extremely useful in identifying associated structures.[16] The correlation described here is more limited in scope and is intended to rationalize some of the more unusual ^{119}Sn Mössbauer data reported over the years for dimethyltin(IV) derivatives. However, the suggested use of the dimethyltin(IV) group as an electronic structure probe and the order of anion basicities, evident from the δ vs. ΔE_Q plot, go beyond the use of ^{119}Sn Mössbauer spectra as a molecular structure probe for organotin(IV) compounds.[20]

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Synthesis and Crystal Structure Determination of a Propylene Glycol Bridged Molybdenum(VI) Peroxo Dimer, $[MoO(O_2)(C_3H_6O_2)(CH_3OH)]_2 \cdot 2CH_3OH$

Sir:

Molybdenum(VI) peroxo complexes are stoichiometric reagents[1] and catalysts[2] for olefin epoxidation. Single-crystal X-ray diffraction studies have shown that the organic ligands contained in this class of compound can be covalently bonded[3-10] or loosely coordinated[11-14] to the Mo(VI) center. Despite the large family of polynuclear peroxomolybdates reported in the literature,[15] all these ligand-stabilized peroxo complexes except the hydroperoxide-bridged $[Mo_2O_2(O_2)_4(OOH)_2]^{2-}$ anion[4] and the tartrate-bridged $[Mo_2O_2(O_2)_4(C_4H_2O_6)]^{4-}$ anion[10] are monomeric. This paper reports the synthesis and solid-state structure of $[MoO(O_2)(C_3H_6O_2)(CH_3OH)]_2 \cdot 2CH_3OH$ (**1**), the first structurally characterized nonionic polynuclear Mo(VI) peroxo complex with a covalently bonded diolate ligand. The unique structural features of this compound provide insights in the design of more effective early-transition-metal peroxo complexes for asymmetric epoxidation of olefinic substrates.

In the synthesis of **1**, the dioxomolybdenum(VI) propylene glycolate complex $MoO_2(C_3H_7O_2)_2$[16] was first prepared from the ligand exchange reaction of $MoO_2(acac)_2$ with 1,2-propanediol in dichloromethane. Dissolution of this propylene glycolate complex in a *tert*-butyl alcohol solution of anhydrous *tert*-butyl hydroperoxide at 70 °C followed by slow diffusion of anhydrous methanol under argon over a 2-day period gave bright yellow crystals of **1** suitable for single-crystal X-ray diffraction study.[17] Alternatively, **1** can be prepared by reacting peroxomolybdic acid[18] with 1,2-propanediol in anhydrous methanol at 25 °C under an inert atmosphere.

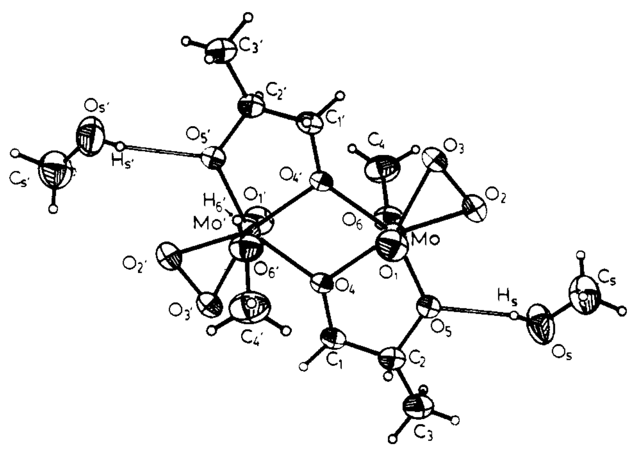

Figure 1. ORTEP drawing of **1** with molybdenum, oxygen, and carbon atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres. Hydrogen atom H_6 is hidden from view in this orientation. Atoms labeled with a prime (′) are related to those without primes by the crystallographic inversion center at $^1/_2$, 0, $^1/_2$. Selected bond lengths and angles: $Mo–O_1$ = 1.665 (2) Å, $Mo–O_2$ = 1.925 (2) Å, $Mo–O_3$ = 1.916 (2) Å, $Mo–O_4$ = 2.070 (2) Å, $Mo–O_4'$ = 2.061 (2) Å, $Mo–O_5$ = 1.944 (2) Å, $Mo–O_6$ = 2.300 (2) Å, $O_2–O_3$ = 1.451 (3) Å, $H_6 \cdots O_S$ = 1.88 (4) Å, $H_S \cdots O_5$ = 2.11 (4) Å, $O_4–Mo–O_5$ = 77.4 (1)°, $O_4–Mo–O_4'$ = 69.5 (1)°.

Compound **1** forms monoclinic crystals: space group $P2_1/n$ (alternate setting of $P2_1/c$-C_{2h}^5 (No. 14)); a = 7.878 (2) Å, b = 9.307 (3) Å, c = 14.194 (4) Å, β = 99.44 (2)°; Z = 2 dimer units; d_{calcd} = 1.825 g cm^{-3}. X-ray diffraction data at 20 °C were collected on a computer-controlled four-circle Nicolet autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structure was solved by heavy-atom Patterson techniques. Of 2353 independent reflections collected to 2θ(Mo K$\bar{\alpha}$) = 55°, 1815 having $I > 3\sigma(I)$ were used in the final least-squares refinement cycle to give R_F and R_w values of 2.4% and 2.6%, respectively.

The title compound depicted in Figure 1 exhibits several distinctive structural features. The two halves of **1** are related by a crystallographic inversion center and bridged by the diolate oxygens of a pair of 1,2-propanediol enantiomers. The binding mode of the glycolate ligand is similar to that of the tartramide and tartrate ester ligands found in the two dinuclear titanium catalysts[19] used for asymmetric epoxidation of allylic alcohols. The planar Mo_2O_2 core is almost a symmetric rhombus with $Mo–O_4$ and $Mo–O_4'$ bond distances of 2.070 (2) and 2.061 (2) Å, respectively; the internuclear Mo---Mo′ separation is 3.395 (1) Å. The peroxy and diolate oxygens form the equatorial plane of a distorted pentagonal bipyramid with a terminal oxygen and the methanol oxygen at the apices. The Mo—peroxo distances, the Mo=O distance, and the O—O distance in the peroxo group are all within the range of distances previously observed for this class of peroxo complexes. The hydroxy proton on each of the coordinated methanol molecules (H_6 or H_6') is hydrogen-bonded to a hydroxy oxygen (O_S or O_S') of a symmetry-related methanol

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(1) Mimoun, H.; Seree de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37.
(2) Westland, A. D.; Haque, F.; Bouchard, J. M. *Inorg. Chem.* **1980**, *19*, 2255.
(3) Stomberg, R. *Acta Chem. Scand.* **1970**, *24*, 2032.
(4) LeCarpentier, J. M.; Mitschler, A.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1288.
(5) Edwards, A. J.; Slim, D. R.; Guerchais, J. E.; Kergoat, R. *J. Chem. Soc., Dalton Trans.* **1977**, 1966.
(6) Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055.
(7) Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1983**, *250*, 291.
(8) Flanagan, J.; Griffith, W. P.; Skapski, A. C.; Wiggins, R. W. *Inorg. Chim. Acta* **1985**, *96*, L23.
(9) Djordjevic, C.; Covert, K. J.; Sinn, E. *Inorg. Chim. Acta* **1985**, *101*, L37.
(10) Dengel, A. C.; Griffith, W. P.; Powell, R. D.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 555.
(11) LeCarpentier, J. M.; Schlupp, R.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1278.
(12) Winter, W.; Mark, C.; Schurig, V. *Inorg. Chem.* **1980**, *19*, 2045.
(13) Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. *Polyhedron* **1984**, *3*, 377.
(14) Djordjevic, C.; Vuletic, N.; Sinn, E. *Inorg. Chim. Acta* **1985**, *104*, L7.
(15) For a listing of the known peroxopolymolybdates, see: Persdotter, I.; Trysberg, L.; Stomberg, R. *Acta Chem. Scand., Sect. A* **1986**, *A40*, 83 and references cited therein.
(16) Sheldon, R. A. *Recl. Trav. Chim.* **1973**, *92*, 367.
(17) Compound **1** is moisture-sensitive and eventually decomposes to molybdenum blue on sitting at room temperature; hence, all manipulations were carried out under an atmosphere of dry argon. A satisfactorily grown crystal with dimensions of 0.30 × 0.40 × 0.75 mm was immediately sealed with the solvent inside a thin-walled capillary for X-ray data collection. The structure determination was carried out by Dr. C. S. Day of Crystalytics, Lincoln, NE 68501.
(18) Kaloustian, J.; Lena, L.; Metzger, J. *Tetrahedron Lett.* **1975**, 559.
(19) Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6430.

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solvent molecule of crystallization that is also hydrogen-bonded to the diolate oxygen (O_5 or O_5') through its hydroxy proton (H_S or H_S').

It is believed that **1** is only the first member of a family of nonionic polynuclear molybdenum(VI) peroxo complexes stabilized by chelating organic ligands. An analogous peroxo complex has been synthesized with homochiral (*S*)-1,2-propanediol. Its crystal structure and peroxo group reactivity are currently under investigation.

Acknowledgment. I am thankful to Professor V. W. Day for helpful discussions on hydrogen bonding.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal structure data, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles, close contacts involving hydrogen atoms, and nonbonding interactions (15 pages); a listing of structure factors (8 pages). Ordering information is given on any current masthead page.

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Articles

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Ligand Isotopic Exchange Kinetics of Tris(acetylacetonato)aluminum(III) in Acetylacetone under Atmospheric and Elevated Pressures

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The rate of ligand isotopic exchange of ^{14}C-labeled tris(acetylacetonato)aluminum(III), Al(acac)$_3$, in acetylacetone (Hacac) was expressed by $R = (k_1 + k_2[H_2O])[Al(acac)_3]$, where $[Al(acac)_3] = 0.0012-0.0057$ mol dm^{-3} and $[H_2O] = 0.022-0.162$ mol dm^{-3} at 15-40 °C under atmospheric pressure and at 25 °C under pressures up to 237 MPa. The rate constants k_1 and k_2 decreased with an increase in pressure, on deuteriation of protolytic hydrogens of water and acetylacetone, and on addition of acetonitrile. The activation parameters, ΔH^*, ΔS^*, and ΔV^*, were 85 ± 5 and 79 ± 4 kJ mol^{-1}, -38 ± 18 and -34 ± 14 J K^{-1} mol^{-1}, and +10 ± 2 and +5 ± 1 cm^3 mol^{-1}, for k_1 and k_2, respectively. An interchange mechanism to form an intermediate containing both a one-ended acac$^-$ and a Hacac or a water molecule are concluded for the rate-determining steps of the k_1 and k_2 paths, respectively.

Introduction

The ligand isotopic exchange of tris(acetylacetonato)aluminum(III), [Al(acac)$_3$], with ^{14}C-labeled acetylacetone (Hacac-[^{14}C]) in toluene, tetrahydrofuran (THF), and ethyl acetate at 0-35 °C gave moderate ΔH^* and negative ΔS^* values and was subject to the catalytic effect of water and acids.[2-4] The activation mode of the substitution process, however, has not been disclosed. The acetylacetonate (acac$^-$) exchange of tris(acetylacetonato)metal complexes in neat acetylacetone (Hacac) is a kind of solvent exchange reaction. We have discussed, taking advantage of the simplicity of the system, the mechanism of the substitution process of neutral complexes of various tervalent metal ions such as vanadium, chromium, iron, cobalt, ruthenium, and rhodium, on the basis of ΔH^* and ΔS^* values, and the deuterium isotope effect on the rates.[5-9]

On the other hand, many workers have studied the solvent exchange of hexakis(unidentate)aluminum(III) cations, e.g. $[Al(H_2O)_6]^{3+}$, $[Al(dmf)_6]^{3+}$ (dmf = *N*,*N*-dimethylformamide), $[Al(Me_2SO)_6]^{3+}$ (Me_2SO = dimethyl sulfoxide), etc., and postulated a dissociative-interchange mechanism.[10-23] Considerably large positive activation volumes, ΔV^*, as well as positive ΔS^*, were understood to be useful in elucidating the mechanism.[10,17,19,20]

We have extended kinetic studies of the ligand isotopic exchange of [Al(acac)$_3$] to that in neat Hacac and applied the pressure technique for clarifying the substitution mechanism.

Experimental Section

Materials. [Al(acac)$_3$] was prepared by the known method,[24] recrystallized, and sublimed at ca. 160 °C at 1 torr (1 torr = 133.3 Pa).[4] The labeled complex was prepared by the ligand exchange method and dried in vacuo (250 mg, ca. 8.1 pCi mg^{-1}).

Hacac was dried with anhydrous calcium sulfate and distilled at 132-138 °C. The water content was determined by Karl Fischer titration to be 0.012 M (M = mol dm^{-3}). Hacac[$^2H_2$] (74% deuteriated at the methylene moiety) was prepared by the reported method.[9]

Kinetic Procedure. Reactions under Atmospheric Pressure. Kinetic runs were carried out similarly to the procedure previously described.[7] The labeled complex (ca. 7 mg) was dissolved in the solvent (ca. 7 cm^3 of Hacac or Hacac[$^2H_2$], with additional water or deuterium oxide, respectively, whenever necessary) and kept thermostated. Six or seven portions (0.50 cm^3 each) were pipetted out at appropriate time intervals and chilled at -60 °C. The solvent was evaporated off in vacuo at ca. 0 °C to recover the complex quantitatively, which was submitted to the liquid scintillation counting. The water content of the reaction mixture remained constant during the kinetic runs within the error of Karl Fischer titration (±2 × 10^{-3} M).

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(1) Present address: Coordination Chemistry Laboratories, Institute for Molecular Science, Okazaki National Research Institutes, Myodaiji, Okazaki 444, Japan.
(2) Saito, K.; Masuda, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 384-389.
(3) Saito, K.; Masuda, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 119-124.
(4) Matsuzawa, K.; Saito, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2777-2779.
(5) Kido, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 82-87.
(6) Kido, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 424-428.
(7) Watanabe, A.; Kido, H.; Saito, K. *Inorg. Chem.* **1981**, *20*, 1107-1112.
(8) Kido, H.; Saito, K. *Inorg. Chem.* **1977**, *16*, 397-400.
(9) Kido, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3545-3548.
(10) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479-1493.
(11) Fiat, D.; Connick, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 608-615.
(12) Neely, J. W. Ph.D. Thesis, University of California, Berkeley, CA, 1971.
(13) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545-554.
(14) Frankel, L. S.; Danielson, E. R. *Inorg. Chem.* **1972**, *11*, 1964-1965.
(15) Movius, W. A.; Matwiyoff, N. A. *Inorg. Chem.* **1967**, *6*, 847-849.
(16) Fratiello, A.; Schuster, R. *J. Phys. Chem.* **1967**, *71*, 1948-1950.
(17) Amman, C.; Moore, P.; Merbach, A. E.; McAteer, C. H. *Helv. Chim. Acta* **1980**, *63*, 268-276.
(18) Thomas, S.; Reynolds, W. L. *J. Chem. Phys.* **1966**, *44*, 3148-3149.
(19) Merbach, A. E.; Moore, P.; Howarth, O. W.; McAteer, C. H. *Inorg. Chim. Acta* **1980**, *39*, 129-136.
(20) Amman, C.; Merbach, A. E. *Inorg. Chim. Acta* **1980**, *40*, X98.
(21) Delpuech, J.-J.; Khaddar, M. R.; Peguy, A. A.; Rubini, P. R. *J. Am. Chem. Soc.* **1975**, *97*, 3373-3379.
(22) (a) O'Brien, J. F. Ph.D. Thesis, University of Minnesota, 1968. (b) O'Brien, J. F.; Alei, M. *J. Phys. Chem.* **1970**, *74*, 743-746.
(23) Richardson, D.; Alger, T. D. *J. Phys. Chem.* **1975**, *79*, 1733-1739.
(24) Young, R. C. *Inorg. Synth.* **1946**, *2*, 25. This procedure was first described in: Biltz, W. *Justus Liebigs Ann. Chem.* **1904**, *331*, 334-358.

0020-1669/86/1325-4330$01.50/0 © 1986 American Chemical Society