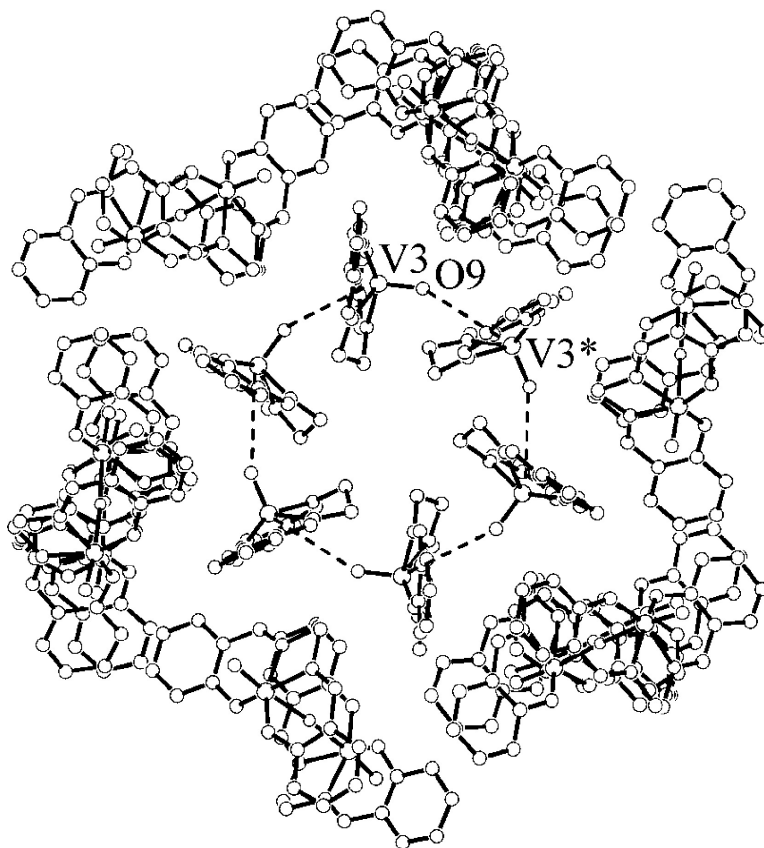


The First Oxovanadium Ring in $[\{OV(salen)\}(\mu-F)]_3[VO(salen)]_3[BF_4] \cdot (CHCl_3)$ Crystals

Kenichi Oyaizu, and Eishun Tsuchida

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The First Oxovanadium Ring in $[\{O=V(\text{salen})\}_2(\mu\text{-F})][VO(\text{salen})][BF_4]\cdot(\text{CH}_2\text{Cl}_2)_x$ Crystals

Kenichi Oyaizu and Eishun Tsuchida*

Advanced Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555, Japan

Received November 22, 2002; E-mail: eishun@mn.waseda.ac.jp

Here, we report the synthesis and crystal structure of a remarkable double salt $[\{O=V^V(\text{salen})\}_2(\mu\text{-F})][V^{IV}O(\text{salen})][BF_4]\cdot(\text{CH}_2\text{Cl}_2)_x$ ($\text{H}_2\text{salen} = N,N'$ -ethylenebis(salicylideneimine)) ($\mathbf{1}_x$). The $[VO(\text{salen})]$ units in the crystal arrange themselves to form a cyclic hexad, a motif never previously seen in oxovanadium complexes.

A ring of functional molecules such as metal complexes and pigments often exhibits exotic properties beyond those of individual molecules. A typical example is the well-designed exciton storage ring of pigment-protein complexes¹ in the bacterial photosynthetic light-harvesting antennas, which allows the coherent delocalization of excitation over the symmetric rings of bacteriochlorophyll (BChl)² and the efficient energy transfer to the photochemical reaction center: the elementary building blocks of the rings are small peptides which arrange themselves in circular structures and noncovalently bind BChls.¹ On the other hand, a synthetic approach to molecular rings without such a protein support is lacking a clear methodology. One must inevitably fall back on the serendipitous use³ of rotational symmetry in crystals without strictly designing the final organizational structure. Thus, molecules should be arranged in a lattice around the circumference of a multifold rotational axis when they occupy general equivalent positions without crystallographic site symmetry.⁴

Leigh et al. reported that $[V^{IV}O(\text{salen})]$ reacted with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ to produce a dinuclear species $[\{O=V^V(\text{salen})\}_2(\mu\text{-F})]^+$, the structure of which was determined as its BF_4^- and $[\text{VO}_2\text{F}_2]^-$ salts.⁵ The cation has also been isolated as a triiodide salt.⁶ Slow diffusion of diethyl ether into an equimolar mixture of $[\{O=V(\text{salen})\}_2(\mu\text{-F})][BF_4]$ and $[VO(\text{salen})]$ in CH_2Cl_2 affords prismatic brown crystals of $\mathbf{1}_x$.⁷ The structure of $\mathbf{1}_x$ ⁸ (Figure 1) reveals the absence of valence scrambling in the crystal. Thus, the V(3) atom lying as far as 0.601 Å above the equatorial N_2O_2 least-squares plane represents a typical square-pyramidal arrangement for vanadium(IV), while the preference of vanadium(V) to be six-coordinate rather than five,⁹ driving the formation of the μ -fluorido dimer, is reflected in the smaller deviation of the V(1) (0.213 Å) and V(2) (0.207 Å) atoms from the respective N_2O_2 planes. The shorter equatorial V–O(phenolate) bond lengths for V(1) and V(2) (1.82–1.85 Å) than those for V(3) (1.92–1.95 Å) are also indicative of the higher oxidation state of V(1) and V(2), because the V–O(phenolate) bond is known to shrink upon the oxidation of vanadium(IV) to vanadium(V).¹⁰

The arrangement of the $[VO(\text{salen})]$ units around the three-fold rotatory-inversion axis in the lattice (Figure 2a) can be described as the result of the self-assembly of $[VO(\text{salen})]$ to yield a cyclic hexad. The six $[\{O=V(\text{salen})\}_2(\mu\text{-F})]^+$ cations are also positioned around the symmetry axis, thereby generating a large hexagonal cavity to accommodate the $[VO(\text{salen})]$ hexad. In the cavity are also contained the noninteger molecules ($x = 0.165$) of the solvated CH_2Cl_2 as well as the necessary charge-balancing but noncoordinating BF_4^- anions which are both highly disordered. We emphasize that the geometrical influence of the BF_4^- anions is vital to the

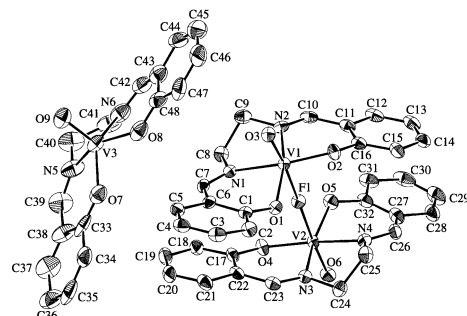


Figure 1. ORTEP view of the oxovanadium complexes in an asymmetric unit of $\mathbf{1}_x$ (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected atom distances (Å) and angles (deg): V1–O1, 1.857(3); V1–O2, 1.823(4); V1–O3, 1.598(3); V1–N1, 2.082(5); V1–N2, 2.103(4); V1–F1, 2.088(2); V2–O4, 1.839(4); V2–O5, 1.844(4); V2–O6, 1.599(3); V2–N3, 2.117(4); V2–N4, 2.065(5); V2–F1, 2.064(2); V3–O7, 1.945(5); V3–O8, 1.922(6); V3–O9, 1.596(5); V3–N5, 2.042(6); V3–N6, 2.055(5); F1–V1–O3, 173.1(2); V1–F1–V2, 174.9(2); F1–V2–O6, 174.0(2).

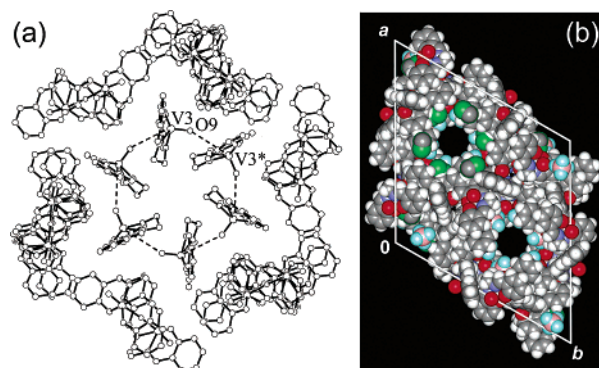


Figure 2. (a) A perspective view of the two concentric rings of the $[\{O=V(\text{salen})\}_2(\mu\text{-F})]$ and $[VO(\text{salen})]$ subunits in $\mathbf{1}_{0.165}$ projected along the three-fold rotatory-inversion axis which is parallel to the c -axis of the trigonal cell ($a/2 < x < a$, $0 < y < b/2$, $0 < z < c/2$). (b) Space-filling representation of the packed structure of $\mathbf{1}_{0.165}$ projected along the c -axis of the trigonal cell showing 1-D channels created perpendicular to the ab plane. The CH_2Cl_2 molecules and the BF_4^- anions are found at the wall of the channel. The central part of the channel is hollow (vacuum) with no atoms or molecules found there. The diameter of this tubular empty space is about 5.3 Å. Yellow, vanadium; red, oxygen; dark blue, nitrogen; gray, carbon; white, hydrogen; purple, boron; light blue, fluorine; green, chlorine.

formation of the curious $[VO(\text{salen})]$ arrangement. A control experiment carried out with $[\{O=V(\text{salen})\}_2(\mu\text{-F})][I_3]$ in place of the tetrafluoroborate salt (same quantities for all of the other components) did not generate the similar phase but yielded a crystal of $[\{O=V(\text{salen})\}_2(\mu\text{-F})][VO(\text{salen})][I_3]$ with a triclinic space group $P\bar{1}$ where the centrosymmetric I_3^- and $[\{O=V^V(\text{salen})\}_2(\mu\text{-F})]^+$ ions both occupied the inversion center in the crystal.⁶ The double salt with the triiodide anion does not possess μ -oxo bridges. A trigonal phase similar to that of the tetrafluoroborate ($\mathbf{1}_x$) appeared when

the triiodide anion was exchanged with the noncentrosymmetric anions such as ClO_4^- by recrystallizing the complex in the presence of an excess amount of tetrabutylammonium perchlorate, although the crystallographic refinement of the perchlorate has so far been unsuccessful. Thus, it may be stated that the crystal can be "engineered" to fabricate the desired $[\text{VO}(\text{salen})]$ ring on the basis of the geometric symmetry of the anions.

Atom-bridged linear chain complexes $[\text{LM}(\mu\text{-X})_n]$ (L = macrocyclic ligand; X = O, F, or N) have received much attention for their conductive,¹¹ liquid crystalline,¹² and nonlinear optical properties.¹³ The μ -oxo-bridged linear polymers are particularly attractive as electrooptical materials, because the linear chain formation could result in unidirectional (head-to-tail) one-dimensional alignment of the $\text{M}-\text{O}$ dipoles to create noncentrosymmetric assemblies. The polarized $\text{V}^{\text{IV}}=\text{O}$ unit is known to condense in a similar way, creating a vast array of molecular assemblies.^{14–16} Liquid crystals with oxovanadium(IV) core groups (metallomesogens) with rodlike tetradentate Schiff base ligands have been reported.¹⁴ The crystal structures of $[\text{V}^{\text{IV}}\text{O}(\text{salpn})]^{15}$ ($\text{H}_2\text{salpn} = N,N'-(1,3\text{-propylene})\text{bis}(\text{salicylideneimine})$) and $[\text{V}^{\text{IV}}\text{O}(\text{salptn})]^{16}$ ($\text{H}_2\text{salptn} = N,N'-(2,2\text{-dimethyl-1,3-propylene})\text{bis}(\text{salicylideneimine})$) consist of molecules packed so that the vanadyl oxygen atom of one molecule occupies the sixth position about the vanadium atom in a neighboring molecule, resulting in the infinite chain of molecules about a two-fold screw axis linked by $\cdots\text{V}^{\text{IV}}-\text{O}-\text{V}^{\text{IV}}\cdots$ bonds. However, to our knowledge, none of the cyclic chain has so far been fashioned from $\text{M}-\text{O}$ building blocks. The unprecedented $[\text{VO}(\text{salen})]_6$ ring in $\mathbf{1}_x$ is composed of a couple of triads associated with the three-fold rotational symmetry; the two triads are alternatively arranged to provide the centrosymmetric hexad. The $\text{V}3^*\cdots\text{O}9$ distance is relatively large (6.70 Å); nevertheless, one could expect a weak interaction of the vanadyl oxygen in $\mathbf{1}_x$ with the neighboring molecule based on the slightly smaller deviation of the $\text{V}(3)$ atom from the equatorial N_2O_2 plane than that of the vanadium(IV) atom (0.609 Å) in a crystal of $[\text{VO}(\text{salen})]$ packed with a purely monomeric arrangement.¹⁷

Another curious feature of the structure is the hollow cavities formed along the symmetry axis. In Figure 2b is displayed a top view of the packing structure of $\mathbf{1}_{0.165}$, showing the cavities that penetrate through the crystal. The diameter of the cavities built by this stacking measures approximately 5.3 Å. The cavity center-to-center distance amounts to 20.9 Å. The solvent CH_2Cl_2 molecules are positioned at the wall of the cavity. The cavity provides a channel for the guest CH_2Cl_2 molecules to travel within the crystal, thus allowing a rapid absorption and desorption of CH_2Cl_2 . Thermogravimetric analysis of the pristine crystal⁷ showed that up to one CH_2Cl_2 molecule per formula unit can reversibly be absorbed in $\mathbf{1}_x$ ($0 \leq x \leq 1$); thus, a weight loss of ca. 7% upon exposure of the pristine crystal to dry air at 50 °C (calcd weight loss based on one CH_2Cl_2 molecule per formula unit: 7.13%) is rapidly set off within a few seconds when the resulting crystals are placed under a CH_2Cl_2 atmosphere at 0 °C. The host lattice maintains its integrity while undergoing such an absorption-desorption cycle. The noninteger molecules of CH_2Cl_2 found by X-ray crystallography⁸ and the smaller density of the derived structure⁸ than that of $[\{\text{O}=\text{V}(\text{salen})\}_2(\mu\text{-F})][\text{VO}(\text{salen})][\text{I}_3]$ (1.773 g/cm³)⁶ indicate that some of the CH_2Cl_2 molecules would have been desorbed during

the course of the diffraction experiment even though it was quickly performed using an area detector at reduced temperature.⁸ A size-selective molecular sievelike behavior of the crystal for guest molecules based on the medium size of the cavity is preliminarily suggested by the lack of absorptivity for larger molecules such as CHCl_3 .

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Supporting Information Available: Tables giving atomic coordinates, equivalent isotropic thermal parameters, anisotropic displacement parameters, bond lengths, and angles for $\mathbf{1}_{0.165}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Into a solution of $[\{\text{O}=\text{V}(\text{salen})\}_2(\mu\text{-F})][\text{BF}_4]$ (77 mg, 0.1 mmol) and $[\text{VO}(\text{salen})]$ (33 mg, 0.1 mmol) in 10 mL of CH_2Cl_2 maintained at room temperature in a closed vessel was slowly diffused diethyl ether. Brown crystals of $[\{\text{O}=\text{V}(\text{salen})\}_2(\mu\text{-F})][\text{VO}(\text{salen})][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ ($\mathbf{1}_x$) were grown from the resulting mixture after 3 days, which were stored under a CH_2Cl_2 atmosphere of 1 atm at 10 °C. Yield: 84 mg (75%). Anal. Calcd for $\text{C}_{49}\text{H}_{44}\text{BCl}_2\text{F}_3\text{N}_6\text{O}_9\text{V}_3$ ($M = 1190.45$, $\mathbf{1}_1$): C, 49.44; H, 3.73; N, 7.06. Found: C, 50.39; H, 3.81; N, 7.46. IR (KBr, cm^{-1}): 979 ($\nu_{\text{V}=\text{O}}$).
- (8) Crystal data for $\mathbf{1}_x$: $M = 1119.59$ ($\mathbf{1}_{0.165}$), trigonal space group $R\bar{3}$ (No. 148), $a = 36.423(5)$ Å, $c = 18.597(4)$ Å, $V = 21366(6)$ Å³, $Z = 18$, $F(000) = 10259.28$, $D_{\text{calcd}} = 1.57$ g/cm³, μ (Mo K α) = 6.80 cm⁻¹. The data were collected at -150 ± 1 °C ($2\theta_{\text{max}} = 55^\circ$) using a Rigaku RAXIS II imaging plate area detector. Of the 42 047 reflections collected, 10 913 were unique ($R_{\text{int}} = 0.076$). The final cycle of the full-matrix least-squares refinement (function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma_o^2(F_o) + 0.00372F_o^2)^{-1}$) was based on 8117 observed reflections ($I > 3\sigma(I)$) and 625 variable parameters and converged with $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.090$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2} = 0.138$. GOF = 2.05.
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