[11] a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636; b) H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 394–400.
[12] a) P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563–594; b) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* **1989**, *91*, 1762–1774.
[13] N. E. Christensen, J. Kollar, *Solid State Commun.* **1983**, *46*, 727–730.
[14] N. J. M. Geibel, B. A. Hess, *Chem. Phys. Lett.* **1997**, *273*, 62–70.
[15] K. Doll, P. Pyykkö, H. Stoll, *J. Chem. Phys.* **1998**, *109*, 2339–2345.
[16] a) P. Pyykkö, N. Runeberg, F. Mendizabal, *Chem. Eur. J.* **1997**, *3*, 1451–1457; b) P. Pyykkö, N. Runeberg, F. Mendizabal, *Chem. Eur. J.* **1997**, *3*, 1458–1465; c) P. Pyykkö, F. Mendizabal, *Inorg. Chem.* **1998**, *37*, 3018–3025; d) P. Pyykkö, T. Tamm, *Organometallics* **1998**, *17*, 4842–4852.
[17] W. E. Dasert in *Nonexistent Compounds*, Marcel Dekker, New York, **1965**, pp. 21–22.
[18] P. Schwerdtfeger, J. S. McFeaters, M. J. Liddell, J. Hrusak, H. Schwarz, *J. Chem. Phys.* **1995**, *103*, 245–252.
[19] G. S. Nunes, P. B. Allen, J. L. Martins, *Phys. Rev. B* **1998**, *57*, 5098–5105; S. Hull, D. A. Keen, *Phys. Rev. B* **1999**, *59*, 750–761.
[20] R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, **1978**.
[21] V. R. Saunders, R. Dovesi, C. Roetti, M. Causà, N. H. Harrison, R. Orlando, C. M. Zicovich-Wilson, *Program CRYSTAL98*, University of Torino, Turin (Italy), **1998**.
[22] C. M. Zicovich-Wilson, *Program LoptCG*, Instituto de Technologia Quimica U.P.V.-C.S.I.C., Valencia, Spain, **1998**.
[23] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*, Van Nostrand, New York, **1979**.

A Metallosupramolecular Capsule with the Topology of the Tetrahedron, 3^3, Assembled from Four Guanidine-Based Ligands and Twelve Cadmium Centers**

Iris M. Müller, Richard Robson,* and Francis Separovic

Coordination chemistry offers scope for the construction by self-assembly of a seemingly limitless range of structures,[1] including cagelike metallosupramolecular species related to polyhedra.[2] We report here a coordinative enclosure with the topology of the tetrahedron in which the four 3-connecting nodes are provided by extensive, approximately flat ligands, each affording three tridentate metal-binding sites, and the six node-to-node connections are provided by pairs of metal centers; the arrangement is represented schematically in Figure 1.

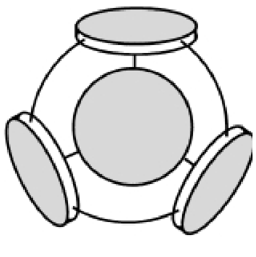
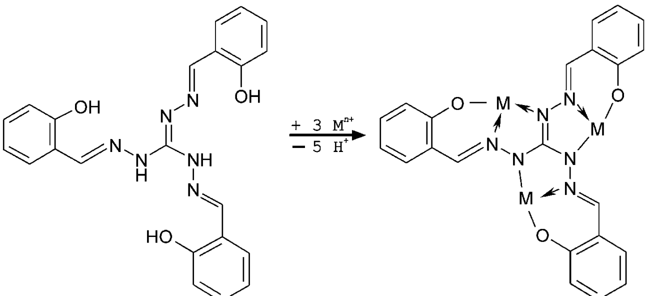


Figure 1. Schematic representation of the cage showing the four almost flat ligands as discs, the central one being at the back. A threefold axis passes throught the center of each disc.

Ligand H_5L (**1**; Scheme 1) is very easy to make and is just one member of a potentially extensive family of Schiff base derivatives of the readily available triaminoguanidine. It has been reported previously that in the presence of appropriate metal cations the central CN_3H_2 core of **1** is readily deprotonated (even by a base as weak as NH_3) to generate a carbonate-like dianionic moiety capable of simultaneously chelating three metal centers in close proximity as in **2** (Scheme 1).[3]

Reaction of the guanidinium chloride salt related to **1**, $[H_6L]Cl$, with cadmium chloride in DMF in the presence of Et_4NOH gives bright yellow rhombic dodecahedral crystals of $(Et_4N)_8[(CdCl)_3L]_4 \cdot 4DMF$ (**3**) in very high yield: the structure was determined by single-crystal X-ray diffraction.[4] Figure 2 shows the immediate environment of one of four symmetry-equivalent ligand units. Four $[L(CdCl)_3]^{2-}$ units are linked by four-membered (-Cd-O-)$_2$ rings to form a cage with the topology of a tetrahedron (Figure 3). All twelve cadmium



H_5L **1** $[M_3L]^{3n-5}$ **2**

Scheme 1.

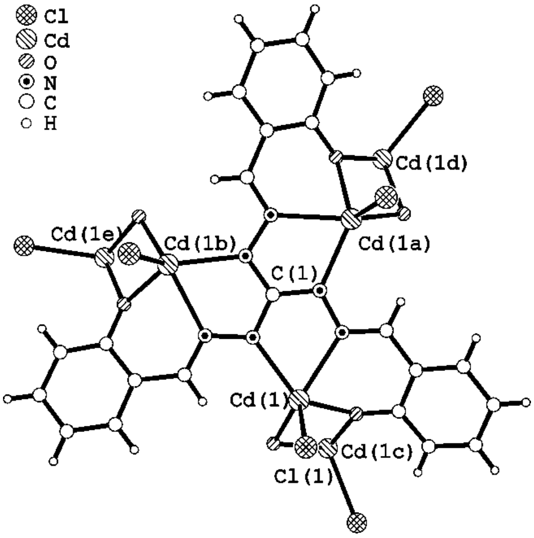


Figure 2. The immediate environment of each of the ligands.

---

[*] Dr. R. Robson, Dr. F. Separovic
School of Chemistry
University of Melbourne
Parkville, Victoria 3052 (Australia)
Fax: (+61)3-9347-5180
E-mail: r.robson@chemistry.unimelb.edu.au
Dr. I. M. Müller
Lehrstuhl für Analytische Chemie
NC 4/27, Ruhr-Universität Bochum
44780 Bochum (Germany)
Fax: (+49)234-321-4420

[**] This work was supported by the "Deutsche Forschungsgemeinschaft" DFG and the Australian Research Council. The authors thank Dr. B. F. Abrahams for help with the X-ray crystallography.

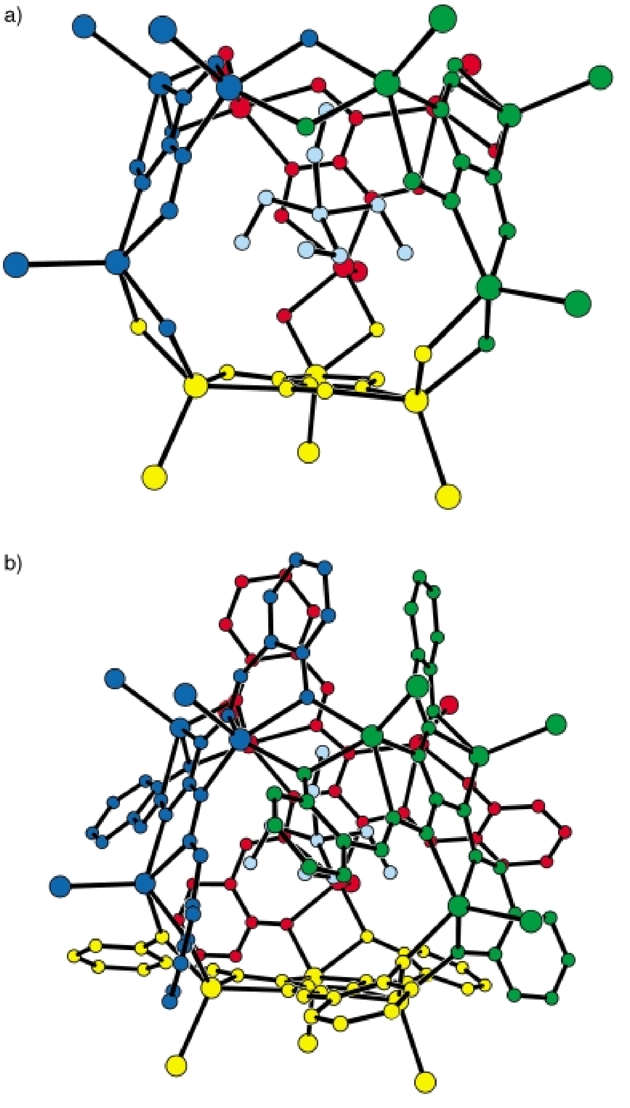


Figure 3. a) Representation of the way in which the four $[(CdCl)_3L]$ units are connected together. For simplicity only the central CN_6 core of each ligand and its three bridging phenoxy oxygen atoms are shown. The entrapped Et_4N^+ ion is also indicated (pale blue). b) View from the same angle as in (a) showing all non-hydrogen atoms in $[\{(CdCl)_3L\}_4 \cdot Et_4N]^{7-}$.

centers are equivalent and are five-coordinate; a chloro ligand is attached to each Cd center on the outside of the cage (Figure 2 and 3). The cage is an octaanion and one of the eight Et_4N^+ countercations is securely locked inside the enclosure; the other seven cations together with the DMF molecules of solvation occupy the spaces in the crystal between the cages in a disordered manner. Individual cages are chiral but the crystal as a whole is racemic.

The solid-state ^{13}C MAS NMR spectrum shows all the features expected for the ligand components, the DMF molecules of solvation, and the Et_4N^+ ions, both trapped and "external". The encaged cations show a methylene signal at $\delta = 59.3$ and a methyl signal at $\delta = 12.5$, whilst the corresponding signals for the "external" cations are at $\delta = 53.6$ and 9.1, respectively; comparison of CP with single pulse ^{13}C MAS experiments using long recycle times confirmed these assignments. The compound unfortunately has very limited solubility in all solvents tested. However it is sufficiently soluble in $[D_6]DMSO$ at 100 °C to afford a ^1H NMR spectrum which reveals that, even under these relatively fierce conditions where it might be suspected that any minimal dissolution might be the result of decomposition, the cage remains intact with its trapped Et_4N^+ ion ($\delta = 0.72$, CH_3) clearly differentiated from the "external" Et_4N^+ ion ($\delta = 1.13$, CH_3); the relative intensities are in the expected 1:7 proportions. The cage would appear to be a very stable entity. As can be seen in Figure 3b salicylaldehyde-derived C_6 rings from three separate ligands make close contact over each face of the imaginary tetrahedron with vertices located at the central guanidine carbon atoms of the four ligands, effectively sealing off the enclosure; the Et_4N^+ prisoner is thereby very securely incarcerated. Analogous products can be isolated with chloride replaced by bromide and with Me_4N^+ encapsulated rather than Et_4N^+.

Experimental Section

$[(C_2H_5)_4N]_8[\{(CdCl)_3(C_{22}H_{15}N_6O_3)\}_4] \cdot 4\,DMF$ (**3**): A solution of tris(2-hydroxybenzylidine)triaminoguanidinium chloride[3] $[H_6L]Cl$ (23.1 mg, 0.051 mmol) in DMF (2 mL) was added to a solution of $CdCl_2 \cdot 2H_2O$ (35.3 mg, 0.161 mmol) in DMF (2 mL). An aqueous solution of Et_4NOH (40 %, 1 mL) was carefully underlayered. Brilliant yellow crystals of **3** were formed over a period of three days. Yield: 56.4 mg (0.012 mmol, 93 %). Elemental analyses (%): calcd: C 37.18, H 5.86, N 9.52, Cd 25.46, Cl 8.03; found: C 37.50, H 5.01, N 9.56, Cd 25.45, Cl 7.78. Solid-state MAS NMR: in addition to signals arising from the ligands (all twelve salicylaldehyde units being equivalent as indicated by the crystallography) at $\delta = 168.0$ (plus shoulder), 147.5, 133.3, 131.7, 125.7, 123.6, 117.7, there are signals arising from DMF at $\delta = 164.0$, 38.6, and 33.6 and signals arising from the trapped Et_4N^+ ion at $\delta = 59.3$ and 12.5 and from "external" Et_4N^+ ions at $\delta = 53.6$ and 9.1.

Crystal structure analysis: Crystals of **3** were small and weakly diffracting. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing the ω-2θ scan method, the data were corrected for Lorentz and polarization effects. The structure of **3** was solved by using direct methods (SHELXS-97)[5] and refined by using a full-matrix least-squares refinement procedure (SHELXL-97).[6] Aromatic protons of the ligand were placed at geometrically estimated positions. The atoms of the cage and its trapped Et_4N^+ ion were well defined but the solvent and cations occupying the regions between the cages displayed a high degree of disorder, despite which it was possible to model some of them. 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-165718. 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).

Received: June 25, 2001 [Z17351]

---

[1] G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483.

[2] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853.

[3] I. M. Müller, R. Robson, *Angew. Chem.* **2000**, *112*, 4527; *Angew. Chem. Int. Ed.* **2000**, *39*, 4357.

[4] Crystal dimensions 0.40 × 0.37 × 0.21 mm^3, cubic, space group $Pn\bar{3}$, $a = 21.257(3)$ Å, $V = 9605(2)$ Å^3, $\rho_{calcd} = 1.532\ g\,cm^{-3}$, $2\theta_{max} = 50°$, $\lambda = 0.71073$ Å, $T = 130$ K, 1867 measured reflections, 1598 independent reflections ($R_{int} = 0.0355$), numerical absorption correction, $\mu = 1.532\ mm^{-1}$, min./max. transmission factors 0.588/0.653, 128 parameters, $R_1 = 0.0607$, $wR2 = 0.1722$, max. residual electron density 0.609 e Å^{-3}.

[5] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Universität Göttingen, **1997**.

[6] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

1433-7851/01/4023-4386 $ 17.50+.50/0