

intramolecular Ar-3' alkylation of **17** with closure of the cyclopropane ring provided duocarmycin SA in excellent yield (3 equiv of NaH, THF-DMF 1:2, 0 °C, 30 min, 87%), and the properties of synthetic **1** proved identical (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, UV, MS/HRMS) or comparable ([α]<sub>D</sub>) with those reported for the natural material.

Resolution of **14** was accomplished by conversion to the bis-(*R*)-*O*-acetylmandelate ester **18** following past protocols<sup>8,12,13</sup> (2.5 equiv of (*R*)-PhCH(OAc)CO<sub>2</sub>H, 3.0 equiv of EDCI, 0.1 equiv of DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 25 °C, 2.5 h, 85%) and chromatographic separation of the resulting diastereomers (preparative HPLC, α = 1.31, 5:95 EtOAc-CH<sub>2</sub>Cl<sub>2</sub>, 250 × 22.5 mm Alltech 10 μm SiO<sub>2</sub>) to provide 1(*S*),2'(*R*),2''(*R*)-**18** and 1(*R*),2'(*R*),2''(*R*)-**18**. Independent hydrolysis of the separated diastereomers (2.5 equiv of NaOMe, MeOH, 0 °C, 1 h, 93%) provided (-)-1(*S*)-**14** possessing the natural configuration of (+)-duocarmycin SA and (+)-1(*R*)-**14**. The conversion of (-)-1(*S*)-**14** to (-)-1(*S*)-**15** and (+)-*N*-BOC-DSA (**2**, [α]<sub>D</sub><sup>22</sup> +144° (c 0.06, CH<sub>3</sub>OH)) and incorporation into natural (+)-duocarmycin SA ([α]<sub>D</sub><sup>22</sup> +197° (c 0.035, CH<sub>3</sub>OH), lit<sup>2</sup> [α]<sub>D</sub><sup>24</sup> +180° (c 0.1, CH<sub>3</sub>OH)) followed the sequence detailed in Scheme I.

The examination of the properties of (+)- and (-)-**1** and the preparation of analogs incorporating the DSA alkylation subunit are in progress and will be reported in due course.

**Acknowledgment.** We gratefully acknowledge the financial support of the National Institutes of Health (CA 55276) and Dr. I. Takahashi, Kyowa Hakko Kogyo Co., Ltd., for copies of the <sup>1</sup>H NMR spectrum of natural duocarmycin SA and a summary of its physical and spectroscopic properties.

**Supplementary Material Available:** Listings of the full characterization of **1-2**, **4-15**, and **17-18** (10 pages). Ordering information is given on any current masthead page.

(20) Synthetic (+)-duocarmycin SA was not completely soluble at this concentration, and this may account for the slightly lower rotation reported for the natural material.

### A High-Nuclearity Polyoxoalkoxomolybdate Cluster Encapsulating a [Na(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> Moiety. Hydrothermal Synthesis and Structure of [Na(H<sub>2</sub>O)<sub>3</sub>H<sub>15</sub>Mo<sub>42</sub>O<sub>109</sub>[(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>OH]<sub>7</sub>]<sup>7-</sup>

M. Ishaque Khan and Jon Zubieta\*

Department of Chemistry  
Syracuse University  
Syracuse, New York 13244

Received July 13, 1992

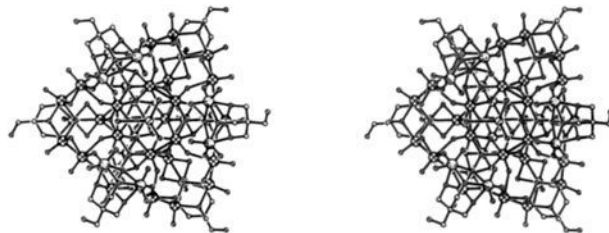
While the chemistries of both the polyoxometalate anions<sup>1</sup> and the polynuclear metal alkoxides<sup>2</sup> have received considerable contemporary attention, the related polyoxoalkoxometalate clusters remain largely unexplored. Despite the emergent nature of this chemistry, a variety of "oxidized" clusters, of which [Ti<sub>7</sub>O<sub>4</sub>(OEt)<sub>20</sub>]<sup>3</sup> and [Nb<sub>8</sub>O<sub>10</sub>(OEt)<sub>20</sub>]<sup>4</sup> are prototypical, and of reduced

(1) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer Verlag: New York, 1983.

(2) Caulton, K. G.; Hubert-Pfalzgraf, J. G. *Chem. Rev.* **1990**, *90*, 969. Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. Mehrotra, R. C. *Transition Metal Alkoxides*. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. G., Sharpe, A. G., Eds.; Academic Press: New York, 1983, Volume 26, p 269.

(3) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, F. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190. Watenpugh, K.; Caughlan, C. N. *J. Chem. Soc., Chem. Commun.* **1967**, 76.

(4) Bradley, D. C.; Hursthouse, M. B.; Rodesila, P. F. *J. Chem. Soc., Chem. Commun.* **1968**, 1112.



**Figure 1.** A stereoview of the molecular anion **1a** approximately along the normal to the central {Mo<sub>6</sub>O<sub>24</sub>} moiety, showing the idealized C<sub>3</sub> symmetry of the structure. Open bonds are used to illustrate the 18 Mo(V)-Mo(V) interactions. Mo(V) centers are shown as crosshatched spheres, while the six Mo(VI) sites are shown as stippled spheres. The central Na<sup>+</sup> cation is shown as a sphere with parallel diagonal lines.

and mixed-valence polynuclear cores, such as [Mo<sub>4</sub>O<sub>8</sub>(OR)<sub>4</sub>(pyridine)<sub>4</sub>]<sup>5</sup> and [Mo<sub>6</sub>O<sub>10</sub>(OR)<sub>12</sub>]<sup>6</sup> have been reported, suggesting that polyoxoalkoxometalates may provide a novel class of clusters with unusual structural and electronic variety. Furthermore, it has been noted that the high-nuclearity polyoxoalkoxomolybdate [Mg<sub>2</sub>Mo<sub>8</sub>O<sub>22</sub>(OR)<sub>6</sub>(HOR)<sub>4</sub>]<sup>2-7</sup> possesses cavities for the incorporation of electropositive cation groups, in a manner reminiscent of the encapsulation of a variety of small guest molecules by polyoxovanadate clusters.<sup>8</sup> As part of our studies of the coordination chemistry of polyoxometalates with alkoxide ligands,<sup>9</sup> we have noted that tris(alkoxy) ligands of the general class (HOCH<sub>2</sub>)<sub>3</sub>CR are effective in stabilizing triangular units [M<sub>3</sub>O<sub>n</sub>[(OCH<sub>2</sub>)<sub>3</sub>CR]<sub>3</sub>], which may in turn aggregate to form high-nuclearity clusters. By combining this feature with the solubility and crystallization advantages afforded by hydrothermal synthesis, we have isolated and structurally characterized a novel mixed-valence cluster, [Na(H<sub>2</sub>O)<sub>3</sub>H<sub>15</sub>Mo<sup>V</sup><sub>36</sub>Mo<sup>VI</sup><sub>6</sub>O<sub>109</sub>[(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>OH]<sub>7</sub>]<sup>7-</sup>, a basket type structure encapsulating a [Na(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> moiety.

The reaction of MoO<sub>3</sub>, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, C(CH<sub>2</sub>OH)<sub>4</sub> (pentaerythritol, H<sub>4</sub>L), (Et<sub>4</sub>N)Cl, Me<sub>3</sub>NHCl, and water in the molar ratio 6:6:10:10:300 at 160 °C for 3 days gave diamagnetic red-brown crystals of (Me<sub>3</sub>NH)<sub>2</sub>(Et<sub>4</sub>N)Na<sub>4</sub>[Na(H<sub>2</sub>O)<sub>3</sub>H<sub>15</sub>Mo<sub>42</sub>O<sub>109</sub>[(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>OH]<sub>7</sub>·15H<sub>2</sub>O (1·15H<sub>2</sub>O) in 30% yield.<sup>10</sup> The X-ray structure of **1** revealed the presence of the discrete molecular anion [Na(H<sub>2</sub>O)<sub>3</sub>H<sub>15</sub>Mo<sub>42</sub>O<sub>109</sub>[(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>OH]<sub>7</sub>]<sup>7-</sup> (**1a**), shown in Figure 1.<sup>11</sup> The structure consists of a framework of edge- and corner-sharing {MoO<sub>6</sub>} octahedra with the organic residues projecting outward from the central core. The anion may be most conveniently described in terms of the three structural motifs shown in Figure 2. Four of the pentaerythritol ligands, HL<sup>3-</sup>, coordinate in the usual tridentate bridging mode to a triangular arrangement of three Mo(V) centers, which in turn are each associated through edge-sharing of oxo groups to an adjacent Mo(V) site (**1b**); the Mo-Mo distances within these binuclear units are in the 2.55-2.65-Å range, corresponding to metal-metal single bonds for Mo. The second

(5) Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C.; Leonelli, J.; Foltling, K. *J. Am. Chem. Soc.* **1981**, *103*, 6093.

(6) Chisholm, M. H.; Foltling, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

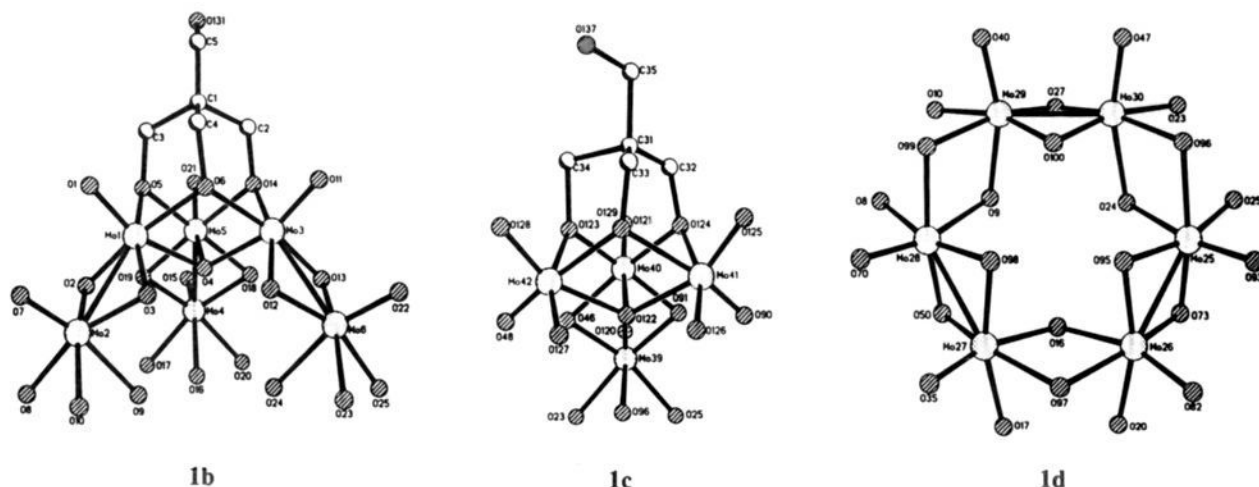
(7) Antipis, M. Yu.; Didenko, L. P.; Kachapina, L. M.; Shilov, A. E.; Shilova, A. K.; Struchkov, Y. T. *J. Chem. Soc., Chem. Commun.* **1989**, 1467.

(8) Klemperer, W. G.; Marquart, T. A.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 49 and references therein. Müller, A. *Nature* **1991**, *352*, 115. Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *Nature* **1991**, *352*, 115. Mitchell, P. C. H. *Nature* **1990**, *348*, 15.

(9) Chen, Q.; Goshorn, D. P.; Scholes, C. P.; Tan X.-L.; Zubieta, J. J. *Am. Chem. Soc.* **1992**, *114*, 4667 and references therein.

(10) Anal. Calcd for C<sub>49</sub>H<sub>154</sub>Mo<sub>42</sub>N<sub>3</sub>Na<sub>5</sub>O<sub>155</sub>: C, 7.93; H, 2.08; N, 0.57; Mo, 54.4. Found: C, 7.30; H, 1.95; N, 0.33; Mo, 54.2. IR (KBr pellet, cm<sup>-1</sup>): 1112 (vs), 1061 (m), 1021 (vs), 986 (vs), 911 (m), 886 (m), 810 (sh).

(11) Crystal data for C<sub>49</sub>H<sub>154</sub>Mo<sub>42</sub>N<sub>3</sub>Na<sub>5</sub>O<sub>155</sub> (**1**): triclinic space group P $\bar{1}$ , *a* = 22.159 (4) Å, *b* = 27.049 (5) Å, *c* = 17.726 (3) Å, α = 98.34 (1)°, β = 112.56 (2)°, γ = 82.81 (1)°, *V* = 9680 (3) Å<sup>3</sup>, *Z* = 2, *D*<sub>calcd</sub> = 2.542 g cm<sup>-3</sup>, *D*<sub>obsd</sub> = 2.51 (2) g cm<sup>-3</sup>. Structure solution and refinement based on 20028 reflections converged at *R* = 0.066. The solvent system is disordered, and some water molecules are highly smeared. The formula is, therefore, approximately 1·15H<sub>2</sub>O.



**Figure 2.** The three building blocks of **1a**: (a, left) the hexanuclear Mo(V)-ligand moiety  $\{\text{Mo}^{\text{V}}_6\text{O}_{22}(\text{HL})\}$  (**1b**) of which there are four in the molecular anion; (b, center) the tetranuclear Mo(V)/Mo(VI)-ligand unit  $\{\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_2\text{O}_{15}(\text{HL})\}$  (**1c**) of which there are three in the molecular anion; (c, right) the central hexanuclear Mo(V) core  $\{\text{Mo}_6\text{O}_{24}\}$  (**1d**).

structural unit, of which there are three present in **1a**, consists of the tridentate ligand bridging a triangular core of one Mo(V) and two Mo(VI) centers (**1c**); the Mo(V) site is in turn associated through edge-sharing by two oxo groups with an exocyclic Mo(V) unit, with the usual short Mo–Mo interaction. Finally, there is a six-membered Mo(V) ring  $\{\text{Mo}_6\text{O}_{24}\}$  of edge-sharing octahedra with alternating short–long Mo–Mo distances (**1d**). The ring **1d** provides the central core of the cluster, with the four hexanuclear (**1b**) and three tetranuclear (**1c**) units disposed about it through edge- and corner-sharing of octahedral motifs.

The tetranuclear units **1c** project outward from the cluster like the arms of a grapple to produce an open cavity. The sides of the cavity are defined by the octahedra of the central ring **1d** and the *cis*-dioxo groups of the six Mo(VI) sites. The  $[\text{Na}(\text{H}_2\text{O})_3]^+$  moiety is located within this cavity.

The structural parameters and valence sum calculations<sup>12</sup> identify the anion as a mixed-valence Mo(V)/Mo(VI) species. The 36 Mo(V) sites are readily identified by the presence of 18 Mo(V)/Mo(VI) binuclear units with short Mo–Mo distances. The six Mo(VI) sites exhibit terminal *cis*-dioxo coordination and the absence of short Mo–Mo distances as unique structural characteristics. Since the overall anion charge of the unit  $[\text{Na}(\text{H}_2\text{O})_3\text{Mo}_6\text{O}_{42}\text{O}_{109}(\text{HL})_7]^-$  is 22– and there are four  $\text{Na}^+$  cations, one  $(\text{Et}_4\text{N})^+$  cation, and two  $(\text{Me}_3\text{NH})^+$  cations associated with the structure, there must be 15  $\text{H}^+$  per formula unit to balance the charge. The 15 protonation sites are readily identified from the metric parameters of **1a** as triply-bridging oxo groups: the oxo groups which connect the ring **1d** to the central **1b** fragment (O24 type), the central oxo groups of each of the ligand-bridged triangular cores of the four **1b** units (O4 type) and the three **1c** units (O122 type), the oxo groups linking the central ring **1d** to the **1c** units (O96, O97, O99) and two of the six triply-bridging oxo groups which are involved in linking octahedra belonging to each of the three structural motifs (O25 type) (13). It is noteworthy that the remaining four triply-bridging oxo groups of this type exhibit close contacts to  $\text{Na}^+$  cations of the lattice to compensate for the absence of a proton. These four  $\text{Na}^+$  cations are imbedded in four of six cavities formed by the fusion of the three peripheral **1b** subunits with the central **1b** subunit and the **1c** fragments.

While the mechanism of compound formation in the hydrothermal synthesis of **1** remains obscure, factors such as pH, the reducing nature of the medium, and templating cations are significant. Thus, **1** could only be isolated in the presence of  $\text{Na}^+$  at low pH. While other cations do yield polyoxoalkoxomolybdate clusters under similar conditions, the compositions are quite

different; we are currently investigating the structures of these species.

**Acknowledgment.** This work was supported by NSF Grant CHE9119910.

**Supplementary Material Available:** Tables of crystal data and experimental conditions, atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors for the X-ray study of **1**, polyhedral views of the structure, and a valence sum discussion (31 pages); tables of calculated and observed structure factors for **1** (71 pages). Ordering information is given on any current masthead page.

#### Fourier-Transform EPR Investigation of Photogenerated Radical Anions of $\text{C}_{60}$ in Solution

M. Ruebsam and K.-P. Dinse\*

*Institute for Physical Chemistry  
Technical University Darmstadt  
D-6100 Darmstadt, Germany*

M. Plueschau

*Physics Institute, University Dortmund  
D-4600 Dortmund, Germany*

J. Fink

*Kernforschungszentrum Karlsruhe, INFP  
D-7500 Karlsruhe, Germany*

W. Kraetschmer and K. Fostiropoulos

*MPI fuer Kernforschung  
D-6900 Heidelberg, Germany*

C. Taliani

*Instituto di Spettroscopia Molecolare  
I-40126 Bologna, Italy*

*Received May 27, 1992*

The new phases of carbon, and in particular its most symmetrical representative  $\text{C}_{60}$ , are attracting intense attention. Although  $^{13}\text{C}$  NMR has been used for an unambiguous identification, EPR experiments have been less successful for a characterization of its paramagnetic derivatives. Early attempts to produce  $\text{C}_{60}$ -related doublet radicals either by photolysis,<sup>1</sup> by alkali metal reduction,<sup>2</sup>

(12) Brown, I. D. In *Structure and Bonding in Crystals*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 2, p 1.

(13) The detailed arguments for these assignments are presented in the supplementary material.