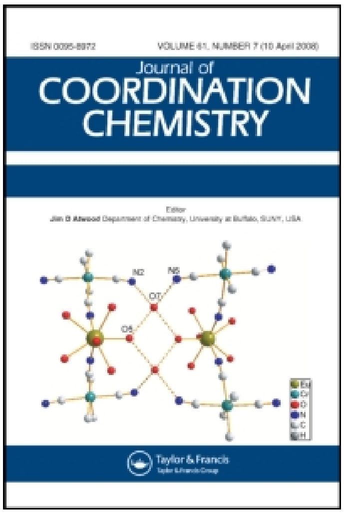

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CRYSTAL AND MOLECULAR STRUCTURE OF THE DIOXO BIS (8-QUINOLINOLATO) VANADIUM(V) ION AND ITS RELATIONS WITH THE MIXED VALENCE μ-OXO-[OXOBIS(8-QUINOLINOLATO) VANADIUM(V)][OXO BIS (8-QUINOLINOLATO) VANADIUM(IV)] ION

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CRYSTAL AND MOLECULAR STRUCTURE OF THE DIOXO BIS (8-QUINOLINOLATO) VANADIUM(V) ION AND ITS RELATIONS WITH THE MIXED VALENCE μ-OXO-[OXOBIS(8-QUINOLINOLATO) VANADIUM(V)][OXO BIS (8-QUINOLINOLATO)VANADIUM(IV)] ION

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The crystal structure of NBu_4^+ $VO_2Q_2^-$ (Q = 8-quinolinol anion) has been determined from three dimensional X-ray data collected with MoKα radiation (λ = 0.71069 Å). Crystal data are as follows: tetragonal, space group $I\bar{4}2d$, a = 19.004(5), c = 19.475(8)Å, Z = 8. The structure has been refined by full matrix least squares methods, using 1265 independent reflections to a conventional weighted R factor of 0.082. The $VO_2Q_2^-$ anion exhibits a C_2 symmetry with a cis VO_2 group (O—V—O angle: 105°). The nitrogen atom of the 8-quinolinolate ligand is trans to an oxo oxygen and the ligand oxygen atoms are trans to each other. The reaction of $VO_2Q_2^-$ upon VOQ_2 giving the mixed valence $V_2O_3Q_4^-$ ion is studied and a structure is proposed for the latter, which would explain the absence of interaction between the two vanadium atoms.

INTRODUCTION

As a part of a research program on mixed valence compounds, we are interested in the synthesis and properties of binuclear species of Mo, W, or V containing oxygen bridges. Few examples of this kind are known in the literature and it is expected that they could be useful models for the study of electron transfer in more complicated systems, such as reduced iso or heteropolyanions, or mixed valence nonstoichiometric oxides. For this reason, we have undertaken a reexamination of the properties of the mixed valence ion $[V^{V}O\,Q_2-O-V^{IV}OQ_2]^-$ (Q = 8-quinolinol anion) first prepared by Sawyer.[1] During the course of this study we have found that the $V^{V}O_2Q_2^-$ anion is involved in the synthesis of the mixed valence dimer, and we have therefore studied its crystal structure and its relations with $V_2O_3Q_4^-$.

EXPERIMENTAL SECTION

Electrochemistry

Polarograms were recorded with Tacussel equipment, including a PRT 30–01 Potentiostat and a GSATP linear scan generator. The current potential curves appeared on a X-Y recorder. The same device was also used to check the reversibility of the waves by cyclic voltammetry. In this case a Tektronix RM564 oscilloscope replaced the X-Y recorder. The solvent was acetonitrile containing 0.1 mol.l^{-1} of tetrabutylammonium tetrafluoroborate as supporting electrolyte.

Spectroscopic Techniques

The UV Visible spectra were obtained with a Beckman 5240 spectrophotometer. IR spectra were recorded with a Perkin Elmer 283 spectrometer and KBr disks. ESR measurements were made on a Varian E 3 spectrometer.

Preparation of Complexes

1) (Tetra-*n*-butylammonium) [dioxo bis (8-quinolinolato) Vanadium (V)]. $NBu_4^+VO_2Q_2^-$ was prepared by mixing equimolar amounts of $VO(OH)Q_2$ (prepared according to Amos and Sawyer[2]) and tetrabutylammonium hydroxide (a 0.1 mol l^{-1} solution in toluene/methanol) in pure acetonitrile. For instance 1.61g of $VO(OH)Q_2$ and 43.4 ml of tetrabutylammonium hydroxide were mixed in 65 ml of acetonitrile. After complete dissolution, the yellow solution was left in the air, and crystallization occurred in a few days. A slow photochemical reduction of V^V by acetonitrile also occurred and the solution turned red after exposure to the day-

light for several days; however the crystals remained yellow and analysis indicated that the product was $NBu_4^+VO_2Q_2^-$. Anal. Calcd. C, 66.56; H.7, 83; N, 6.85. Found: C, 66.16; H, 8.01, N, 7.01.

2) Oxobis (8-quinolinolato) vanadium (IV). VOQ_2 was prepared by the method of Bielig and Bayer[3] and dried in vacuum. Anal. Calcd. C, 60.85; H, 3.43; N, 7.88. Found: C, 60.67; H, 3.43; N, 7.91.

3) (Tetrabutylammonium) {μ-oxo-[oxobis (8-quinolinolato) vanadium (V)] [oxo bis(8-quinolinolato) vanadium (IV)] }. This compound (abbreviated by $NBu_4^+V_2O_3Q_4^-$) was prepared by a modification of Sawyer's method.[1] Stoichiometric amounts of $VO(OCH_3)Q_2$,[4] VOQ_2 and tetrabutylammonium hydroxide (solution in toluene/methanol) were mixed in a solvent such as acetonitrile or toluene. (Contrary to Sawyer's results, we found this reaction to be impossible in methanol). Then the solvent was evaporated, leaving a green powder. Anal. Calcd: C, 64.46; H, 6.19; N, 7.23. Found: C, 64.29; H, 6.15; N, 7.36. Electrochemical studies on a mercury electrode revealed the presence of the reversible oxidation wave described by Sawyer near 0 volt and the IR spectrum exhibited the same V=0 band at 882nm.

Crystallographic Study of $NBu_4^+VO_2Q_2^-$

The single crystal used was a 0.35 x 0.66 x 1.25mm prism. Precession and Laue photographs showed tetragonal symmetry. Systematic absences $h + k + 1 = 2n + 1$ for all reflections, and $2h + 1 \neq 4n$ in $h\ h\ 1$ planes, combined with the Laue class $4\ m\ m\ m$, yielded two possible non-centrosymmetric space groups: $I\,4_1\,md$ and $I\,\bar{4}\,2d$. The lattice constants were obtained from a least squares refinement of the setting angles of 8 strong reflections centered manually on a 4-circle diffractometer: $a = 19.004(5)$, $c = 19.475(8)$Å. The wavelength for these measurements was 0.71069 Å. The calculated density, 1.17g.cm^{-3} for 8 molecules of $NBu_4^+VO_2Q_2^-$ per unit cell is in good agreement with the measured value 1.20 obtained by flotation in a dimethylsulfoxyde/methylene chloride mixture.

1710 independent reflections, including 282 zeros, with a Bragg angle lower than 25°, were recorded at room temperature with an automatic 4-circle diffractometer, using MoK_α radiation with a graphite monochromator set in front of the counter ($\lambda = 0.71069$Å). The $\theta/2\theta$ scan technique was used with a scan rate of 1.07°/min. Intensities were measured with a scintillation counter and a single channel analyser. Lorentz and polarization corrections were applied to all intensity measurements. No absorption correction was performed in view of the low linear absorption coefficient (3.68cm^{-1}). Each structure factor Fo was assigned a standard deviation $\sigma = \text{Fo}\ \Delta I/2I$ where ΔI was the error on the integrated intensity I. Of the 1710 reflections, 445 with $\text{Fo} < 3\sigma$ were not included in the subsequent calculations.

Computations were performed using standard programs[5] on a C I I IRIS 80. Scattering factors were taken from International Tables, including $\Delta f'$ and $\Delta f''$ for vanadium. Full-matrix least squares methods were used to minimize $\Sigma(w|F_{obs} - F_{calc}|)^2$ where weight $w = 1/\sigma$.

A three dimensional Patterson map immediately ruled out the $I\,4_1\,md$ space group and yielded the position of the vanadium atom which was found on a C_2 axis. At this stage, a least squares refinement gave a Rw value of 0.44, and this vanadium position was used to phase an initial Fourier map. Then, all other non-hydrogen atoms showed up. The nitrogen atom of the tetrabutylammonium cation was also found on a C_2 axis, so that only two C_4H_9 chains were independent. Each C_4H_9 chain end exhibited a crystallographic disorder: the isotropic temperature factors increased along each chain and finally the ending carbon atoms appeared in 3 different positions. These were refined with the occupancy factor as a variable. A Fourier difference map revealed the presence of a disordered acetonitrile molecule with two possible orientations, near a C_2 axis. This molecule was refined with a constrained geometry (C—C = 1.50 and C—N = 1.15 Å and a variable occupancy factor. The stoichiometry of the salt was thus found to be $(NBu_4^+)\ [VO_2Q_2^-]\ .\ 0.6\ CH_3CN$. Finally, most hydrogen atoms appeared on a Fourier difference map and were located at a distance of 1.0 Å of the corresponding carbon atom, but not refined. They were assigned an isotropic temperature factor one unit greater than the one of the corresponding carbon atom (isotropic B in Å^2 units).

A secondary extinction correction appeared necessary since systematic divergences with $F_{obs} < F_{calc}$ were observed for low angle reflections. The extinction factor refined to a value of $2.8.10^{-7}$. The final agreement factors were $R = 0.077$ and $Rw = 0.082$, where the agreement factors are defined as

$$R = \Sigma(|F_{obs} - F_{calc}|)/\Sigma|F_{obs}|$$

and

$$Rw = \{\Sigma(w|F_{obs} - F_{calc}|)^2/\Sigma w|F_{obs}|^2\}^{1/2}$$

Atomic parameters with their standard deviations are given in Table I.

TABLE I
Positional and anisotropic thermal parameters with estimated standard deviation in parentheses.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$VO_2Q_2^-$ anion									
V	.16736 (9)	.25	.125	4.33 (8)	5.3 (1)	4.94 (8)	.0	.0	−1.57 (8)
O_1	.2197 (3)	.2087 (3)	.0713 (3)	6.0 (3)	6.9 (3)	6.0 (3)	−.0 (3)	1.3 (2)	−1.7 (3)
O_2	.1424 (3)	.1661 (3)	.1791 (3)	7.1 (3)	6.7 (3)	6.0 (3)	.2 (3)	.2 (3)	− .1 (3)
N_1	.0704 (3)	.2839 (4)	.1881 (4)	4.6 (3)	7.9 (4)	6.6 (4)	−.1 (3)	− .3 (3)	−2.9 (3)
C_2	.0358 (5)	.3454 (6)	.1881 (4)	5.6 (4)	10.5 (7)	8.5 (5)	1.3 (5)	−1.0 (4)	−4.3 (5)
C_3	−.0226 (6)	.353 (1)	.2368 (7)	6.4 (6)	14 (1)	8.5 (7)	1.4 (6)	.7 (5)	−4.8 (7)
C_4	−.0453 (6)	.305 (1)	.2727 (7)	6.1 (6)	15 (1)	8.7 (7)	−.4 (7)	1.5 (5)	−3.8 (7)
C_5	−.026 (1)	.180 (1)	.3154 (8)	11 (1)	19 (2)	7.4 (7)	−4 (1)	3.1 (7)	−3 (1)
C_6	.012 (1)	.121 (1)	.3107 (8)	15 (1)	16 (1)	8.0 (8)	−6 (1)	3.8 (9)	−1.4 (9)
C_7	.0705 (8)	.1132 (7)	.2625 (6)	12.3 (9)	10.0 (8)	7.5 (6)	−2.6 (7)	.3 (6)	.3 (6)
C_8	.0890 (5)	.1675 (6)	.2256 (5)	7.6 (5)	8.3 (6)	6.7 (5)	−2.5 (5)	−.2 (4)	−1.7 (5)
C_9	−.0083 (6)	.236 (1)	.2743 (5)	7.2 (6)	16	6.7 (5)	−4.1 (8)	.5 (5)	−3.5 (7)
C_{10}	.0484 (4)	.2318 (6)	.2299 (4)	5.4 (4)	10.0 (7)	5.4 (4)	−1.2 (4)	.1 (4)	−2.5 (4)
Tetrabutylammonium Cation. Occupation probabilities are given in parentheses for each position of the last carbon atoms C_{14} and C_{24}									
N_2	.25	.2702 (7)	−.125	11.0 (8)	9.7 (7)	7.8 (6)	.0	2.4 (7)	.0
C_{11}	.1859 (7)	.2256 (7)	−.1108 (6)	10.7 (7)	11.4 (8)	8.4 (6)	.8 (5)	3.9 (6)	.6 (6)
C_{12}	.170 (1)	.170 (1)	−.168 (1)	14 (1)	22 (2)	10.6 (9)	−5 (1)	3.3 (9)	−2 (1)
C_{13}	.094 (1)	.143 (1)	−.161 (1)	18 (2)	20 (2)	11 (1)	−5 (1)	3 (1)	−1 (1)
$C_{14}A$ (.39)	.035 (2)	.190 (3)	−.185 (2)	13 * (1)					
$C_{14}B$ (.27)	.076 (5)	.095 (5)	−.174 (5)	13 * (2)					
$C_{14}C$ (.34)	.064	.16027	−.2087	16 * (2)					
C_{21}	.243 (1)	.3162 (8)	−.1881 (5)	14 (1)	11.9 (8)	6.2 (5)	−.6 (9)	3.1 (6)	.0 (5)
C_{22}	.179 (1)	.365 (1)	−.186 (1)	18 (2)	16 (1)	10 (1)	0 (1)	2 (1)	4 (1)
C_{23}	.180 (2)	.416 (2)	−.246 (1)	27 (3)	21 (2)	11 (1)	6 (3)	7 (2)	5 (2)
$C_{24}A$ (.46)	.143 (2)	.483 (2)	−.248 (2)	13 * (1)					
$C_{24}B$ (.31)	.088 (5)	.439 (5)	−.249 (5)	18 * (2)					
$C_{24}C$ (.23)	.228 (5)	.464 (5)	−.247 (5)	13 * (3)					
Acetonitrile molecule									
C_{31} (CH_3)	.341	.334	.158	14 *					
C_{32} (Cen)	.361	.256	.160	14 *					
N	.369	.196	.162	14 *					

Anisotropic thermal parameters enter the following expression for the temperature factor, where B are in Å^2 units:

$$\exp\left[-0.25\left(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hk\,a^*b^* + 2B_{13}hl\,a^*c^* + 2B_{23}kl\,b^*c^*\right)\right]$$

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* Isotropic value of B.

RESULTS AND DISCUSSION.

The Structure of $VO_2Q_2^-$

The crystal structure consists of $VO_2Q_2^-$ and NBu_4^+ ions, and disordered acetonitrile molecules (see Figure 1). The vanadium atom of the anion and the nitrogen atom of the cation lie on a crystallographic C_2 axis. The acetonitrile molecule is found near this C_2 axis, with crystallographic disorder between two possible orientations. On each axis, the sequence $VO_2Q_2^-$... ...CH_3CN......NBu_4^+...$VO_2Q_2^-$ repeats indefinitely, with the oxygen atoms of the anion facing the acetonitrile molecule. The binary axes are found at the $z = 1/8$ (shown on Figure 1), $z = 3/8$, $z = 5/8$ and $z = 7/8$ levels, and are oriented alternately along the x and y directions.

The $VO_2Q_2^-$ anion is shown on Figure 2. The two oxo-type oxygen atoms ($O_{(1)}$) are cis to each other, with an $O_{(1)}$–V–$O_{(1)}$ angle of 105.4°. Each 8-quinolinolate ligand coordinates the vanadium atom with its nitrogen atom trans to $O_{(1)}$, and the oxygen atoms of the two ligands ($O_{(2)}$) are trans to each other. This arrangement is identical to the one observed in MoO_2Q_2.[6] The cis disposition of oxygen atoms in MO_2 groups with M a metal in d^0 electronic configuration has been rationalized by Griffith[7] and Guerchais[8] who have emphasized that it allows a maximum use of d orbitals in $p\pi$–$d\pi$ bonding. Several other vanadium (V) complexes containing the cis VO_2 group have been described, for example $VO_2(C_2O_4)_2^{3-}$ [9,12], $VO_2(H_2EDTA)^-$ [10], $VO_2(EDTA)^{3-}$ [11] and $VO_2F(C_2O_4)^{2-}$ [13].

The six ligated atoms around the vanadium atom form a nearly regular octahedron with the distances between vertices ranging from 2.61 to 2.84 Å (Table II), which are less than the sum of the usual Van der Waals radii for O (1.40 Å) and N(1.50 Å). Inside this small octahedron, the vanadium atom exhibits a marked off-center displacement along the crystallographic 2-fold axis, toward the O(1)–O′(1) edge as shown by the $O_{(2)}$–V–$O'_{(2)}$ angle of 152° and the distance between the vanadium atom and the $O_{(2)}$...$O'_{(2)}$ line, which is 0.475 Å. The V–$O_{(1)}$ distance is 1.64 Å and thus has a strong double bond

TABLE II
Closest ligand-ligand distances with their standard deviation for the VO_4N_2 octahedron.

O_1–O'_1	2.61 (1)	O_2–O'_1	2.79 (1)
O_1–O_2	2.68 (1)	O_2–N'_1	2.82 (1)
O_1–O'_2	2.79 (1)	N_1–N'_1	2.77 (1)
O_1–N'_1	2.84 (1)	N_1–O'_2	2.82 (1)
O_2–N_1	2.63 (1)	N_1–O'_1	2.84 (1)

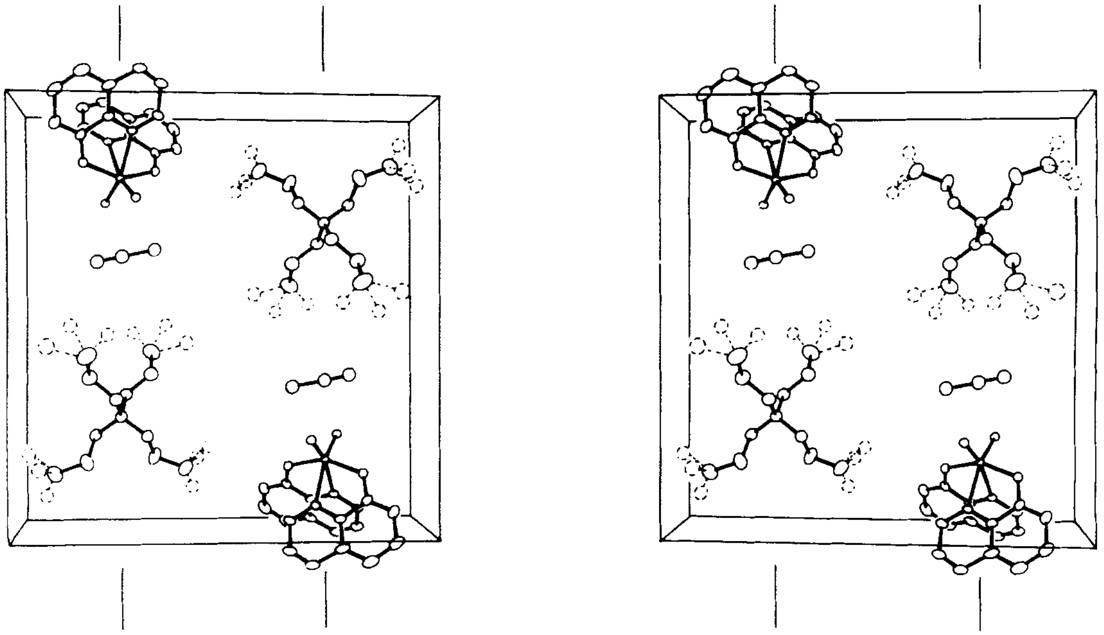


FIGURE 1 Stereoscopic view along the *c* axis of the crystal packing. Only one quarter of the unit cell, from $z = 0$ to $z = 0.25$ has been shown, for clarity. The two binary axes are at the $z = 0.125$ level. Thermal ellipsoids are shown at the 8% probability level. Dotted circles represent the disordered ending carbon atoms of the tetrabutylammonium cation.

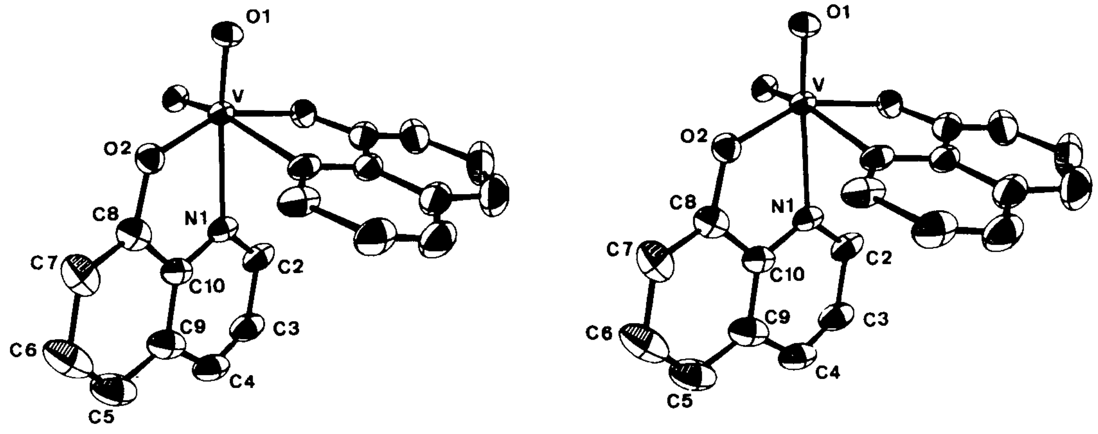
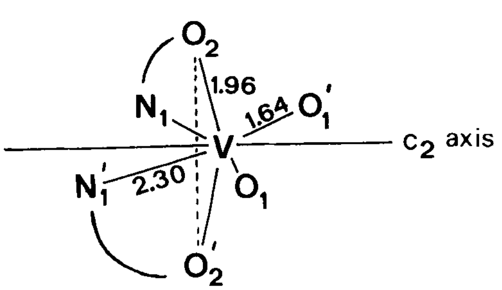


FIGURE 2 Stereoscopic ORTEP drawing of the $VO_2Q_2^-$ ion. Thermal ellipsoids are shown at the 17% probability level.



character, while the trans V—N distance is 2.30 Å.

It is well known that the small size of vanadium(V) is responsible for its tendency to give a strongly distorted octahedral coordination.[14] In the present case, a further reason is provided by the presence of the two oxo-type oxygen atoms which attract the vanadium atom by forming π-bonds, while the trans nitrogen atoms are kept away by the Van der Waals contact of the ligated atoms.

The 8-quinolinolate anion exhibits an alternating pattern of long and short bonds which has already been observed in $VO(MeQ)_2$[15] (MeQ = 2 methyl-8-quinolinolate) and $Al_2O(MeQ)_4$.[16] Finally it can be pointed out that the $VO_2Q_2^-$ ion is chiral; however both enantiomers are present in the crystal, related by the S_4 axis.

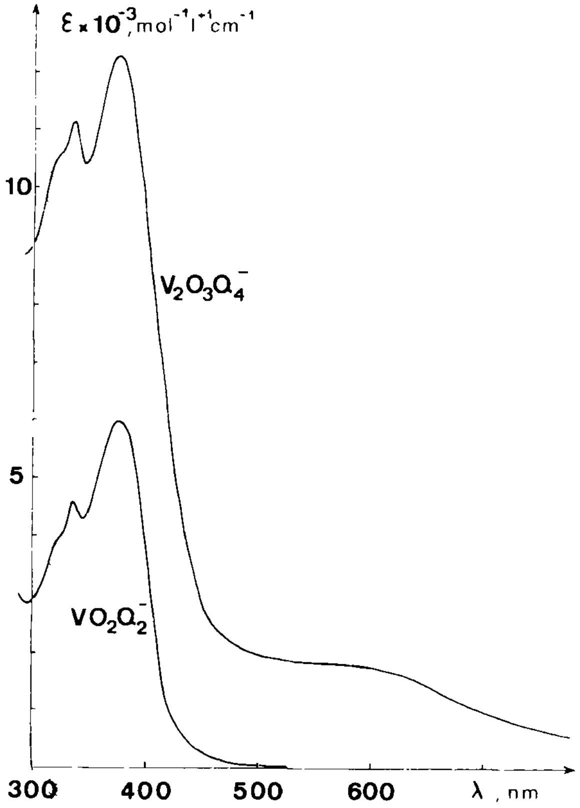


FIGURE 3 UV-visible spectra of $VO_2Q_2^-$ and $V_2O_3Q_4^-$. The latter has been obtained from the spectrum of a mixture of $VO_2Q_2^-$ and $V_2O_3Q_4^-$ after subtraction of the $VO_2Q_2^-$ absorption.

Synthesis of $V_2O_3Q_4^-$

The preparation of $V_2O_3Q_4^-$ involves the reaction of a vanadium(V) species with VOQ_2 and OH^- ions. The

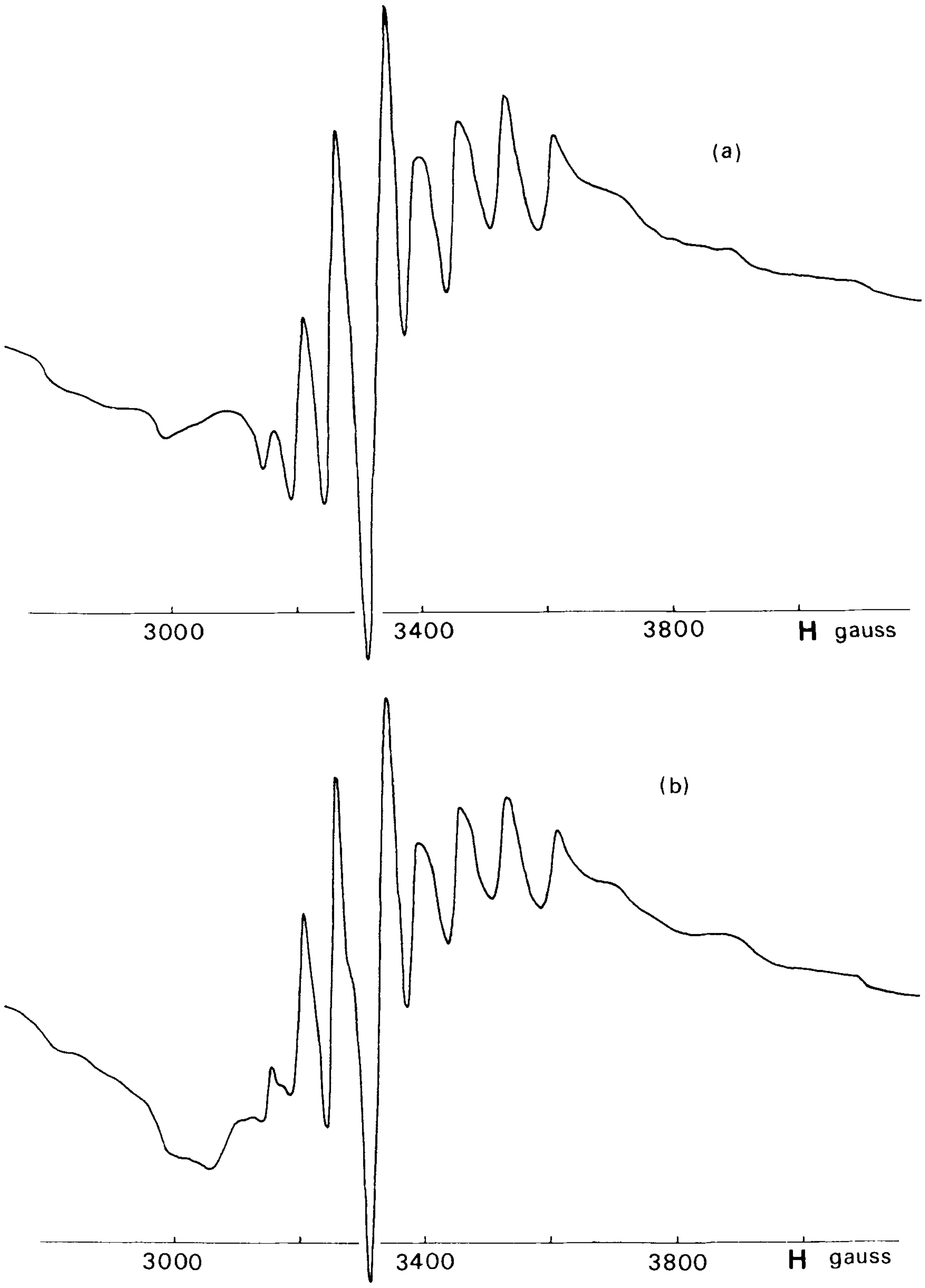


FIGURE 4 Powder ESR spectrum of $NBu_4^+V_2O_3Q_4^-$ at room temperature (a) and 100° C (b).

best results are obtained with the methyl ester $VO(OCH_3)Q_2$ as a source of vanadium(V). We have noticed that the ester alone reacts quickly with OH^- ions to yield the $VO_2Q_2^-$ ion. For instance a mixture of $VO(OCH_3)Q_2$ and acetonitrile, in which the former is incompletely soluble, rapidly turns yellow upon addition of tetrabutylammonium hydroxide and the dissolution of $VO(OCH_3)Q_2$ proceeds to completion. The UV spectrum shows the characteristic spectrum of $VO_2Q_2^-$, obtained through the saponification reaction:

$$VO(OCH_3)Q_2 + OH^- \rightarrow VO_2Q_2{}^- + CH_3OH$$

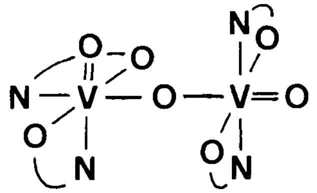
It is thus very likely that this reaction is the first step in the synthesis of $V_2O_3Q_4^-$, the second being the reaction of $VO_2Q_2^-$ on VOQ_2.

Reaction between $V^vO_2Q_2^-$ and $V^{iv}OQ_2$

A freshly prepared solution of $VO_2Q_2^-$ in acetonitrile does not display any polarographic wave in acetonitrile on a mercury electrode between +0.4 and −1.8 volts *vs* SCE. This is not surprising since the *cis* MO_2 structure implies that the three t_{2g} orbitals are extensively involved in π-bonding and thus acquire a considerable antibonding character. There is thus no low lying orbital available for an easy and reversible reduction.[17] The solution is yellow and its spectrum is given on Figure 3. There are two maxima at 375 and 335 nm and a shoulder near 320 nm.[18]

While VOQ_2 is almost insoluble in acetonitrile, it dissolves slowly in an acetonitrile solution of $VO_2Q_2^-$. The reaction is never complete but the formation of $V_2O_3Q_4^-$ is shown by polarography since this species exhibits a characteristic reversible anodic wave at 0.0 V *vs* SCE and a cathodic irreversible wave at −1.1 volts. This polarogram is identical to the one of the product prepared by our modification of Sawyer's method. The UV-visible spectrum also shows the formation of $V_2O_3Q_4^-$: a new band appears near 600 nm and the intensity of the UV bands increases markedly. Indeed $VO_2Q_2^-$ and $V_2O_3Q_4^-$ exhibit the same UV bands but the latter is characterized by higher extinction coefficients (Figure 3).

The most probable formation mechanism is a mere addition reaction, one of the oxo oxygens of $VO_2Q_2^-$ coordinating the sixth position of the VOQ_2 molecule. In the related $VO(MeQ)_2$ molecule (MeQ = 2 methyl-8-quinolinolate anion), it has been shown that the vacant position is trans to the oxo-group;[15] therefore we believe that the structure of $V_2O_3Q_4^-$ is very likely as follows:



It can be noticed that the interaction between the two d_{xy} orbitals (each one perpendicular to a V=O axis) is strictly zero in such a case. This would explain why no delocalization has been observed by Sawyer in the ESR of this compound in solution at room temperature. We have recorded the powder ESR spectrum of $NBu_4^+V_2O_3Q_4^-$ at temperatures up to 100°C and no delocalization was neither found; the spectrum presented the usual 8-line pattern of a mononuclear vanadium(IV) compound (Figure 4). By contrast the mixed valence $[(NTA)V^{iv}O{-}O{-}V^{v}\text{-}O(NTA)]^{3-}$ compound (NTA = nitrilotriacetate) prepared by Saito et al,[19] exhibits a 15-line ESR spectrum and an intervalence band at 1000 nm. In this latter case, the bridging oxygen atom is *cis* to both V=O groups, allowing the interaction between the two d_{xy} orbitals.

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