geometries involve equatorial methyl substituents and *lel* conformations, just as was found in the structure of isomer (F) (Searle & Tiekink, 1989). These stereochemical arrangements generally give lower-energy structures in cobalt(III) complexes with pn, meen and en (pn is propane-1,2-diamine), although some instances of axial methyls and *ob* conformations have been found in $[Co(meen)_3]^{3+}$ complexes (Searle & Tiekink, 1989).

There are several significant interionic contacts in the crystal lattice arising from numerous potential hydrogen-bonding sites and a brief description of these follows. The perchlorate group with Cl(1) makes close contact with the amine groups $N(11)H_2$ and $N(13)H_2$ of cation (1). The second perchlorate makes three contacts with amines $N(21)H_2$, $N(22)H_2$ and $N(25)H_2$ of cation (2) and makes a fourth contact with a solvent water molecule, $H_2O(w1)$. The chlorides Cl(1), Cl(2), Cl(3) and Cl(4) make three, four, two and two contacts respectively in the lattice. The two solvent water molecules are involved in four and two significant contacts respectively.

Support from the Australian Research Grants Scheme is acknowledged.

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Structure of Hydrogen Bis(2-methyl-8-quinolinolato)dioxovanadate(V)

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Abstract. $H[V(C_{10}H_8NO)_2O_2].3H_2O$, $M_r = 454{\cdot}4$, monoclinic, $P2_1/c$, $a = 8{\cdot}544\,(1)$, $b = 22{\cdot}401\,(2)$, $c = 11{\cdot}488\,(1)$ Å, $\beta = 109{\cdot}95\,(1)^\circ$, $V = 2066{\cdot}7\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}470$, $D_x = 1{\cdot}460$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 46{\cdot}5$ cm^{-1}, $F(000) = 944$, $T = 298$ K, $R = 0{\cdot}068$ for 2823 observed reflections. The title compound is yellowish and has a monomeric structure, in contrast with the dimeric structure of μ-oxo-bis[oxobis(8-quinolinolato)vanadium(V)], which is black in color. The V atom is in a five-coordinate distorted trigonal-bipyramidal environment, where two vanadyl O atoms and an O atom from the chelating ligand define the equatorial plane. The N atom of the other methylquinolinol is not coordinated toV^V but protonated.

Introduction. The black color of vanadium(V) 8-quinolinolate has been considered a mysterious phenomenon, since most other metal complexes of this ligand are yellow in color except for the black iron(III) complex (Borrel & Pâris, 1950; Bielig & Bayer, 1953; Hollingshead, 1956). This question was clearly resolved by X-ray crystallography demonstrating that the vanadium(V) complex is an oxo-bridged dimer (Yamada, Katayama, Tanaka & Tanaka, 1984), which is quite consistent with the presence of dimeric species in non-aqueous solutions as proved by the solvent extraction technique (Yuchi, Yamada & Tanaka, 1980). Methyl substitution at the 2-position, however, leads to a yellowish vanadium(V) compound, which is quite sparingly soluble in both aqueous and non-aqueous solvents. The present study aims to determine the structure of the 2-methyl-8-quinolinolate complex and to explain the different colors of these homologs.

Experimental. Yellowish transparent crystals grown from an acetone solution containing only a little

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water in a crystallizer similar to that already described (Yamada *et al.*, 1984). Elemental analysis: (calc. for $C_{20}H_{23}N_2O_7V$) C 52·87, N 6·17, H 5·10%; (found) C 52·53, N 6·13, H 5·06%. Crystal of dimensions 0·35 × 0·15 × 0·10 mm used. D_m by flotation in $C_6H_{12}/C_2H_2Br_4$. Rigaku AFC-5R diffractometer, graphite-monochromated Cu $K\alpha$. Cell dimensions from 2θ for 25 reflections ($40 < 2\theta \leq 45°$). Intensities measured up to $2\theta = 130°$ with h 0/10, k −26/0, l −13/12. $R_{\text{int}} = 0·029$. Three standard reflections monitored after every 100 scans, no variation in intensity. Total of 3510 unique reflections measured. Absorption corrections for ψ scans, relative absorption coefficients 0·835–0·996. Structure solved by the heavy-atom method. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least-squares technique. H atoms located on a difference density map. Temperature factor of each H atom set to B_{eq} of the bonded atom. $\sum(w|\Delta F|^2)$ minimized, $w = [\sigma^2(F_o) + 0·00448\ |F_o|^2]^{-1}$ for reflections with $w^{1/2}|F_o| > 3$ and $w^{1/2}|\Delta F| < 3$, $w = 0$ otherwise. Final $R = 0·068$, $wR = 0·093$, $S = 1·163$ for 2823 observed reflections with $|F_o| > 3\sigma(F_o)$. No significant peaks in final difference map, $\Delta\rho_{\max} = 0·45$ e Å^{-3}. $(\Delta/\sigma)_{\max} = 0·24$. Atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ ($i = 1,...,4$) (*International Tables for X-ray Crystallography*, 1974). Calculations performed on Facom M340R computer at Shionogi Research Laboratories with programs *XPACK*.

Discussion. Atomic coordinates and equivalent isotropic temperature factors of non-H atoms are given in Table 1.* Bond lengths and angles are listed in Table 2. The numbering system and the molecular structure appear in Fig. 1, where the unidentate ligand has primed labels. The crystal structure consists of a three-dimensional hydrogen-bonded network, as shown in Fig. 2. Figures were drawn with the aid of the program *PLUTO* (Motherwell & Clegg, 1978).

The most interesting finding in this study may be the monomeric structure of the complex, making a striking contrast with the dimeric skeleton of the vanadium(V)–8-quinolinolate complex (Yamada *et al.*, 1984). In the latter complex, the two V^V ions are bridged by one O atom, are chelated with two bidentate ligands, have a V═O bond, and are in a

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10) *with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
V	8931·6 (8)	1704·7 (3)	810·9 (6)	29·5 (2)
N(1)	11395 (4)	2098 (2)	1155 (3)	35 (1)
C(2)	11786 (7)	2567 (2)	609 (5)	47 (2)
C(3)	13459 (8)	2771 (2)	982 (6)	60 (2)
C(4)	14665 (7)	2485 (3)	1902 (6)	62 (2)
C(5)	15397 (6)	1635 (3)	3448 (5)	58 (2)
C(6)	14872 (6)	1147 (3)	3919 (4)	54 (2)
C(7)	13177 (6)	970 (2)	3463 (4)	43 (1)
C(8)	12050 (5)	1295 (2)	2554 (3)	32 (1)
C(9)	12596 (5)	1805 (2)	2071 (4)	34 (1)
C(10)	14283 (6)	1979 (2)	2495 (5)	47 (2)
C(11)	10450 (8)	2889 (2)	−405 (6)	62 (2)
O(12)	10421 (3)	1180 (1)	2067 (2)	35 (1)
N(1′)	5684 (5)	301 (2)	1788 (3)	39 (1)
C(2′)	4946 (7)	−142 (2)	2169 (5)	53 (2)
C(3′)	3289 (8)	−273 (3)	1520 (6)	69 (2)
C(4′)	2421 (7)	57 (3)	561 (7)	73 (2)
C(5′)	2265 (6)	945 (3)	−760 (6)	68 (2)
C(6′)	3066 (7)	1418 (3)	−1078 (5)	65 (2)
C(7′)	4770 (6)	1511 (2)	−456 (4)	48 (2)
C(8′)	5698 (5)	1137 (2)	477 (4)	34 (1)
C(9′)	4839 (5)	668 (2)	818 (4)	36 (1)
C(10′)	3111 (5)	563 (2)	175 (5)	49 (2)
C(11′)	5983 (10)	−491 (3)	3290 (5)	68 (2)
O(12′)	7311 (3)	1172 (1)	1081 (2)	35 (1)
O(13)	8188 (4)	2345 (1)	1028 (3)	47 (1)
O(14)	8557 (4)	1610 (2)	−660 (3)	48 (1)
O(15)	8993 (4)	414 (1)	3307 (3)	47 (1)
O(16)	8881 (7)	519 (2)	5744 (4)	79 (2)
O(17)	8180 (8)	1503 (2)	6880 (4)	80 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

V—N(1)	2·189 (5)	V—O(12)	1·957 (3)
V—O(12′)	1·932 (3)	V—O(13)	1·622 (4)
V—O(14)	1·623 (5)		

	Unprimed	Primed		Unprimed	Primed
N(1)—C(2)	1·324 (7)	1·328 (7)	C(5)—C(10)	1·410 (9)	1·371 (9)
N(1)—C(9)	1·362 (6)	1·375 (6)	C(6)—C(7)	1·418 (8)	1·401 (8)
C(2)—C(3)	1·420 (9)	1·388 (9)	C(7)—C(8)	1·364 (7)	1·378 (7)
C(2)—C(11)	1·508 (9)	1·509 (10)	C(8)—C(9)	1·417 (6)	1·411 (6)
C(3)—C(4)	1·359 (10)	1·324 (11)	C(8)—O(12)	1.336 (5)	1·317 (5)
C(4)—C(10)	1·417 (9)	1·417 (10)	C(9)—C(10)	1·410 (7)	1·427 (7)
C(5)—C(6)	1·362 (10)	1·377 (10)			

N(1)—V—O(12)	76·4 (1)	N(1)—V—O(12′)	156·5 (2)
N(1)—V—O(13)	91·1 (2)	N(1)—V—O(14)	94·4 (2)
O(12)—V—O(12′)	80·3 (1)	O(12)—V—O(13)	127·4 (2)
O(12)—V—O(14)	122·5 (2)	O(12′)—V—O(13)	100·5 (2)
O(12′)—V—O(14)	100·9 (2)	O(13)—V—O(14)	109·1 (2)

	Unprimed	Primed
V—N(1)—C(2)	128·1 (4)	
V—N(1)—C(9)	111·7 (3)	
C(2)—N(1)—C(9)	120·2 (5)	122·5 (5)
N(1)—C(2)—C(3)	120·2 (6)	119·5 (6)
N(1)—C(2)—C(11)	119·9 (5)	117·5 (6)
C(3)—C(2)—C(11)	119·9 (6)	122·9 (6)
C(2)—C(3)—C(4)	120·1 (6)	120·5 (7)
C(3)—C(4)—C(10)	120·9 (6)	122·2 (7)
C(6)—C(5)—C(10)	121·4 (6)	120·8 (6)
C(5)—C(6)—C(7)	120·7 (6)	120·2 (6)
C(6)—C(7)—C(8)	119·9 (5)	121·9 (5)
C(7)—C(8)—C(9)	119·3 (4)	116·9 (4)
C(7)—C(8)—O(12)	125·4 (4)	126·5 (4)
C(9)—C(8)—O(12)	115·3 (4)	116·6 (4)
N(1)—C(9)—C(8)	115·4 (4)	119·4 (4)
N(1)—C(9)—C(10)	123·1 (4)	119·0 (4)
C(8)—C(9)—C(10)	121·5 (4)	121·5 (4)
C(4)—C(10)—C(5)	127·3 (6)	125·5 (6)
C(4)—C(10)—C(9)	115·5 (5)	115·9 (5)
C(5)—C(10)—C(9)	117·2 (5)	118·6 (5)
V—O(12)—C(8)	121·0 (3)	129·1 (3)

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* Lists of structure factors, anisotropic temperature factors of non-H atoms, atomic coordinates and isotropic temperature factors of the H atoms and a stereoview of the molecular packing have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51864 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pseudo-OH environment. On the other hand, the methyl-substituted ligand offers a five-coordinate environment around the central metal ion, and an N atom from one ligand is not coordinated and is protonated. These differences may well explain the different coloration between the two vanadium(V) complexes.

Several authors have assumed the chemical formula of $VO(OH)(C_9H_5CH_3NO)_2$ which is consistent with the present results (Borrel & Pâris, 1951), but none has been able to assign the position of the proton. In this respect the dissociation of the N atom seems rather peculiar, even allowing for the general affinity of vanadium toward oxygen. Dreiding models, however, exclude the octahedral structure owing to the steric hindrance of the methyl group, which should make the nitrogen dissociation more favorable in this compound. Nakamura, Shimura & Tsuchida (1961) concluded from IR and UV evidence that V^V ions are bound only to oxygen donors of 2-methyl-8-quinolinol in the solid state, whereas Amos & Sawyer (1974) stated that there apparently is no, or extremely little, metal–nitrogen bonding in the Mo^{VI} and V^V chelates with the 2-methyl derivative in Me_2SO. These findings are consistent, at least partially, with the presence of uni- and bidentate ligands in the complex as shown in this study.

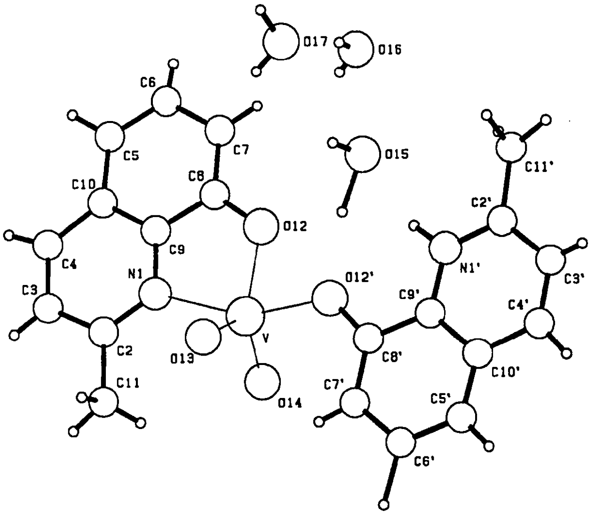

Fig. 1. A perspective view of the molecular structure of hydrogen bis(2-methyl-8-quinolinolato)dioxovanadate(V). The unidentate ligand has primed atom labels.

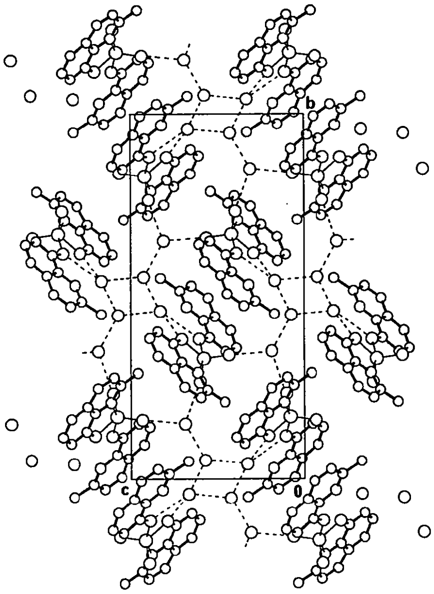

Fig. 2. Crystal structure of hydrogen bis(2-methyl-8-quinolinolato)dioxovanadate(V), viewed down the *a* axis. Dotted lines indicate hydrogen bonds.

The molecular structure of an isopropyl ester of V^V–8-quinolinolate has been proved to have a quasi-octahedral environment by X-ray crystallography (Scheidt, 1973), while the trigonal bipyramid has already been found for a 2-methyl-8-quinolinolate compound with quadrivalent vanadium, $[VO(C_{10}H_8NO)_2]$ (Shiro & Fernando, 1971*a*,*b*). In the latter complex the three O atoms are in the equatorial plane and the two N-atom donors occupy the apical positions. For the present vanadium(V) complex, the donors O(12), O(13) and O(14) define the equatorial plane, while the O atom from the unidentate ligand O(12′) and the N-atom donor occupy the apical positions of the quasi-trigonal bipyramid. The central V atom is only slightly above the equatorial plane, *i.e.* 0·099 (1) Å from it toward O(12′). O(12′) is 1·984 Å above and N(1) 2·051 (4) Å below the plane.

The protonated and dissociated N(1′) atom participates in the intermolecular hydrogen bonding, with a bond length to O(15) of water of 2·781 (6) Å. This water molecule forms a multiply-H-bonded network, with O(15)—H···O(12) 2·766 (4), O(15)—H···O(12′) 2·997 (4), O(15)—H′···O(16) 2·843 (7), O(15)···H—O(16^{i}) 2·740 (7) Å. Other H bonds are O(16)—H′···O(17) 2·730 (9), O(17)—H···O(14^{ii}) 2·743 (8) Å, and O(17)—H′···O(13^{iii}) 2·761 (8) Å [(i) $2-x$, $-y$, $1-z$; (ii) x, y, $1+z$; (iii) x, $1/2-y$, $1/2+z$].

Recrystallization of the 2-methyl-8-quinolinol complex from water has not been successful in obtaining a crystal suitable for structure determination because of insufficient solubility. The specially made crystallizer alone permitted dissolution of the solid in an organic solvent to supersaturation, although otherwise the complex is not readily soluble. Thus acetone and dimethyl sulfoxide gave amber-colored solutions, but the yellowish crystals of reasonable size appeared only in the presence of a certain quantity of water. Hence, water molecules seem to play an important role in crystallization of this monomeric complex, which is consistent with the transition to the dimer on loss of water molecules, as shown by thermogravimetric studies (Borrel & Pâris, 1951; Yuchi *et al.*, 1980).

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The Structure of Acetylarsenocholine Bromide*

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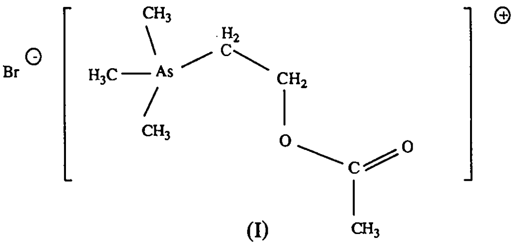
Abstract. $[C_7H_{16}AsO_2]^+.Br^-$, $M_r = 287{\cdot}03$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}121$ (3), $b = 11{\cdot}745$ (2), $c = 9{\cdot}530$ (1) Å, $V = 1132{\cdot}8$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}682$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6{\cdot}86$ mm^{-1}, $F(000) = 568$, $T = 296$ K, $R = 0{\cdot}034$ for 919 observed reflections. Crystalline acetylarsenocholine bromide exists in the *trans–gauche* conformation which is similar to the solution conformation of acetylcholine. The cationic structure is compared with known crystalline acetylcholine salts. In the crystal structure, each Br^- ion appears to link the arsonium ends of four cations.

Introduction. Recent innovations in nuclear medicine imaging using tomographic techniques have shown that regional brain metabolism and biochemical function can be studied *in vivo*. Therefore the structural properties of various molecules active in the neuromuscular system have been studied. Acetylcholine, the natural intercellular transmitter substance in most intercellular peripheral nervous junctions, stimulates both muscarinic and nicotinic receptor sites. The title compound (I) is an acetylcholine analog which demonstrates preferential affinity for muscarinic receptors over nicotinic receptors. The determination of the active conformation of acetylcholine in the muscarinic receptor of the parasympathetic and central nervous systems is an ongoing problem in neurochemical research. Numerous crystal structures have been completed by various researchers on acetylcholine salts, analogs and derivatives in an effort to discover which of the several stable conformers was most commonly associated with pharmacological activity and from which the active conformation could be inferred.

A crystallographic study of the title compound, (I), was undertaken in an effort to learn more about the structural features which lead to muscarinic activity of an acetylcholine-like molecule.



(I)

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* Trimethyl-2-(acetoxy)ethylarsonium bromide.

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