Inorg. Chem. **1998,** *37,* 5380−5382

Diastereoselective Self-Assembly and Crystal Structure of the Chiral, Anionic Molybdenum-Based [2+2] Molecular Square $[\{MoO_2(C_{21}H_{20}O_4)\}_2]^{4-}$

Anne-K. Duhme,[*,†] **Sian C. Davies,**[‡] **and David L. Hughes**[‡]

Anorganisch-Chemisches Institut der Universität,
Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany, and
Nitrogen Fixation Laboratory, John Innes Centre,
Norwich Research Park, Colney, Norwich NR4 7UH, U.K.

Received October 23, 1997

Introduction

Bis(catecholates) react not only with metal cations[1] but also with molybdate[2,3] to form chiral mono- as well as dinuclear complexes depending on the structure of the linker between the catecholate subunits. The alternative formation of polymeric arrays has not yet been observed; discrete complexes are apparently entropically favored. Even in the presence of excess catecholate, two oxo ligands remain coordinated to the molybdenum, invariably cis to each other, thereby sealing up two adjacent coordination sites of the octahedral metal center.[4] This distinctive feature of the MoO_2^{2+} unit prompted us to investigate its shape-defining potential as a metal center in supramolecular assemblies[2] (Figure 1).

Recently, the self-assembly of diverse molecular squares, in which transition metals,[5] the main group element iodine in its trivalent I^{III} form,[6] or organic frameworks[7] provide the approximate 90° angles at the corners of the square, has been a subject of increasing activity in supramolecular chemistry.[8] To achieve such an efficient and controlled assembly, a particular metal−ligand combination should give only one optimal metallo-supramolecular structure. In our case, such a design requires a ligand with the correct orientation of coordination sites to form defined closed structures with MoO_2^{2+}, ruling out the formation of complexes of undesired nuclearity.[3,9]

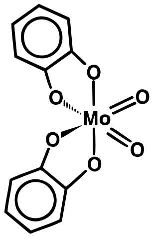
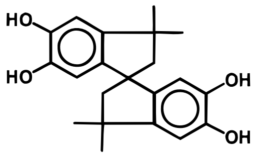


Figure 1. Schematic representation of a catecholate complex containing the *cis*-dioxo MoO_2^{2+} unit.

For this purpose, the conformationally rigid, chiral spiro ligand $\mathbf{L^1}$ was chosen as a promising dinucleating ligand.[10] The preorientation of $\mathbf{L^1}$ should favor the formation of a square-shaped [2+2] complex on coordination to MoO_2^{2+} with a high degree of asymmetric induction. It has been reported that configurational control of octahedral complexes can be achieved with chiral ligands such as siderophore analogues,[11−13] binaphtholate derivatives,[14,15] or bipyridine containing "chiragens".[16]



3, 3, 3', 3'-Tetramethyl-1, 1'- spirobisindane-5, 5', 6, 6'-tetrol

L^1

Here we describe the synthesis and structural characterization of a MoO_2^{2+}-based, homochiral dinuclear molecular square, obtained in a one-step self-assembly process by simple mixing of metal ion and ligand solutions. The shape-defining corner units consist of *cis*-MoO_2^{2+} cores and the orthogonal connections of two catecholates via spiro junctions. Consequently, a complementary structural control is achieved by choice of the ligand and the metal center.

---

[*] To whom correspondence should be addressed.

[†] Universität Münster.

[‡] Nitrogen Fixation Laboratory.

(1) (a) Enemark, E. J.; Stack, T. D. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 996. (b) Albrecht, M.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 3134. Albrecht, M.; Kotila, S. *J. Chem. Soc., Chem. Commun.* **1996**, 2309. Albrecht, M.; Schneider, M.; Röttele, H. *Chem. Ber./Rec.* **1997**, *130*, 615. (c) Huang, S.-P.; Franz, K. J.; Olmstead, M. M.; Fish, R. H. *Inorg. Chem.* **1995**, *34*, 2820. (d) Kersting, B.; Telford, J. R.; Meyer, M.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 5712.

(2) Duhme, A.-K.; Dauter, Z.; Hider, R. C.; Pohl, S. *Inorg. Chem.* **1996**, *35*, 3059.

(3) Duhme, A.-K. *J. Chem. Soc., Dalton Trans.* **1997**, 773.

(4) Albrecht, M.; Franklin, S. J.; Raymond, K. N. *Inorg. Chem.* **1994**, *33*, 5785.

(5) (a) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. Fujita, M.; Ogura, K. *Coord. Chem. Rev.* **1996**, *148*, 249. (b) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. Stang, P. J.; Persky, N. E. *J. Chem. Soc., Chem. Commun.* **1997**, 77. (c) Duan, C.; Liu, Z.; You, X.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1997**, 381. (d) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096. (e) Stricklen, P. M.; Volcko, E. J.; Verkade, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 2494.

(6) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1993**, *115*, 9808. Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. Stang, P. J.; Chen, K.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 8793. Olenyuk, B.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 8221.

(7) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313.

(8) (a) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995. (b) Hunter, C. A. *Angew. Chem.* **1995**, *34*, 1079.

(9) Fujita, M.; Sasaki O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1535.

(10) To our knowledge no metal complexes of $\mathbf{L^1}$ have yet been described although the compound has been known for a long time (*Beilstein* **1967**, *6* (Part 8, Suppl. 3), p 6791) and is commercially available (Aldrich). No entries in the Cambridge Structural Database are present (May 1998). Spirobisindanol has been used as auxiliary in building a chiral cavity in combination with oligobipyridine strands: Woods, C. R.; Benaglia, M.; Cozzi, F.; Siegel, J. S. *Angew. Chem.* **1996**, *35*, 1830.

(11) Tor, Y.; Libman, J.; Shanzer, A.; Lifson, S. *J. Am. Chem. Soc.* **1987**, *109*, 6517. Tor, Y.; Libman, J.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 6518. Dayan, I.; Libman, J.; Agi, Y.; Shanzer, A. *Inorg. Chem.* **1993**, *32*, 1467.

(12) Stack, T. D. P.; Karpishin, T. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1512. Karpishin, T. B.; Stack, T. D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6115.

(13) Enemark, E. J.; Stack, T. D. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 996.

(14) Dietz, S. D.; Eilerts, N. W.; Heppert, J. A.; Morton, M. D. *Inorg. Chem.* **1993**, *32*, 2, 1698.

(15) Baret, P.; Beaujolais, V.; Gaude, D.; Coulombeau, C.; Pierre, J.-L. *Chem. Eur. J.* **1997**, *3*, 969.

(16) Hayoz, P.; von Zelewsky, A.; Stoeckli-Evans, H. *J. Am. Chem. Soc.* **1993**, *115*, 5111.

S0020-1669(97)01349-9 CCC: $15.00

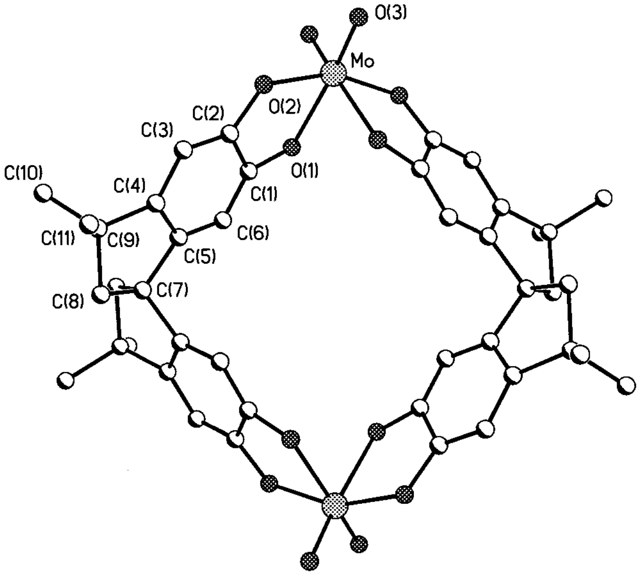


Figure 2. Structure of Λ, Λ-$[\{MoO_2(R\text{-}\mathbf{L^1})\}_2]^{4-}$ showing the atom-labeling scheme. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mo−O(1), 2.144(15); Mo−O(2), 1.974(15); Mo−O(3), 1.757(15); O(1)−Mo−O(2), 74.3(6); O(1)−Mo−O(3), 161.1(6); O(2)−Mo−O(3), 89.0(6); O(2)−Mo−O(2A), 157.1(6); O(3)−Mo−O(3A), 102.8(7).

Experimental Section

General Methods. Starting materials were commercially available (Aldrich, Fluka) and used as supplied. NMR data were recorded on a Bruker AM-400 and IR spectra on a Bruker IFS 113 v spectrometer. Electrospray ionization mass spectrometry (ESI-MS) spectra were taken with a Finnigan MAT LCQ spectrometer. Elemental analyses were performed by the Microanalytical Service of the Organic Chemistry Department, University of Münster, and the Mikroanalytisches Laboratorium Beller, D-37004 Göttingen, Germany.

Synthesis of $\mathbf{Na_4[\{MoO_2(L^1)\}_2]}$. A solution of 242 mg (1.0 mmol) $Na_2MoO_4\cdot 2H_2O$ in 1 mL of water was added to a vigorously stirred solution of 340 mg (1.0 mmol) $\mathbf{L^1}$ in 10 mL of methanol at ambient temperature. The resulting dark red solution was filtered before 3 mL of ethanol was added. The product crystallized overnight in form of dark red needles, and these were filtered off, washed with ethanol, and dried in a desiccator over silica gel to yield 439 mg (0.43 mmol, 86%). Crystals suitable for single-crystal X-ray structure determination were obtained by crystallization of the product from a 0.3 M solution in methanol/H_2O 10:1 by slow diffusion of ethanol. IR (KBr) $\nu = 857$, 890 cm^{-1} (*cis*-MoO_2); ESI-MS (−) molecular ion ($M^{4-} + H_3O^+ + 2\,H^+$) 949 *m*/*z*; ^{1}H NMR ([D$_6$]DMSO) δ 1.23, 1.25 (2 × s, 6H each, C-10H_3, C-11H_3), 2.00, 2.16 (2 × d, 2H each, $J = 12.8$ Hz, C-8H_2), 5.40 (s, 2H, C-3*H*), 5.97 (s, 2H, C-6*H*); ^{13}C NMR (D_2O) δ 30.5, 32.2 (C-10, C-11), 43.4 (C-9), 57.3 (C-7), 60.6 (C-8), 106.6 (C-6), 109.1 (C-3), 141.0 (C-4), 144.4 (C-5), 155.6 (C-2), 156.6 (C-1) (numbering scheme analogue Figure 2, assignment according to 2D experiments). Anal. Calcd for $C_{42}H_{40}Mo_2Na_4O_{12}\cdot C_{10}H_{40}O_{10}$: C, 46.57; H, 6.01; Mo, 14.31; Na, 6.86. Found: C, 46.48; H, 5.89; Mo, 14.02; Na, 6.50.

X-ray Structure Determination. Crystal data for $Na_4[\{MoO_2(\mathbf{L^1})\}_2]$: $C_{42}H_{40}Mo_2Na_4O_{12}$, solv. (where solv. is a mixture of water, methanol, and ethanol, equivalent to 10 methanol), $M = 1341.0$, dark red square prisms (0.35 × 0.30 × 0.30 mm), orthorhombic, space group *Ccca* (No. 68), $a = 9.839(2)$ Å, $b = 28.509(12)$ Å, $c = 29.519(16)$ Å, $V = 8280(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.08$ g cm^{-3}, $F(000) = 2784$, μ(Mo Kα) = 3.8 cm^{-1}, $T = 293$ K. The crystal was coated with paraffin oil and sealed in a glass capillary. After preliminary photographic examination, this was transferred to an Enraf-Nonius CAD4 diffractometer for determination of cell parameters (settings of 25 reflections, $\theta = 8{-}10°$, each centered in four orientations) and for measurement of diffraction intensities (1902 unique reflections to $\theta_{max} = 20°$; 839 were observed with $I > 2\sigma_I$). During processing, corrections were applied for Lorentz−polarization effects, crystal deterioration (ca. 20% overall), and to eliminate negative net intensities (by Bayesian statistical methods). No absorption correction was necessary. The structure was determined by direct methods (SHELXS[17]) and refined by full-matrix least-squares methods in SHELXL.[18] The non-hydrogen atoms of the complex were clearly resolved and refined with anisotropic thermal parameters. The hydrogen atoms on the ligand were included in idealized positions with isotropic temperature factors. The region between the anions, occupied by sodium cations and a mixture of solvent molecules, was less well resolved. At the conclusion of the refinement, $wR_2 = 0.244$ and $R_1 = 0.105$ for 967 reflections (with $I > 1.5\sigma_I$) weighted $w = [\sigma^2(F_o^2) + (0.15P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the observed data only, $R_1 = 0.092$. In the final difference map, the highest peaks (to ca. 0.47 e Å^{-3}) were close to a sodium ion and in the solvent region.

Results and Discussion

Synthesis, Spectroscopic, and Physical Characterization of $\mathbf{Na_4[\{MoO_2(L^1)\}_2]}$. Reaction of a methanolic solution of $\mathbf{L^1}$ with an aqueous solution of sodium molybdate in a 1:1 ratio gave the dinuclear anionic molecular square $[\{MoO_2(\mathbf{L^1})\}_2]^{4-}$ via self-assembly. The spectral data as summarized in the Experimental Section are consistent with the above formula as is the elemental analysis.

The optically active spiro ligand $\mathbf{L^1}$ was used in its racemic form. However, the ^{1}H and ^{13}C NMR spectra of the product show only one set of sharp signals with a pattern close to that of the free ligand. In the ^{1}H NMR spectrum, the diastereotopic protons of the methylene groups show the expected four-line AB pattern. Since quick exchange processes seem to be unlikely with a rigid and preoriented ligand like $\mathbf{L^1}$ this provides evidence for a highly symmetrical and diastereomerically pure complex. Consequently, the highly preorganized ligand $\mathbf{L^1}$ is obviously able to direct the stereochemical outcome of the self-assembly process.

Crystal Structure of $\mathbf{Na_4[\{MoO_2(L^1)\}_2]}$. An X-ray crystallographic study confirmed the existence of enantiomeric, entirely homochiral macrocyclic anions with formulas Δ,Δ-$[\{MoO_2(R\text{-}\mathbf{L^1})\}_2]^{4-}$ and Λ,Λ-$[\{MoO_2(S\text{-}\mathbf{L^1})\}_2]^{4-}$ (Figure 2). The dinuclear complexes lie around points of 222 symmetry; one 2-fold axis of symmetry passes through both molybdenum atoms, the second passes through the two spiro carbon atoms C(7), and the third is perpendicular to the plane of the ring. The geometry around the octahedral MoO_6 centers is distorted in a way typical for MoO_2^{2+} core structures. Due to the strong structural trans-effect of the oxo-ligands, these adopt the usual cis-configuration and the Mo−O single bonds trans to the oxo ligands are significantly longer [2.144(15) Å] than the cis-oriented ones [1.974(15) Å].

The planar $Mo_2C(7)_2$ square is slightly distorted toward a rhomoid-like geometry with a Mo−Mo diagonal distance of 10.08 Å and a C(7)−C(7) diagonal distance of 8.94 Å. The Mo−C(7) distance is 6.74 Å. These dimensions are smaller than those ovserved for the tetranuclear cationic molecular square $[Pt(dppp)(4,4'\text{-bipyridyl})OSO_2CF_3]_4$ (dppp = 1,3-bis(diphenylphosphino)propane) which has a lateral length of 11.2 Å and a metal-to-metal diagonal distance of 14.6 Å.[19] Interestingly, these complexes both form microchannels in the solid state due to alignment of the square macrocycles (Figure 3).

---

(17) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(18) Sheldrick, G. M. *SHELXL: Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1993.

(19) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

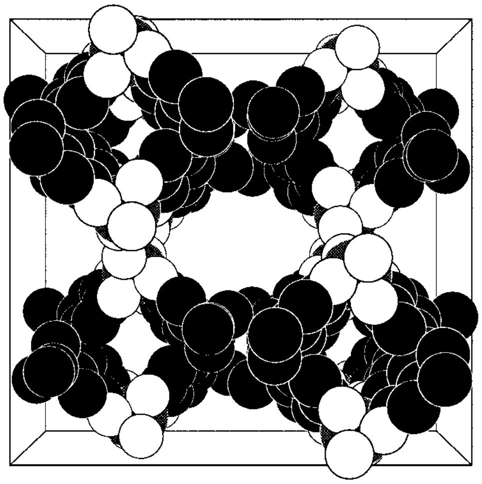


Figure 3. Packing diagram of the molecular squares looking down the microchannels as viewed along the *a* axis.

A special feature of the oxo ligands in the molybdenum complex is their ability to serve as “exo-receptors” of the square anions by acting as components of the disordered network formed by sodium counterions and solvent oxygen atoms that links the squares, through hydrogen bonds and Na···O coordination, in planes normal to the *c* axis.

Unfortunately, the quality of the structural parameters obtained from the X-ray structure determination is limited due to disordered counterions and solvent molecules in the lattice. Some solvent of crystallization may have been lost during mounting and the crystal showed a 20% degradation of intensities during the data collection. Similar problems in obtaining high-quality data have been reported in the X-ray crystallographic characterization of several molecular squares[6,9] and metallomacrocycles,[20] perhaps as an unwelcome side effect of the microchannel formation.

Conclusions

This novel anionic molecular square represents a chiral self-assembling system that can be prepared in high yields from readily available precursors. The configuration (Δ or Λ) of the octahedral metal centers is controlled by the chirality of the rigid spiro ligand. Thereby, the unusual stereoelectronic preferences of the MoO_2^{2+} unit allow the one-step assembly of an unusual structure that is not easily accessible with other metal ions. The entirely homochiral macrocycles are of interest with regard to host−guest chemistry, catalysis, and biomimetic studies. Investigations in these directions are currently under way.

Acknowledgment. This work was supported by the European Commission (TMR Marie Curie Research Training Grant for A.K.D.) and the Fonds der Chemischen Industrie. We thank Professors B. Krebs and R. L. Richards for helpful discussions and Dr. H. Luftmann for the ES mass spectrum.

Note Added in Proof

We also draw the attention of the reader to the following recent publications: Masood, M. A.; Enemark, E. J.; Stack, T. D. P. *Angew. Chem.* **1998**, *37*, 928; Enemark, E. J.; Stack, T. D. P. *Angew. Chem.* **1998**, *37*, 932.

IC971349Z

---

[20] Houghton, M. A.; Bilyk, A.; Harding, M. M.; Turner, P.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2725.