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The First "Vanadate Hexamer" Capped by Four Pentamethylcyclopentadienylrhodium or -iridium Groups

Yoshihito HAYASHI, Yoshiki OZAWA, and Kiyoshi ISOBE*
Institute for Molecular Science, Myodaiji, Okazaki 444

The organometallic oxide clusters $[(MCp^*)_4V_6O_{19}]$ (M=Rh, Ir; $Cp^*=C_5Me_5$) were prepared and characterized by elemental analyses, SIMS as well as IR and NMR (^1H, ^{13}C, ^{17}O, ^{51}V) spectroscopy. Single crystal X-ray analysis showed that $[(RhCp^*)_4V_6O_{19}]\cdot 4CH_3CN\cdot H_2O$ contains the vanadate hexamer core (V_6O_{19}). The rhodium cluster displays site selective oxygen exchange with free water at the bridging oxygen atoms.

Organometallic oxide clusters containing transition metals in both high and low oxidation states are expected to have multi-functional properties and cooperative effects on reactivity owing to the mixed multi-metal center systems.1) We have recently demonstrated that the neutral oxide clusters, $[MCp^*MoO_4]_4$ (M=Rh, Ir; $Cp^*=C_5Me_5$), have a novel triple-cubane core which is very similar in structure to that of fragments of MoO_3, and may prove to be a good model for metal oxide surfaces.2) We report here the first example of "vanadate hexamer," $[(MCp^*)_4V_6O_{19}]$, which displays a unique interaction with water, leading to the site-selective oxygen exchange with water at the bridging oxygen atom sites and dissociation of the organometallic group $[RhCp^*]^{2+}$.

An aqueous suspension (10 cm^3) of $NaVO_3$ (0.63 g, 5.2×10^{-3} mol) was added dropwise to a suspension of $[RhCp^*Cl_2]_2$ (0.32 g, 5.2×10^{-4} mol) in water (10 cm^3) at 25 °C, and the mixture was stirred for 30 min to result in a very deep red solution, which was then extracted with CH_2Cl_2. The CH_2Cl_2 solution was evaporated to leave a deep red solid. In the case of $[IrCp^*Cl_2]_2$, a blue black solid was similarly obtained. Recrystallization from CH_2Cl_2 gave black crystals formulated as $[(MCp^*)_4V_6O_{19}]\cdot nH_2O$ (n=4 for M=Rh(**1**) and 0 for Ir(**2**)) in 90 and 96% yields, respectively. The water of crystallization is easily lost under vacuum at room temperature.3)

X-Ray structure analysis4) of the rhodium cluster revealed that the V_6O_{19} framework is composed of an octahedral arrangement of vanadium atoms around a central oxygen atom, each vanadium being surrounded by six oxygen atoms (Fig. 1). Rhodium atoms in the $RhCp^*$ units form a tetrahedral array, each being bound to the alternate triangular cluster face comprised of bridging oxygen atoms. The overall molecular symmetry is T_d. Each vanadium is bound peripherally to neighboring vanadium atoms through an oxygen bridge to form a cage-like structure and retains three distinct types of bonding: one bond to a terminal oxygen (O^t) [$V-O^t$=1.61 (2, 2, 3, 3,) Å5)], four bonds to bridging oxygen atoms (O^b), each of which is shared by another vanadium and rhodium atoms [V-O^b=1.913 (8, 7, 12, 4) Å], and one to a central oxygen (O^c) which is shared by all six vanadium atoms [V-O^c=2.25 (1, 3, 4, 3) Å]. The V-O^t and V-O^c distances are very close to the corresponding values in $V_{10}O_{28}^{6-}$ (V-O^t=1.61 Å, V-O^c=2.23 Å), but the V-O^b distances are longer than those in $V_{10}O_{28}^{6-}$ (the averaged bond distance: V-O^b=1.85 Å).[6)] The lengthening of V-O^b bonds is caused by binding of the $[RhCp^*]^{2+}$ group to the bridging oxygen atoms in $V_6O_{19}^{8-}$. The rhodium atom has an octahedral geometry and achieves the 18-electron configuration by ligating three adjacent bridging O atoms as observed previously.[2, 7)] The V1i•••V1ii (3.175 (5) Å), Rh1i•••V1i (2.995 (3) Å), and Rh1i•••Rh1ii (5.927 (3) Å) distances indicate no bonding interaction between the respective metal atoms. Each of four acetonitrile molecules is located on the center of triangular cluster face comprised of the bridging oxygen atoms. The methyl group of acetonitrile is directed toward the triangular face. Cluster **1** is the first vanadate hexamer with the V_6O_{19} framework.[8)]

Samples of **1** and **2** enriched with ^{17}O were prepared in ^{17}O-enriched water, with which VO_3^- readily exchanged oxygen at pH ca. 7. The ^{17}O NMR spectra display three completely resolved signals in $CDCl_3$ as shown in Fig. 2 for **1**.[9)] These

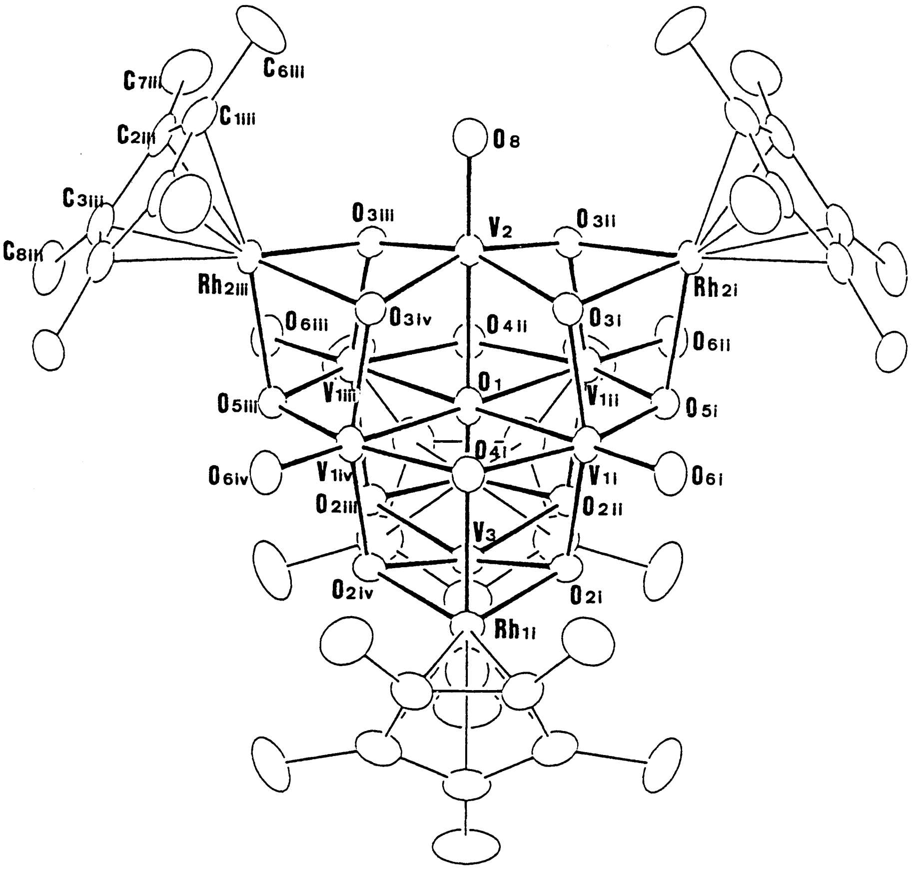

Fig. 1. Molecular structure of $[(RhCp^*)_4V_6O_{19}]$: ORTEP diagram with the numbering scheme. Important bond lengths (Å) and angles (deg) not mentioned in the text are as follows: Rh1i-O2i, 2.111(9); V1i-O6i, 1.61(1); V1i-O1, 2.248(2); V1i-O2i, 1.904(9); V2-O1, 2.29(2); V3-O1, 2.21(2); V2-O1-V3, 180(1); Rh1i-Rh1ii-Rh2i, 60.31(3); V1i-V2-V1ii, 59.9(1); V1i-O1-V3, 91.0(5).

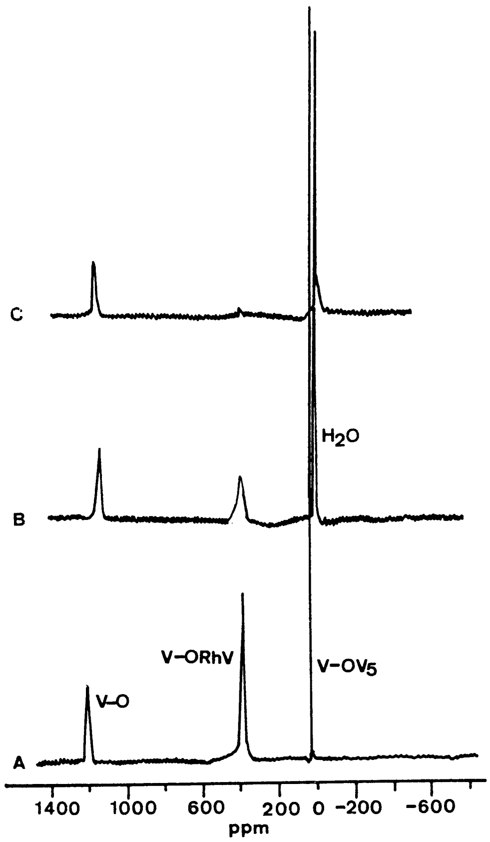

Fig. 2. ^{17}O NMR spectra of $[(RhCp^*)_4V_6O_{19}]$ in $CDCl_3$ at 25 °C (A), in H_2O at 25 °C (B), and in H_2O at 25 °C after heating at 90 °C for 4 h (C).

resonances are assigned on the basis of the general correlation between chemical shift and the π-bond order of V-O which increases with decreasing bond length.$^{10)}$ Cluster **1** also gives a similar ^{17}O NMR spectral pattern in H_2O at 25 °C,$^{11)}$ but the signal of O^b is very broad ($\Delta\upsilon 1/2$: O^b, 1192 Hz; O^t, 525 Hz; O^c, 14 Hz) compared with that in $CDCl_3$ (Fig. 2). This broadening of the O^b signal is caused by interaction of the bridging oxygen in the cluster with free H_2O. The ^{17}O NMR spectrum measured at 25 °C after standing at 90 °C for 4 h displayed an anomalous decrease in the O^b signal intensity although the intensities of the O^t and O^c signals remained unaltered (Fig. 2). The ^{51}V NMR spectra measured between at 25 °C and 90 °C showed only one signal.$^{12)}$ These results indicate that site-selective oxygen exchange with free water occurs at the bridging oxygen atoms without any change in the cluster skeleton (as follows):$^{13)}$

$$[(RhCp^*)_4V_6{}^{17}O^c\,{}^{17}O^t{}_6\,{}^{17}O^b{}_{12}] + H_2{}^{16}O \rightleftharpoons [(RhCp^*)_4V_6{}^{17}O^c\,{}^{17}O^t{}_6\,{}^{16}O^b\,{}^{17}O^b{}_{11}] + H_2{}^{17}O \quad (1)$$

The strong interaction of the O^b atom with water molecule weakens both the V-O^b and Rh-O^b bonds. Dissociation of the $[RhCp^*]^{2+}$ group from **1** is not observed in neutral aqueous solution, but becomes appreciable around pH 3.8 (Eq. 2).

$$[(RhCp^*)_4V_6O_{19}] + 2nH^+ \longrightarrow [(RhCp^*)_{4-n}V_6O_{19}H_{2n}] + n[(RhCp^*)L_3]^{2+} \quad (2)$$

By virtue of this reaction we can obtain mixed clusters of $[(RhCp^*)_{4-n}(IrCp^*)_n$-$V_6O_{19}]$ (n=1-4) from the reaction of **1** with $[IrCp^*(L)_3]^{2+}$ (L=H_2O or CH_3CN).

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References

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3) **1**: Anal. Found: C, 30.59; H, 4.28%. Calcd for $C_{40}H_{60}O_{19}Rh_4V_6$ (anhydrous): C,

30.75; H, 3.87%. SIMS showed $[M+1]^+$ ion peaks with an isotopic distribution. IR (Nujol, 1000-400 cm^{-1}) 934 cm^{-1} (s) [ν V-O^t], 722 (s), 677 (s), 559 cm^{-1} (m) [ν V-O^b], 483 cm^{-1} (s) [ν V-O^c] (O^t: terminal oxygen, O^b: bridging oxgen, O^c: central oxygen). ^1H NMR ($CDCl_3$) C_5Me_5 δ 1.94 s. ^{13}C NMR ($CDCl_3$) $C_5\underline{Me}_5$ δ 9.4 s; $\underline{C}_5Me_5$ δ 93.7 d (J_{C-Rh}=8.9 Hz). **2**: Anal. Found: C, 24.78; H, 3.18%. Calcd for $C_{40}H_{60}Ir_4O_{19}V_6$: C, 25.03; H, 3.15%. SIMS showed $[M+1]^+$ ion peaks with an isotopic distribution. IR (Nujol, 1000- 400 cm^{-1}) 940 cm^{-1} (s) [ν V-O^t], 748 (m), 672 (m), 562 cm^{-1} (m) [ν V-O^b], 500 cm^{-1} (m) [ν V-O^c]. ^1H NMR ($CDCl_3$) C_5Me_5 δ 1.90 s. ^{13}C NMR ($CDCl_3$) $C_5\underline{Me}_5$ δ 9.8 s; $\underline{C}_5Me_5$ δ 87.1 s.

4) The crystal used in the X-ray study was obtained as the acetonitrile and water solvate, $[(RhCp^*)_4V_6O_{19}]\cdot 4CH_3CN\cdot H_2O$, from an acetonitrile solution. Crystal data are as follows: orthorhombic, space group $\underline{P}_{\underline{mmn}}$, $\underline{a}$=15.151(2) Å, $\underline{b}$=18.611(2) Å, $\underline{c}$=11.682(2) Å, $\underline{V}$=3294.2(7) Å^3, $\underline{Z}$=2, $\underline{D}_x$=1.759 g cm^{-3}. Intensity data were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation in the $2\theta \leqq 60°$ range. The structure was solved by a direct method (Multan 78) and refined by a block diagonal least-squares technique. The current $\underline{R}$ value is 0.047 for 1484 independent absorption-corrected reflections.

5) The numbers in parenthese are written according to the Klemperer's method. The first, second, and third numbers are the average of the standard deviations, the average and maximum deviations from the averaged value of bond lengths, respectively. The fourth number represents the number of data. See Ref. 7.

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9) ^{17}O NMR chemical shifts referred to D_2O at 25 °C (lower field positive) are as follows: (a) anhydrous **1** in $CDCl_3$, δ 1213 (OV), 386 ($ORhV_2$), and 27 (OV_6); **2** in $CDCl_3$, δ 1236 (OV), 360 ($OIrV_2$), and 37 (OV_6); (b) **1** in D_2O, δ 1176 (OV), 404 ($ORhV_2$), and 27 (OV_6).

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11) The spectra was measured by the water-suppression technique.

12) ^{51}V NMR (H_2O): δ 648 at 25 °C, δ 655 at 90 °C. The chemical shifts vary slightly with temperature and are referred to neat $VOCl_3$.

13) A different site selective oxygen exchange at the terminal oxygen atom has been observed for the aqueous $Ta_6O_{19}^{8-}$ system. See Ref. 10b.

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