Further study of the magnetic properties of these irregular alternating systems are planned but a general law may be easily envisaged for homometallic systems with sequences of more than one F/AF interaction. Ferromagnetism emerges, as observed for **2**, if $2n+1$ AF interactions are followed by one or more F interactions; the ground state here is always $S=0$. An alternative possibility consists of an even number of AF interactions ($2n$) followed by one or more (m) F interactions, as observed for **1**, which induces net ferrimagnetic behavior with ground state $S_T = \mathrm{m}S$ for each ($2n+m$) local S spin carrier.

Received: November 16, 1999 [Z 14284]

---

[1] a) O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**, chap. 11; b) P. Day, *J. Chem. Soc. Dalton Trans.* **1997**, 701–705.

[2] a) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–195*, 1027–1068; b) M. A. S. Abu-Youssef, A. Escuer, M. A. S. Goher, F. A. Mautner, R. Vicente, *J. Chem. Soc. Dalton Trans.* **2000**, 413–416, and references therein.

[3] Crystal data for **1** ($C_{12}H_{14}MnN_8$) and **2** ($C_{14}H_{14}MnN_8O_4$; in square brackets), monoclinic, $P2_1/n$ [$P2_1/a$], $a=11.201(3)$, $b=14.499(4)$, $c=14.308(4)$ Å [$a=15.556(2)$, $b=16.831(2)$, $c=17.595(2)$ Å], $\beta=106.05(2)°$[$110.80(1)°$], $V=2233.1(11)$ Å^3 [$4306.6(9)$ Å^3], $Z=6$ [10], $\rho_{calc}=1.451\,\mathrm{g\,cm^{-3}}$ [$1.593\,\mathrm{g\,cm^{-3}}$], crystal size $0.15\times0.28\times0.50$ mm [$0.30\times0.60\times1.0$ mm], $\mu=0.893\,\mathrm{mm^{-1}}$ [$0.807\,\mathrm{mm^{-1}}$]. Of 4887 [17574] reflections collected, 3164 [6593] were observed with $I>2\sigma(I)$; 289 [612] parameters. $R(F)=0.0363$ [0.0641], $wR(F^2)=0.0943$ [0.1861], min./max. residual electon density $\rho=-0.22/0.21\,\mathrm{e\,Å^{-3}}$ [$-1.94/1.80\,\mathrm{e\,Å^{-3}}$]. The data were collected on a modified STOE [IPDS] diffractometer with $Mo_{K\alpha}$ irradiation 0.71069 Å [0.71073 Å] at room temperature. Lorentz polarization effects, intensity decay, and absorption (DIFABS) [Lorentz polarization effects and numerical absorption (X-SHAPE, min./max. transmission 0.604/0.803)] corrections were made. Both structures were solved by direct methods and refined by full-matrix least-squares method on F^2 values. Refinement used the SHELXTL/PC package [SHELXL-97 for **2**, which was a twinned crystal; twin ratio 0.244/0.756(1)]. Nonhydrogen atoms were refined anisotropically; hydrogen atoms were included by a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136997 and -136998. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

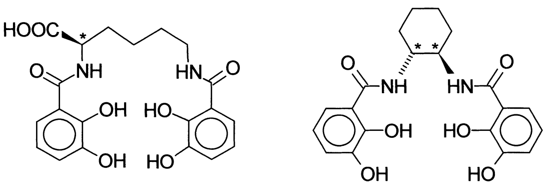
[4] A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1998**, *37*, 782–787.

[5] a) J. L. Manson, A. M. Arif, J. S. Miller, *Chem. Commun.* **1999**, 1479–1480; b) M. A. S. Abu-Youssef, A. Escuer, D. Gatteschi, M. A. S. Goher, F. A. Mautner, R. Vicente, *Inorg. Chem.* **1999**, *38*, 5716–5723.

Stereoselectivity in the Formation of a Cyclic Trinuclear *cis*-Dioxomolybdenum(VI) Complex of a Chiral Siderophore Analogue[**]

Anne-Kathrin Duhme-Klair,* Guido Vollmer,
Craig Mars, and Roland Fröhlich

The stereoselective synthesis of coordination compounds can be achieved by using enantiomerically pure ligands, which, on metal binding, transfer their chiral information to the metal center.[1] Siderophores, high-affinity chelators synthesized by microorganisms to solubilize iron(III) for uptake into the cell, represent a biologically important example of this ligand type.[2] Most siderophores are enantiomerically pure amino acid derivatives, and the chirality of the molecules can play an important role in their biological activity. This is well documented for enterobactin, the native siderophore of *Escherichia coli*: Only the naturally occurring complex, having an L-seryl ligand backbone and a Δ configuration at the metal center, is able to supply iron to the cells.[3, 4] Interestingly, the N_2-fixing cells of *Azotobacter vinelandii* secrete azotochelin (Scheme 1), a tetradentate iron siderophore which also binds molybdenum.[5, 6] The structures of relevant model complexes have been reported.[7, 8] Molybdenum, as well as iron, is a component of the conventional nitrogenase, and in *A. vinelandii* the siderophore production depends not only on the amount of iron in the environment but also on the concentration of molybdenum.[5b, 6b] We report here that the L-lysine derivative azotochelin shows a high diastereoselectivity in forming the two possible Δ and Λ *cis*-dioxomolybdenum complexes. Use of the azotochelin analogue H_4-(1*R*,2*R*)-dachcam (Scheme 1) allowed us to investigate the chiral induction on molybdenum binding in the solid state and to compare the CD spectra of the model complex



Azotochelin

H_4-(1*R*,2*R*)-dachcam

Scheme 1.

---

[*] Dr. A.-K. Duhme-Klair, C. Mars
Department of Chemistry
The University of York
York YO10 5DD (UK)
Fax: (+44) 1904-43-2516
E-mail: akd1@york.ac.uk

G. Vollmer
Anorganisch-chemisches Institut der Universität
Wilhelm-Klemm-Strasse 8, 48149 Münster (Germany)

R. Fröhlich
Organisch-chemisches Institut der Universität
Corrensstrasse 40, 48149 Münster (Germany)

[**] This work was supported by the Fonds der Chemischen Industrie. We thank Dr. T. A. Dransfield, York, for the ES mass spectrum and Dr. T. Vogel and B. Beermann, Münster, for recording the CD spectra.

with the spectra obtained for the naturally occurring azotochelin complex under analogue conditions.

The reaction of a solution of H_4-(1*R*,2*R*)-dachcam in DMSO with an aqueous solution of sodium or potassium molybdate in a 1:1 ratio resulted in the formation of orange complexes which could be precipitated by addition of acetone and THF. Microanalyses of the isolated solids were consistent with a 1:1:2 ratio of molybdenum, ligand, and counterions. The electrospray (ES) mass spectrum of a solution of the sodium salt of the complex in acetonitrile showed three peaks at *m*/*z* 533, 811 (base peak), and 1645 corresponding to a trinuclear complex $[\{MoO_2((1R,2R)\text{-dachcam})\}_3]^{6-}$ (**1**) associated with three, four, and five sodium counterions, respectively. The 1/3, 1/2, and 1 spacing between isotopic components of the peaks confirmed the charges of the species involved. An additional peak at *m*/*z* 1090 originating from a dinuclear complex $[\{MoO_2((1R,2R)\text{-dachcam})\}_2]^{4-}$ associated with three sodium cations was also observed.

Suitable single crystals for X-ray diffraction could be obtained from the potassium salt of **1**. The crystal structure showed the complex to be trinuclear in the solid state (Figure 1).[9] The molybdenum atoms form an approximately equilateral triangle with intramolecular Mo(1)–Mo(2), Mo(1)–Mo(3), and Mo(2)–Mo(3) distances of 11.221(4), 11.104(4), and 11.236(4) Å, respectively. Atom Mo(3) lies on a pseudo-twofold axis of symmetry, and the coordination mode of the two catecholamide units corresponds to the C_2-symmetrical *cis,trans,cis* isomer shown in Scheme 2. In contrast, the catecholamide units coordinated to Mo(1) and Mo(2) are bound in *cis,cis,cis* orientation, thereby allowing the formation of the cyclic structure. In the rapidly developing field of supramolecular coordination chemistry[10] examples of molecular triangles with metal atoms in vertex positions are still relatively rare and have so far been concentrated on noble metals,[11–15] copper,[16] and ligands based on nitrogen-containing heterocycles. In contrast, the novel molecular triangle **1** consists of catecholate ligands in combination with *cis*-MoO_2^{2+} units, demonstrating the versatility of these components as building blocks in supramolecular assemblies.[17] On complex formation the enantiomerically pure ligand (1*R*,2*R*)-dachcam predetermines the chirality of the metal centers, giving rise to an entirely homochiral cyclic trimer Δ,Δ,Δ-**1**. The absolute configuration at the metal centers could be assigned unambiguously since the absolute configuration of the ligand is known.

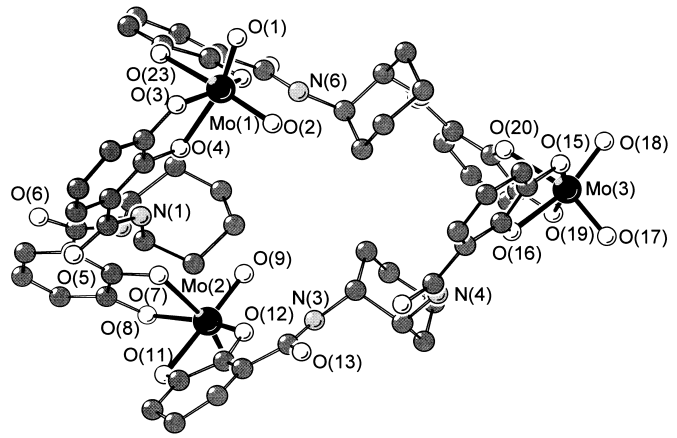
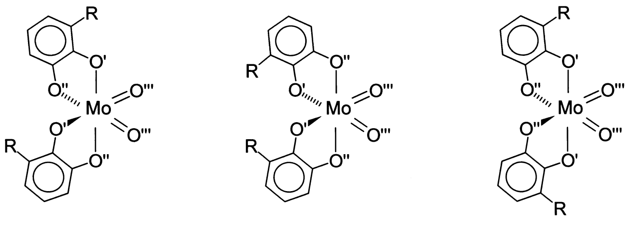


Figure 1. Structure of Δ,Δ,Δ-$[\{MoO_2((1R,2R)\text{-dachcam})\}_3]^{6-}$ showing the atom labeling scheme. Projection along the *a* axis. Hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Mo(1)–O(2) 1.71(2), Mo(1)–O(1) 1.72(2), Mo(1)–O(3) 2.02(2), Mo(1)–O(24) 2.04(2), Mo(1)–-O(4) 2.10(2), Mo(1)–O(23) 2.12(2), Mo(2)–O(10) 1.70(2), Mo(2)–O(9) 1.70(2), Mo(2)–O(12) 2.02(2), Mo(2)–O(8) 2.02(2), Mo(2)–O(7) 2.13(2), Mo(2)–O(11) 2.16(2), Mo(3)–O(17) 1.71(2), Mo(3)–O(18) 1.72(2), Mo(3)–O(15) 1.98(2), Mo(3)–O(19) 2.02(2), Mo(3)–O(16) 2.12(2), Mo(3)–O(20) 2.13(2); O(23)-Mo(1)-O(24) 75.1(6), O(3)-Mo(1)-O(4) 75.7(7), O(1)-Mo(1)-O(2) 101.1(8), O(7)-Mo(2)-O(8) 75.2(7), O(11)-Mo(2)-O(12) 76.2(6), O(9)-Mo(2)-O(10) 102.5(9), O(19)-Mo(3)-O(20) 75.2(6), O(15)-Mo(3)-O(16) 75.5(6), O(17)-Mo(3)-O(18) 103.5(8).



cis,cis,cis *cis,trans,cis* *trans,cis,cis*

Scheme 2. Schematic representation of the three possible *cis/trans* isomers that can be formed on coordination of two asymmetrically substituted catecholate ligands to a *cis*-dioxomolybdenum(VI) unit (all shown in Λ configuration).

To investigate if the intramolecular chiral induction observed for Δ,Δ,Δ-**1** in the solid state also occurs in aqueous solution at pH 7, a CD spectroscopic investigation has been carried out. A time-dependent study revealed that **1** rapidly inverts its configuration on dissolution of the crystalline solid in water. After equilibration in 4-(2-hydroxyethyl)-1-piperazinethanesulfonic acid (HEPES) buffer at pH 7 the Λ-configured complex dominates, giving rise to a CD band with a minimum at around 360 nm (Figure 2). Since the Δ- and Λ-configured complexes of (1*R*,2*R*)-dachcam are diastereomers [Eq. (1)], not enantiomers, they have different physical

$$\Delta\text{-}[\{MoO_2((1R,2R)\text{-dachcam})\}_n]^{2n-} \rightleftharpoons \Lambda\text{-}[\{MoO_2((1R,2R)\text{-dachcam})\}_n]^{2n-} \qquad (1)$$

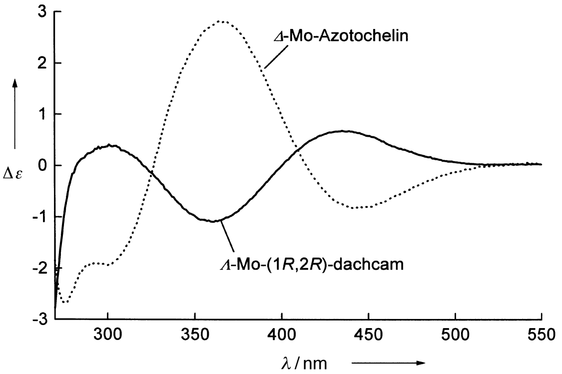


Figure 2. CD spectra of the molybdenum complexes of H_4-(1*R*,2*R*)-dachcam and azotochelin in buffered aqueous solution (0.2 mM) at neutral pH.

properties, including solubilities.[18] Consequently, the $(+)_{360}$ diastereomer present in the solid state inverts its configuration on dissolution to form the $(-)_{360}$ diastereomer, which is the more stable form in aqueous solution. In solution, however, the trimer appears to dissociate partially. The diastereomerisation process does not exhibit first-order kinetics and, in accordance with the ES mass spectrum, a molecular weight distribution analysis by gel filtration (LH20, methanol) shows evidence for the presence of a minor amount of a dinuclear species in solution.

An intramolecular chiral induction was also observed on binding of molybdenum by the naturally occurring L-lysine derivative azotochelin. In this case the CD spectrum of the equilibrium mixture in aqueous solution at pH 7 shows a strong band with a maximum at 360 nm (Figure 2). According to this comparison, the preferred configuration of the molybdenum complex of the naturally occurring L-lysine derivative azotochelin in aqueous solution and at neutral pH is likely to be the Δ form. Interestingly, this would correspond to the biologically active Δ form of the iron(III) – enterobactin complex.

Experimental Section

H_4-(1*R*,2*R*)-dachcam: The ligand was synthesized by analogy to published procedures[19] by activation of 2,3-di(benzyloxy)benzoic acid with 2-(1-*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium (HBTU) hexafluorophosphate and subsequent reaction with (1*R*,2*R*)-diaminocyclohexane. Removal of the protecting groups was achieved by hydrogenation (catalyst: 5 % Pd on charcoal). Yield: 85 %. Satisfactory elemental analysis for $C_{20}H_{22}N_2O_6$; ^1H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.13$ (m, 2H; C-CH$_2$-C), 1.53 (m, 2H; C-CH$_2$-C), 1.75 (m, 2H; C-CH$_2$-C*), 1.92 (m, 2H; C-CH$_2$-C*), 3.76 (m, 2H; C-*CH-N), 6.61 (t, 2H; ArH), 6.84 (d, 2H; ArH), 7.17(d, 2H; ArH), 8.48 (d, 2H; NH); MS (70 eV): *m*/*z* (%): 386 (94) $[M]^+$.

$K_6[\{MoO_2((1R,2R)\text{-dachcam})\}_3]$ and $Na_6[\{MoO_2((1R,2R)\text{-dachcam})\}_3]$: The molybdenum complexes were synthesized by addition of a solution of H_4-(1*R*,2*R*)-dachcam (0.25 mmol) in DMSO (2 mL) to a solution of potassium or sodium molybdate (0.25 mmol) in water (2 mL). After addition of acetone (10 mL) and THF (20 mL) microcrystalline products precipitated which could be isolated in 78 and 80 % yield, respectively. Satisfactory elemental analyses for $C_{60}H_{54}N_6K_6Mo_3O_{24} \cdot 7\,C_2H_6OS \cdot 6\,H_2O$ and $C_{60}H_{54}N_6Mo_3Na_6O_{24} \cdot 7\,C_2H_6OS \cdot 6\,H_2O$; IR (KBr): $\tilde{\nu} = 870$, 897 cm^{-1} (*cis*-MoO$_2$); MS (ES, Na salt in acetonitrile): *m*/*z* (%): 533 (50) $[M_{\text{trimer}}+3\,Na]^{3-}$, 811 (100) $[M_{\text{trimer}}+4\,Na]^{2-}$, 1090 (25) $[M_{\text{dimer}}+3\,Na]^-$, 1645 (10) $[M_{\text{trimer}}+5\,Na]^-$.

Received: October 7, 1999 [Z 14126]

---

[1] Recent review: U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 313; *Angew. Chem. Int. Ed.* **1999**, *38*, 303.

[2] "Iron Transport and Storage in Microorganisms, Plants and Animals": A.-M. Albrecht-Gary, A. L. Crumbliss in *Metal Ions in Biological Systems, Vol. 35* (Eds.: A. Sigel, H. Sigel), Marcel Dekker, New York, **1998**, p. 239.

[3] J. B. Neilands, T. J. Erickson, W. H. Rastetter, *J. Biol. Chem.* **1981**, *256*, 3831.

[4] P. Thulasiraman, S. M. C. Newton, J. Xu, K. N. Raymond, C. Mai, A. Hall, M. A. Montague, P. E. Klebba, *J. Bacteriol.* **1998**, *180*, 6689.

[5] a) W. J. Page, M. von Tigerstrom, *J. Bacteriol.* **1982**, *151*, 237; b) A. S. Cornish, W. J. Page, *BioMetals* **1995**, *8*, 332.

[6] a) A.-K. Duhme, R. C. Hider, H. H. Khodr, *BioMetals* **1996**, *9*, 245; b) A.-K. Duhme, R. C. Hider, M. Naldrett, R. N. Pau, *J. Biol. Inorg. Chem.* **1998**, *3*, 520.

[7] M. Albrecht, S. J. Franklin, K. N. Raymond, *Inorg. Chem.* **1994**, *33*, 5785.

[8] A.-K. Duhme, Z. Dauter, R. C. Hider, S. Pohl, *Inorg. Chem.* **1996**, *35*, 3059.

[9] X-ray crystal structure analysis of $K_6(\mathbf{1}) \cdot 7\,C_2H_6OS \cdot 6\,H_2O$: $C_{60}H_{54}K_6Mo_3N_6O_{24} \cdot 6\,C_2H_6OS \cdot 2/2\,C_2H_6OS \cdot 6\,H_2O$, $M_r = 2420.5$, red crystal, $0.50 \times 0.35 \times 0.22$ mm, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 14.041(3)$, $b = 15.690(3)$, $c = 47.573(10)$ Å, $V = 10480(4)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.534$ g cm^{-3}, $2.50° < 2\theta < 24.63°$, $F(000) = 4968$, $\mu = 8.12$ cm^{-1}, ω scans, $T = 223$ K. The data set was collected on an Enraf Nonius CAD4 diffractometer equipped with a rotating anode generator ($\lambda = 0.71073$ Å). Of 9711 reflections measured $(+h,+k,+l)$, $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 9711 were independent and 4253 observed $[I \geq 2\sigma(I)]$. An empirical absorption correction with φ scan data was applied. The structure was solved using the program SHELXS-86 and refined against $|F^2|$ using the program SHELXL-97 (601 parameters). $R1 = 0.092$, $wR2 = 0.206$, max./min. residual electron density 1.67/ – 0.87 e Å^{-3}, Flack parameter – 0.05(13). Due to the limited number of observed data only Mo and K atoms were refined anisotropically. Some of the DMSO molecules are heavily disordered. The hydrogen atoms of the water molecules could not be located, other hydrogens atoms were refined using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135301. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**.

[11] a) D. P. Smith, E. Baralt, B. Morales, M. M. Olmstead, M. F. Maestre, R. H. Fish, *J. Am. Chem. Soc.* **1992**, *114*, 10647; b) H. Chen, M. M. Olmstead, D. P. Smith, M. F. Maestre, R. H. Fish, *Angew. Chem.* **1995**, *34*, 1590; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1514.

[12] a) S. Rüttimann, G. Bernadinelli, A. F. Williams, *Angew. Chem.* **1993**, *105*, 432; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 392; b) C. Provent, S. Hewage, G. Brand, G. Bernadinelli, L. H. Charbonniere, A. F. Williams, *Angew. Chem.* **1997**, *109*, 1346; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1287.

[13] a) R.-D. Schnebeck, L. Randaccio, E. Zangrando, B. Lippert, *Angew. Chem.* **1998**, *110*, 128; *Angew. Chem. Int. Ed.* **1998**, *37*, 119; b) R.-D. Schnebeck, E. Freisinger, B. Lippert, *Chem. Commun.* **1999**, 675.

[14] S.-W. Lai, M. C.-W. Chan, S.-M. Peng, C. M. Che, *Angew. Chem.* **1999**, *111*, 696; *Angew. Chem. Int. Ed.* **1999**, *38*, 669.

[15] L. Schenetti, G. Bandoli, A. Dolmella, G. Trovo, B. Longato, *Inorg. Chem.* **1994**, *33*, 3169.

[16] P. Chaudhuri, I. Karpenstein, M. Winter, C. Butzlaff, E. Bill, A. X. Trautwein, U. Flörke, H. J. Haupt, *J. Chem. Soc. Chem. Commun.* **1992**, 321.

[17] A.-K. Duhme, S. C. Davies, D. L. Hughes, *Inorg. Chem.* **1998**, *37*, 5380.

[18] P. Biscarini, R. Kuroda, *Inorg. Chim. Acta* **1988**, *154*, 209.

[19] A.-K. Duhme, R. C. Hider, H. H. Khodr, *Chem. Ber.* **1997**, *130*, 969.