

Cubane-Type Clusters as Potential Models for Inorganic Solid Surfaces

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Cubic structures had been observed in inorganic chemistry before cubane, a hydrocarbon with the formula C_8H_8 , was first prepared in 1964 by Eaton and Cole;¹ the simple cubic structure was observed as early as 1936.² Compounds with incomplete cubane structures³ and homocubane⁴ structures have also been reported, as have those with integrated cubane structures (Figure 1).⁵ These cubane-type clusters have attracted much attention:⁶⁻⁸ some are capable of multielectron transfer,^{6c} and others exhibit interesting magnetic⁷ and optical⁸ properties. Compounds that have the cubic Fe_4S_4 or Mn_4O_4 core have been under extensive research because of their link to biological systems.^{5f,9}

The chemistry of cubane-type clusters has another important aspect—its potential relevance to that of inorganic solids. Many structures commonly found in inorganic solids are derived from a cubic framework, such as the rock salt structure (MgO , NiO , MnS), $CsCl$ structure ($CsSH$, $TlSb$), fluorite structure (ZrO_2 , CeO_2 , RhO_2), corundum structure (Sc_2O_3 , Mn_2O_3 , Al_2S_3), pyrite structure (FeS_2 , RhS_2 , CoS_2), pyrochlore structure ($NaCaNb_2O_6F$, $Na_2Sb_2O_5(OH)_2$), perovskite structure ($CaTiO_3$, $SrFeO_3$, $BaSnO_3$), ReO_3 structure (ReO_3 , WO_3), and so on. Many of these solids are important catalysts for organic substrate transformation.¹⁰ Most, if not all, of these catalytic reactions take place on the surface of the catalysts. Hence we need to elucidate the geometry and electronic structure of both substrate and catalyst if we are to understand and improve these catalytic reactions. This is easier said than done. The surfaces of inorganic solids are complicated systems and are extremely difficult to characterize. Apparently, we need a simpler model system which is easier to characterize.

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Atsushi Yagasaki was born on October 16, 1958, in Osaka, Japan. He received his B.A. from the University of Tokyo in 1982 and his Ph.D. from the same university in 1987 with Yukiyoshi Sasaki. After postdoctoral work at University of Illinois with Walter G. Klumperer, he moved to the Institute for Molecular Science as a research associate in 1989. He joined the faculty of Kwansai Gakuin University in 1991, where he is currently Assistant Professor of Chemistry. His research interest is focused on synthesis of new polyoxo compounds and study of their behavior in solution.

Cubane-type clusters would make a good model system for the study of these solid oxides. As mentioned earlier, cubane-type units are the building blocks of many oxide structures. In addition, single or integrated cubane-type clusters have been successfully used as models of inorganic solids in recent theoretical works.¹¹ The present review tries to summarize the recent development of cubane-type oxide cluster chemistry and displays its relevance to solid oxide catalysts.

Integrated Cubane-Type Clusters of Group 5 and 6 Metals

Many cubane-type oxide clusters including hydroxide and alkoxide clusters have been synthesized so far,^{6b} but few of them were synthesized "rationally". It is important to overcome this lack of control and to develop methodology for the rational synthesis of the clusters. Some people have approached this problem

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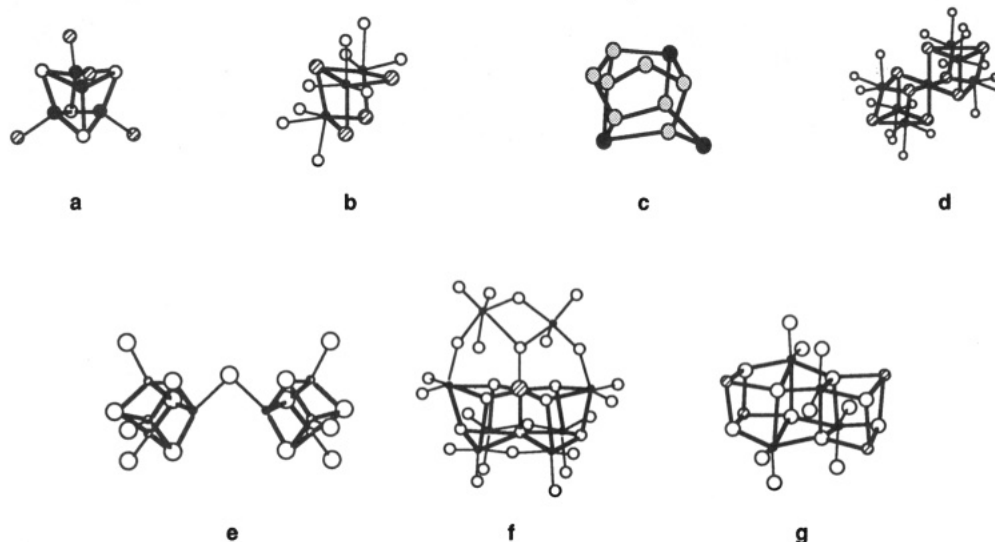
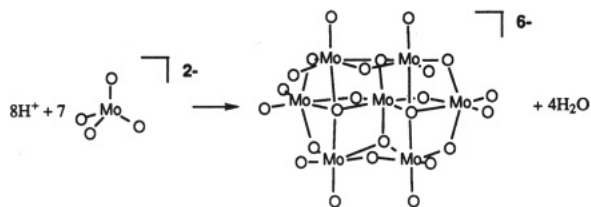


Figure 1. Schematic drawings of different cubane-type clusters. Organic and carbonyl moieties are omitted for clarity: a, simple cube; b, incomplete cube; c, extended cube (homocubane); d, corner-shared cubes; e, cubes connected by a ligand; f, edge-shared cubes; g, face-shared cubes.

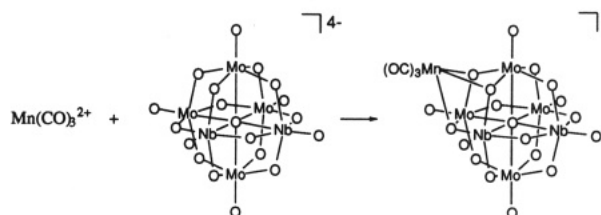
through "controlled hydrolysis" of metal alkoxides^{12a-c} and carboxylates.^{12d-f} We approached the problem through the chemistry of polyoxoanions.

Polyoxoanions form a well-defined class of oxide clusters.¹³ Traditionally they are prepared by condensation of monomeric oxometalates (MoO_4^{2-} , WO_4^{2-} , VO_4^{3-}) in acidic aqueous solution. The reaction is



basically a dehydration process, where protons act as oxygen abstractors. Unfortunately, we do not have good control of the reaction here, either. It is usually not possible to predict the product from the reactant because the number of oxygen atoms changes. On the other hand, Klemperer and co-workers recently showed that many organometallic complexes can be incorporated into a polyoxoanion framework by simple addition

reactions.¹⁴ Here, the polyoxoanion unit is prepared



first and then reacted with an organometallic moiety. The former behaves as a Lewis base and the latter as a Lewis acid: the vacant coordination sites of the carbonyl cation are simply filled by the surface oxygen atoms of $[\text{Nb}_2\text{W}_4\text{O}_{19}]^{4-}$. Thus the structure of the product can be predicted easily.

What will happen, then, if we mix these two kinds of reactions together? Is it possible to trigger the oligomerization reaction by Lewis acids? If so, we would be able to build an oxide cluster framework directly on a Lewis acidic coordination compound which has vacant coordination sites. In this way we should have some control over the reaction through the number of vacant sites, the size of the nonlabile ligand, and the metal ion charge of the Lewis acidic coordination compound. Also, it would be easier to predict the product, since no dehydration would take place. Our recent experiments show that such reactions are indeed possible. Moreover, these reactions yield several new cubane-type oxide clusters.

The complex $[\text{RhCp}^*(\mu\text{-Cl})\text{Cl}]_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$)¹⁵ has potentially three vacant sites on each rhodium atom because the Cl ligands are readily removed from the coordination sphere. We have tried to construct an oxide framework on these sites. Treatment of $[\text{RhCp}^*(\mu\text{-Cl})\text{Cl}]_2$ with Na_2MoO_4 in water gave $[(\text{RhCp}^*)_4\text{Mo}_4\text{O}_{16}]$ in ca. 90% yield.^{5c}

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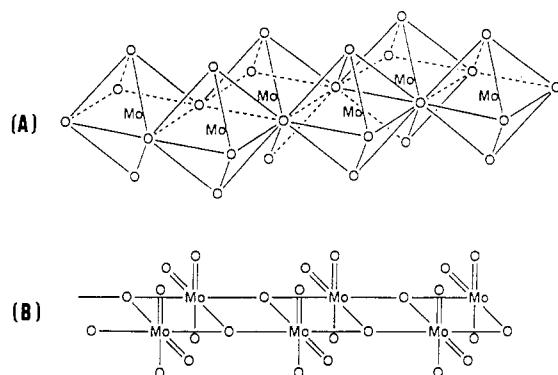
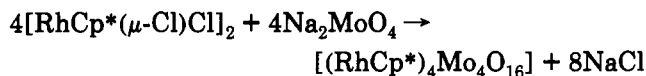


Figure 2. Part of the infinite layer structure of MoO_3 . (A) Polyhedral model and (B) simplified drawing.



Note that formally no dehydration took place. Analogous compounds $[(\text{MCp}^*)_4\text{M}'_4\text{O}_{16}]$ ($\text{M} = \text{Rh}, \text{Ir}$ and $\text{M}' = \text{Mo}, \text{W}$) have also been isolated. X-ray structure analyses of these clusters revealed that these crystals are isomorphous and contain a triple cubane framework (see Figure 1g for $[(\text{RhCp}^*)_4\text{Mo}_4\text{O}_{16}]$: striped circles, Rh; filled circles, Mo; open circles, O). The RhCp^* groups occupy the vertices of the cubes and are coordinated by three oxygen atoms. The cluster has three types of Mo–O bonds: Mo–O(t), Mo–O(Rh_2), and Mo–O(Mo_2Rh). The ^{17}O NMR spectrum of the compound indicated that the charge density is highest on the Mo–O(Mo_2Rh) oxygens and lowest at the Mo–O(t) oxygens.¹⁶

This triple cubane-type structure represents a part of the infinite layer structure of MoO_3 (see Figure 2),¹⁷ which has been used as a heterogeneous catalyst in a variety of organic substrate transformations.¹⁰ One of the most important catalytic reactions over the MoO_3 surface is dehydrogenation of MeOH to HCHO with O_2 .¹⁸ Two different mechanisms have been proposed for the formation of HCHO . One suggests the dissociative adsorption of methanol across a molybdenum–oxygen double bond as the key step (Scheme Ia).^{18a,b,d} The other claims that the addition of methanol across a molybdenum–oxygen single bond is important (Scheme Ib).^{18e}

The compound $[(\text{RhCp}^*)_4\text{Mo}_4\text{O}_{16}]$ reacts with MeOH in the presence of *p*-hydroquinone to give the incomplete double cubane-type cluster $[(\text{RhCp}^*)_2\text{Mo}_3\text{O}_9(\text{OMe})_4]$, as shown in Figure 3.¹⁹ The structure suggests that methanol molecules attack the bridging oxygens of $[(\text{RhCp}^*)_4\text{Mo}_4\text{O}_{16}]$ to remove the $(\text{RhCp}^*)_2\text{MoO}_7$ part from its framework. This supports the mechanism of methanol addition across a molybdenum–oxygen single bond in the catalytic reaction. The incomplete double

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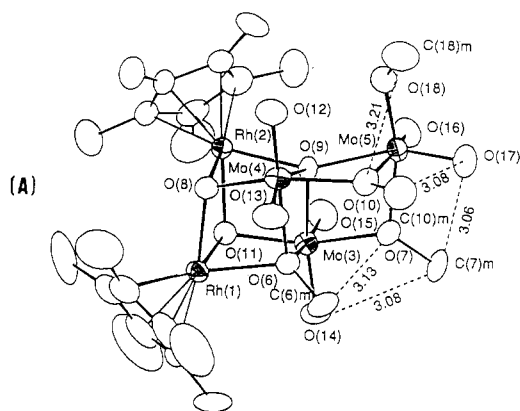
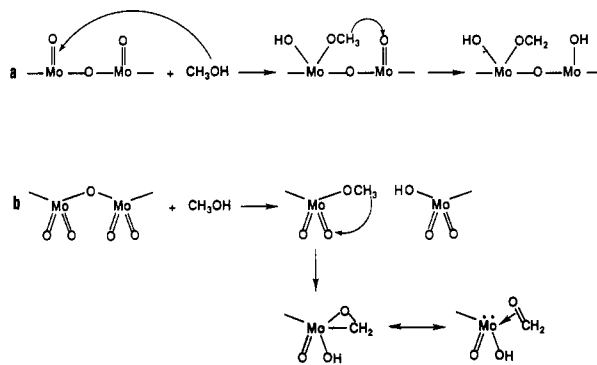


Figure 3. Molecular structure of $[(\text{RhCp}^*)_2\text{Mo}_3\text{O}_9(\text{OMe})_4]$: (A) ORTEP diagram and (B) simplified drawing. Reproduced with permission from ref 19. Copyright 1991 American Chemical Society.

Scheme I



cubane-type cluster is stable in the solid state in air at room temperature. However, upon dissolution in CH_2Cl_2 it condenses to yield the quadruple cubane-type cluster $[(\text{RhCp}^*)_4\text{Mo}_6\text{O}_{22}]$ (Figure 4),¹⁹ releasing methanol. A small amount of formaldehyde is formed at the same time. The incomplete double cubane-type cluster released organic compounds on heating. A typical product composition at 386 °C was MeOH (56%), HCOOMe (28%), Me_2O (12%), and Me_2CO (4%).²⁰ A small amount of aromatic compounds was also detected.

Both of the mechanisms depicted in Scheme I assume the terminal methoxy group as the key intermediate. Our results with the incomplete double cubane cluster suggest otherwise. There are several short interactions (≈ 3 Å) between doubly bridged methoxy carbons and terminal Mo=O oxygens in the structure of $[(\text{RhCp}^*)_2\text{Mo}_3\text{O}_9(\text{OMe})_4]$, indicating the existence of short C–H...O intramolecular contacts. The proton transfer between these methoxy groups and oxygen atoms would

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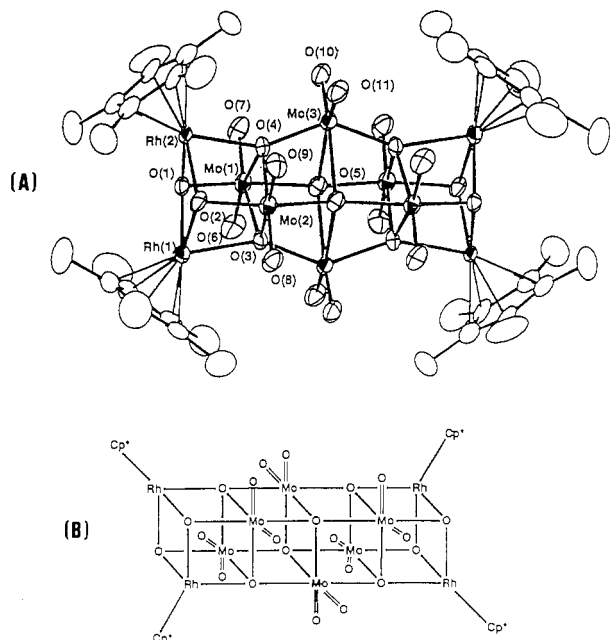
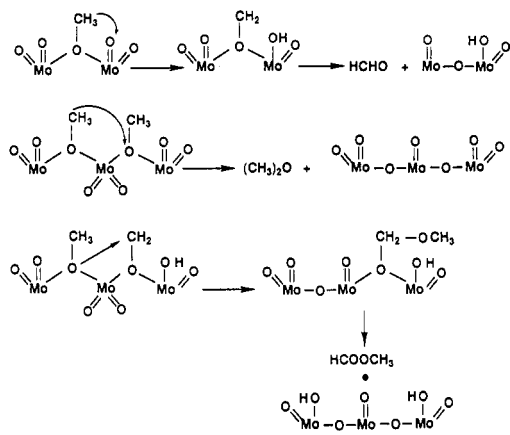


Figure 4. Molecular structure of $[(\text{RhCp}^*)_4\text{Mo}_6\text{O}_{22}]$: (A) ORTEP diagram and (B) simplified drawing. Reproduced with permission from ref 19. Copyright 1991 American Chemical Society.

Scheme II



lead to the formation of HCHO molecules, which is observed on dissolving the cluster in CH_2Cl_2 . Short contacts are also observed between the oxygen atom of a bridging methoxy group and the carbon atom of another (3.13–3.21 Å). Methyl transfer between these methoxy groups would yield Me_2O and other organic molecules observed on heating the compound. Thus, we propose that the bridging methoxy group is the key species in the formation of HCHO, Me_2O , and HCOOMe (Scheme II).²⁰

The series of reactions just mentioned are also interesting from a synthetic point of view. As is shown in Scheme III, the cubic framework is maintained throughout, and no drastic metal-oxygen bond rearrangement seems to take place. This triple and quadruple cubane systems may serve as starting points for the rational synthesis of lattice compounds.

The quadrupole cubane-type cluster mentioned above is a linear compound where cubic units fuse together by sharing faces. There is another kind of quadruple cubane framework²¹ in which cubic units are fused together sharing edges to make a molecule of tetrahedral symmetry (Figure 5). The cluster $[(\text{MCp}^*)_4\text{V}_6\text{O}_{19}]$ (M

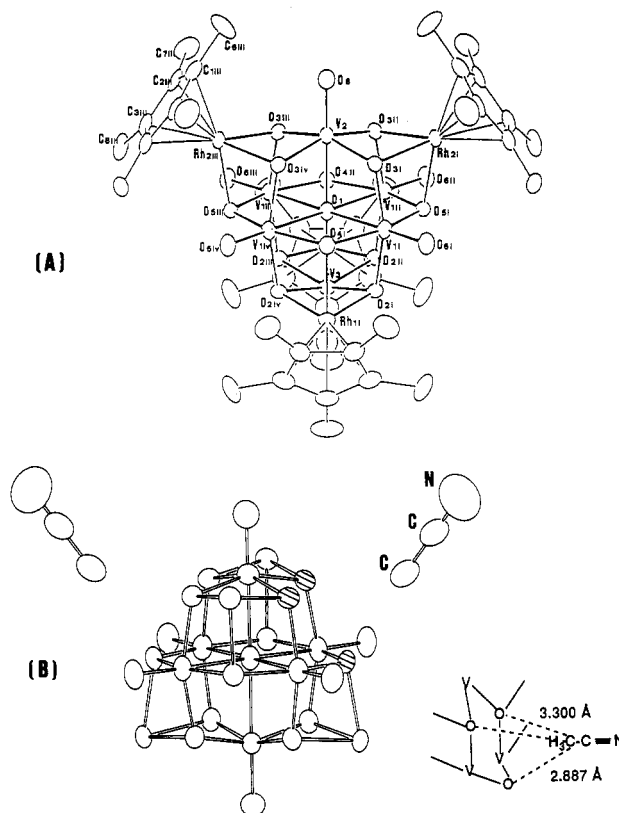


Figure 5. Molecular structure of $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$: (A) ORTEP diagram and (B) interaction between $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$ and acetonitrile molecules in $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}] \cdot 3\text{MeCN} \cdot \text{H}_2\text{O}$. One of the acetonitrile molecules, H_2O , and Cp^* groups are omitted for clarity. Reproduced with permission from ref 21 c. Copyright 1991 American Chemical Society.

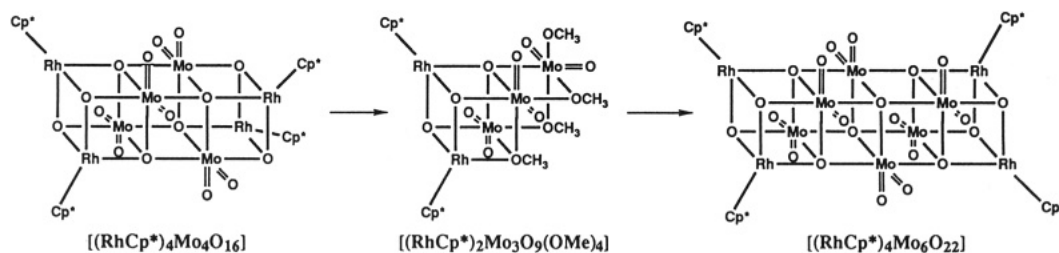
$= \text{Rh, Ir}$)^{21a,c} is obtained from the reaction of $[\text{MCp}^*(\mu\text{-Cl})\text{Cl}]_2$ ¹⁵ with NaVO_3 . The compound $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$ is amphiphilic, soluble in CH_2Cl_2 , $\text{C}_6\text{H}_5\text{Me}$, and H_2O . Its ¹⁷O NMR spectrum shows that the oxygen exchange with free water molecules occurs selectively at the oxygen atoms shared by rhodium and vanadium. In acidic solutions (pH < 4), the cluster liberates the $[\text{RhCp}^*(\text{H}_2\text{O})_3]^{2+}$ group sequentially. Reaction of this acidic aqueous solution with $[\text{IrCp}^*(\text{H}_2\text{O})_3]^{2+}$ gives a mixture of clusters $[(\text{RhCp}^*)_{4-n}(\text{IrCp}^*)_n\text{V}_6\text{O}_{19}]$ ($0 \leq n \leq 4$).^{21c}

These results suggest that the bridging oxygens in $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$ are activated and prone to the attack of solvent molecules. Even aprotic solvents like acetonitrile interact with these oxygen atoms. In the $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}] \cdot 3\text{MeCN} \cdot \text{H}_2\text{O}$ crystals, acetonitrile molecules are located very close to the bridging oxygen atoms (Figure 5B). The existence of C—H...O intermolecular contacts as short as 1.78 Å is anticipated from the carbon-oxygen distances. This is interesting in view of the fact that acetonitrile is selectively oxygenated by O_2 to glycolonitrile, HOCH_2CN , over vanadium oxide.²² Molecular contacts similar to these obtained in the model system may be present in the initial step of this catalytic reaction prior to proton abstraction from acetonitrile on the vanadium oxide surface.

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Scheme III



The observed dynamic behavior of $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$ is interesting in connection with new hydroformylation catalysts. The catalysts prepared by supporting a RhCp^* complex on oxide surfaces have been found to have higher reactivity and selectivity than classical impregnation catalysts.²³ The dynamic behavior of the RhCp^* groups has been suggested to be responsible for the high reactivity and selectivity. Also, the relative inertness of $[(\text{IrCp}^*)_4\text{V}_6\text{O}_{19}]$ compared to $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$ may have some relevance to the finding that IrCp^* on zeolites is inactive for C—H bond activation.²⁴

Other Oxide-Related Cubane-Type Clusters

Surface-modified silicas are another important class of oxides. They have been used extensively as stationary phases in chromatography²⁵ and as heterogeneous catalysts for the oxidation,²⁶ oxidative coupling,²⁷ and polymerization of hydrocarbons.²⁸ Several attempts have been made to model silica surfaces using siloxanes.²⁹ Here again, we can find cubane-like compounds which have interesting properties. Feher *et al.* have recently reported the synthesis of a silsesquioxane $[\text{C}_7\text{Si}_7\text{O}_9(\text{OH})_3]$ (Cy = cyclohexyl) which has an incomplete cubane-like framework.³⁰ The structure of this siloxane has a remarkable similarity to that of β -cristobalite (Figure 6).³¹ More interesting, the siloxane reacts with metal compounds and incorporates metal atoms into a cubane-like framework.³² One of them, $[\text{C}_7\text{Si}_7\text{O}_{12}(\text{VO})]$, undergoes dimerization in

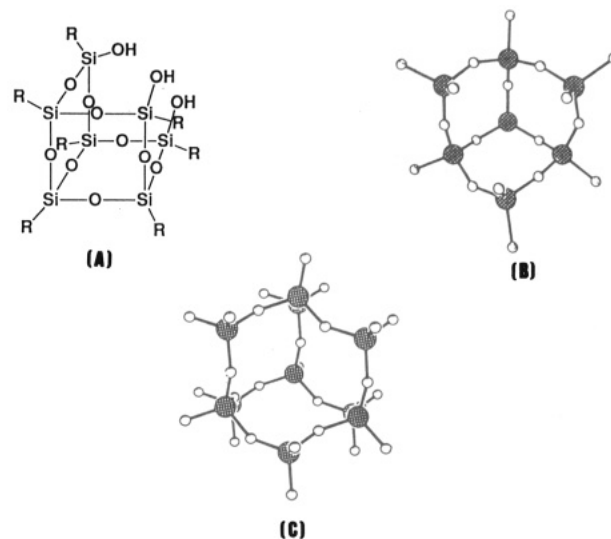
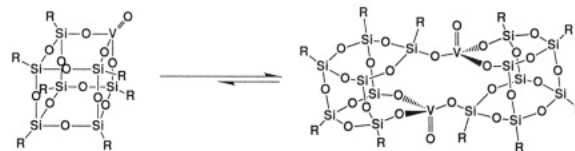


Figure 6. Molecular structure of $[\text{C}_7\text{Si}_7\text{O}_9(\text{OH})_3]$: (A) simplified drawing and (B) perspective view. Structure (C) is the perspective view of the idealized (111) octahedral face of β -cristobalite. Reproduced with permission from ref 30. Copyright 1989 American Chemical Society.

Scheme IV



solution (Scheme IV).³³ The dimer is capable of polymerizing olefins and can be considered a model for silica-supported metal catalysts.

There are several single cubane-type clusters which incorporate metal carbonyls. Examples are $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OR})_4]^+$ ($\text{R} = \text{H}, ^{34}\text{Me}^{35}$), $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$,³⁶ and $[\text{Mo}_4(\text{CO})_8(\text{NO})_4(\mu_3\text{-OH})_4]$.³⁷ The reaction chemistry of these single cubane compounds has not been examined in detail yet. Such clusters might, however, serve as model compounds for metal carbonyls supported on oxide surfaces, which have been drawing increasing attention recently.³⁸ Hieber's acid, $[\text{W}_4(\text{CO})_{12}(\mu_3\text{-$

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$(\text{OH})_4\text{H}_4$],³⁹ which is formed by reacting $[\text{W}_2(\mu\text{-OH})_3(\text{CO})_6]^{3-}$ with protons, is reminiscent of the initial step of CO reduction on oxide surfaces in the Fischer-Tropsch reaction.⁴⁰

The cluster $[\text{CrCp}(\mu_3\text{-O})_4]$ ($\text{Cp} = \text{C}_5\text{Me}_5, \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{-Me}$)⁷ is magnetically interesting in that the Cr atoms are antiferromagnetically coupled. In the cubane-type copper complex $[\text{Cu}(\text{bpy})(\text{OH})_4](\text{PF}_6)_4$,⁸ on the other hand, there is ferromagnetic coupling between metal atoms.

A series of compounds that consist of Mo_4O_4 cubes have been synthesized recently.⁴¹⁻⁴³ In these compounds, the Mo_4O_4 cubes are connected together to form chain $([\text{NET}_4][\text{MoO}_4(\mu_3\text{-O})_4(\text{PO}_4)_{2/2}(\text{H}_{1.5}\text{PO}_4)_2]\cdot 2\text{H}_2\text{O})$,⁴¹ sheet $([\text{N}(\text{C}_3\text{H}_7)_4(\text{NH}_4)][(\text{MoO}_4)(\mu_3\text{-O})_4(\text{PO}_4)_2])$,⁴² and three-dimensional $([(\text{NMe}_4)_{1.3}(\text{H}_3\text{O})_{0.7}][(\text{MoO}_4)(\mu_3\text{-O})_4(\text{PO}_4)_2]\cdot 2\text{H}_2\text{O})$,^{43a} $[\text{NH}_4]_3(\text{MoO}_4)(\mu_3\text{-O})_4(\text{P}_3\text{O}_8)]$ ^{43b} structures. These compounds are drawing attention as possible shape-selective catalysts. Related molecular Mo_4O_4 cubane-type compounds have also been isolated as $[(\text{MoO}_4)(\mu_3\text{-O})_4(\text{OSiMe}_3)_4(\text{NHMe}_2)_4]$ ⁴⁴ and $[(\text{MoO}_4)(\mu_3\text{-O})_4(\text{PMe}_2\text{OS})_4]$.⁴⁵

Outlook

The study of the chemistry of cubane-type clusters related to inorganic solid surfaces has just been started with the hope of developing a new field in the understanding of surface reactions on molecular levels. Although the cubane-type clusters described here are relatively simple, they offer useful information on the precise structural data as well as the nature and reactivities of the M-O bonds. Particularly, integrated cubane-type clusters have several kinds of M-O bonds with oxygen atoms of different charge density and

basicity. This is important because the surface acidity and basicity, which are essential factors in determining the behavior of solid surfaces,⁴⁶ are based on the nature of the surface M-O bonds.

Recently, integrated cubane-type compounds with coordinatively unsaturated metal centers have been synthesized (see Figure 1f for $[\text{TeMo}_8\text{O}_{29}(\text{OH}_2)]^{4-}$: striped circle, Te; filled circles, Mo; open circles, O. The top right of the Mo atom is 5-coordinate and has a vacant coordination site).^{5b,47,48} Also, the chemistry of incomplete cubane-type clusters, which show unique reactivity, has developed rapidly during the last decade.^{7f} The behavior of these compounds is of much interest in connection with modeling active sites on solid surfaces. Inorganic solid surfaces are not homogeneous and consist of terraces, kinks, steps, and so on, in which there are defects with metal atoms in a variety of coordination numbers.⁴⁹ Particularly, coordinatively unsaturated atoms at defects in the kinks and steps often play an important role in activating substrates. Incomplete cubane-type clusters will give a much more accurate model corresponding to such active sites in defects and then enable us to obtain information on the dynamic behavior of active centers during catalytic reactions. Finally, we hope that synthetic studies of cubane-type clusters will make an impact on those theoretical studies using cubic models for specific surfaces of metal oxides to get new insights into surface dynamics.

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