Data collection

Siemens CCD area-detector diffractometer	2884 reflections with $I > 2\sigma(I)$
ω rotation scans with narrow frame	$R_{int} = 0.075$
Absorption correction:	$\theta_{max} = 27.53°$
SADABS (Sheldrick, 1996)	$h = -28 \rightarrow 28$
$T_{min} = 0.515$, $T_{max} = 0.839$	$k = -12 \rightarrow 11$
23 897 measured reflections	$l = -25 \rightarrow 16$
4627 independent reflections	Intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R(F) = 0.056$	$\Delta\rho_{max} = 1.048$ e Å^{-3}
$wR(F^2) = 0.150$	$\Delta\rho_{min} = -0.418$ e Å^{-3}
$S = 1.088$	Extinction correction: none
4627 reflections	Scattering factors from
208 parameters	*International Tables for*
H atoms: see below	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

Ti1—O3	1.784 (2)	Ti1—O4	1.938 (2)
Ti1—O2	1.793 (2)	Ti1—O4'	2.117 (2)
Ti1—O1	1.812 (2)		
O3—Ti1—O2	99.59 (10)	O1—Ti1—O4	126.35 (10)
O3—Ti1—O1	97.58 (10)	O3—Ti1—O4'	168.38 (9)
O2—Ti1—O1	111.85 (11)	O2—Ti1—O4'	88.26 (9)
O3—Ti1—O4	96.72 (9)	O1—Ti1—O4'	87.29 (9)
O2—Ti1—O4	116.18 (9)	O4—Ti1—O4'	72.01 (8)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 10 s exposure. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at $\varphi = 0, 90$ and $180°$, with the area detector held at $2\theta = -29°$. The crystal-to-detector distance was 4.974 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed. H atoms were included in the model in idealized sp^2 or sp^3 geometries, riding on their attached C atom.

Data collection: *SMART* (Siemens, 1995b). Cell refinement: *SAINT* (Siemens, 1995b). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995a). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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[N,N'-Ethylenebis(3-*tert*-butyl-5-methyl-salicylideneaminato)]oxovanadium(IV)†

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Abstract

[VO($C_{26}H_{34}N_2O_2$)] was synthesized in order to study its reactivity in the oxygen-transfer catalysis of alkyl hydroperoxides to a wide array of substituted olefins. The geometry about the V center is nearly square pyramidal, with an axial oxo ligand and a four-coordinate substituted Schiff base ligand. The axial V—O bond distance of 1.592 (3) Å is indicative of double-bond character.

Comment

The crystal structure of the title compound, (I), is formed by essentially discrete molecules with only one intermolecular interaction between any two molecules.

(I)
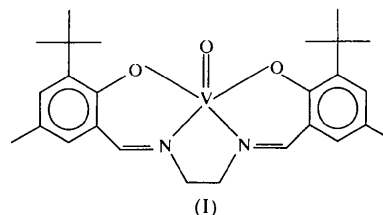
The unique molecule contains a central V atom, which exhibits square-pyramidal coordination where the phenolate O atoms and the imino N atoms are *cis* due to geometrical constraints of the backbone ligand (Fig. 1). The axial V=O bond is essentially perpendicu-

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† Alternative name: {6,6'-di-*tert*-butyl-2,2'-[1,2-ethanediylbis(nitrilomethylidyne-*N*)]-4,4'-dimethyldiphenolato-*O,O'*}oxovanadium(IV).

lar [89.2 (3)°] to the plane formed by the N and O ligand atoms of the backbone. The V atom sits 0.62 (1) Å above the least-squares basal plane of the four coordinating atoms. The axial V=O bond distance of 1.592 (3) Å is typical of bonds exhibiting double-bond character, and correlates well with its observed stretching frequency in the IR at 990 cm^{-1}. V=O distances range from 1.587 (1) to 1.595 (5) Å in the parent OV(salen) complex (Riley et al., 1986), in [N,N'-ethylenebis(3-ethoxysalicylideneaminato)]oxovanadium(IV) (Zamian et al., 1995), and in [N,N'-bis(3-methoxysalicylidene)-cyclohexane-1,2-diaminato]oxovanadium(IV) (Schmidt et al., 1996). The basal-plane V—O and V—N bond distances given in Table 1 are also within the ranges reported previously [1.921 (1)–1.938 (2) and 2.036 (6)–2.060 (2) Å, respectively; Riley et al., 1986; Zamian et al., 1995; Schmidt et al., 1996]. No unusual bond distances are observed in the salen-derivative backbone of the title compound; average distances and angles include: phenyl C—C = 1.40 (2) Å, phenyl C—C—C = 120 (3)°, tert-butyl C—C = 1.53 (1) Å, tert-butyl C—C—C = 109 (2)°, C—O = 1.32 (1) Å, C—N = 1.479 (6) Å, C=N = 1.281 (5) Å and ethylenediamine C—C = 1.490 (7) Å. These values are within the expected ranges for coordinated salen derivatives (Riley et al., 1986; Zamian et al., 1995; Schmidt et al., 1996).
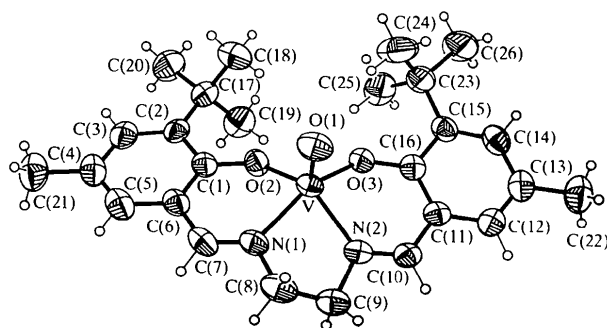

Fig. 1. View of the molecular unit of (I). Displacement ellipsoids are shown at the 60% probability level and H atoms are shown as small spheres.

The packing of molecules of (I) results in only one intermolecular interaction under 3 Å. A distance of 2.55 (1) Å is observed between the axial O(1) atom and H(8), which is bound to C(10) of a symmetry-related molecule at (2 − x, 2 − y, 1 − z). This interaction appears to be weak or negligible since no significant change is observed in the axial V=O bond distance.

Experimental

Single crystals of (I) were obtained from the reaction of vanadyl acetylacetonate (281 mg, 1.06 mmol), dissolved in 50 ml of methylene chloride to make a 5–6% solution, with salen. This aqua-colored solution was stirred at room temperature for 30 min prior to addition of the salen ligand. The previously synthesized vanadyl (o-tert-butyl-p-methylsalicylaldehyde)ethylenediamine ligand (500 mg, 1.06 mmol) was dissolved in 50 ml of methylene chloride to give a brilliant yellow solution, and was subsequently added slowly to the vanadium solution. The resulting solution turned green and was stirred at room temperature for 2 h under an inert argon atmosphere. The solvent was pumped off to yield a crude green crusty powder. This crusty powder was redissolved in 5 ml of methylene chloride, layered with 80 ml of petroleum ether, and stored at 273 K overnight. Suitable crystals were obtained after two similar recrystallizations and were finally isolated by filtration.

Crystal data

Table 1. Selected geometric parameters (Å, °)

V—O(1)	1.592 (3)	V—N(1)	2.056 (4)
V—O(2)	1.919 (3)	V—N(2)	2.061 (4)
V—O(3)	1.929 (3)		
O(1)—V—O(2)	113.3 (2)	O(2)—V—N(1)	85.7 (1)
O(1)—V—O(3)	105.5 (1)	O(2)—V—N(2)	135.4 (1)
O(1)—V—N(1)	103.1 (2)	O(3)—V—N(1)	150.7 (1)
O(1)—V—N(2)	110.7 (2)	O(3)—V—N(2)	86.1 (1)
O(2)—V—O(3)	88.9 (1)	N(1)—V—N(2)	77.9 (2)

All H atoms were generated in idealized positions, with C—H = 0.96 Å and isotropic displacement parameters fixed at 1.2 times the value of the attached C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1114). Services for accessing these data are described at the back of the journal.

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Na₂[(μ-N,N'-C₁₀H₁₂N₂O₈)(μ-O)(μ-S)-Mo₂O₂].2H₂O

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Abstract

Analogs of bridging-oxo complexes of dimolybdenum(V) where sulfide replaces one or both bridges are known. After reduction of [(MoO₃)₂(μ-edta)]⁴⁻ (edta is ethylenediaminetetraacetate) with dithionite at pH 6 in the absence of dioxygen, slow replacement of bridging oxide with sulfide produced *in situ* produces the title

compound, disodium μ-(ethylenediaminetetraacetato)-μ-oxo-μ-sulfido-bis[oxomolybdenum(V)] dihydrate, Na₂-[Mo₂O₃S(C₁₀H₁₂N₂O₈)].2H₂O. IR and NMR spectroscopic analyses are consistent with an unsymmetrical complex. In the molecular structure, the Mo centers have distorted octahedral coordination, with an average Mo—S distance of 2.320(1) Å and an average bridging Mo—O distance of 1.938(3) Å. The Mo···Mo contact distance [2.666(1) Å] is intermediate between those in comparable di-μ-oxo and di-μ-sulfido complexes. The two Na⁺ ions have five and six nearest O atoms in their coordination spheres, which each include one disordered water oxygen.

Comment

Complexes of ethylenediaminetetraacetate (edta) with bridged dinuclear molybdenum(V) cores are known with a variety of bridging and coordinated group types. Chief among bridging chalcogenides are di-μ-oxo, di-μ-sulfido, and ordered μ-oxo-μ-sulfido. Spectroscopic (IR and electronic) properties are sensitive to the type of bridging group (Ott *et al.*, 1977; Shibahara *et al.*, 1982, 1983, 1987; Barber *et al.*, 1996). With coordinated edta, Mo^V forms all three chalcogenide bridge types (Ott *et al.*, 1977). [Mo₂O₂(μ-O)₂(μ-edta)]²⁻ can be formed from [MoOCl₅]²⁻ and Na₂[H₂edta].2H₂O (Ikari *et al.*, 1989). Di-μ-oxo and di-μ-sulfido complexes can be made by reacting Mo^V in aqueous acid (pH 5–6) with water or aqueous H₂S/Na₂S, respectively, followed by treatment with edta (Ott *et al.*, 1977). A single bridging oxide in the Mo^VI–edta complex can be replaced stoichiometrically by H₂S or polysulfide (Spivak & Dori, 1970). Replacement of oxo with sulfido in the Mo^V–edta complex has not been verified. In the present case, (I), replacement of one bridging oxo ligand of the di-μ-oxo–edta complex of oxomolybdenum(V) is accomplished slowly with sulfur originating in the form of the relatively oxidized dithionite.
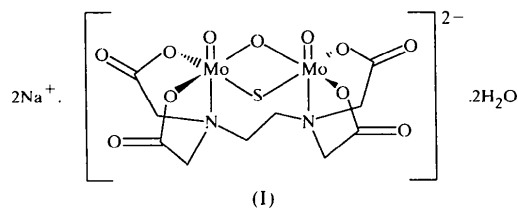
(I)

It has been established that edta stabilizes molybdenum(V) in solution below pH 7 (Pescok & Sawyer, 1956). Synthesis of the dihydrated sodium salt of the di-μ-oxo–edta complex (Ott & Schultz, 1975) was preceded by the synthesis and structure determination of the dihydrated dicaesium di-μ-sulfido–edta salt (Spivak & Dori, 1973) formed from a dimeric Mo^VI–edta complex, and followed by a report of the crystal structure of the hydrated barium di-μ-oxo–edta salt (Khalil & Sheldrick,