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Acta Cryst. (1985). C**41**, 1726–1728

Structure of Aquaoxo(*N*-salicylidene-L-alaninato)vanadium(IV)

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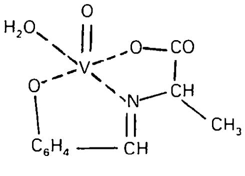
(*Received* 29 *March* 1985; *accepted* 13 *August* 1985)

Abstract. $[V(C_{10}H_9NO_3)O(H_2O)]$, $M_r = 276\cdot14$, monoclinic, $P2_1$, $a = 8\cdot514$ (3), $b = 7\cdot394$ (2), $c = 9\cdot210$ (3) Å, $\beta = 101\cdot85$ (3)°, $V = 567\cdot4$ (3) Å^3, $Z = 2$, $D_m = 1\cdot61$ (flotation), $D_x = 1\cdot616$ (4) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·94 mm^{-1}, $F(000) = 282$, $T = 295$ K, $R = 0\cdot030$ for 1217 reflections. A tridentate Schiff-base ligand forms, together with one water molecule and the O atom of the vanadyl ion, square-pyramidal coordination geometry around the V^{IV} atom. The shortest hydrogen-bonding interactions, 2·714 (4) and 2·720 (5) Å, are formed between the carboxylate O atom and the coordinated water molecules of the neighbouring complex units.

Introduction. The Schiff bases have been found to yield numerous stable complexes with the oxovanadium(IV) ion, where the V atom has square- or tetragonal-pyramidal stereochemistry. Occasionally a weaker donor group may coordinate in the sixth position to form distorted octahedral structures. We have prepared a tridentate ligand from an amino acid and salicylaldehyde and allowed it to react with the oxovanadium(IV) ion. The analysis of the resulting crystals continues our structural studies of transition-metal Schiff-base complexes.



Experimental. 0·04 mol of L-alanine (E. Merck AG) and 0·04 mol of salicylaldehyde in aqueous ethanol solution were refluxed on a waterbath for about 0·5 h. To this Schiff-base solution 0·04 mol of $VOSO_4.5H_2O$ in aqueous solution was added gradually with stirring. At the end of the synthesis, dilute sodium hydroxide was added dropwise until the solution was nearly neutral and clear and dark greenish. On standing at 298 K for a few days the filtrate yielded plate-like crystals, which were filtered, washed with ethanol and dried in air (Mukherjee & Ray, 1955).

Cell parameters calculated by least-squares method from 16 reflections in the range $12 < 2\theta < 20°$. 1490 unique reflections with $5\cdot0 < 2\theta < 55\cdot0°$; $h,k,\pm l$ set with maximum values 11,9,11 respectively. 1217 observed unique reflections with $|F_o| \geq 6\sigma(|F_o|)$. $(\sin\theta)/\lambda \leq 0\cdot65$ Å^{-1}, ω-scan technique, Nicolet $P3$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Two standard reflections after every 58 intensities showed no systematic variation. Measuring speed 2·0 to 20·0° min^{-1}. Data corrected for Lp effects and an empirical absorption correction based on the φ-scan method was applied (min. 0·726, max. 1·00). Main part of the structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); remaining C atoms located with Fourier methods of the *XRAY*76 program system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Overall structure refined anisotropically to $R = 0\cdot041$ by least-squares technique minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1/(60\cdot0 + |F_o| + 0\cdot01|F_o|^2)$. H atoms located on $\Delta\rho$ map and partly in calculated positions and refined isotropically, together with anisotropic refinement of the nonhydrogen atoms, to final $R = 0\cdot030$, $wR = 0\cdot030$ and $(\Delta/\sigma)_{\max} = 0\cdot66$. Final difference map showed peaks between −0·5 and 0·4 e Å^{-3}. No correction for secondary extinction.

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Atomic scattering factors for nonhydrogen and H atoms from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), respectively. Anomalous-dispersion correction for V (Cromer & Liberman, 1970). The alternative enantiomeric structure was refined separately, and converged to $R = 0{\cdot}032$ and $wR = 0{\cdot}032$ (Hamilton, 1965).

Discussion. The atomic coordinates with $B_{\rm eq}$ values (Hamilton, 1959) are given in Table 1 and bond lengths and angles in Table 2.* The molecular conformation and numbering scheme are illustrated in Fig. 1. The Schiff-base ligand has the usual dimensions. The vanadyl V=O bond length is 1·578 (3) Å, which agrees well with bond lengths found in related systems (Dodge, Templeton & Zalkin, 1961; Hon, Belford & Pfluger, 1965). The V atom deviates 0·614 (2) Å from the basal plane towards the vanadyl O atom; this is slightly more than is usual in corresponding complexes with coordination number five (0·48–0·58 Å), but, for example, still in the range 0·48–0·72 Å predicted by extended Hückel molecular-orbital calculations for porphin systems (Zerner & Gouterman, 1966). The basal plane and the benzene ring are almost coplanar, the interplanar angle being only 6·3 (5)°.

A stereoview of the molecular packing is presented in Fig. 2. There are two notable hydrogen bonds in the structure, *viz* $\text{O(2)}\cdots\text{O(4}^{\text{i}})= 2{\cdot}714\,(4)$ Å [(i) $-x+2$, $y+\frac{1}{2}$, $-z+2$], where $\text{O(2)}\cdots\text{H(11)} = 2{\cdot}02\,(6)$, O(4)–H(11) = 0·74 (6) Å and angle O(2)···H(11)–O(4) = 157 (7)°; and $\text{O(2)}\cdots\text{O(4}^{\text{ii}}) = 2{\cdot}720\,(5)$ Å [(ii) $x, y+1, z$], where O(2)···H(10) = 1·79 (6), O(4)–H(10) = 0·94 (6) Å and angle O(2)···H(10)–O(4) 171 (5)°. Two other intermolecular contact distances less than 3·2 Å are $\text{O(1)}\cdots\text{O(4}^{\text{ii}}) = 3{\cdot}119\,(4)$ and $\text{O(2)}\cdots\text{O(1}^{\text{ii}}) = 3{\cdot}127\,(4)$ Å.

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters*

	x	y	z	$B_{\rm eq}$(Å²)
V	8045 (1)	5700	7014 (1)	2·35
O(1)	8816 (4)	7660 (4)	8448 (3)	2·98
O(2)	9138 (4)	10580 (6)	8858 (3)	3·62
O(3)	8611 (4)	4331 (4)	5438 (3)	3·13
O(4)	9586 (4)	4170 (4)	8437 (3)	3·42
O(5)	6272 (4)	5192 (5)	7122 (3)	3·54
N(1)	7844 (4)	7900 (5)	5640 (3)	2·46
C(1)	8698 (5)	9317 (6)	8021 (4)	2·60
C(2)	7926 (5)	9653 (6)	6403 (4)	2·55
C(3)	6256 (5)	10432 (8)	6323 (5)	3·88
C(4)	7599 (5)	7851 (6)	4209 (4)	2·89
C(5)	7525 (5)	6224 (6)	3352 (4)	2·97
C(6)	6922 (6)	6350 (8)	1795 (4)	4·10
C(7)	6771 (6)	4825 (9)	937 (4)	4·67
C(8)	7275 (7)	3191 (8)	1557 (5)	4·54
C(9)	7912 (6)	3039 (7)	3064 (5)	3·88
C(10)	8010 (5)	4542 (6)	3984 (4)	2·77

Table 2. *Interatomic distances* (Å) *and angles* (°)

V–O(1)	1·980 (3)	C(2)–N(1)	1·469 (5)
V–O(3)	1·911 (3)	C(4)–N(1)	1·292 (5)
V–O(4)	2·003 (3)	C(4)–C(5)	1·433 (6)
V–O(5)	1·578 (3)	C(5)–C(6)	1·423 (5)
V–N(1)	2·047 (4)	C(5)–C(10)	1·399 (6)
O(1)–C(1)	1·285 (5)	C(6)–C(7)	1·368 (8)
O(2)–C(1)	1·220 (5)	C(7)–C(8)	1·368 (8)
O(3)–C(10)	1·341 (4)	C(8)–C(9)	1·388 (6)
C(1)–C(2)	1·521 (5)	C(9)–C(10)	1·389 (7)
C(2)–C(3)	1·522 (6)		
O(1)–V–O(3)	142·5 (1)	V–O(1)–C(1)	120·0 (2)
O(1)–V–O(4)	83·9 (1)	V–N(1)–C(2)	114·6 (2)
O(1)–V–O(5)	108·8 (1)	V–N(1)–C(4)	125·7 (3)
O(1)–V–N(1)	78·7 (1)	V–O(3)–C(10)	126·4 (3)
O(3)–V–O(4)	87·9 (1)	N(1)–C(4)–C(5)	124·4 (4)
O(3)–V–O(5)	108·4 (1)	C(2)–N(1)–C(4)	119·7 (4)
O(3)–V–N(1)	87·3 (1)	C(4)–C(5)–C(6)	117·8 (4)
O(4)–V–N(1)	144·5 (1)	C(4)–C(5)–C(10)	122·8 (3)
O(4)–V–O(5)	109·3 (1)	C(5)–C(6)–C(7)	120·0 (5)
O(5)–V–N(1)	105·6 (1)	C(5)–C(10)–O(3)	122·6 (4)
O(1)–C(1)–O(2)	122·8 (3)	C(5)–C(10)–C(9)	118·8 (4)
O(1)–C(1)–C(2)	116·5 (3)	C(6)–C(7)–C(8)	120·2 (4)
O(2)–C(1)–C(2)	120·6 (4)	C(7)–C(8)–C(9)	120·9 (5)
N(1)–C(2)–C(1)	107·1 (3)	C(8)–C(9)–C(10)	120·5 (5)
N(1)–C(2)–C(3)	111·0 (3)	C(9)–C(10)–O(3)	118·6 (4)
C(1)–C(2)–C(3)	108·7 (3)	C(10)–C(5)–C(6)	119·5 (4)

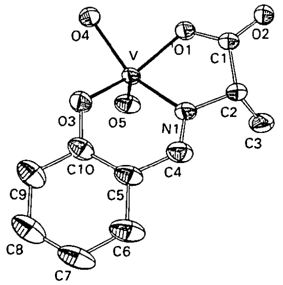

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the molecule and the atom labelling.

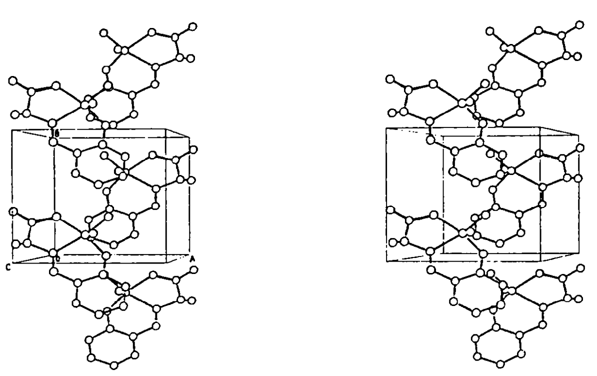

Fig. 2. A stereoview of the unit-cell packing.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42436 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1985). C**41**, 1728–1730

Structure of (Benzoato-*O,O′*)bis(2-dimethylaminoethanol)copper(II) Benzoate

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(*Received* 7 *March* 1985; *accepted* 15 *August* 1985)

Abstract. $[Cu(C_7H_5O_2)(C_4H_{11}NO)_2][C_7H_5O_2]$, M_r = 484·05, orthorhombic, $P2_12_12_1$, a = 9·166 (3), b = 13·293 (7), c = 19·274 (7) Å, V = 2348 (2) Å^3, D_x = 1·37 g cm^{-3}, Z = 4, λ(Mo $K\alpha$) = 0·71069 Å, μ = 10·1 cm^{-1}, $F(000)$ = 1020, T = 293 K, R = 0·049 for 1610 observed reflections. The Cu atom has an unusual distorted octahedral environment with two approximately collinear short Cu—N bonds of 2·060 (6) and 2·058 (6) Å, three intermediate Cu—O bonds of 2·126 (6), 2·168 (6) and 2·179 (6) Å, and one longer Cu—O bond of 2·370 (6) Å from the asymmetrically chelated carboxylate group.

Introduction. Several tetrameric complexes have been obtained from reactions between 2-dimethylaminoethanol and Cu^{II} carboxylates (Turpeinen, Hämäläinen & Ahlgrén, 1980; Ahlgrén, Turpeinen & Hämäläinen, 1982). Blue and green crystals crystallized simultaneously during slow evaporation of ethanol solution containing Cu^{II} benzoate and 2-dimethylaminoethanol. The present study shows that the blue form of the complex is the title compound.

Experimental. Blue, rhombic crystal 0·3 × 0·3 × 0·4 mm. Nicolet $P3$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions obtained from 20 reflections in θ range 6–13°. Intensity data 4° < 2θ < 50°. ω-scan technique. Scanning speed varied according to the prescanned peak intensities from 2 to 30° min^{-1}. Three standard reflections every 80 reflections showed no significant change in intensity. Lp correction, no absorption or extinction corrections. 2425 unique reflections measured, 1610 with $I > 3\sigma(I)$; index range h 0–10, k 0–15, l 0–22. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Least squares (*XRAY76*, Stewart, 1976), minimizing $\sum w(\Delta F)^2$, with anisotropic thermal parameters for non-H atoms, isotropic for H atoms of the hydroxyl groups located from difference synthesis. The other 30 H atoms with U = 0·08 Å^2 included at idealized positions (C—H 1·0 Å) and held fixed. Final R = 0·049, wR = 0·032 for observed data (the rejected enantiomeric structure had R = 0·056, wR = 0·040); $w = 1/\sigma^2(F_o)$ based on counting statistics. Residual electron density within ±0·3 e Å^{-3}. Largest Δ/σ = 0·56. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic coordinates and temperature factors are listed in Table 1 and interatomic distances

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