$Zr(OiPr)_4$ (109 mg, 0.28 mmol) in CH_2Cl_2 (5 mL) with 4 Å molecular sieves at $-20\,^{\circ}C$ (salt/ice bath), followed by *tert*-butyl hydroperoxide (3.8 M solution in toluene, 0.085 mL, 0.32 mmol). The reaction mixture was stirred at $-20\,^{\circ}C$ for 0.5 h before addition of diallylic alcohol **12** (30 mg, 0.094 mmol) in CH_2Cl_2 (5 mL) which was also cooled to $-20\,^{\circ}C$. The reaction mixture was then stirred for a further 0.5 h before transfer to a freezer at $-20\,^{\circ}C$ for 3 days. H_2O (2.5 mL) and saturated aqueous Na_2SO_3 (2.5 mL) were added to the reaction mixture. The resulting biphasic system was stirred vigorously for 0.5 h at ambient temperature and the aqueous layer extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were dried ($MgSO_4$), filtered through Celite, and concentrated under vacuum. Flash column chromatography (elution with EtOAc:petroleum ether (1:3)) gave epoxy alcohol (+)-**13** as a colorless oil (14 mg, 44 %). (see Supporting Information for analytical data,).

Received: October 23, 2000 [Z15980]

[1] O. Munoz, A. Penaloza, A. G. González, A. G. Ravelo, I. L. Bazzocchi, N. L. Alvarenga, *Stud. Nat. Prod. Chem.* **1996**, *18*, 739 – 783.

[2] For previous synthetic approaches to polyhydroxylated *Celastraceae* cores, see: a) C. Descoins, G. V. Thanh, F.-D. Boyer, P.-H. Ducrot, C. Descoins, J.-Y. Lallemand, *Synlett* **1999**, 240 – 242; b) J. D. White, H. Shin, T.-S. Kim, N. S. Cutshall, *J. Am. Chem. Soc.* **1997**, *119*, 2404 – 2419, and references therein.

[3] a) Y. Takaishi, K. Ujita, H. Tokuda, H. Nishino, A. Iwashima, T. Fujita, *Cancer Lett.* **1992**, *65*, 19 – 26; b) Y. Kuo, L. Yang Kuo, *Phytochemistry* **1997**, *44*, 1275 – 1281.

[4] Y. L. Zheng, Y. Xu, J. F. Lin, *Acta Pharm. Sin.* **1989**, *24*, 568 – 572.

[5] M. Beroza, G. T. Bottger, *J. Econ. Entomol.* **1954**, *47*, 188 – 189.

[6] a) N. Wakabayashi, W. J. Wu, R. M. Waters, R. E. Redfern, G. D. J. Mills, A. B. Demilo, W. R. Lusby, D. Andrzejewski, *J. Nat. Prod.* **1988**, *51*, 537 – 542; b) I. Kubo, M. Kim, G. De Boer, *J. Chromatogr.* **1987**, *402*, 354 – 357.

[7] a) H. Duan, Y. Takaishi, Y. Imakura, Y. Jia, T. Li, L. M. Cosentino, K.-H. Lee, *J. Nat. Prod.* **2000**, *63*, 357 – 361; b) H. Duan, Y. Takaishi, M. Bando, M. Kido, Y. Imakura, K.-H. Lee, *Tetrahedron Lett.* **1999**, *40*, 2969 – 2972.

[8] For asymmetric desymmetrization of acyclic secondary diallylic alcohols by Sharpless AE, see: T. Honda, H. Mizutani, K. Kanai, *J. Chem. Soc. Perkin Trans. 1* **1996**, 1729 – 1739, and references therein.

[9] The natural product acnistin-H; see: J. G. Luis, F. Echeverri, A. G. Gonzalez, *Phytochemistry* **1994**, *36*, 769 – 772. An elegant ring-closing metathesis approach to simple decalin diallylic alcohols has recently been disclosed; see: M. Lautens, G. Hughes, *Angew. Chem.* **1999**, *111*, 160 – 162; *Angew. Chem. Int. Ed.* **1999**, *38*, 129 – 131.

[10] a) E. Vogel, W. Klug, A. Breuer, *Org. Synth.* **1974**, *54*, 11 – 18; b) E. Vogel, W. Klug, A. Breuer, *Org. Synth.* **1976**, *55*, 86 – 90.

[11] W. Nagata, M. Yoshioka, T. Okumura, *Tetrahedron Lett.* **1966**, *8*, 847 – 852.

[12] a) K. B. Sharpless, T. Katsuki, *J. Am. Chem. Soc.* **1980**, *102*, 5976 – 5978; b) T. Katsuki, V. S. Martin, *Org. React.* **1996**, *48*, 1 – 299.

[13] Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, K. B. Sharpless, *J. Am. Chem. Soc.* **1987**, *109*, 5765 – 5780.

[14] L. D.-L. Lu, R. A. Johnson, M. G. Finn, K. B. Sharpless, *J. Org. Chem.* **1984**, *49*, 731 – 733.

[15] Z.-C. Yang, X.-B. Jiang, Z.-M. Wang, W.-S. Zhou, *J. Chem. Soc. Perkin Trans. 1* **1997**, 317 – 321, and references therein.

[16] a) S. Takano, Y. Iwabuchi, K. Ogasawara, *Tetrahedron Lett.* **1991**, *32*, 3527 – 3528, and references therein; b) D. C. Dittmer, R. P. Discordia, Y. Ahang, C. K. Murphy, A. Kumar, A. S. Pepito, Y. Wang, *J. Org. Chem.* **1993**, *58*, 718 – 731.

[17] Stoichiometric $Zr(OnPr)_4$/dicyclohexyltartramide effects AE of homoallylic alcohols but in poor yield and with low *ee* value; see: S. Ikegami, T. Katsuki, M. Yamaguchi, *Chem. Lett.* **1987**, 83 – 84.

[18] Catalytic $Zr(OnBu)_4$ in conjunction with a C_3-symmetric chiral ligand effects asymmetric oxidation of alkyl aryl sulfides to sulfoxides; see: M. Bonchio, G. Licini, F. Di Furia, S. Mantovani, G. Modena, W. A. Nugent, *J. Org. Chem.* **1999**, *64*, 1326 – 1330.

[19] Unfortunately, attempts to employ sub-stoichiometric amounts of $Zr(OiPr)_4$ have so far been unsuccessful.

[20] Use of $Ti(OiPr)_4$ with D-(−)-DIPT gives (−)-**6**/**13** and with L-(+)-DIPT gives (+)-**6**/**13**, whereas $Zr(OiPr)_4$ with D-(−)-DIPT gives (+)-**6**/**13** and with L-(+)-DIPT gives (−)-**6**/**13**. This reversal in the sense of induction between the two metals suggests that topologically distinct complexes may be involved. We have yet to establish the absolute configurations of the products but, by analogy with Ti-based AE of other cyclic allylic alcohols, and allowing for the reversal of sense of induction with $Zr(OiPr)_4$, the configurations drawn in Schemes 3 and 5 would correspond to the levorotatory enantiomers. See: a) V. S. Martin, S. S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda, K. B. Sharpless, *J. Am. Chem. Soc.* **1981**, *103*, 6237 – 6240; b) J. A. Marshall, K. E. Flynn, *J. Am. Chem. Soc.* **1982**, *104*, 7430 – 7435.

[21] J. K. Cha, W. J. Christ, Y. Kishi, *Tetrahedron* **1984**, *40*, 2247 – 2255.

[22] Base-promoted cyclization of the axial hydroxyl group onto the nitrile moiety to give an imidolactone ensues if this reaction is allowed to proceed too long or if the conditions summarized in step (g) are employed for this step.

[23] Details of this structure determination, full experimental details for all transformations in Schemes 2 and 4, and details of additional studies which led to the selection of this synthetic route will be published in a forthcoming full account of this work.

[24] *meso*-Bis-epoxide **14** is also formed in 21 % yield. After just 24 h the *ee* value of epoxy alcohol (+)-**13** is 82 % and there are just traces of *meso*-bis-epoxide **14**. Enhancement of the *ee* value as a function of conversion is expected in this type of reaction; see: S. L. Schreiber, T. S. Schreiber, D. B. Smith, *J. Am. Chem. Soc.* **1987**, *109*, 1525 – 1529.

The First Crystalline Calcium Porphyrin and Tetrakis(*tert*-butylphenyl)porphyrinato Calcium(II): Its Synthesis, Structure, and Binding Properties Towards Alkali and Alkaline Earth Metal Salts**

Lucia Bonomo, Marie-Line Lehaire, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

The study of alkaline earth metals and particularly of calcium in porphyrin systems is of great importance because of their relationship to the role of magnesium and iron porphyrin derivatives in naturally occurring systems. This notwithstanding, information available on the synthesis, structure, and spectroscopic properties of calcium porphyrin is practically nonexistent,[1] with only UV/Vis data being available.[1a]

The field of alkali metal porphyrin and porphyrin analogues has burgeoned in recent years,[2] with a significant example being that of calcium porphyrinogen chemistry.[3] The isolation and characterization of alkaline earth metal porphyrin systems have failed so far because of the use of protic conditions in their synthesis.[1] Therefore, we turned our

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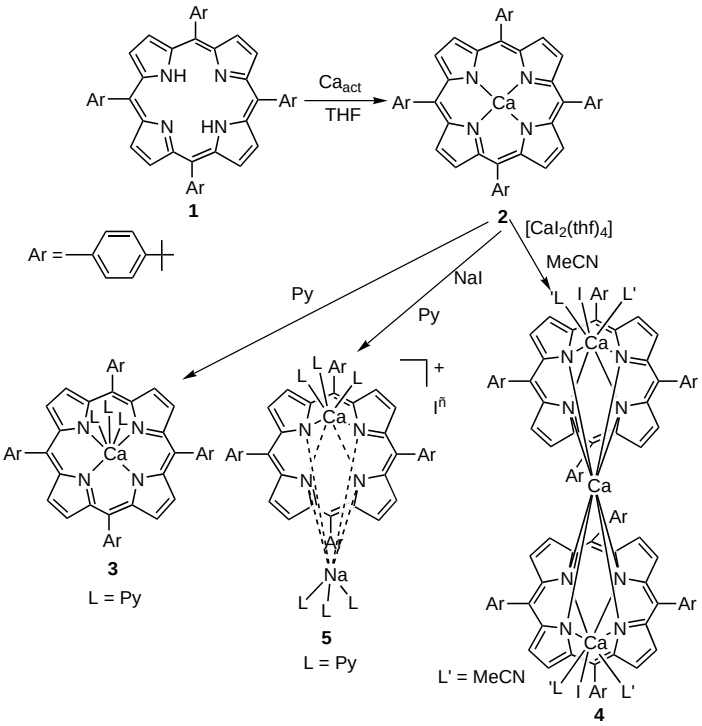
[**] This work was supported by the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-53336.98) and Action COST D9 (European Programme for Scientific Research, OFES No. C98.008).

attention to the synthesis of a calcium porphyrin using nonprotic conditions and a suitably substituted porphyrin, namely 5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin (**1**, H_2(*t*BuPP);[4] Scheme 1). The synthesis of **2**[5] was performed



Scheme 1. Synthesis of the calcium porphyrin **2** and salt complexation.

by treating the free porphyrin **1** in THF with an activated form of calcium metal.[6] The reaction led to a weakly solvated form of calcium porphyrin **2**,[7] which dissolves in both THF and benzene to give red-brown solutions. Its structure in solution (^{1}H NMR) was analyzed in MeCN and pyridine. Its UV/Vis spectrum was of the expected normal type, with bands at 430, 572, and 612 nm. The solvated form **3**[5] was isolated from pyridine and structurally characterized.

The coordinative unsaturation of the calcium ion in **2** is proved by its binding to three pyridine molecules, which have a significant effect on the chemical shift of the β-protons of the pyrrole moieties and the *meso*-aryl protons.[5] The structure analysis of **3**[8] shows (Figure 1) there is a significant

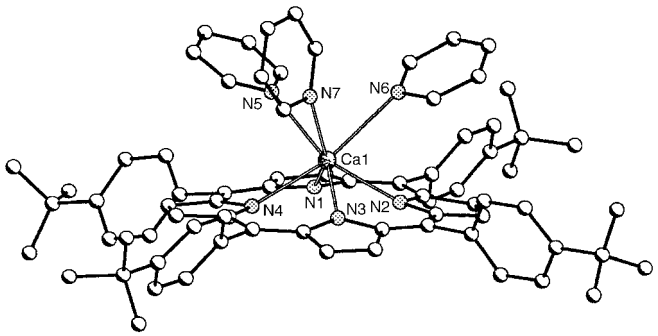


Figure 1. Ball and stick diagram for complex **3** (solvent molecules and hydrogen atoms are omitted). Selected bond lengths [Å]: Ca1-N1 2.382(4), Ca1-N2 2.391(3), Ca1-N3 2.397(3), Ca1-N4 2.416(3), Ca1-N5 2.640(4), Ca1-N6 2.723(4), Ca1-N7 2.663(4).

displacement of the calcium ion from the N_4 plane (−1.208(2) Å). The N(pyrrole)−Ca bond lengths range from 2.382(4) to 2.416(3) Å, with the other structural parameters being in the expected range.

The N_4 core of the porphyrin skeleton in **3** maintains some extra-binding ability towards metal ions. Such a behavior has been emphasized by adding a solution of [CaI_2(thf)$_4$][9] in acetonitrile to the solution of **2** in acetonitrile (Scheme 1). The ^{1}H NMR spectrum of the resulting solution showed, regardless of the CaI_2/**2** ratio employed, the appearance of a single new compound (**4**), the amount of which depends exclusively on the reaction time and the temperature. The significant change in the chemical shifts of the β-protons of the pyrrole rings and the pattern of the *meso*-aryl protons, which are well known from the formation of double-decker structures in the tetraarylporphyrin series,[10] allows the conversion of **2** into **4** to be easily followed. After 24 hours at room temperature, 50% of **2** was converted into **4**, while a complete conversion was observed when the solution was refluxed overnight (Figure 2). The addition of toluene (C_7H_8) to the acetonitrile solution led to crystals of **4**[11] ([(MeCN)$_2$ICa(*t*BuPP)Ca(*t*BuPP)CaI(MeCN)$_2$]·4MeCN·C_7H_8) which were suitable for X-ray analysis. The ^{1}H NMR spectrum of **4** in acetonitrile is identical to that observed when **2** is mixed with [CaI_2(thf)$_4$][11] (Figure 2).

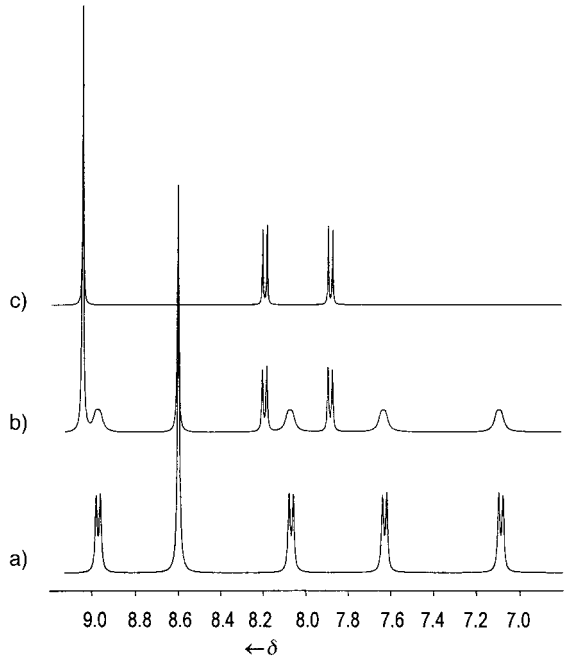


Figure 2. ^{1}H NMR spectra showing the pyrrole and aryl protons of a) **2** in CD_3CN; b) **2** + [CaI_2(thf)$_4$] (2:1) after 24 h at room temperature; c) **2** + [CaI_2(thf)$_4$] (2:1) after 24 h in refluxing CD_3CN.

The structure of **4**[8] is shown in Figure 3. The molecule can be viewed as a complex of a Ca^{2+} ion sandwiched between two [Ca(*t*BuPP)I(MeCN)$_2$]$^-$ ions. The terminal calcium ions protrude from the N_4 plane by 1.577(5) Å, and a coordination geometry quite close to that of the calcium ion in **2** is obtained. In the present case, the Ca−N(pyrrole) bond lengths range from 2.557(10) to 2.589(10) Å. The central calcium ion

  1433-7851/01/4004-0772 $ 17.50+.50/0

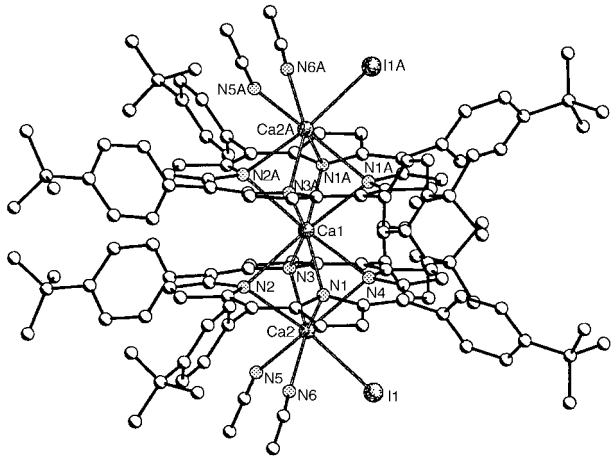


Figure 3. Ball and stick representation of compound **4** (solvent molecules and hydrogen atoms are omitted). Selected bond lengths and distances [Å]: Ca1-N1 2.659(9), Ca1-N2 2.652(9), Ca1-N3 2.557(10), Ca1-N4 2.608(9), Ca2-I1 3.087(3), Ca2-N1 2.589(10), Ca2-N2 2.557(10), Ca2-N3 2.560(9), Ca2-N4 2.571(10), Ca2-N5 2.509(14), Ca2-N6 2.516(12), Ca1···Ca2 3.234(3). The letters A refer to the symmetry transformation $x, -y+1/2, -z+1/2$.

is symmetrically bound to the two N_4 cores, with an average Ca–N bond length of 2.619(9) Å and at a distance of −1.657(5) Å out of the N_4 plane. The coordination geometry of the N_8 cage is square antiprismatic. The N_4 core in the alkali metal porphyrin series behaves as a doubly bridging ligand, as shown by analyzing the structures of $[Na_2(OEP)(thf)_4]$[4, 12] and $[K_2(OEP)(thf)_4]$.[4, 13] The coordination of the alkali metal cation by the nitrogen atoms of anionic transition metal porphyrins has been observed in $[\{Na(THF)_3\}_2Fe(TPP)]$,[4, 13] $[\{Na(THF)_3\}_2Co(TPP)]$,[4, 14] and $[Li_2\{Ru(OEP)Np\}]$.[4, 15] Thallium is also able to sit on another porphyrin moiety, as shown in $[Tl\{Pr(OEP)_2\}]$.[4, 16]

The structure is reminiscent of the one of [AcOHg(Etio)-Hg(Etio)HgOAc] (Etio = octaalkylporphyrin),[17] which, however, was only assigned from ^{1}H NMR data. The binding capability of **2** towards CaI_2 emphasizes for the first time the possibility of metallaporphyrins functioning as salt carriers in moderately polar solvents. The reaction of **2** with NaI confirmed such an assumption with the formation of **5**, whose structure has been supported by an X-ray analysis.[18] The results presented above prove the stability of the calcium porphyrin derivatives even in quite polar coordinating solvents, except in the protic ones. An interesting perspective is now open for the use of the polar metallaporphyrins as metallaligands for complexing and transporting alkali or alkaline earth metal salts.[19] This type of complexation can be monitored in CD_3CN by ^{1}H NMR spectroscopy, since the interaction of the calcium porphyrin with salts causes a significant downfield shift of the protons at the β-position of the pyrrole rings as a function of the specific charge of the cation, while the aryl protons, which give rise to four doublets in **2**, appear as two doublets upon salt complexation, similar to the related metalloporphyrin double-decker structures.[10]

Experimental Section

2 and **3:** Complex **1** (3.00 g, 3.57 mmol) was added to a suspension of active calcium (3.57 mmol) in THF (250 mL). The reaction mixture was refluxed for about 24 h. The resulting solution was evaporated to dryness and benzene (250 mL) was added to remove the undissolved NaI. Then the solution was evaporated to dryness to give **2** as a dark violet solid (3.05 g, 97%). The red crystals of **3** suitable for X-ray diffraction were grown in pyridine. ^{1}H NMR (400 MHz, CD_3CN, 70 °C, TMS): $\delta = 8.97$ (d, J(H,H) = 7.83 Hz, 4H; CH_{arom}), 8.60 (s, 8H; $CH_{pyrrole}$), 8.07 (d, J(H,H) = 7.83 Hz, 4H; CH_{arom}), 7.63 (d, J(H,H) = 7.83 Hz, 4H; CH_{arom}), 7.03 (d, J(H,H) = 7.83 Hz, 4H; CH_{arom}), 1.69 (s, 36H; *t*Bu); ^{1}H NMR (400 MHz, C_5D_5N, 80 °C, TMS): $\delta = 9.04$ (s, 8H; $CH_{pyrrole}$), 8.34 (d, J(H,H) = 6.85 Hz, 8H; CH_{arom}), 7.91 (d, J(H,H) = 6.85 Hz, 8H; CH_{arom}), 1.74 (s, 36H; *t*Bu); UV/Vis (CH_3CN): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 430 (181 582), 572 (9619), 612 (7941); UV/Vis (pyridine): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 438 (324 960), 574 (11 900), 616 (11 208); elemental analysis calcd (%) for **2** ($C_{60}H_{60}CaN_4$): C 82.15, H 6.89, N 6.39; found: C 82.01, H 6.79, N 6.42.

4: $[CaI_2(thf)_4]$ (0.163 g, 0.28 mmol) was added to a solution of **2** (0.50 g, 0.57 mmol) in acetonitrile (50 mL). After 24 h of stirring at room temperature, the ^{1}H NMR spectrum of the reaction mixture recorded at $T = 70$ °C showed the presence of a mixture of **4** and **2** in a 1:2 ratio. After an overnight reflux, the reaction was complete (80%). The black crystals of **4** suitable for X-ray diffraction were grown from a mixture of acetonitrile and toluene. ^{1}H NMR (400 MHz, CD_3CN, 70 °C, TMS): $\delta = 9.04$ (s, 8H; $CH_{pyrrole}$), 8.19 (d, J(H,H) = 8.31 Hz, 8H; CH_{arom}), 7.88 (d, J(H,H) = 8.31 Hz, 8H; CH_{arom}), 1.63 (s, 36H; *t*Bu); ^{1}H NMR (400 MHz, C_5D_5N, 80 °C, TMS): $\delta = 9.29$ (s, 8H; $CH_{pyrrole}$), 8.48 (d, J(H,H) = 6.85 Hz, 8H; CH_{arom}), 7.94 (d, J(H,H) = 6.85 Hz, 8H; CH_{arom}), 1.73 (s, 36H; *t*Bu); UV/Vis (acetonitrile): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 422 (195 053), 563 (8241), 603 (5491); elemental analysis calcd (%) for **4** ($C_{128}H_{132}Ca_3I_2N_{12}$): C 69.50, H 6.01, N 7.60; found: C 69.31, H 6.12, N 7.82.

Salt complexation: An excess of salt (CaI_2, $CaCl_2$, BaI_2, NaI) was added directly to the NMR tubes containing solutions of **2** in CD_3CN. The tubes were sealed and heated at 70 °C overnight. ^{1}H NMR spectrum of **2** in the presence of $CaCl_2$ (400 MHz, CD_3CN, 70 °C, TMS): $\delta = 9.07$ (s, 8H; $CH_{pyrrole}$), 8.17 (d, J(H,H) = 8.0 Hz, 8H; CH_{arom}), 7.90 (d, J(H,H) = 8.0 Hz, 8H; CH_{arom}), 1.65 (s, 36H; *t*Bu); ^{1}H NMR spectrum of **2** in the presence of BaI_2 (400 MHz, CD_3CN, 70 °C, TMS): $\delta = 8.97$ (s, 8H; $CH_{pyrrole}$), 8.24 (d, J(H,H) = 7.6 Hz, 8H; CH_{arom}), 7.88 (d, J(H,H) = 7.6 Hz, 8H; CH_{arom}), 1.63 (s, 36H; *t*Bu). ^{1}H NMR spectrum of **2** in the presence of NaI (400 MHz, CD_3CN, 70 °C, TMS): $\delta = 8.70$ (s, 8H; $CH_{pyrrole}$), 8.06 (br s, 8H; CH_{arom}), 7.78 (d, J(H,H) = 8.8 Hz, 8H; CH_{arom}), 1.56 (s, 36H; *t*Bu).

Received: October 23, 2000 [Z15983]

[1] a) J. B. Allison, R. S. Becher, *J. Phys. Chem.* **1963**, *65*, 2675; b) J. W. Buchler, J. Hüttermann, J. Löffler, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 71; c) J. W. Buchler in *Porphyrins and Metalloporphyrins* (Ed.: K. M. Smith), Elsevier, New York, **1975**, Chap. 5, p. 157; d) J. W. Buchler in *The Porphyrins*, *Vol. 1* (Ed.: D. Dolphin), Academic, New York, **1978**, Chap. 10, p. 389.

[2] a) J. Arnold in *The Porphyrin Handbook*, *Vol. 3* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, Chap. 17, p. 113; b) J. W. Buchler, *J. Porphyrins Phthalocyanines* **2000**, *4*, 337.

[3] L. Bonomo, O. Dandin, E. Solari, C. Floriani, R. Scopelliti, *Angew. Chem.* **1999**, *111*, 963; *Angew. Chem. Int. Ed.* **1999**, *38*, 913.

[4] Abbreviations used: H_2(*t*BuPP) = 5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin, H_2(OEP) = octaethylporphyrin; H_2(TPP) = tetraphenylporphyrin.

[5] For the synthesis and spectroscopic data of **2** and **3**, see the Experimental Section.

[6] Active calcium prepared according to a known procedure was employed: T. C. Wu, H. Xiong, R. D. Rieke, *J. Org. Chem.* **1990**, *55*, 5045.

[7] Solvation of calcium by aromatic hydrocarbons or acetonitrile seems quite plausible.

[8] Crystal structure analysis of **3**: $(C_{75}H_{75}CaN_7)\cdot C_5H_5N$, $M_r = 1193.60$, monoclinic, space group *I*2/*a* (No. 15), $a = 25.536(5)$, $b = 16.139(3)$, $c = 32.367(7)$ Å, $\beta = 95.17(3)°$, $V = 13285(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.194$ g cm^{-3}, $F(000) = 5088$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), $\mu(Mo_{K\alpha}) = 0.146$ mm^{-1}; crystal dimensions $0.23 \times 0.20 \times 0.15$ mm. Diffraction data were collected on a mar345 Imaging Plate at 143 K. The structure was solved with direct methods and refined using the full-matrix least-squares analysis on F^2 with all non-hydrogen atoms

anisotropically refined. For 4420 observed reflections [$I > 2\sigma(I)$] and 804 parameters the conventional R factor is 0.0593 ($wR_2 = 0.1627$ for 9410 independent reflections). Crystal structure analysis of **4**: $(C_{128}H_{132}Ca_3I_2N_{12}) \cdot C_7H_8 \cdot 4(C_2H_3N)$, $M_r = 2468.85$, orthorhombic, space group *Pnna* (No. 52), $a = 16.566(3)$, $b = 34.562(7)$, $c = 24.996(5)$ Å, $V = 14312(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.146$ g cm^{-3}, $F(000) = 5152$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), $\mu(Mo_{K\alpha}) = 0.598$ mm^{-1}; crystal dimensions $0.13 \times 0.10 \times 0.07$ mm. Data collection and solution of the structure was done as above. For 4480 observed reflections [$I > 2\sigma(I)$] and 742 parameters the conventional R factor is 0.1138 ($wR_2 = 0.3662$ for 9138 independent reflections). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153000 (**3**) and -153001 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] K. F. Tesh, D. J. Burkey, T. P. Hanusa, *J. Am. Chem. Soc.* **1994**, *116*, 2409.

[10] J. W. Buchler, D. K. P. Ng in *The Porphyrin Handbook*, *Vol. 3* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, Chap. 20, p. 284.

[11] For the synthesis and spectroscopic data of **4**, see the Experimental Section.

[12] J. Arnold, D. Y. Dawson, C. G. Hoffman, *J. Am. Chem. Soc.* **1993**, *115*, 2707.

[13] T. Mashiko, C. A. Reed, K. J. Haller, W. R. Scheidt, *Inorg. Chem.* **1984**, *23*, 3192.

[14] S. Ciurli, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Angew. Chem.* **1986**, *98*, 553; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 553.

[15] C. S. Alexander, S. J. Rettig, B. R. James, *Organometallics* **1994**, *13*, 2542.

[16] J. W. Buchler, B. Scharbert, U. Englert, J. Strähle, *Chem. Ber.* **1988**, *121*, 2077.

[17] M. F. Hudson, K. M. Smith, *Tetrahedron* **1975**, *31*, 3077.

[18] L. Bonomo, E. Solari, C. Floriani, R. Scopelliti, unpublished results.

[19] Complexation of NaI, CaI_2, $CaCl_2$, and BaI_2 by **2** has so far been observed.

$[W_{16}S_{16}O_{16}(OH)_{16}(H_2O)_4(C_5H_6O_4)_2]^{4-}$: A Flexible, Pillared Oxothiotungstate Wheel**

Emmanuel Cadot,* Jérôme Marrot, and Francis Sécheresse

The design of clusters containing a large number of metal centers represents an intellectually stimulating challenge for the chemist since these compounds are situated at the boundary of molecular and condensed matter. The properties of such compounds are expected to envelop diverse fields such as biochemical processes,[1] catalysis,[2] and material science.[3] In this context, transition metal ringlike clusters based on the $\{M_2S_2O_2\}$ building block represent a fascinating emerging class of compounds.[4] Two years ago, we reported the synthesis and characterization of the neutral ring-shaped polyoxothio molybdenum compound $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$.[5] The cyclic architecture of this cluster delimits a central cavity which has a significant cationic character and is the origin of striking properties related to supramolecular[6] or host–guest chemistry.[7] Anionic reagents such as phosphate or dicarboxylate ions have been inserted into the cavity replacing the water molecules which initially line the cavity. This substitution led to size-controlled molecular wheels, distorted to a greater or lesser extent, and containing from eight[8] to twelve[9] molybdenum atoms. However, compared to heteropolyoxometalates, which are generally built upon Mo, W, and V centers,[10] cyclic oxothiocompounds are restricted exclusively to molybdenum, herein we aim to fill this void.

By acido–basic self-condensation of the $\{W_2S_2O_2\}^{2+}$ building block we have prepared compound **1** which is the largest

$[W_{16}S_{16}O_{16}(OH)_{16}(H_2O)_4(C_5H_6O_4)_2]^{4-}$ **1**

known discrete cyclic oxothioanion. The W_{16} anion was synthesized through successive steps consisting of the formation of the oxothio precursor $[(S_x)_2W_2S_2O_2]^{2-}$ ($x = 2, 4$)[11] followed by the selective oxidation of the two terminal polysulfido ligands with stoichiometric amounts of iodine in DMF.[12] The acido–basic self-condensation was performed in the presence of glutarate which acts as a templating agent. The cesium salt of **1** was isolated as a pale yellow precipitate and after recrystallization at room temperature gave two types of crystals (**1a** and **1b**). A minimum of three weeks was required for the crystallization of orthorhombic crystals of **1a** while the monoclinic phase **1b** crystallized within two or three days.

The compositions of **1a** and **1b** are quite similar, differing only in the water content. The molecular structure of **1** (Figure 1) consists of a cyclic neutral backbone $\{W_{16}S_{16}O_{16}(OH)_{16}\}$ (noted W_{16}) encapsulating two glutarate ions $[C_5H_6O_4]^{2-}$ (noted glu^{2-}). Eight $[W_2S_2O_2]^{2+}$ units are mutually connected by hydroxo double bridges giving two types of W···W separations in the cluster: short W–W distances within the building blocks (2.825(1)–2.818(1) Å) for **1a**; 2.813(1)–2.789(1) Å for **1b**) and long inter-block distances (3.413(1)–3.415(1) Å for **1a** and 3.298(1)–3.403(1) Å for **1b**. The two carboxylate groups are symmetrically arranged in the open cavity and exhibit the same type of binding mode with oxygen atoms bonded to the tungsten atoms. The cavity contains four water molecules, each being bonded to a tungsten atom through long W–OH_2 bonds (2.376(9) Å for **1a** and 2.363(10)–2.403(9) Å for **1b**). Probably because of steric constraints induced by the presence of the two glutarate ions in the cavity, four tungsten atoms adopt a pyramidal arrangement. Compounds **1a** and **1b** differ in their packing, the symmetry of the wheel is also significantly affected. In **1a** (orthorhombic), the discrete $\{W_{16}\}$ cluster has D_{2h} symmetry (Figure 1a) while in **1b** (monoclinic), the symmetry of the wheel is lowered to C_2 (Figure 1b). Both the structures are formally related through "soft" deformations which can be described as antiparallel stretching modes

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[**] We thank Dr. G. Chottard for recording Raman spectra.

  1433-7851/01/4004-0774 $ 17.50+.50/0