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Preparation, Properties and Crystal Structure of Dioxane-bis-{μ-oxobis[oxovanadium(V) 2-(2'-hydroxyphenyl)iminomethylphenato]}

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The title compound has been prepared by oxydation of vanadyl(IV) 2-(2'-hydroxyphenyl)iminomethylphenato. The crystal structure has been determined by X-ray analysis from diffractometer data and refined to R 0.085. The crystals are triclinic, space group $P\bar{1}$, *with* $a = 12.98(1)$, $b = 11.99(1)$, $c = 11.97(1)$ Å, $\alpha = 94.12(4)^\circ$, $\beta = 97.99(4)^\circ$ *and* $\gamma = 102.13(4)^\circ$. *Two five-coordinate vanadium atoms are oxygen bridged to form the binuclear asymmetric unit of the cell. Such units are additionally bridged in pairs by a dioxane molecule which makes two weak bonds with two symmetry related vanadium atoms forming a tetramer. Axial V=O distances are 1.55 and 1.56 Å, whereas V–O distances to the terminal oxygen atoms average 1.85 Å and those to the bridging oxygens average 1.78 Å. The V–O(dioxane) bond (2.51 Å) is opposite to the axial bond.*

Introduction

The field of dinuclear complexes has seen extensive growth, stimulated by interest in areas such as metallo-enzymes, homogeneous catalysis, electrical conductance and magnetic exchange processes [1, 2].

Semiquantitative correlations between the structures of polynuclear complexes and their magnetic properties have been reported [3]. In particular, in studies of several hydroxo-bridged Cu(II) compounds, a significant correlation was found between the Cu–O–Cu angle and the exchange constant, J [3].

Some dinuclear oxovanadium(IV) complexes of tridentate Schiff bases have been well characterized by infrared spectra and magnetic measurements [4–6], but practical difficulties (mainly due to the low solubility in most solvents and to the easy oxidation to vanadium(V) compounds) prevented a complete determination of their structures. In this optique the binuclear complex bis[oxovanadium(IV)-2-(2'-hydroxyphenyl)iminomethylphenato], $(VO)_2L_2$, was prepared, and, after several attempts to crystallize it from different solvents, dark brown crystals were obtained from a dioxane–diethylether solution. The X-ray analysis and other physico-chemical measurements of these crystals show that the crystallized compound is a vanadium(V) complex which is the product of an oxidation reaction. An alternative route to obtain the same vanadium(V) complex starting from vanadium(IV) diacetate has also been examined.

Experimental

Preparation of Compounds

2-(2'-hydroxyphenyl)iminomethylphenol, H_2L

Equimolar amounts of 2-hydroxyaniline and salicylaldehyde were mixed in methanol solution. The ligand was obtained and used as crude product without further purification. Its purity was checked by elemental analysis, mp and ir, and mass spectrum. (Found: C, 73.60; H, 5.22; N, 6.39. $C_{13}H_{11}NO_2$ calcd.: C, 73.24; H, 5.16; N, 6.57%).

Bis[oxovanadium(IV)2-(2'-hydroxyphenyl)iminomethylphenato], $(VO)_2L_2$

The ligand H_2L (4 mmol) and LiOH (8 mmol) were dissolved in methanol (100 ml) under a nitrogen atmosphere and heated at reflux temperature. Solid vanadyl(IV) diacetate (4 mmol) was added and the suspension stirred during 5 hr, till no more unreacted vanadyl(IV) diacetate was present. A green-brown precipitate was separated after cooling. (Found: C, 56.14; H, 3.19; N, 4.90. $C_{26}H_{18}N_2O_6V_2$ calcd.: C, 56.11; H, 3.24; N, 5.04%). The magnetic moment at room temperature was 1.55 B.M.

This compound, when treated with 1,4-dioxane at room temperature in air, gave a dark brown solution (while a major amount remained undissolved) from which black crystals were obtained by addition of diethylether (1:1 by volume). These crystals were suitable for X-ray work.

Repetition of the reaction under the same conditions yielded, in several instances, varying amounts of soluble fractions. The insoluble residue ranged from less than 5% to almost 100% of the total weight. No significant variation of composition, spectral properties and magnetic moment was observed in combination with the strongly variable solubilities.

μ-oxo-bis[oxovanadium(V) 2-(2'-hydroxyphenyl)iminomethylphenato] dihydrate, $(VOL)_2O\cdot 2H_2O$ and dioxane-bis-[μ-oxo-bis-oxovanadium(V)2-(2'-hydroxyphenyl)iminomethylphenato], $[(VOL)_2O]_2$ dioxane

The ligand H_2L (4 mmol) and LiOH (8 mmol) were dissolved in methanol (100 ml). Solid oxovanadium(IV) diacetate (4 mmol) was added. The solution was stirred at reflux temperature and a continuous stream of air was bubbled into the solution during 1 hr. At the end no solid product was present. The dark brown solution was cooled and the solvent evaporated under reduced pressure. A portion of the black residue was treated with dichloromethane. From the solution a brown powder (a) precipitated by evaporating part of the solvent. (Found: C, 51.00; H, 3.52; N, 4.38. $(VOL)_2O\cdot 2H_2O$, $C_{26}H_{22}N_2O_9V_2$ calcd.: C, 51.32; H, 3.62; N, 4.61%).

A second portion was washed with cold water to eliminate lithium acetate and the elemental analysis was made of the residue (b) (Found: C, 51.62; H, 3.74; N, 4.55%).

The infrared spectra of both samples were characterized by the presence of a strong broad band at 750 cm^{-1}.

Both fractions (a) and (b) were recrystallized from a 1,4-dioxane/diethyl ether mixture (1:1), yielding black powders of $[(VOL)_2O]_2\cdot$dioxane. (Found: C, 54.97; H, 3.81; N, 4.15% and C, 54.20; H, 3.80; N, 4.17% respectively. $C_{56}H_{44}N_4O_{16}V_4$ calcd.: C, 54.55; H, 3.57; N, 4.55%).

The infrared spectra showed strong bands at the following frequencies: 1600, 1535, 1465, 1455, 1280, 1250, 1110, 985, 795 and 740 (vs) cm^{-1}.

Attempted Oxidation of $(VO)_2L_2$

A suspension of the insoluble $(VO)_2L_2$ complex (100 mg) in dioxane (50 ml) was stirred at room temperature during 12 hr. All this time a continuous air stream was bubbled into the suspension. The starting $(VO)_2L_2$ was isolated at the end by filtration in almost quantitative amount. By evaporating the dark filtrate only traces of a black oily product could be obtained.

X-ray Data

Crystals suitable for the X-ray work were obtained from a dioxane solution of $(VO)_2L_2$ as black prisms. The crystals belong to the space group $P\bar{1}$ of the triclinic system. The cell constants were determined from a least-squares refinement of the setting angles of 25 medium-angle reflections measured on a Philips PW 1100 automated diffractometer. The density was measured by flotation. Crystallographic data are given in Table I.

TABLE I. Crystal Data of $[(VOL)_2O]_2$ dioxane.

$C_{26}H_{18}N_2O_7V_2\cdot 1.5C_4H_8O_2\cdot H_2O$	FW 576 + 132 + 18
Triclinic	Space group $P\bar{1}$
$a = 12.98(1)$ Å	$\alpha = 94.12(4)°$
$b = 11.99(1)$ Å	$\beta = 97.99(4)°$
$c = 11.97(1)$ Å	$\gamma = 102.13(4)°$
$D_m = 1.33$ g cm^{-3}	F(000) = 1464
$D_x = 1.34$ g cm^{-3}	$Z = 2$
$\mu(MoK\alpha) = 5.7$ cm^{-1}	$\lambda(MoK\alpha) = 0.7107$ Å

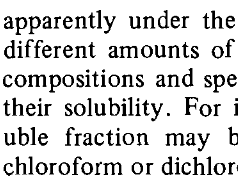
Intensity data were collected on the diffractometer with MoKα radiation by the $\omega-2\vartheta$ scan mode with a scan rate of 2° min^{-1}. A total of 6442 independent reflections, of which 2906 had $I > 3\sigma(I)$, were recorded up to $2\vartheta = 50°$. Usual Lorentz and polarization factors were applied, but no absorption correction was made. Two standard reflections, monitored before every 100 measurements, were constant within counting statistics. Scattering factors for neutral atoms were taken from Cromer and Mann [7], and for vanadium allowance was made for the anomalous dispersion [8].

A sharpened three-dimensional Patterson function was calculated and used to determine the positions of the two independent V atoms. Fourier synthesis was then computed assuming the centric space group and using phases determined by these atoms. The remaining non-hydrogen atoms, including those of two dioxane molecules, were located in three successive Fourier syntheses, and their positions refined isotropically. However, the temperature factors of N(1) and N(7) were abnormally high if compared with those of the remaining light atoms, and especially with the corresponding N(2) and C(20), suggesting the possibility of disorder in the structure. An accurate inspection of a difference Fourier synthesis confirmed the presence of alternative positions for these atoms but only showed poorly resolved residuals of electronic density near the rings carbon atoms of this ligand. Probably this molecule is packed in two equivalent but opposite orientations, in which most carbon atoms are completely or partially superimposed so that their alternative peaks are scarcely resolved.

Refinement of positional and population parameters assigning a fixed isotropic temperature factor of 5 Å^2 resulted in a mean occupancy of 0.64 and 0.36 for the alternative positions with a very good accordance for both atoms. Refinement of positional and anisotropic temperature factors with these occupancy factors reduced the conventional R factor to 0.092. A difference Fourier synthesis calculated at this stage suggested the additional presence of an ill-defined water molecule in the asymmetric unit. Also this molecule is disordered, and successive attempts showed that it is statistically present with occupancy factors of 0.53 and 0.46 respectively. Further refinement with inclusion of these positions improved the reliability index R to the final value of 0.085. All calculations were performed using the X-ray '73 program system [9]. Final atomic coordinates are listed in Table II. Intramolecular distances and angles are tabulated in Tables III and IV. Mean planes through selected atomic groupings are in Table V and selected contact distances are in Table VI.

Results and Discussion

Reaction of 2-(2'-hydroxyphenyl)iminomethylphenol (H_2L) with LiOH (in molar ratio 1:2) and vanadyl(IV) diacetate under nitrogen atmosphere yields a green-brown compound, whose elemental analysis, infrared spectrum and magnetic moment at room temperature are in agreement with the structure (I) proposed by Ginsberg [5] and which will be indicated as $(VO)_2L_2$.



The reaction is irreproducible in that it yields, apparently under the same experimental conditions, different amounts of two fractions having the same compositions and spectral properties but differing in their solubility. For instance a soluble and an insoluble fraction may be separated from 1,4-dioxane, chloroform or dichloromethane.

Upon adding diethyl ether to the dioxane solution dark crystals, suitable for X-ray studies, were obtained. As will be later described in detail, this compound is dimeric and can be correctly formulated as $[(VOL)_2O]_2$·dioxane.

The possibility that oxovanadium compounds form μ-oxocomplexes by reaction with dioxygen is known [10]; in particular the reaction

$$2VO(Q_2)(py) + 1/2O_2 \longrightarrow [VO(Q_2)]_2O + 2py$$

(where HQ represents 8-quinolinol) was observed.

It is noteworthy that when a suspension of the dioxane-insoluble fraction is stirred under oxygen flow, $(VO)_2L_2$ remains unaffected. This parallels the behaviour of the almost insoluble $VO(Q_2)$ whose oxidation reaction with dioxygen is much slower than the one of the soluble $VO(Q_2)(py)$ [10].

Owing to the irreproducibility of the reaction of H_2L with LiOH and vanadyl diacetate an alternative synthesis of $(VOL)_2O$ was looked for.

Reproducible results were obtained by stirring the ligand (H_2L), lithium hydroxide and vanadyl diacetate in refluxing methanol while bubbling an air stream into the solution. By evaporating the solvent and treating with dichloromethane the dark brown $(VOL)_2O·2H_2O$ could be isolated. Further recrystallization of $(VOL)_2O·2H_2O$ with a 1,4-dioxane/diethylether mixture yielded the black powder $[(VOL)_2O]_2$·dioxane in which no more water was present.

On performing the above reaction in air the precipitation of $(VO)_2L_2$ is prevented by a fast oxidation to vanadium(V); $(VO)_2L_2$ was not isolated at the end of the heating and no precipitate was observed during the reaction.

The infrared spectra of $(VO)_2L_2$, $(VOL)_2O·2H_2O$ and $[(VOL)_2O]_2$·dioxane show several similarities but also interesting differences. Intense bands at 1602 cm^{-1} (νC=N) and 985 cm^{-1} (νV=O) are present in the spectra of the three compounds; the shape of the absorptions due to the ligand is also comparable. Very intense broad bands lie at 750 cm^{-1} for $(VOL)_2O·2H_2O$ and at 740 cm^{-1} for $[(VOL)_2O]_2$·dioxane and may be associated with the group VO–O–VO in agreement with the observation of Pasquali *et al.* [10] about $[VO(Q_2)]_2O$; $(VO)_2L_2$, instead, shows in this region a much less intense absorption at 745 cm^{-1}, with a shoulder at 755 cm^{-1}, due to the phenyl C–H out of plane bending.

It is difficult to explain correctly the different behaviours of the two $(VO)_2L_2$ fractions and their formation in variable ratios under the same experimental conditions. On the basis of the available results we suggest a binuclear structure for the more soluble compound, as already reported in the literature, and a more complex (perhaps polymeric) structure for the less soluble one due to intermolecular interactions between dimers.

Description of the Structure of $[(VOL)_2O]_2$·dioxane

Two five-coordinate vanadium atoms are oxygen bridged to form the binuclear asymmetric unit of the cell. Both vanadium atoms are displaced (by 0.46

TABLE II. Fractional Atomic Coordinates and Estimated Standard Deviations.

Atom	X	Y	Z	σ(X)	σ(Y)	σ(Z)
V1	0.2039	0.1016	0.1308	0.0001	0.0002	0.0002
V2	0.3314	−0.1193	0.1972	0.0002	0.0002	0.0002
O1	0.1341	0.0628	0.2538	0.0007	0.0008	0.0009
O2	0.1982	0.0824	−0.0238	0.0008	0.0008	0.0008
O3	0.2923	0.0101	0.1576	0.0006	0.0007	0.0008
O4	0.4651	−0.0583	0.2725	0.0006	0.0008	0.0008
O5	0.2362	0.7884	0.0751	0.0006	0.0007	0.0007
O6	0.2708	−0.1527	0.2984	0.0007	0.0007	0.0008
O7	0.2675	0.2272	0.1651	0.0006	0.0007	0.0008
O8	0.6267	0.2685	0.3006	0.0009	0.0009	0.0012
O9	0.5374	0.4521	0.2703	0.0010	0.0010	0.0012
O10	0.4333	−0.0970	0.0337	0.0006	0.0007	0.0008
*O11	0.0684	0.5340	0.3529	0.0017	0.0019	0.0019
*O11A	0.2490	0.4851	0.3983	0.0030	0.0033	0.0034
*N1	0.0451	0.1294	0.1015	0.0019	0.0022	0.0021
*N1A	0.0663	0.1443	0.0435	0.0029	0.0033	0.0035
N2	0.3869	−0.2766	0.1871	0.0008	0.0009	0.0009
C1	0.0480	0.0965	0.2781	0.0010	0.0011	0.0013
C2	0.0222	0.0922	0.3854	0.0011	0.0011	0.0013
C3	−0.0722	0.1212	0.4065	0.0012	0.0013	0.0014
C4	−0.1372	0.1537	0.3229	0.0011	0.0012	0.0016
C5	−0.1118	0.1599	0.2128	0.0012	0.0012	0.0017
C6	−0.0174	0.1308	0.1975	0.0013	0.0011	0.0013
*C7	−0.0011	0.1576	0.0084	0.0019	0.0017	0.0026
*C7A	−0.0205	0.1517	0.0878	0.0034	0.0039	0.0060
C8	0.0569	0.1636	−0.0918	0.0012	0.0011	0.0013
C9	0.0027	0.2123	−0.1798	0.0012	0.0012	0.0016
C10	0.0406	0.2224	−0.2734	0.0014	0.0014	0.0016
C11	0.1374	0.1897	−0.2877	0.0014	0.0015	0.0014
C12	0.1907	0.1446	−0.2043	0.0011	0.0013	0.0014
C13	0.1521	0.1296	−0.1068	0.0011	0.0011	0.0012
C14	0.5316	−0.0991	0.3483	0.0008	0.0012	0.0011
C15	0.6058	−0.0238	0.4293	0.0009	0.0012	0.0012
C16	0.6738	−0.0682	0.5018	0.0010	0.0013	0.0012
C17	0.6737	−0.1844	0.4982	0.0010	0.0015	0.0012
C18	0.6029	−0.2561	0.4183	0.0010	0.0012	0.0013
C19	0.5314	−0.2162	0.3407	0.0010	0.0011	0.0012
C20	0.4574	−0.2985	0.2548	0.0010	0.0012	0.0012
C21	0.2354	0.6770	0.0507	0.0010	0.0010	0.0012
C22	0.1540	0.6049	−0.0260	0.0011	0.0012	0.0012
C23	0.1546	0.4932	−0.0528	0.0013	0.0013	0.0015
C24	0.2411	0.4502	−0.0015	0.0017	0.0013	0.0014
C25	0.3239	0.5279	0.0805	0.0013	0.0014	0.0014
C26	0.3156	0.6371	0.1045	0.0010	0.0010	0.0012
C27	0.5464	−0.0870	0.0429	0.0009	0.0011	0.0013
C28	0.6020	0.0390	0.0633	0.0009	0.0011	0.0012
C29	0.6587	0.3425	0.2236	0.0018	0.0018	0.0020
C30	0.6468	0.4642	0.2524	0.0017	0.0020	0.0028
C31	0.4995	0.3692	0.3414	0.0015	0.0015	0.0020
C32	0.5191	0.2612	0.3066	0.0014	0.0015	0.0024

Anisotropic Thermal Parameters

	Atom	U11	U22	U33	U12	U13	U23
UIJ	V1	0.0434	0.0436	0.0706	0.0168	0.0014	−0.0023
UIJ	V2	0.0454	0.0448	0.0674	0.0174	0.0048	0.0030
UIJ	O1	0.0717	0.0694	0.1128	0.0179	0.0472	0.0011

(continued overleaf)

TABLE II. *(continued)*

	Atom	U11	U22	U33	U12	U13	U23
UIJ	O2	0.1107	0.0848	0.0748	0.0510	0.0016	0.0085
UIJ	O3	0.0430	0.0616	0.0755	0.0208	0.0078	0.0041
UIJ	O4	0.0560	0.0727	0.0836	0.0209	0.0031	0.0181
UIJ	O5	0.0472	0.0546	0.0771	0.0170	0.0140	0.0120
UIJ	O6	0.0678	0.0611	0.0818	0.0143	0.0177	0.0033
UIJ	O7	0.0576	0.0495	0.0996	0.0176	−0.0018	0.0000
UIJ	O8	0.1043	0.0959	0.1674	0.0517	0.0505	0.0377
UIJ	O9	0.1510	0.1072	0.1609	0.0745	0.0390	0.0451
UIJ	O10	0.0579	0.0642	0.0680	0.0196	0.0136	0.0089
UIJ	N1	0.0390	0.0436	0.0327	0.0028	0.0119	−0.0008
UIJ	N1A	0.0290	0.0255	0.0786	0.0176	−0.0106	0.0089
UIJ	N2	0.0583	0.0623	0.0706	0.0212	0.0212	0.0229
UIJ	C1	0.0481	0.0556	0.0669	0.0113	0.0145	0.0106
UIJ	C2	0.0755	0.0537	0.0610	0.0161	0.0061	0.0067
UIJ	C3	0.0640	0.0741	0.0783	0.0152	0.0180	0.0116
UIJ	C4	0.0612	0.0597	0.0938	0.0172	0.0069	−0.0010
UIJ	C5	0.0666	0.0494	0.1009	0.0073	−0.0083	0.0083
UIJ	C6	0.0918	0.0428	0.0406	−0.0003	0.0147	−0.0026
UIJ	C7	0.0491	0.0177	0.0846	−0.0031	−0.0014	−0.0084
UIJ	C7A	0.0395	0.0529	0.1267	−0.0031	0.0210	−0.0302
UIJ	C8	0.0740	0.0403	0.0682	−0.0009	0.0211	−0.0099
UIJ	C9	0.0663	0.0554	0.0854	0.0177	0.0052	−0.0047
UIJ	C10	0.0924	0.0823	0.0823	0.0221	0.0080	0.0106
UIJ	C11	0.0901	0.0904	0.0693	0.0119	0.0197	0.0064
UIJ	C12	0.0607	0.0829	0.0614	0.0178	0.0205	0.0076
UIJ	C13	0.0713	0.0514	0.0532	0.0234	−0.0058	−0.0038
UIJ	C14	0.0307	0.0727	0.0475	0.0183	0.0099	0.0054
UIJ	C15	0.0331	0.0828	0.0620	0.0198	0.0039	−0.0045
UIJ	C16	0.0424	0.0827	0.0592	0.0084	0.0140	−0.0141
UIJ	C17	0.0467	0.1063	0.0469	0.0248	0.0064	0.0149
UIJ	C18	0.0537	0.0674	0.0763	0.0238	0.0115	0.0230
UIJ	C19	0.0553	0.0476	0.0568	0.0013	0.0225	−0.0004
UIJ	C20	0.0645	0.0626	0.0705	0.0182	0.0269	0.0212
UIJ	C21	0.0505	0.0394	0.0776	0.0029	0.0135	−0.0004
UIJ	C22	0.0669	0.0588	0.0668	0.0151	0.0116	0.0086
UIJ	C23	0.0826	0.0555	0.1040	0.0125	0.0132	0.0153
UIJ	C24	0.1624	0.0564	0.0635	0.0323	0.0373	−0.0020
UIJ	C25	0.0954	0.0698	0.0761	0.0173	0.0054	0.0110
UIJ	C26	0.0629	0.0404	0.0621	0.0004	0.0145	−0.0002
UIJ	C27	0.0425	0.0535	0.0918	0.0253	0.0095	0.0002
UIJ	C28	0.0418	0.0633	0.0656	0.0097	−0.0020	0.0112
UIJ	C29	0.1561	0.1114	0.1481	0.0782	0.0684	0.0137
UIJ	C30	0.1168	0.1213	0.3080	0.0598	0.1181	0.0665
UIJ	C31	0.1024	0.0790	0.1748	0.0320	0.0548	0.0298
UIJ	C32	0.0950	0.0708	0.2743	0.0434	0.0980	0.0398
U	**O11	0.1132					
U	**O11A	0.1258					

*Population parameters for these atoms are O11 0.53, O11A 0.46, N1 0.64, N1A 0.36, C7 0.64, C7A 0.36. **These atoms were refined isotropically. Thermal parameters ($\times 10^3$) in the form $\exp[-2\pi^2 \Sigma U_{ij} a_i^* a_j^* h_i h_j]$.

and 0.33 Å) from the average plane of the four base atoms in the typical square pyramidal geometry. In addition V(2) makes a relatively short contact of 2.51 Å, with the oxygen atom of a dioxane molecule located opposite to the axial oxygen. If this contact is considered a weak bond, as it seems to be, then the whole structure is formed by tetramers (as shown in the bonding scheme of Fig. 1) in which important bond distances and angles are reported, and in Fig. 2, where the structure is projected down the *b* axis of the cell. As shown in this figure, another dioxane molecule is present in the asymmetric unit as crystallization solvent. A different view of the structure, where the clathrate solvent molecules are omitted for

TABLE III. Bond Distances (Å).

Coordination			
V(1)–O(1)	1.87(1)	V(2)–O(3)	1.81(1)
V(1)–O(2)	1.83(1)	V(2)–O(4)	1.81(1)
V(1)–O(3)	1.76(1)	V(2)–O(5)	1.90(1)
V(1)–N(1)	2.17(3)	V(2)–N(2)	2.16(1)
V(1)–N(1A)	2.09(4)	V(2)–O(6)	1.56(1)
V(1)–O(7)	1.55(1)	V(2)–O(10)	2.51(1)
O(1)–C(1)	1.32(1)	O(4)–C(14)	1.35(2)
O(2)–C(13)	1.32(1)	O(5)–C(21)	1.34(2)
N(1)–C(6)	1.49(3)	N(2)–C(26)	1.45(2)
N(1)–C(7)	1.26(3)	N(2)–C(20)	1.22(2)
C(7)–C(8)	1.51(3)	C(20)–C(19)	1.44(2)
N(1A)–C(8)	1.67(4)	O(10)–C(27)	1.44(1)
N(1A)–C(7A)	1.33(4)	C(27)–C(28)	1.53(2)
C(7A)–C(6)	1.30(7)	C(28)–O(10^{i})	1.46(1)
O(8)–C(28)	1.37(1)	O(9)–C(31)	1.41(1)
C(29)–C(30)	1.51(2)	C(31)–C(32)	1.43(3)
C(30)–O(9)	1.45(2)	C(32)–O(8)	1.39(1)

TABLE IV. Bond Angles (°).

O(1)–V(1)–O(3)	94(1)	O(4)–V(2)–O(3)	100(1)
O(1)–V(1)–N(1)	70(1)	O(4)–V(2)–N(2)	84(1)
O(2)–V(1)–O(3)	94(1)	O(5)–V(2)–O(3)	93(1)
O(2)–V(1)–N(1)	88(1)	O(5)–V(2)–N(2)	76(1)
O(1)–V(1)–O(7)	105(1)	O(6)–V(2)–O(10)	171(1)
O(2)–V(1)–O(7)	104(1)	O(3)–V(2)–O(6)	104(1)
O(3)–V(1)–O(7)	108(1)	O(4)–V(2)–O(6)	101(1)
N(1)–V(1)–O(7)	100(1)	O(5)–V(2)–O(6)	100(1)
O(1)–V(1)–O(2)	146(1)	N(2)–V(2)–O(6)	93(1)
O(3)–V(1)–N(1)	151(1)	O(4)–V(2)–O(5)	152(1)
V(1)–O(1)–C(1)	126(1)	O(3)–V(2)–N(2)	161(1)
V(1)–O(2)–C(13)	132(1)	V(2)–O(4)–C(14)	133(1)
V(1)–O(3)–V(2)	156(1)	V(2)–O(5)–C(21)	122(1)
V(1)–N(1)–C(6)	118(1)	V(2)–N(2)–C(26)	111(1)
V(1)–N(1)–C(7)	125(2)	V(2)–N(2)–C(20)	125(1)
C(6)–N(1)–C(7)	116(2)	C(26)–N(2)–C(20)	123(1)
N(1)–C(7)–C(8)	119(1)	N(2)–C(20)–C(19)	127(1)
O(1)–V(1)–N(1A)	91(1)	V(2)–O(10)–C(27)	125(1)
O(2)–V(1)–N(1A)	68(1)	V(2)–O(10)–C(28^{i})	121(1)
N(1A)–V(1)–O(7)	96(1)	C(28^{i})–O(10)–C(27)	108(1)
O(3)–V(1)–N(1A)	153(1)	O(10)–C(27)–C(28)	108(1)
V(1)–N(1A)–C(8)	121(2)	C(27–C(28)–O(10^{i})	109(1)
V(1)–N(1A)–C(7A)	127(3)		
C(8)–N(1A)–C(7A)	112(3)		
N(1A)–C(7A)–C(6)	114(2)		
C(32)–O(8)–C(29)	110(1)	C(30)–O(9)–C(31)	115(2)
O(8)–C(29)–C(30)	112(2)	O(9)–C(31)–C(32)	111(2)
C(29)–C(30)–O(9)	105(2)	C(31)–C(32)–O(8)	111(1)

TABLE V. Least-squares Planes and Distances (Å) of Atoms from the Planes. The equation of a plane is PX + QY + RZ = S with coordinates referred to the crystallographic axes.

Plane I:	O(1), O(2), O(3), N(1) 4.29X + 9.77Y + 1.51Z = 1.60 Å [O(1) 0.00, O(2) 0.00, O(3) 0.00, N(1) 0.00, V(1)[a] 0.46, N(1A)[a] 0.12]
Plane IA:	O(1), O(2), O(3), N(1A) 4.64X + 9.55Y + 1.59Z = 1.68 Å [O(1) −0.02, O(2) −0.03, O(3) 0.03, N(1A) 0.03, V(1)[a] 0.44, N(1)[a] −0.09]
Plane II:	O(3), O(4), O(5), N(2) −7.74X + 0.15Y + 10.50Z = −0.84 Å [O(3) 0.24, O(4) 0.08, O(5) −0.08, N(2) −0.24, V(2)[a] 0.33]
Plane III:	C(1) to C(6) 3.43X + 10.27Y + 1.28Z = 1.54 Å [C(1) −0.01, C(2) 0.01, C(3) −0.01, C(4) 0.01, C(5) −0.01, C(6) 0.01]
Plane IV:	C(8) to C(13) 3.80X + 9.58Y + 2.83Z = 1.53 Å [C(8) 0.01, C(9) 0.00, C(10) 0.00, C(11) 0.00, C(12) 0.00, C(13) −0.01]
Plane V:	C(14) to C(19) 0.75X + 0.12Y − 0.65Z = 2.02 Å [C(14) −0.01, C(15) 0.02, C(16) −0.01, C(17) 0.00, C(18) 0.01, C(19) 0.00]
Plane VI:	C(21) to C(26) −7.49X − 2.58Y + 10.12Z = −2.98 Å [C(21) −0.04, C(22) 0.02, C(23) 0.01, C(24) −0.03, C(25) 0.02, C(26) 0.02]

Angles between the planes

Planes	Angle (°)	Planes	Angle (°)
I–II	85.0	I–III	4.4
I–IA	1.8	I–IV	6.5
III–IV	8.2	II–V	13.2
V–VI	14.5	II–VI	13.5

[a]Atoms not defining the plane.

TABLE VI. Selected Contact Distances (Å).

V(1)···V(2)	3.49	O(1)···O(3)	2.65
O(1)···N(1)	2.33	O(2)···O(3)	2.63
O(1)···N(1A)	2.82	O(4)···O(3)	2.77
O(2)···N(1)	2.78	O(5)···O(3)	2.68
O(2)···N(1A)	2.22	O(8)···O(9)	2.72
O(4)···N(2)	2.67	O(10)···O(10^{i})	2.84
O(5)···N(2)	2.52	i = 1 − x, $\bar{y}$, $\bar{z}$	

clarity, is reported in Fig. 3. Least-squares calculations show that the base planes of the two coordination pyramides make an angle of 85 degrees. The axial V=O distances (1.55 and 1.56 Å) are among the shortest found in similar complexes and are characteristic of a double bond. TheV–O distances to the terminal oxygen atoms of the tridentate ligands average 1.85 Å whereas those to the bridging oxygen are somewhat shorter (1.76 and 1.81 Å), but all V–O distances, except V–O(10), are significantly shorter than the V–N distances (2.17 and 2.16 Å); a feature already observed which has been

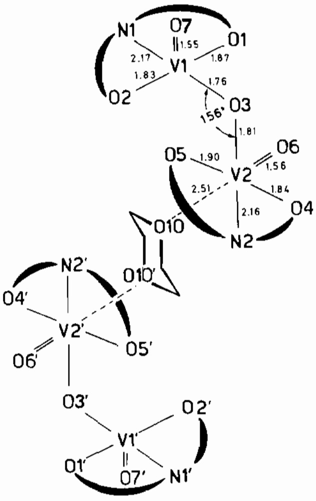


Fig. 1. Bonding scheme in $[(VOL)_2O]_2$·dioxane.

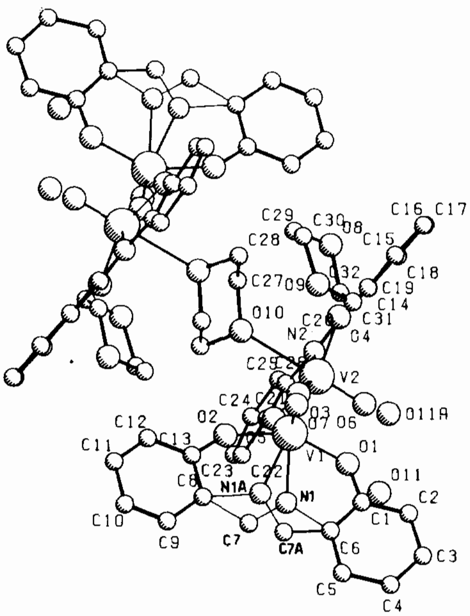


Fig. 2. Projection of the structure down the *b* axis of the cell.

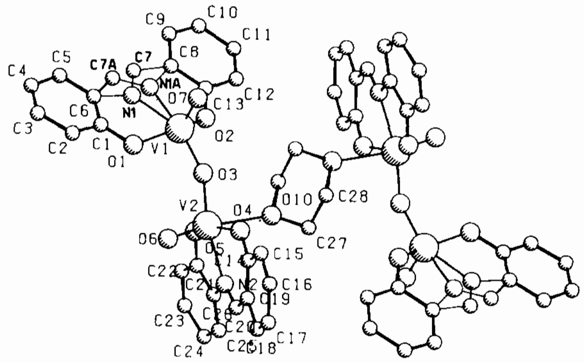


Fig. 3. Projection of the structure along [110]. For clarity clathrate solvent molecules are omitted.

attributed to several factors, including a relatively low affinity of the VO_2^+ ion for imino nitrogen [11]. Each ligand makes with the metal atom a six-membered and a five-membered ring. Angles at the oxygen atoms of the six-membered rings are comparable (132° and 133°) and larger than those of the corresponding atoms in the five-membered rings (126° and 122°) whereas V–O distances are shorter (1.83 and 1.81 Å against 1.87 and 1.90 Å respectively). The adjacent O···O bite distances of 2.68 Å (average) agree with the values found in other five-coordinate vanadyl complexes, but the N···O bite distances as well as the N–V–O angles are largely determined by the ligand geometry. The O–V–O angles with the base oxygens are comparable in the two coordination polyhedrons (mean 94° and 96°), but O(7)–V(1)–O angles involving the apical oxygen (mean 106°) are significantly larger than the corresponding O(6)–V(2)–O (mean 102°), this being probably related to the additional presence of the dioxane oxygen atom in the V(2) coordination sphere. A survey of the apex-to-base-angles shows that they are comprised between 100 and 108 degrees (or 96 and 108 degrees if we consider also the statistical presence of the nitrogen atom) in the V(1) pyramid, and between 100 and 104 degrees in the V(2) pyramid. It is noteworthy that in both cases the O(apex)–V–N angles have the smallest values and the O(apex)–V–O(3) angles have the largest ones. This could be a consequence of the presence of repulsive forces between the electronic valency pairs of these oxygens, which are not adequately counterbalanced by the corresponding repulsive forces between the apex oxygens and the more distant nitrogen atoms, according with the hypothesis of Gillespie [12].

The nitrogen atoms and the bonded chain carbon atoms are sp^2 hybridized but, as expected, the nitrogen atom angles in the six-membered ring (125°) are larger than in the five-membered ring (mean 115°). Bond distances show that the N=C (chain) bond (1.26 and 1.22 Å) is double whereas the N–C ring bond lengths (1.49 and 1.45 Å) are comparable with the value (1.47 Å) assumed for a pure $N(sp^2)$–$C(sp^2)$ single bond [13]. All the C–O distances are in the range 1.32–1.35 Å, that is they have the typical partial-double bond character of the C=O bonds when they are weakened by the adduct formation. The phenylene rings of the organic moiety are tilted to each other by 8 and 14 degrees respectively. As expected it is impossible for the ligands to be planar in this coordination geometry.

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