Tetrahedral Cobalt(II) and Zinc(II) Chloride with Tetravanadate through a Tripod Coordination Mode

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Polyoxometalate derivatives, $((n\text{-}C_4H_9)_4N)_3[(MCl)V_4O_{12}]$ (**1**, M = Co and **2**, M = Zn), have been synthesized from reactions of a tetravanadate with $CoCl_2{\cdot}6H_2O$ and $ZnCl_2$, respectively. From the variable-temperature ^{51}V and ^{17}O NMR studies of **2**, a dynamic behavior of the tetrahedral metal group on the surface of oxide mimic tetravanadate was observed in acetonitrile solution.

Currently, polyoxometalate has attracted much attention in diverse areas such as ion-transport models, oxide catalysis, and materials science.[1] Organometallic-group-supported polyoxometalate has a fundamental importance as a key model species for understanding mechanisms of catalysis.[2] However, it is necessary to develop synthetic methods for the supported polyoxovanadates of various coordination modes to establish a model schemes for catalytic processes.[3] Simple model compounds are the tetravanadate supported with an organometallic Rh or Ir unit, $[(LM)_2V_4O_{12}]^{2-}$.[4] In these examples, tetravanadate unit is coordinated as a bidentate ligand to the individual organometallic group that has a square-planar coordination environment of Rh^I or Ir^I with π coordination of diolefin groups such as those of COD (cyclooctadiene).

In a typical catalytic cycle on the oxide surface, four key steps are necessary to consider; (1) the formation of supported organometallic compound on oxides, (2) the migration of substrates, (3) the elimination of the products from the metal center which releases the supported coordination compound on oxides, (4) the reproduction of supported organometallic compounds on oxides with the reaction of organic substrates.[5] To model such a catalytic reaction on oxides, the supported polyoxovanadates that have an available coordination site through the presence of leaving group are required. In this paper, we describe such a new coordination mode of cyclic tetravanadate, $[V_4O_{12}]^{4-}$, upon binding to a tetrahedral metal center.

Treatment of $(n\text{-}Bu_4N)VO_3$ with $CoCl_2{\cdot}6H_2O$ in a 4:1 ratio in acetonitrile gave green compound $(n\text{-}Bu_4N)_3[(CoCl)V_4O_{12}]$ (**1**), while the reaction with $ZnCl_2$ gave colorless compound $(n\text{-}Bu_4N)_3[(ZnCl)V_4O_{12}]$ (**2**).[6] The X-ray quality crystals were prepared by vapor diffusion of ether or ethyl acetate into an acetonitrile solution of each complex at room temperature.[7] The structures of **1** and **2** determined by the X-ray analysis[8] reveal identical anionic fragments with a general formula of $[(MCl)V_4O_{12}]^{3-}$. Both clusters crystallize in space group $P2_1$. Cluster **1** has one cluster anion with three counter cations in the asymmetric unit, while cluster **2** has two independent cluster anions whose structures are nearly identical to that of **1**, with six counter cations in the asymmetric unit. The anionic cluster consists of a $V_4O_{12}{}^{4-}$ fragment with the MCl^+ (M = Co for **1**, Zn for **2**) group attached directly to the tetravanadate through three oxygen bridges, resulting in the tetrahedral arrangement of the metal.

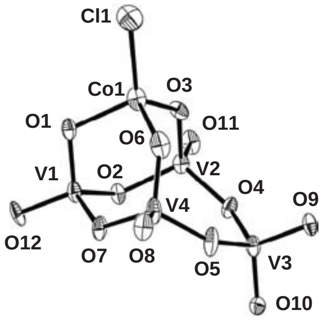

Figure 1. ORTEP representation of cluster anion **1**. Selected distances (Å) are as follows: Co1–Cl1, 2.183(5); Co1–O1, 1.988(8); Co1–O3, 1.910(9); Co1–O6, 1.913(7); V1–O1, 1.683(8); V1–O2, 1.829(8); V1–O7, 1.797(7); V1–O12, 1.637(8); V2–O2, 1.810(8); V2–O3, 1.691(11); V2–O4, 1.768(7); V2–O11, 1.633(8); V3–O4, 1.819(7); V3–O5, 1.814(8); V3–O9, 1.623(8); V3–O10, 1.652(9); V4–O5, 1.760(8); V4–O6, 1.691(8); V4–O7, 1.804(8); V4–O8, 1.632(8).

The precedented $[(MR)_2V_4O_{12}]^{2-}$ type[4] complexes have a similar conformation in which the four vanadium atoms nearly sit on a plane. On the other hand, the four vanadiums in **1** and **2** are arranged in a butterfly shape (V2 and V4 at a hinge position) with dihedral angles of 139° for **1** and 142° for **2**. These are significantly larger when compared with the value of 128° reported[9] for $[HV_4O_{12}]^{3-}$ which has a butterfly conformation in its protonated form. In cluster **1**, one of the VO_4 units (V3 in Figure 1) is not coordinated to the cobalt atom and has different oxygen atoms, terminal oxygens ($V\text{–}O_t$, 1.623(8)–1.652(9) Å) and bridging oxygens ($V\text{–}\mu\text{-}O_V$, 1.814(8)–1.819(7) Å). The three remaining VO_4 units of V1, V2, and V4 have three different oxygen atoms, the terminal oxygens ($V\text{–}O_t$, 1.632(8)–1.637(8) Å) and two kinds of bridging oxygens ($V\text{–}\mu\text{-}O_V$, 1.797(7)–1.829(8) Å; $V\text{–}\mu\text{-}O_{Co}$, 1.683(8)–1.691(8) Å). The five atoms on part of the butterfly wing, V2, O4, V3, O5, and V4 lie on the same plane, which is a characteristic feature for this conformation. The structure of cluster **2** is geometrically the same as that of **1**. The distances of the bridging oxygen $V\text{–}O_{Zn}$ (1.678(6)–1.691(6) Å) in **2** are comparable to that of the $V\text{–}O_{Co}$ in **1**, indicating the weaker interactions between the tetravanadate and the metal units. The Zn–Cl distances (2.183(3) and 2.191(3) Å) are shorter than the Co–Cl distance, reflecting the difference in ionic radius. These complexes provide an example of all-inorganic coordination chemistry[10] of a well-defined soluble species where polyanions act as a *ligand*.

The variable-temperature ^{51}V and ^{17}O NMR spectra of **2** are represented in Figure 2 in a temperature range between −40 and 50 °C. The ^{17}O-enriched sample of **2** was prepared from the synthesis of the enriched tetravanadate. The ^{17}O NMR spectrum at 50 °C presents signals at 1067, 817, and 526 ppm, attributed to

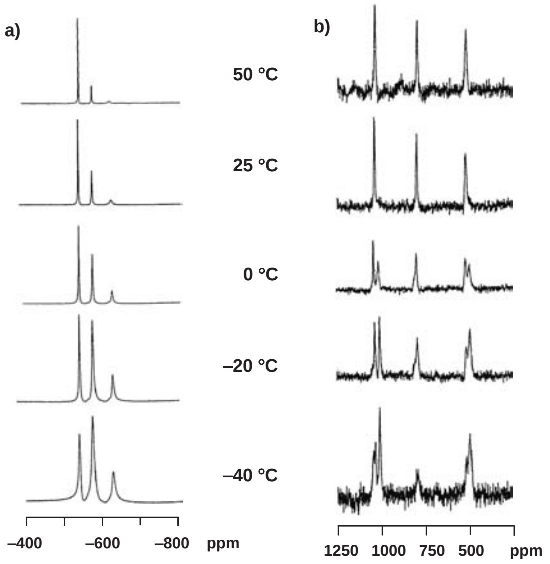

Figure 2. Variable temperature NMR spectra of **2** in acetonitrile-d_3: (a) ^{51}V NMR; (b) ^{17}O NMR.

the terminal oxygens, the bridging oxygens between V and Zn atoms, and those between vanadium atoms, respectively. At −40 °C, the dynamic process slows down and splittings of signals are observed, corresponding to the expected structural features observed for the crystal structure of **2**; two kinds of terminal oxygens at 1092 and 965 ppm, two kinds of bridging oxygens (V–O–Zn bridge) at 838 and 728 ppm, and two kinds of bridging oxygens (V–O–V bridging) at 548 and 526 ppm, with the intensity ratio of 5:4:3, are observed. These fluxional phenomena are reversible as the lines retrieve when returning to the initial temperature. The fluxionality of the organometallic fragments on the tetravanadate has been reported[11] with a pivoting mechanism. A similar dynamic process is suggested without the dissociation of the MCl^+ group from the evidence that the ^{17}O NMR signals of bridging oxygens (V–O–Zn) are well separated from the V–O–V bridging oxygens even at 50 °C. The ^{51}V NMR at −40 °C exhibits three lines with intensity ratio of 1:2:1, at −533, −570, and −622 ppm assigned to the vanadium with coordination to the zinc at the butterfly wing position (V1), the vanadiums at the hinge positions (V2 and V4), and the vanadium without coordination to the zinc (V3), respectively. At 50 °C, the signals almost become superimposed into a rapidly exchanged singlet at −533 ppm which is close to the reported values of the tetravanadate with the bonding of M^I species.[12] Unfortunately, it was not possible to reach the fast exchange regime exhibiting one coalesced line because of the limitation of the solvent boiling point. The NMR spectra of **2** are not informative owing to the paramagnetism of the Co^{2+} center.

In summary, the supported polyoxovanadates with a terminal chloride ligand have been isolated and the fluxional behaviors of the tetrahedaral metal units have been characterized.[13] These oxide-supported complexes are intriguing molecular systems in which the terminal coordination site occupied by the chloride ion may serve as an active site for a certain catalytic process. Studies concerning such issues are now in progress.

References and Notes

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6 A 0.136 g (0.40 mmol) of $(n\text{-}Bu_4N)[VO_3]$ was dissolved in 0.5 mL of acetonitrile, and 0.024 mg (0.1 mmol) of $CoCl_2{\cdot}6H_2O$ in 0.5 mL of acetonitrile was slowly added to the solution. The resulting green mixture was stirred for 30 min. Any insoluble material was removed by filtration, and the filtrate was left to crystallize with the addition of 5 mL of ethyl acetate. Isolated yield was 74% (90 mg) based on vanadium. Compound **2** was prepared by the same method using $ZnCl_2$. **1**: Anal. Calcd for $(n\text{-}Bu_4N)_3[(CoCl)V_4O_{12}]{\cdot}H_2O$: C, 46.66; H, 8.97; N, 3.40%. Found: C, 46.66; H, 8.72; N, 3.48%. IR (KBr, 500–1500 cm^{-1}): 615(w), 744(s), 854(s), 925(m), 949(s), 970(m). **2**: Yield of colorless crystals was 41%. Anal. Calcd for $(n\text{-}Bu_4N)_3[(ZnCl)V_4O_{12}]{\cdot}H_2O$: C, 46.42; H, 8.93; N, 3.38%. Found: C, 46.72; H, 8.80; N, 3.42%. IR (KBr, 500–1500 cm^{-1}): 619(w), 723(w), 756(s), 846(s), 860(sh), 896(m), 925(m), 947(s), 970(m).

7 The diffraction data were collected with a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71070$ Å) at −150 °C. Crystal data for **1**: $C_{48}H_{108}N_3CoClO_{12}V_4$, 1217.5 g mol^{-1}, monoclinic $P2_1$, $a = 12.014(2)$ Å, $b = 21.109(3)$ Å, $c = 12.479(2)$ Å, $\beta = 93.229(5)^\circ$, $V = 3159.8(8)$ Å^{-3}, $Z = 2$, $D_{calcd} = 1.280$ g cm^{-3}, $\mu = 0.92$ cm^{-1}, $F(000) = 1298$, $2\theta_{max} = 52^\circ$, $S = 0.90$. The structure was solved by direct methods and refined on F^2 to $R_1(wR_2)$ 0.084(0.239) using 10615 reflections with $I > 2\sigma(I)$. Crystal data for **2**: $C_{48}H_{108}N_3ClO_{12}V_4Zn$, 1224.0 g mol^{-1}, monoclinic $P2_1$, $a = 12.4961(7)$ Å, $b = 21.0756(12)$ Å, $c = 24.0205(14)$ Å, $\beta = 93.039(1)^\circ$, $V = 6317.2(6)$ Å^{-3}, $Z = 4$, $D_{calcd} = 1.287$ g cm^{-3}, $\mu = 1.04$ cm^{-1}, $F(000) = 2608$, $2\theta_{max} = 55^\circ$, $S = 0.76$. **2** was treated as a racemic twin by using the TWIN command in SHELX. The structure was solved by direct methods and refined on F^2 to $R_1(wR_2)$ 0.053(0.161) using 14648 reflections with $I > 2\sigma(I)$.

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