinolato)vanadium(V)], $[V_2O_3(C_9H_6NO)_4]$, (III). The compound was prepared by heating the ethoxy-complex (II) at 130°.[4d] (Found: C, 59.2; H, 3.3; N, 7.5; V, 14.0. Calculated for $C_{36}H_{24}N_4O_7V$: C, 59.5; H, 3.3; N, 7.7; V, 14.0%).

Bis(5,7-dichloro-8-quinolinolato)hydroxooxovanadium(V), $[VO(OH)(C_9H_4Cl_2NO)_2]$, (IV). A solution of ammonium metavanadate (1.2 g) in 2M sulphuric acid (50 ml) was added to a solution of 5,7-dichloro-8-quinolinol (4.5 g) in 2M acetic acid (100 ml) at 80°. The solution was adjusted to pH 4.0 with ammonia solution and digested for 90 min at 75°. The yellow brown precipitated complex was washed with hot water and dried at 120°. (4.5 g). Found: C, 42.7; H, 1.8; Cl, 27.1; N, 5.6; V, 10.1. $C_{18}H_9Cl_4N_2O_4V$

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Table I. I.r. spectra: V-O_t stretching vibration (ν/cm^{-1}).

$VO(OH)(C_9H_6NO)_2$ 955 [a]	$VO_2(C_9H_6NO)_2^-$ 910-940, 860-900 [a,b]	$VO(OMe)(C_9H_6NO)_2$ 950 [b]
$VO(OEt)(C_9H_6NO)_2$ 955 [a]	$VO(OBu)(C_9H_6NO)_2$ 950-960 [b]	$VO(OH)(C_9H_6NO)_2 4HCl$ 995 [b]
$V_2O_3(C_9H_6NO)_4$ 955 [a]	$VO(OH)(2Me\text{-}C_9H_5NO)_2$ 960 [b]	$VO(OH)(5Me\text{-}C_9H_5NO)_2$ 960 [b]
$VO(OH)(5,7\text{-}Cl_2\text{-}C_9H_4NO)_2$ 960 [a]		

[a] This work. [b] Ref. 7.

Table II. Electronic spectra [a]

	I	II	III
$VO(OH)(C_9H_6NO)_2$	15,800	24,600	36,000
$VO(OEt)(C_9H_6NO)_2$	18,000	24,600	35,000
$V_2O_3(C_9H_6NO)_4$	17,100	24,600	36,000
$VO(OH)(5,7\text{-}Cl_2\text{-}C_9H_4NO)_2$	13,400	24,600	36,500

[a] Reflectance spectra against a magnesium oxide standard. Peak positions ν_{max}/cm^{-1}.

requires: C, 42.5; H, 1.8; Cl, 27.6; N, 5.5; V, 10.0%).

Physical Measurements. I.r. spectra were measured for Nujol mulls and potassium bromide discs using a Unicam SP 200 spectrophotometer. U.V. and visible spectra were measured by diffuse reflectance against a magnesium oxide standard using a Unicam SP 700 spectrophotometer.

Analysis. A weighed sample of the complex was decomposed by heating with a perchloric acid-sulphuric acid mixture (3:2). Vandium(V) was reduced to vanadium(IV) with sodium sulphite and reoxidised with an excess of cerium(IV) which was titrated with iron(II) using ferroin indicator.

Results and Discussion

We have prepared complexes $[VO(OR)(C_9H_6NO)_2]$ (I, R = H; II, R = Et), $[V_2O_3(C_9H_6NO)_4]$(III), and $[VO(OH)(C_9H_4Cl_2NO)_2]$(IV). The complexes (I-III) have been prepared before:[4] we found that the preparative procedures of Blair et al consistently gave products with satisfactory analyses.[4d]

I.r. Spectra. (a) V–O_t stretching wavenumbers. Data for our complexes and other complexes are in Table I. We assign to V–O_t stretching vibrations (where O_t represents terminal oxide, i.e. oxide bonded only to vanadium) strong bands in the region 900-1000 cm^{-1}. We note: (i) The V–O_t stretching wavenumber hardly changes when R is changed in the complexes $[VO(OR)(ligand)_2]$ or with substituents in 8-quinolinolate (see Table I). (ii) In salts containing the anion $[VO_2(C_9H_6NO)_2]^-$ the V–O_t stretching wavenumber is less than in the hydroxo-complex (I)[7] and there was an additional shoulder or band at 860-900 cm^{-1} which, in our view (see below), should also be assigned to a V–O_t stretching vibration. (iii) In the adducts with hydrogen halides, $[VO(OH)(C_9H_6NO)_2](HX)_4$ (X = F, Cl) the V–O_t stretching wavenumber is greater than in the hydroxo-complex (I).[7]

(b) O-H vibrations. Complexes (I) and (IV) and other complexes in Table I formulated with –OH groups have strong bands at 3450 cm^{-1} which we assign to the O–H stretching vibration of coordinated hydroxide. (For 8-quinolinol a broad band at ca. 3030 cm^{-1} is assigned to the O–H stretching vibration.[8])

Electronic Spectra. Peak positions are given in Table II. We assign peak (I), which does not occur in the spectra of the free ligands, to a charge-transfer transition from an orbital associated mainly with 8-quinolinolate to an orbital of vanadium. Replacing –OH in complex (I) by –OEt or bridging oxide shifts band (I) to higher wave numbers indicating that the acceptor orbital of vanadium in the charge-transfer transition has been raised in energy, i.e. become more anti-bonding presumably as a result of increased π-donor bonding from the –OR group. We assign peaks (II) and (III) to internal transitions ($\pi \rightarrow \pi^*$) of the 8-quinolinolate ligands, with peak (II) (ca. 25000 cm^{-1}) corresponding to the ^1L_a band of 8-quinolinolate (28600 cm^{-1}) and peak (III) to the ^1L_b band (30000 cm^{-1}).[9] The ^1L_a transition has considerable charge-transfer character, $-O^- \rightarrow$ hetero-ring, and its shift when 8-quinolinolate coordinates depends on the relative inductive (σ-bonding) effect of a cation at nitrogen (which withdraws charge from the hetero-ring and so stabilises the excited state) and at oxygen (from which withdrawal of charge by σ– and π–bonding of oxygen to the cation stabilises the ground state).[9d] When the inductive effect of a cation at the nitrogen of 8-quinolinolate is greater than at oxygen the excited state is lowered in energy by more than the ground state and the energy of the transition is therefore less for the complex than for the free ligand. The shifts with oxovanadium(IV) and (V) and oxo-

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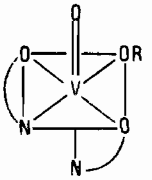
molybdenum(V)[9c] are of the same order (ca. –3000 to –4000 cm^{-1}) as with cobalt(II) and nickel(II) but less than with chromium(III) (–4770 cm^{-1}) and iron(III) (–7270 cm^{-1}).[9]

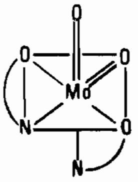
We suggest that the fact that the shift of the ^1L_a transition caused by high-valent vanadium is *not* greater than the shift caused by di- and tri-valent cations is due to (a) weaker bonding of nitrogen of 8-quinolinolate to vanadium as a consequence of trans-repulsion by terminal oxide bonded to vanadium and so a smaller inductive effect at nitrogen and less lowering of the excited state, (b) strong bonding, including π–bonding, of oxygen of 8-quinolinolate to vanadium and so greater lowering of the ground-state.

The shift in the ^1L_b transition of 8-quinolinolate on coordination to oxovanadium(V) (+6000 cm^{-1}) is much greater than and in the opposite direction to the shift observed with divalent and trivalent ions of the later elements of the first transition series and also greater than with oxovanadium(IV) (+1400cm^{-1}) and oxomolybdenum(V) (+ 2800 cm^{-1}). The direction of the shift (i.e., to higher wavenumbers) is the same as with unsaturated, electron-withdrawing substituents (–CO_2H, –CHO) at the 5-position of 8-quinolinate which stabilises the ground state in the $\pi \rightarrow \pi^*$ transition. If there is a π-bonding contribution to the interaction of vanadium with $-O^-$ of 8-quinolinolate, then the effect of vanadium on the ^1L_b transition would be similar to that of electron-withdrawing 5-substituents, i.e., stabilisation of the ground-state and shift of the transition to higher wavenumber as observed. Consistent with this is the fact that the shift to higher wavenumbers is less with oxovanadium(IV) and oxomolybdenum(V) than with oxovanadium(V) and oxomolybdenum(VI), the latter being the better π-acceptors.[9]

Structures and Bonding. None of the structures of the vanadium(V) complexes of 8-quinolinolate and its derivatives have been determined by X-ray crystallography. Possible structures, including isomers, have been summarised by Bielig and Bayer.[4c] It has generally been assumed that in the complexes [VO(OR)(ligand)$_2$] the –OR group is *trans* to terminal oxide. However, for the following reasons, a more likely structure is that in which the –OR group and ionised –OH group are *cis* to terminal oxide ((a) below):



(a)



(b)

(i) In the i.r. spectra of complexes [VO_2(ligand)$_2$]$^-$ there are two bands in the region 900-1000 cm^{-1} which we assign to the symmetric and anti-symmetric stretching vibrations of the *cis*-VO_2 group (cf. *cis*-MoO_2 complexes[1,2]). For a *trans*-VO_2 group only one V-O_t stretching vibration would be expected. (ii) The V-O_t stretching wave number does not vary with the donor ability of the –OR group (increasing R = H to R = alkyl). Thus there is no *trans*-effect as there is, for example, in a series of adducts of the complex [VOQ_2] with substituted pyridines.[11] (iii) The *cis*-configuration is commonly found in dioxo-complexes of the early transition metals in high oxidation states, e.g. molybdenum(VI) and tungsten(VI).[1,2] The structure of [MoO_2Q_2] is shown above (b).[10] (iv) The *cis*-structure is preferred on theoretical grounds. π-Donor bonding will occur from OH^- and OR^- as well as from O^{2-} and the structure in which there is the maximum possibility of O→V bonding will be the more stable: this is the *cis*-structure since in the *cis*-configuration three metal d-orbitals have the correct symmetry to act as acceptor orbitals in π-bonding wih two oxygens. (v) Since *trans* repulsion would be greater for $-O^-$ than for nitrogen of 8-quinolinolate the $-O^-$ groups will avoid the positions *trans* to terminal oxygen so giving structure (a) similar to that of [MoO_2Q_2]. We propose also that the binuclear complex, [$V_2O_3Q_4$], has terminal and bridging oxide in a *cis*-configuration as in, for example, complexes of molybdenum(V) having the Mo_2O_3 group.[2]

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