only carbonyl ligands, have been isolated is not due to energetic factors related to the electronic structure of the cluster itself but more probably to extra stabilization supplied by the solvation sphere or by the ionic lattice in the solid state. The anionic clusters gain in stability more than the neutral ones as the nuclearity increases, and this is probably the reason anionic clusters of only relatively high nuclearity have been successfully isolated.

The results concerning the two-atom contributions to the cluster stability are to be compared with other suggestions made on the basis of different approaches. In the review paper of Connor,[10] the thermochemical data for a series of iron and cobalt carbonyl clusters were analyzed and relations between the strength of different bonds within the cluster have been established. These relations, assumed to be valid also for other transition-metal clusters, may be summarized as follows: (a) the strength of the unique M–T bond and the sum of the two M–B bond strengths are similar; (b) the mean value of the energy of the M–L bond (L = T, B) is independent of the nuclearity; (c) the empirical relation M–M = 0.68(M–T) is assumed as approximately valid.

The experimental data available for nickel clusters are insufficient to obtain a set of relations similar to those presented above. Nevertheless, from the trend observed in ref 10, bond energy values for nickel compounds may be estimated to be as follows: M–T, 30–40 $\text{kcal}\cdot\text{mol}^{-1}$; M–B, 15–20 $\text{kcal}\cdot\text{mol}^{-1}$; M–M, 20–27 $\text{kcal}\cdot\text{mol}^{-1}$. On the basis of the results of Table VIII (and other results not reported here for brevity) the M–T and M–B values fall into ranges wider than those reported above and are dependent on the molecular charge and structure. Furthermore, our computed values for the M–M contributions are definitely smaller than those obtainable by extrapolation to the nickel case of the data of ref 10.

Another attempt to evaluate the M–M energy interaction has been made by Housecroft et al.[9] In this case the metal–metal interaction is smaller than in Connor's treatment but the qualitative description of the bond remains unaltered. In the approach of ref 9, it must be noted that an interaction potential of the type $E(\text{M–M}) = AR_{\text{M-M}}^{-k}$, where A and k are determined from length and strength of the bonds in the bulk metal, cannot be transferred to a molecular cluster without significant modifications. In particular, the analytical form of this potential is such that the contribution of the metal–metal interaction is always of bonding character, while when a more flexible potential is used (as is the INDO one, even if approximate), such terms may be either attractive or repulsive. Finally, the model of ref 9 seems to neglect every energy variation accompanying changes in coordination mode and valence configuration of the metal atoms. We have shown, on the contrary, that M–M interactions are strongly influenced by the particular geometric and electronic situation of each metal atom.

We note that the results of the present theoretical investigation are not in disagreement with those of other theoretical investigations,[5,6] in which the contribution of the direct M–M interaction is found to be much less important than that required by the usual qualitative arguments.

Moreover, in very recent X-ray diffraction studies, the presence of a strong metal–metal bond has not been confirmed for several cluster compounds of nickel,[21] cobalt,[22] and osmium.[23]

All these aspects considered, we feel that a more careful analysis of the commonly accepted concepts used in the description of the bonds within the clusters is in order.

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Notes

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Molecular Structure of (μ-Oxo)bis[oxobis(8-quinolinolato)vanadium(V)]

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The structural chemistry of vanadium(V), like that of the other early transition metals in higher oxidation state, is dominated by the presence of oxo complexes. However, oxo-bridged V(V) species are rare compared to those of Ti(IV), Mo(V), and Mo(VI), where binuclear species are found bridged by one or two oxo or oxygen ligands.[1,2]

Vanadium(V) reacts with 8-quinolinol (HQ) to give a 1:2 water-insoluble complex in weakly acidic media. It has been known that the black solution of this complex dissolved in organic solvents causes a pronounced color change in the presence of various types of substances by forming the corresponding monomeric derivatives.[3] Among them, the structures have been established crystallographically for a red isopropyl ester[4] and yellow sodium[5] and tetrabutylammonium[5,6] salts. On the other hand, for the black complex dried at about 130 °C, the conflicting formulas of $V_2O_3Q_4$[7,8] and $VO(OH)Q_2$[9–11] have been assigned from the elemental analysis. Extensive studies involving the black complex have been carried out with the monomeric composition assumed for this complex.[3,9–19]

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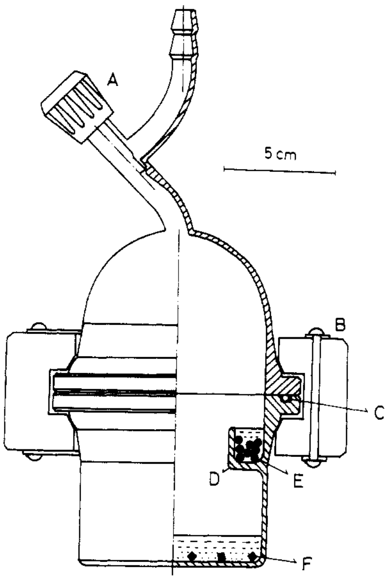

Figure 1. Schematic diagram of the crystallizer: A, stopcock (ROTAFLO-TF 2/13); B, chain-type clamp; C, Teflon O-ring; D, inner cylinder; E, raw crystal; F, single crystal.

Table I. Crystal Data for $(VOQ_2)_2O$

mol formula	$C_{36}H_{24}N_4O_7V_2$
mol wt	726.45
cryst dimens, mm	0.31 × 0.08 × 0.01
cryst system	monoclinic
space group	*C*2/*c*[a]
cell consts	
a, Å	25.034 (5)
b, Å	9.674 (3)
c, Å	14.003 (6)
β, deg	112.03 (2)
V, Å³	3144 (3)
cell const determn	10 reflcns, 60 < 2*θ* < 80°
Z	4
ρ_{calcd}, g cm^{-3}	1.54
ρ_{measd}, g cm^{-3}	1.53 by flotation in CCl_4/C_6H_5Cl
temp, °C	20 ± 2
μ, cm^{-1}	53.5

[a] Successful refinement shows that this monoclinic cell belongs to space group *C*2/*c*.

Recently we have revealed[20-22] this complex to be the oxo-bridged dimer, VOQ_2–O–VOQ_2. Though such a dimeric vanadium(V) 8-quinolinolate complex has been postulated previously,[5,11,16,18] solution equilibria, reactivity, and structural characterization of this dimeric complex have not been investigated, except for the dissociation equilibrium into 1:1 monomeric species in chlorobenzene[22] and the kinetics and equilibria of the esterification with butyl alcohols.[23] In this paper we present the first single-crystal X-ray diffraction study on a *μ*-oxo dimeric vanadium(V) complex.

Experimental Section

(*μ*-Oxo)bis[oxobis(8-quinolinolato)vanadium(V)], $[VO(C_9H_6NO)_2]_2O$, was prepared according to the method of Blair et al.[11]. Chlorobenzene, 8-quinolinol, and ammonium metavanadate were purified as described previously.[20,21]

Table II. Data Collection and Refinement Details for $(VOQ_2)_2O$

diffractometer	Rigaku AFC-5
monochromator	graphite
reflcns measd	$\pm h, +k, +l$
radiation (λ, Å)	Cu K*α* (1.54178)
scan type	ω–2θ
scan width, deg	$1.0 + 0.142 \tan\theta$
scan speed, deg min^{-1}	3.0
bkgd time, s	10 × 2
std reflcns	(10,0,2), (12,0,0), $(\bar{2}42)$
standardizn period, h	3
2*θ* range, deg	$0 \leqslant 2\theta \leqslant 126$
range of transmission factors	0.05–1.7
no. of data collected	2854
no. of data used in final refinement	1707, with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$
no. of variables	223
$R_1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.075
$R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.072, with $w = 1/\sigma^2(F_o)$

Table III. Positional Parameters for $(VOQ_2)_2O$

atom	*x*	*y*	*z*
V(1)	0.4300 (1)	0.3649 (1)	0.1518 (1)
O(3)	0.5000	0.3542 (8)	0.2500
O(2)	0.4247 (3)	0.2354 (6)	0.0792 (5)
O(1)	0.4410 (2)	0.4879 (5)	0.0557 (4)
N(1)	0.4239 (2)	0.5806 (6)	0.2179 (5)
C(2)	0.4182 (3)	0.6240 (11)	0.3016 (7)
C(3)	0.4186 (4)	0.7647 (12)	0.3295 (8)
C(4)	0.4209 (4)	0.8606 (12)	0.2586 (9)
C(5)	0.4362 (4)	0.9067 (9)	0.0892 (9)
C(6)	0.4445 (4)	0.8537 (11)	0.0070 (9)
C(7)	0.4471 (4)	0.7135 (9)	−0.0064 (7)
C(8)	0.4400 (3)	0.6267 (8)	0.0663 (6)
C(9)	0.4304 (3)	0.6781 (8)	0.1528 (7)
C(10)	0.4284 (4)	0.8224 (8)	0.1694 (8)
O(1′)	0.3960 (2)	0.2946 (6)	0.2447 (5)
N(1′)	0.3382 (3)	0.4150 (7)	0.0728 (5)
C(2′)	0.3117 (4)	0.4765 (10)	−0.0148 (7)
C(3′)	0.2516 (4)	0.4975 (11)	−0.0539 (9)
C(4′)	0.2199 (4)	0.4491 (12)	−0.0004 (9)
C(5′)	0.2191 (4)	0.3242 (14)	0.1533 (9)
C(6′)	0.2506 (5)	0.2606 (14)	0.2419 (10)
C(7′)	0.3112 (4)	0.2434 (12)	0.2793 (8)
C(8′)	0.3392 (4)	0.3013 (10)	0.2189 (7)
C(9′)	0.3073 (3)	0.3662 (9)	0.1278 (6)
C(10′)	0.2473 (4)	0.3809 (11)	0.0929 (8)

Crystal Growth of $(VOQ_2)_2O$. A closed-system evaporation crystallizer[24] transferring the material from a solid source to a solution has been developed for growing single crystals of the black complex (Figure 1). The recycle of chlorobenzene for 4 weeks under reduced pressure and at about 70 °C enabled us to obtain flaky single crystals suitable for X-ray analysis.

X-ray Crystallography. The refined cell constants and other pertinent crystal data and the routine aspects of data collection are presented in Tables I and II, respectively. Statistical analysis of the standard reflections indicated that there was no crystal decomposition during 40-h radiation. The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu\bar{r} = 0.3$) and extinction.

The structure was solved by using MULTAN[25] and refined by the block-diagonal least-squares procedure with the function minimized being $\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2$. The refined parameters included anisotropic thermal parameters for the non-hydrogen atoms.[26] During refinement hydrogen atoms were included in precalculated positions (C–H bond distance 1.0 Å) with $B = 7.0$ Å^2 and were not refined.[27] Drawing

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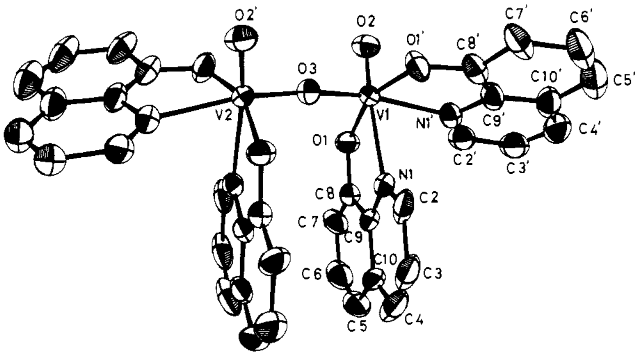

Figure 2. Molecular structure of $(VOQ_2)_2O$ (ORTEP 30% probability ellipsoids).

Table IV. Selected Bond Distances and Bond Angles for $(VOQ_2)_2O$

(a) Distances, Å			
V(1)-O(2)	1.587 (6)	V(1)-N(1)	2.310 (6)
V(1)-O(3)	1.779 (2)	V(1)-O(1′)	1.925 (6)
V(1)-O(1)	1.893 (6)	V(1)-N(1′)	2.199 (7)
(b) Angles, deg			
O(1)-V(1)-O(1′)	157.2 (3)	O(3)-V(1)-O(1)	102.8 (3)
O(2)-V(1)-O(1′)	92.3 (3)	O(3)-V(1)-O(1′)	90.8 (2)
O(2)-V(1)-O(1′)	101.7 (3)	V(1)-O(3)-V(2)	173.4 (4)
O(3)-V(1)-O(2)	105.7 (3)		

of the molecular structure was made with the use of ORTEP-II.[28] The final positional parameters for the non-hydrogen atoms, together with their estimated standard deviations, are listed in Table III. The final thermal parameters for the non-hydrogen atoms and the observed and calculated structure factor amplitudes are listed in Tables SI and SII, respectively (supplementary material).

Results and Discussion

The dimeric molecule was found to lie on a 2-fold axis (crystallographically imposed, at $^1/_2, y, ^1/_4$), which coincides with the center point of the V(1)-O(3)-V(2) linkage. The two VOQ_2 units are therefore crystallographically equivalent. The molecular structure and the atomic labeling scheme are illustrated in Figure 2. Selected intramolecular distances and interatomic angles with their estimated standard deviations are presented in Table IV. Additional bond distances and angles (Table SIII) are available as supplementary material.

The distorted octahedral six-coordination around the vanadium atom in a VO_2Q_2 unit is completed by the terminal oxygen atom, the oxygen atom bridging two vanadium atoms, and the two nitrogen and the two oxygen atoms of 8-quinolinolate. As expected,[4-6,29,30] the two nitrogen atoms are coordinated trans to the terminal and the bridging oxygen atoms, and these two oxygen atoms are in the cis configuration. The O(2)-V(1)-O(3) angle of 105.7 (3)° is close to that found for the yellow salts (105.4-106.1°),[5,6] but it is slightly larger than for the red ester (101.9°). In the yellow salts, the VO_2 group is found to occur as an ion pair (sodium salt) or a free anion (tetrabutylammonium salt), whereas in the red ester and the μ-oxo dimer, the VO_2 group is covalently bonded to the isopropyl group and the other VOQ_2 unit via the bridging oxygen atom, respectively. This suggests that the O-V-O angle in a VO_2Q_2 unit would not be affected by the ionic character of the VO_2 group. The terminal oxygen-vanadium bond distance is 1.587 (6) Å and thus has a strong double-bond character. This value is quite close to that reported for the isopropyl ester and somewhat shorter than the 1.62-1.66 Å range found for the other VO_2 complexes with the same coordination geometry.[4-6,29,30] The bridging oxygen-vanadium bond distance of 1.779 (2) Å is comparable to the 1.774 (2) Å vanadium-isopropoxy oxygen distance in the isopropyl ester[4] and the 1.76 Å average vanadium-methoxy oxygen distance in $VO(OCH_3)_3$.[31]

As a result of the structural trans effect exerted by the two types of oxygen atoms present in the VO_2 group, the two V-N bond distances are significantly different. The V-N bond distances trans to the terminal oxygen and trans to the bridging oxygen are 2.310 (6) and 2.199 (7) Å, respectively. This characteristic structural pattern, also found in the isopropyl ester, is correlated with the difference in electron-donating properties between the terminal and the bridging oxygen atoms.

The average bond distance between 8-quinolinol oxygen and vanadium increases in the order μ-oxo dimer ~ isopropyl ester < sodium salt < tetrabutylammonium salt. The same trend is observed in the average bond distance between 8-quinolinol nitrogen and vanadium, and it is most likely attributable to the decrease of formal charge on the vanadium center.

When the unsymmetrically bidentate 8-quinolinolate ligands are allowed to chelate the remaining coordination site on the V_2O_3 framework, there should be many possible isomers. However, the basic pattern of the coordination group, the nitrogen atoms of the 8-quinolinolate ligands being expected to be trans to the oxo groups, appears to rather completely specify the way in which the remaining coordination sites on the V_2O_3 framework will be used. What is yet to be specified is the relative orientations of the two corner-shared octahedra. Examination of Figure 2 along with the listing in Table SIV (supplementary material) of the atomic displacements of the important planes in the molecule shows that the complex has the skewed cis-directed terminal oxygens in which the dihedral angle formed by the O(2), V(1), O(3) and O(3), V(2), O(2′) planes is 66.1°. In the complex, the maximum deviation of an atom from the least-squares planes of the chelated 8-quinolinolate is 0.07 Å and one pair of these ligands adopts a parallel arrangement with the dihedral angle of 0.5° and the mean separation of 3.35 Å. The geometry adopted here results in appreciable ligand overlap in which, when viewed normal to the plane through one of the ligands, C(2) and C(8) lie upon C(8) and C(2) of the other 8-quinolinolate chelated to V(2), respectively. This would suggest that the aromatic interaction between these quinoline rings favors this configuration.

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Note Added in Proof. After the submission of the present paper the attention of the authors was drawn to structural studies on (μ-oxo)bis[oxobis(*N,N*-dimethylhydroxylamino)vanadium(V)]: Saussine, L.; Mimoun, H.; Mitschler, A.; Fisher, J. *Nouv. J. Chim.* **1980**, *4*, 253-7.

Registry No. $(VOQ_2)_2O$, 70748-61-7.

Supplementary Material Available: Listings of anisotropic thermal parameters for the non-hydrogen atoms (Table SI), observed and calculated structure factor amplitudes (Table SII), molecular dimensions not included in Table IV (Table SIII), atomic displacements from selected least-squares mean planes (Table SIV), and positional parameters for the hydrogen atoms (Table SV) and stereoscopic views of the molecule (Figure S1) and the unit cell (Figure S2) (15 pages). Ordering information is given on any current masthead page.

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