Synthesis and Structure of Novel Vanadium(III) Compounds Having a Cyclic Core

Hitoshi Kumagai and Susumu Kitagawa*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami Ohsawa, Hachiouji, Tokyo 192-03

(Received March 5, 1996)

Treatment of $VCl_3(thf)_3$ with dipyridylamine, sodium hydride and sodium acetate yields a novel cyclic octanuclear vanadium(III) complex; the X-ray structure analysis reveals a cyclic vanadium core. The vanadium ions are alternatively bridged by hydroxide, ethoxide and carboxylate.

A growing number of dinuclear vanadium(III) compounds with oxygen donor ligands have been synthesized and structurally characterized as interest in related biological units and magnetic properties.[1-10] Our interest in vanadium(III) chemistry stems in part from synthesis of polynuclear vanadium(III) aggregates. However, few examples of high-nuclearity vanadium(III) complexes are known. Binding ability of carboxylato, alkoxo and/or oxo ligands is widely employed for the assemblage of di- and poly-metallic units. In the present communication acetate and benzoate were used to afford a tri- and octanuclear vanadium(III) complexes, $[V_8(\mu\text{-OH})_4(\mu\text{-OEt})_8(\mu\text{-CH}_3COO)_{12}]$ (**1**) and $[V_3(\mu\text{-O})(\mu\text{-C}_6H_5COO)_6(EtOH)_3]^+$ (**2**), which were characterized crystallographically.[11,12] All complexes were prepared under an Ar atmosphere using standard Schlenk techniques. $VCl_3(thf)_3$ was prepared according to the literature methods.[13] For the compound **1**, NaH (0.02g, 5mmol) and dpya (dpya = di-2-pyridylamine) (0.09g, 5mmol) were stirred in thf, followed by the addition of sodium acetate (0.08g, 10mmol). Then the ethanolic solution of $VCl_3(thf)_3$ (0.2g, 5mmol) was added to the suspension. Hexane was layered slowly on the filtrate. Small amount of black crystals were obtained. The compound **2** was synthesized by adding ethanol solution of $VCl_3(thf)_3$ (0.2g, 5mmol) to ethanol solution of dpya (0.09g, 5mmol) and benzoic acid (0.13g, 10mmol). Single crystals of **2** were obtained from the hexane-layered ethanol solution.

The molecular structure of **1** is shown in Figure 1, indicative of an octameric form having eight distorted octahedral vanadium ions of O_6 environment. The molecule has an crystallographic C2 axis passing through the center of the cavity. All vanadium atoms, O(1), O(5), O(6), O(7), O(10) and O(12) are sitting on the crystallographic mirror plane. The near D_{4h} symmetry of the whole molecule is clearly seen.

There are no other small anions in the lattice and therefore the molecule is neutral, indicating that the possible oxidation states of vanadium atoms are V(IV) or V(III); V(III) states occur when the inner oxygen atoms of O(1), O(1'), O(7) and O(7') are protonated to be hydroxo-bridges. There are three possible valence states; (1) all V(III) atoms and all hydroxo bridges, (2) n(V(III))/n(V(IV)) = 3 and the ratio of the number of OH^- to O^{2-} is 1, and (3) n(V(III))/n(V(IV)) = 1 and all oxo bridges (n denotes the number of atoms or groups). The vanadium(III) compounds having a $[V(III)(\mu\text{-X})(\mu\text{-RCOO})_2V(III)]^{2+}$ core have so far been synthesized and characterized X-ray crystallographically. Their V-O distances and V-O-V angles for X = O^{2-} fall within the range of 1.777Å to 1.792(4)Å and 130.2(2)° to 143.7(13)°, respectively while those values for X = OH^- range from 1.934(2)Å to 1.959(10)Å, and from 123.5(3)° to 133.1(5)°, respectively.[4,5,14] The V-O(hydroxo) distances are longer than the V-O(oxo) distance,[1] supporting that the moieties of O(1), O(1') O(7) and O(7') are hydroxo groups. The angles of **1** also fall within the range of the case for X = OH^-. Therefore the oxidation state III for all the vanadium ions is most possible.

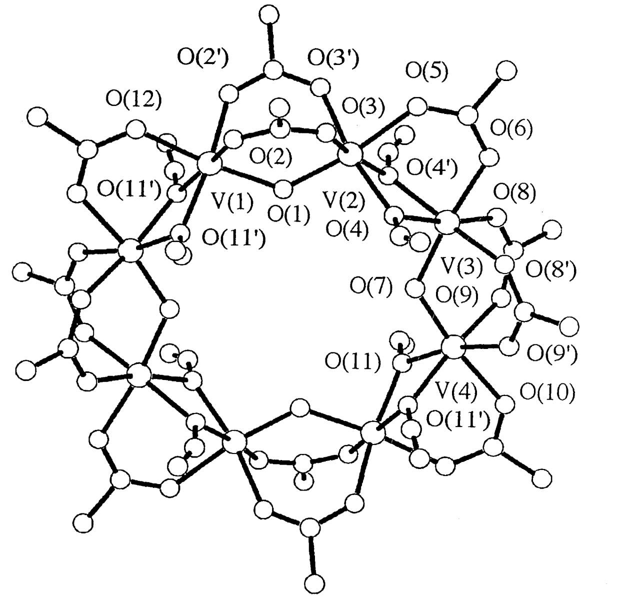

Figure 1. CHARON drawing of **1** showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity in this figure. Selected Bond Distances (Å) and Angles (deg) are as follows: V(1)-O(1), 1.951(7); V(1)-O(2), 2.011(6); V(1)-O(11'), 1.981(5); V(1)-O(12), 2.025(7); V(2)-O(1), 1.865(8); V(2)-O(3), 2.006(6); V(2)-O(4), 1.968(5); V(2)-O(5), 2.037(8); V(3)-O(4), 1.981(5); V(3)-O(6), 2.026(8); V(3)-O(7), 1.942(7); V(3)-O(8), 2.011(6); V(4)-O(7), 1.875(7); V(4)-O(9), 2.006(6); V(4)-O(10), 2.032(8); V(4)-O(11), 1.967(5); V(1)-O(1)-V(2), 127.5(4); V(2)-O(4)-V(3), 99.9(3); O(4)-V(3)-O(7), 95.2(2); V(3)-O(7)-V(4), 127.3(4)

The compound **1** has two characteristic features. Firstly, **1** has two types of grouped bridging ligands; one is $(OH)(CH_3COO)_2$ (type A) and the other is $(C_2H_5O)_2(CH_3COO)$ (type B). These types are arranged alternatively to form a cyclic compound. Therefore the two distances of vanadium atoms are obtained; 3.4Å and 3.0Å for V-type A-V and V-type B-V, respectively.

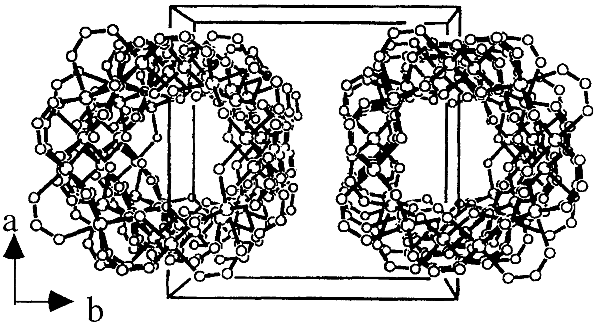

Figure 2. View of the structure of **1** parallel to the crystallographic c axis, showing the infinite channel passing through the interior holes. Carbon atoms of ethoxo ligands and methyl groups are omitted for clarity.

Secondly, the cyclic compounds are stacked along the c axis in the crystal lattice to produce an infinite channel passing through the interior holes. The diameter of the ring is 6Å, which is defined as the average distance of O(1)•••O(1') and O(7)•••O(7'). The four oxygen groups, directed toward the center of the hole, could be able to trap ionic species such as metal ions, organic and inorganic ions.[15] To our knowledge, one vanadium(IV) cyclic compound, $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$, has been isolated[16] which has oxalate as a template in the cavity indicating no more space to trap anions. The macrocyclic framework in **1** is, thus, one of host candidates for host-guest chemistry, such as $[NaFe_6(OCH_3)_{12}(dbm)_6]Cl$ (dbm = dibenzoylmethane) and $\{[TiO(O_2CC_6F_5)_2]_8\}nC_7H_8$.[17,18]

Throughout the synthesis of cyclic polynuclear compounds, we also found a new synthetic route for oxo-centered trivanadium(III) complexes,[19-21] by which the corresponding benzoate form provides a single crystals. The structure of trinuclear cations is shown in Figure 2. The vanadium atoms show octahedra formed by VO_6 coordination geometry.

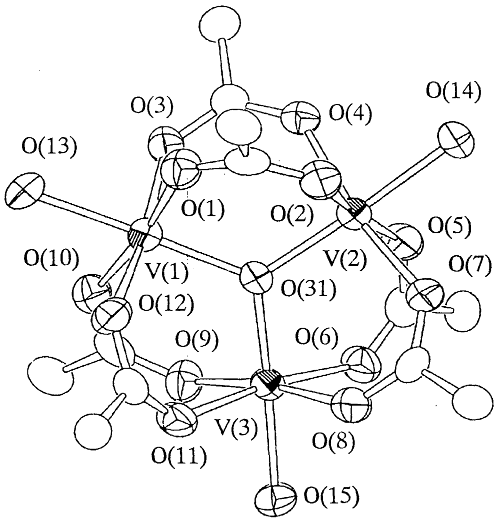

Figure 2. ORTEP drawing of **2** showing the atom-labeling scheme. Phenyl groups, carbon atoms of ethanol and hydrogen atoms are omitted for clarity. Atoms are represented by their 50% probability ellipsoids. Selected Bond Distances (Å) and Angles (deg) are as follows:
V(1)-O(1), 1.990(7); V(1)-O(3), 2.025(6); V(1)-O(10), 1.995(7); V(1)-O(12), 2.010(7); V(1)-O(13), 2.064(6); V(1)-O(31), 1.929(6); O(1)-V(1)-O(3), 90.5(3); O(3)-V(1)-O(10), 89.0(3); O(3)-V(1)-O(12), 173.4(3); O(3)-V(1)-O(13), 88.7(3); O(3)-V(1)-O(31), 93.6(3); O(1)-V(1)-O(10), 172.0(3); O(1)-V(1)-O(12), 87.5(3); O(1)-V(1)-O(13), 85.7(3); O(1)-V(1)-O(31), 93.4(3); O(10)-V(1)-O(12), 92.2(3); O(10)-V(1)-O(13), 86.3(3); O(10)-V(1)-O(31), 94.7(3); O(12)-V(1)-O(13), 84.9(3); O(12)-V(1)-O(31), 92.8(3); O(13)-V(1)-O(31), 177.5(3); V(1)-O(31)-V(2), 119.6(3); V(1)-O(31)-V(3), 119.9(3); V(2)-O(31)-V(3), 120.5(3)

This research was supported in part by a Grant-in-Aid for scientific research (No. 07640757) from the Ministry of Education, Science and Culture of Japan.

References and Notes

1 K. Kanamori, T. Okayasu, and K. Okamoto, *Chem.Lett.*, **1995**, 105.

2 K. Kanamori, M. Teraoka, H. Maeda, and K. Okamoto, *Chem.Lett.*, **1993**, 1731.

3 K. Kanamori, K. Yamamoto, and K. Okamoto, *Chem.Lett.*, **1993**, 1253.

4 M. R. Bond, R. S. Czernuszewicz, B. C. Dave, Q. Yan, M. Mohan, R. Verastegue, and C. J. Carrano, *Inorg.Chem.*, **34**, 5857, (1995).

5 C. J. Carrano,R. Verastgue, and M. R. Bond, *Inorg.Chem.*, **32**, 3589, (1993).

6 P. Knopp and K. Wieghardt, *Inorg.Chem.*, **30**, 4061, (1991).

7 R. Hotzelmann and K. Wieghardt, *Inorg.Chem.*, **32**, 114, (1993).

8 R. Hotzelmann, K. Wieghardt, J. Ensling,H. Romstedt, P. Gutlich,E. Bill, U. Florke, and H.-J. Haupt, *J.Am.Chem.Soc.*, **114**, 9470, (1992).

9 R. Hotzelmann, K. Wieghardt, U. Floerke, H.-J. Haupt, D. C. Weatherburn, J. Bonvoisin, G. Blondin, and J.-J. Girerd, *J.Am.Chem.Soc.*, **114**, 1681, (1992).

10 N. S. Dean, S. L. Bartley,W. E. Streib, E. B. Lobkovsky, and G. Christou, *Inorg.Chem*, **34**, 1608, (1995).

11 Crystal data; Empirical Formula, $C_{20}H_{46}O_{18}V_4$; Formula Weight, 778.34; Crystal System, orthorhombic; Space Group, Pccm; a = 14.306(2)Å; b = 14.306(1); c = 18.681(2)Å; V = 3823.2(5)Å^3; Z = 4; Dc = 1.352gcm^{-3}; No. of Reflections Measured, Total: 3216; Unique, 3215; No. Observations ($I>3.00\sigma(I)$) = 2484; No. Variables = 229; R(Rw) = 0.064(0.101); Toward the end of the development of the structure, the thermal ellipsoids on C(4) and C(10) atoms indicated disorder. From the difference Fourier peaks each site was remodeled as the C(4) and C(14) (C(10) and C(15)) with the site occupancies of 50%, respectively. These four carbon atoms were refined anisotropically. In the difference Fourier map, the residual electron density (1.1 and 1.0 e$^-$/Å^3) were found around the O(1) and O(7) atoms, respectively. However, the hydrogen atoms of the hydroxo groups were not located at these positions due to the long O-H distances (ca. 1.6Å).

12 Crystal data; Empirical Formula, $C_{106}H_{100}O_{32}Cl_3N_3V_6$; Formula Weight, 2339.96; Crystal System, monoclinic; Space Group, $P2_1/n$; a = 21.797(5)Å, b = 22.588(9)Å, c = 25.679(6)Å, β = 111.51(2)°, V = 11762(5)Å^3; Z = 4, Dc = 1.321gcm^{-3}; No. of Reflections Measured, Total: 28619; Unique: 27742; No. Observations ($I>3.00\sigma(I)$) = 11953; No. Variables = 1351; R(Rw) = 0.071(0.100).

13 E. Kurras, *Naturwissenschaften*, **46**, 171, (1959).

14 K. Wieghardt, M. Koppen, B. Nuber, and J. Weiss, *J.Chem.Soc., Chem.Commun.*, **1986**, 1530.

15 S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, and M. Munakata, *Inorg.Chem.*, **34**, 1455, (1995).

16 Q. Chen, S. Liu, and J. Zubieta, *Inorg.Chem.*, **28**, 4433, (1989).

17 A. Caneschi, A. Cornia, and S. J. Lippard, *Angew.Chem.Int.Ed.Engl.*, **34**, 467, (1995).

18 H. Barrow, D. A. Brown, N. W. Alcock, H. J. Clase, and M. G. H. Wallbridge, *J.Chem.Soc.,Chem.Commun.*, **1995**, 1231.

19 F. A. Cotton, G. E. Lewis, and G. N. Mott, *Inorg.Chem.*, **21**, 3127, (1982).

20 F. A. Cotton, G. E. Lewis, and G. N. Mott, *Inorg.Chem.*, **21**, 3316, (1982).

21 F. A.Cotton, L. R. Falvello, E. Libby, C. A. Murillo, and W. Schwotzer, *Inorg.Chem.*, **25**, 3423, (1986).