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Complexes of Vanadium(IV) with 8-Quinolinolate and Adducts with Donor Molecules

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The following complexes have been prepared: VOQ_2 (Q = 8-quinolinolate), $[VOQ_2A]$ (A = pyridyl-N-oxide, 4-cyanopyridine, aniline, pyridine, 4-methylpyridine, 4-aminopyridine, N-methylaniline, N,N-dimethylaniline, 2-methylpyridine, 2,4-dimethylpyridine), $[AH][VOQ_3]$ (A = morpholine, piperidine, pyrrolidine), and $[VOQ_2(QH)]2H_2O$. Their magnetic moments, i.r., and electronic spectra are reported and interpreted. For the complexes $[VOQ_2A]$ there are correlations between the pK's of the compounds A and vanadium-oxygen stretching wave numbers and the wave number separations of the first two d-d transitions. The following structures are proposed: for $[VOQ_2]$, trigonal bipyramidal; for $[VOQ_2A]$, octahedral with A trans to terminal oxygen; for $[VOQ_3]^-$, octahedral with one monodentate 8-quinolinolate bonded through nitrogen.

Introduction

Vanadium in oxidation state +4 forms many complexes containing the oxovanadium(IV) ion, VO^{2+}.[1] The wavenumbers of the V-O_t stretching vibrations and the 'd-d' transitions in the electronic spectra depend on the ligand coordinated to vanadium. Attempts have been made to interpret, in terms of their donor properties, the electronic effects of ligands coordinated in the position *trans* to oxygen, especially for complexes of VO^{2+} with acetylacetone.[1,2] In this paper we report a study of the *trans*-effect of ligands, A, in complexes $[VOQ_2A]$, where Q is 8-quinolinolate.

Experimental Section

Preparations. Oxobis(8-quinolinolato)vanadium(IV), $[VO(C_9H_6NO)_2]$, (I). The compound was precipitated by mixing aqueous solutions of 8-quinolinol and oxovanadium(IV) sulphate under nitrogen.[3] The precipitate was washed with hot water and dried in vacuo at 100° over P_2O_5. (Found: C, 60.7; H, 3.6; N, 8.0; V, 14.4. Calculated for $C_{18}H_{12}N_2O_3V$: C, 60.8; H, 3.4; N, 7.9; V, 14.4%).

Oxo(pyridine)bis(8-quinolinolato)vanadium(IV), (II), $[VO(C_9H_6NO)_2(C_5H_5N)]$. Analar pyridine (100 ml) was added to a solution of 8-quinolinol (5.8 g) in water (500 ml). Nitrogen was passed through the solution. To the solution was added a solution of oxovanadium(IV) sulphate (4.0 g) in water (100 ml). The solution was heated and stirred for one h. The olive green precipitate was filtered and washed with hot water. The product was dried in vacuo over concentrated sulphuric acid (5.2 g). (Found: C, 63.4; H, 4.0; N, 9.3; V, 11.7. Calculated for $C_{23}H_{17}N_3O_3V$: C, 63.6; H, 4.0; N, 9.7; V, 11.7%).

The following complexes were prepared by a procedure similar to that used for the pyridine adduct (II).

(4-Methylpyridine)oxobis(8-quinolinolato)vanadium (IV), $[VO(C_9H_6NO)_2(4\text{-}MeC_5H_4N)]$, (III). (Found: C, 63.6; H, 4.7; N, 8.9; V, 11.4. Calculated for $C_{24}H_{19}N_3O_3V$: C, 64.3; H, 4.3; N, 9.4; V, 11.4%).

(4-Cyanopyridine)oxobis(8-quinolinolato)vanadium (IV), $[VO(C_9H_6NO)_2(4\text{-}CNC_5H_4N)]$, (IV). (Found: C, 63.2; H, 3.5; N, 11.9; V, 13.5. $C_{24}H_{16}N_4O_3V$ requires: C, 62.7; H, 3.5; N, 12.2; V, 13.6%).

Oxo(pyridyl-N-oxide)bis(8-quinolinolato)vanadium (IV), $[VO(C_9H_6NO)_2(C_5H_5NO)]$, (V). Found: C, 61.7; H, 4.0; N, 9.4; V, 11.5. $C_{23}H_{17}N_3O_4V$ requires: C, 61.5; H, 3.8; N, 9.3; V, 11.3%).

(4-Aminopyridine)oxobis(8-quinolinolato)vanadium (IV), $[VO(C_9H_6NO)_2(4\text{-}NH_2C_5H_4N)]$, (VI). (Found: C, 60.7; H, 4.1; N, 12.0; V, 11.3. $C_{23}H_{18}N_4O_3V$ requires: C, 61.5; H, 4.0; N, 12.5; V, 11.4%).

(Aniline)oxobis(8-quinolinolato)vanadium(IV), $[VO(C_9H_6NO)_2(C_6H_5NH_2)]$, (VII). (Found: C, 63.9; H, 4.0; N, 9.2; V, 11.4. $C_{24}H_{19}N_3O_3V$ requires: C, 64.3; H, 4.2; N, 9.4; V, 11.4%).

Piperidinium oxotris(8-quinolinolato)vanadate(IV), $(C_5H_{12}N)[VO(C_9H_6NO)_3]$, (VIII). The compound precipitated when piperidine (50 ml) was added to an aqueous solution (600 ml) of 8-quinolinol (5.6 g) and oxovanadium(IV) sulphate (4.0 g). The pH of the final solution was 9.0. (Found: C, 65.5; H, 4.9; N, 9.6; V, 8.7. $C_{33}H_{30}N_4O_4V$ requires: C, 65.8; H, 5.0; N, 9.6; V, 8.7%).

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(1) (a) J. Selbin, *Chem. Rev.*, 65, 153 (1965), (b) *Coordination Chem. Rev.*, *1*, 293 (1966).

(2) R.L. Dutta and S. Ghosh, *J. Indian Chem. Soc.*, *44*, 273, 290, 296, 306, 369, 377, 381 (1967); (b) R.G. Garvey and R.O. Ragsdale, *J. Inorg. Nuclear Chem.*, *29*, 745 (1967); (c) R.G. Garvey and R.O. Ragsdale, *Inorg. Chim. Acta*, *2*, 191 (1968); (d) J.J.R. da Silva and R. Wooton, *Chem. Comm.*, 421 (1969); (e) C.J. Popp and R.O. Ragsdale, *J. Chem. Soc.* (*A*), 1892 (1969); (f) A. Syamal, *Z. Anorg. Chem.*, 373, 204 (1970).

(3) H.J. Beilig and E. Bayer, *Liebigs Ann.*, *584*, 96 (1953).

Pyrrolidinium Oxotris(8-quinolinolato)vanadate-(IV), $(C_4H_{10}N)[VO(C_9H_5NO)_3]$, (IX). The procedure was similar to that for the piperidinium salt, (VIII). (Found: C, 65.2; H, 5.2; N, 9.5; V, 9.2. $C_{31}H_{28}N_4O_4V$ requires: C, 65.3; H, 4.7; N, 9.8; V, 8.8%).

Morpholinium Oxotris(8-quinolinolato)vanadate-(IV), $(C_4H_{10}NO)[VO(C_9H_6NO)_3]$, (X). The procedure was similar to that for the piperidinium salt, (VIII). (Found: C, 63.7; H, 4.8; N, 9.2; V, 8.7. $C_{31}H_{27}N_4O_5V$ requires: C, 63.5; H, 4.6; N, 9.6; V, 8.7%).

Hydrogen Oxotris(8-quinolinolato)vanadate(IV) dihydrate, $H[VO(C_9H_5NO)_3]2H_2O$, (XI). The compound was obtained in an attempt to prepare the pyridinium analogue of compounds (VIII), (IX), and (X). The procedure was similar to that for the pyridine adduct (II) except that the pH of the final solution was adjusted to 9.0 with sodium hydroxide. (Found: C, 59.0; H, 3.9; N, 7.9; V, 9.7. $C_{27}H_{23}N_3O_6V$ requires: C, 60.4; H, 4.1; N, 7.8; V, 9.5%).

Attempted preparations of other adducts. We attempted to prepare according to the procedure for the pyridine adduct (II) compounds $[VO(C_9H_5NO)_2A]$ for A = 2-methylpyridine, 2,6-dimethylpyridine, N-methylaniline, and N,N-dimethylaniline. Analyses indicated that the precipitates obtained were mixtures of the desired adducts and $[VO(C_9H_6NO)_2]$.

Physical Measurements. I.r. spectra were measured for nujol mulls and potassium bromide discs using a Unicam SP200 spectrophotometer. U.v. and visible spectra were measured by diffuse reflectance against a magnesium oxide standard using a Unicam SP 700 spectrophotometer. Magnetic susceptibilities were measured on solid samples at room temperature with a Newport Instruments Gouy balance system.

Analysis. Samples of the complexes were decomposed by a perchloric acid-sulphuric acid mixture (3:2). Vanadium(V) was reduced to vanadium(IV) with sodium sulphite and the vanadium was determined by adding an excess of cerium(IV) sulphate and back titration with iron(II).

Results and Discussion

Compounds Prepared. We have prepared three types of complex of oxovanadium(IV) with 8-quinolinolate: $[VOQ_2]$, $[VOQ_2A]$, and $AH^+[VOQ_3]^-$ (HQ = 8-quinolinol, A = adduct molecule). The complexes are insoluble in water and organic solvents and are precipitated from aqueous solutions containing 8-quinolinol, the oxovanadium(IV) ion, and the compounds A. Formation of the complexes can be represented by the following equations. Figures in parentheses are pK's which provide a basis for comparing the donor abilities of the ligands in σ-bonding.[4]

$$VO^{2+} + 2HQ = [VOQ_2] + 2H^+ \tag{1}$$

[(HQ = 8-quinolinol (9.81 (–OH), 4.91 (–NH⁺))]

$$2VO^{2+} + 4HQ + A = [VOQ_2] + [VOQ_2A] + 4H^+ \tag{2}$$

[A = N-methylaniline (4.85), N,N-dimethylaniline (5.06), 2-methylpyridine (5.97), 2,5-dimethylpyridine (6.99)]

$$VO^{2+} + 2HQ + A = [VOQ_2A] + 2H^+ \tag{3}$$

[A = pyridyl-N-oxide (0.79), 4-cyanopyridine (1.45), aniline (4.58), pyridine (5.23), 4-methylpyridine (6.02), 4-aminopyridine (9.17)]

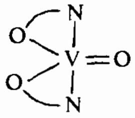
$$VO^{2+} + 3HQ = [VOQ_2(HQ)] + 2H^+ \tag{4}$$

$$VO^{2+} + 3HQ + A = [VOQ_3]^- + AH^+ + 2H^+ \tag{5}$$

[A = morpholine (8.70), piperidine (11.22), pyrrolidine (11.27)].

Equation (2) represents reactions in which we obtained mixtures of the parent compound $[VOQ_2]$ and adducts $[VOQ_2A]$. Equation (3) represents reactions in which adducts $[VOQ_2A]$ were the only products. The tendency to form adducts is less for the ligands of equation (2) than for the ligands of equation (3), a consequence of steric restrictions on coordination due to the methyl substituents. Equations (4) and (5) represent reactions in which we obtained tris-complexes. For the compounds A of equation (5) protonation occurs in preference to coordination to vanadium presumably because the hydrogen atoms of the –NH groups of morpholine, etc. impose steric restrictions on coordination to vanadium.

Attempts to prepare adducts directly from the 8-quinolinolate complex (I) were unsuccessful, e.g., complex (I) did not dissolve in pyridine. A possible explanation is that complex (I) has a trigonal bipyramidal structure like that of bis(2-methyl-8-quinolinolato)-oxovanadium(IV) in which the vanadium is not accessible to potential donors:[5]



Magnetic Moments. All the complexes had magneton numbers at ca. 293 K close to the spin-only value for one unpaired electron (1.73) and so contain vanadium(IV).

I.r. Spectra. (a) V-O_t stretching wavenumbers. The V-O_t stretching wavenumbers are lower in the adducts $[VOQ_2A]$ than in the parent compound $[VOQ_2]$ and decrease as the pK's of the ligands A (see Figure 1) increase, i.e., as their σ-donor abilities increase. So the effect of ligands A is to reduce the acceptor ability of vanadium with respect to terminal oxygen so that the order of the V-O bond and the V-O_t stretching wavenumber decrease. Similar correlations have been observed for adducts of oxobis(acetylacetonato)vanadium(IV) with pyridyl-N-oxides.[2e] The V-O_t stretching wavenumbers in the adducts of N-methylaniline, and of the other bases listed under equation (2) above, were higher than expected from the pK's (see Figure 1). This is consistent with

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(4) 'Stability Constants of Metal-Ion Complexes', Special Publication No 17, Chemical Society, London, 1964.

(5) M. Shiro and Q. Fernando, *Chem. Comm.*, 63 (1971).

our suggestion that coordination of these ligands to vanadium in complexes of the type [VOQ_2A] is sterically hindered.

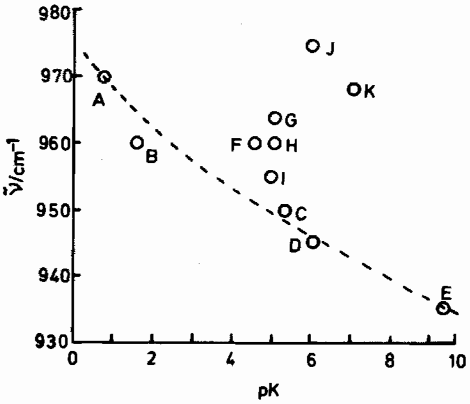

Figure 1. V-O_t stretching wavenumbers (ν/cm^{-1}) for compounds [VOQ_2A] plotted against pK's of the compounds A for: A, pyridyl-N-oxide; B, 4-cyanopyridine; C, pyridine; D, 4-methylpyridine; E, 4-aminopyridine; F, aniline; G, N,-N-dimethylaniline; H, N-methylaniline I, 8-quinolinolate (i.e., the ion [VOQ_3] assuming Q bonded through nitrogen with pK 4.9; J, 2-methylpyridine; K, 2,6-dimethylpyridine.

(b) Organic ligands. The i.r. spectra of the complex [VOQ_2] (I), and adducts [VOQ_2A] (II)-(VII), were characteristic of chelated 8-quinolinolate.[6] The spectra of the tris-complexes [AH][VOQ_3], (VIII)-(XI), differed from that of the bis-complex [VOQ_2], (I), as follows: (i) In the range 700-850 cm^{-1} (CH out-of-plane deformations[7]) the tris-complexes had two additional bands (730 and 760 cm^{-1}). (ii) In the range 1570-1640 cm^{-1} (ring C=C and C=N streching vibrations[10]) the bis-complex had two bands and the tris-complexes had four bands. Thus, in the tris-complexes, at least one of the three 8-quinolinolate ligands is bonded differently from the two equivalent ligands of the bis-complex. (iii) In the region 2200-3000 cm^{-1} complexes (AH)[VOQ_3], (VIII)-(X), and also the salts (AH)Cl and (AH)Q (which slowly crystallised from solutions of 8-quinolinol in the bases, A), had three bands (ca. 2400, 2500, 2640 cm^{-1}) which were not observed for the bis-complex, (I), or for complex H[VOQ_3], (XI). So we assign these bands to NH stretching vibrations of the $-NH_2^+$ groups of the AH^+ cations. Thus the compounds A are present in the tris complexes as cations AH^+. (iv) The spectrum of the compound H[VOQ_3] . $2H_2O$, (XI), had three bands at 3300, 3450, and 3600 cm^{-1} which were not observed in the spectra of the bis-complexes and the other tris-complexes. We assign the band at 3600 cm^{-1} to the OH stretching vibration of water, that at 3450 cm^{-1} to the OH stretching vibration of the phenolic group of 8-quinolinol, and that at 3300 cm^{-1} to intermolecular hydrogen bonding.[7] Thus in complex (XI) an oxygen of 8-quinolinolate is protonated, and the complex should be formulated [VOQ_2-(HQ)]$2H_2O$ with the 8-quinolinol molecule bonded to vanadium through nitrogen only.

Electronic Spectra. Because of the insolubility of our compounds diffuse reflectance spectra of the solids were recorded. Peak positions are given in Table II. By analogy with other oxovanadium(IV) complexes of approximately C_{4v} symmetry[1] we assign band I (12,000-14,000 cm^{-1}) to the transitions $b_2(d_{xy}) \rightarrow e_\pi^*$ (d_{xz},d_{yz}), $b_1^*(d_{x^2-y^2})$ and band II (16,000-18,000 cm^{-1}) to the transition $b_2 \rightarrow 1a_1^*$ (d_{z^2}). The main contribution to band I is from the transition to e_π^*.[8] For the complexes [VOQ_2A] the separation of bands I and II increases as the pK of compound A increases (see Figure 2) and hence also as the V-O_t stretching wavenumber decreases. The separation of bands I and II measures the relative energies of the e_π^* and $1a_1^*$ orbitals at constant energy of the b_2 orbital and for the separation to increase as the donor ability of the molecules A increases indicates that the e_π^* orbitals are becoming less anti-bonding, a consequence of the decreasing acceptor ability of vanadium with respect to terminal oxygen. For the complexes [AH][VOQ_3] the separation of bands I and II (ca. 4000 cm^{-1}) is of the order expected if nitrogen of the third 8-quinolinolate (pK 4.9) is bonded to vanadium (cf. Figure 2).

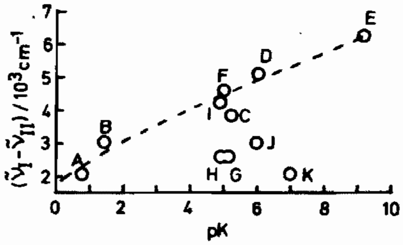

Figure 2. Separation of peaks II and I in the electronic spectra of complexes [VOQ_2A] plotted against pK's of compounds A for: A, pyridyl-N-oxide; B, 4-cyanopyridine; C, pyridine; D, 4-methylpyridine; E, 4-aminopyridine; F, aniline; G, N,N-dimethylaniline; H, N-methylaniline; I, 8-quinolinolote J, 2-methylpyridine; K, 2,6-dimethylpyridine.

We assign band III to the first $\pi \rightarrow \pi^*$ transition (^1L_a) of the 8-quinolinolate ligands.[6b,9] This transition has charge-transfer character, $-O^- \rightarrow$hetero-ring, and shifts when Q– coordinates to an extent dependent on the relative inductive effects (σ-bonding) of an acceptor cation at oxygen and nitrogen.[9] Band III is at higher wavenumbers in compounds [VOQ_2A] compared with [VOQ_2] in agreement with the expected lower acceptor ability of vanadium in the former. For the compounds [AH][VOQ_3] band III is split into two components. We assign the higher wavenumber component to the ^1L_a transition of chelated 8-quinolinolate as in the bis-complexes and to 8-quinolinolate bonded through nitrogen only.

Structures and bonding. The complex bis(2-methyl-8-quinolinolato)oxovanadium(IV) has a trigonal bipyramidal structure (cf. earlier). The reluctance of

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[6] (a) R.J. Magee and L. Gordon, *Talanta, 10*, 851, 967 (1963); (b) P.C.H. Mitchell, *J. Chem. Soc.* (A), 146 (1969).

[7] L.J. Bellamy, 'The Infra-red Spectra of Complex Molecules', Methuen, London, 1954.

[8] C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, *1*, 111 (1962).

[9] L. Morpurgo and R.J.P. Williams, *J. Chem. Soc.* (A), 73 (1966).

Table I.[a] I.r. spectra: V-O$_t$ stretching vibrations (ν/cm^{-1}).

[VOQ$_2$] 975	[VOQ$_3$]$^-$ 955		
[VOQ$_2$A],	A = pyridyl-N-oxide 970	4-CN pyridine 960	aniline 960
	pyridine 950	4-Me pyridine 945	4-NH$_2$ pyridine 935
	N-Me aniline[b] (975) 960	N,N-diMe aniline[b] (975) 964	2-Me pyridine 975
	2,6-diMe pyridine[b] (975) 968		

[a] Q is 8-quinolinolate. Ligands A are in order of increasing pK's. [b] The products were mixtures of the required adducts and [VOQ$_2$].

Table II. Electronic spectra[a].

Compound	Peak Positions I	 II	 III
[VOQ$_2$]	14,000	(18,000)	25,000
[VOQ$_2$(pyridyl-N-oxide)]	(14,400)	16,400	26,000
[VOQ$_2$(4-CN pyridine)]	14,000	(17,000)	25,000
[VOQ$_2$(aniline)]	13,000	18,000	25,400
[VOQ$_2$(pyridine)]	14,200	(18,000)	25,400
[VOQ$_2$(4-Me pyridine)]	13,600	(18,800)	25,000
[VOQ$_2$(4-NH$_2$ pyridine)]	12,200	(18,600)	25,400
[VOQ$_2$(N-Me aniline)]	(14,400)	17,000	25,000
[VOQ$_2$(N,N-diMe aniline)]	14,400	17,000	25,000
[VOQ$_2$(2-Me pyridine)]	14,000	(17,000)	26,000
[VOQ$_2$(2,6-diMe pyridine)]	14,400	17,000	25,000
[morH][VOQ$_3$]	13,200	17,600	25,400 (22,600)
[pipH][VOQ$_3$]	13,000	17,000	26,000 (22,600)
[pylH][VOQ$_3$]	12,800	17,000	26,000 (22,800)
[VOQ$_2$(QH)]2H$_2$O	12,800	17,200	25,000

[a] Peak positions, ν/cm^{-1}. Shoulders in parenthesis. Abbreviations: Q, 8-quinolinolate; morH, morpholinium; pipH, piperidinium; pylH, pyrrolidinium.

the complex [VOQ$_2$] to undergo addition reactions indicates that this complex has the same structure. For the adducts [VOQ$_2$A] the correlation of V-O$_t$ stretching wavenumbers with pK's indicates that the ligands A are coordinated *trans* to terminal oxygen. There is no evidence for *cis*- and *trans*-isomers as suggested for pyridine adducts of VO(acetylacetonate)$_2$.[2d] For the tris-complexes containing the anion [VOQ$_3$]$^-$ we propose a structure in which one 8-quinolinolate is unidentate and bonded to vanadium through nitrogen in the *trans* position to terminal oxygen. On basis we are able satisfactorily to interpret the i.r. and u.v. spectra of the tris complexes. Bonding of nitrogen rather than oxygen is also consistent with our earlier suggestion that the oxygens of 8-quinolinolate avoid positions *trans* to multiply bonded terminal oxygen[10]

Conclusions

Reaction of oxovanadium(IV) sulphate with 8-quinolinolate (Q$^-$) and organic N-donor bases (A) gave complexes [VOQ$_2$A], (AH)[VOQ$_3$], and [VOQ$_2$(OH)].2H$_2$O. Compared with the parent compound [VOQ$_2$], the complexes [VOQ$_2$A] exhibited lower V–O$_t$ stretching wavenumbers, increased separation of the first two d–d transitions, and a shift to higher wavenumber of the $\pi \rightarrow \pi^*$ transition of 8-quinolinolate. These spectroscopic changes are attributed to a decrease, caused by the ligand A, in the acceptor ability of vanadium towards terminal oxygen and 8-quinolinolate. The effect of coordinating the bases A to vanadium increased with increasing pK of the bases except for those bases with substituents which caused coordination to vanadium to be sterically hindered. The following structures are proposed for the complexes: [VOQ$_2$], trigonal bipyramidal; [VOQ$_2$A], octahedral with A *trans* to terminal oxygen; [VOQ$_3$]$^-$, octahedral with two bidentate 8-quinolinolate ligands and one unidentate bonded through nitrogen.

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(10) R.P. Henry, P.C.H. Mitchell, and J.E. Prue, to be published.