Linear, Divergent Molecular Receptors – Subtle Effects of Transition Metal Coordination Geometry

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Reaction between deprotonated *p-tert*-butyltetrathiacalix[4]arene and Co^{II} or Zn^{II} under strictly defined conditions leads to the formation of sandwich species in which a trimetallic unit is held between two opposed, divergently oriented, staggered *O*- and *S*-bound calixarene ligands in the cone conformation. Despite the isomorphous nature of the crystalline compounds, there is a subtle difference in the coordination of Co^{II} and Zn^{II}, presumably related to the differences in metal radius and electron configuration combined with structural restrictions imposed by the calixarene framework, in that whereas all three Co atoms may be considered six-coordinate (and approximately octahedral), only two of the Zn atoms appear so, the third being five-coordinate and more nearly trigonal bipyramidal in its coordination geometry.

Introduction

The pursuit of the rational design of solid state structure, with the ultimate aim of producing new materials with properties of true utility, can be based upon the exploitation of various chemical forces.[1,2] We have previously demonstrated the feasibility of using (presumably) weak CH_3-π interactions to form one-dimensional "koilates" in which binuclear calix[4]arene metal complexes provide opposed-divergent, double-cavity receptors.[2] A difficulty in this approach arises because of the relatively limited range and possibly the limited stability of appropriate binuclear calix[4]arene derivatives.[2–4] The initial report[5] of the superior transition metal binding properties of *p-tert*-butyltetrathiacalix[4]arene therefore aroused our interest and we have recently characterised[6] an antiferromagnetically coupled dicopper(II) derivative of this calixarene which proved to have a dimeric form in the solid state in which a tetracopper square is sandwiched between opposed, eclipsed calixarene cones, thus justifying our optimism that compounds useful in koilate construction might be obtained. The coordination geometry of the copper atoms in this compound is, however, considerably distorted from any regular form of six-coordination and, in attempting to extend our studies of coordination of the tetrathiacalixarene to the elements adjacent to copper, we have found that this may be an important factor determining the metal/ligand stoichiometry, though not necessarily the opposed double-cavity form of the resultant complex. Thus, we have found that for cobalt(II) and zinc(II), compounds of the stoichiometry $M_3(calH)_2$ (where $calH^{3-}$ is the three-times deprotonated tetrathiacalixarene, $calH_4$) may be isolated. Subsequent structure determinations[7] have shown that the isomorphous cobalt and zinc compounds can indeed be regarded as containing molecular units of this stoichiometry (Figure 1) with, as in the case of the Cu^{II} compound, a small cluster of metal ions sandwiched between two opposed, quasi-staggered calixarene cones. The differences from the copper system may be associated with a stronger tendency to retain a regular octahedral coordination geometry around Co and Zn, with the incompatibility of structural demands being more readily accommodated by the Jahn–Teller accessible Cu^{II} adduct, though this can at best be considered only a partial rationalisation of the detailed differences between these three complexes.

For the preparation of these complexes it is important to adhere closely to a particular procedure to obtain a particular product and to convert it to a crystalline form suitable for X-ray diffraction. With a variety of other metals we have experienced considerable complications due to either polymorphism or alternate stoichiometries. In our initial efforts to obtain the Co and Zn complexes described herein we obtained heterogeneous materials showing only partial solubility in CH_2Cl_2. Interestingly, the ^1H NMR spectrum reported for a Zn^{II} complex[5] isolated from a solvent extraction experiment, is identical to that for the Zn species reported here after recrystallisation. The NMR spectra are consistent with a similar trinuclear species that exists in the solid state (Figure 1) persisting in solution, and where all the protons within each calixarene are chemically inequiva-

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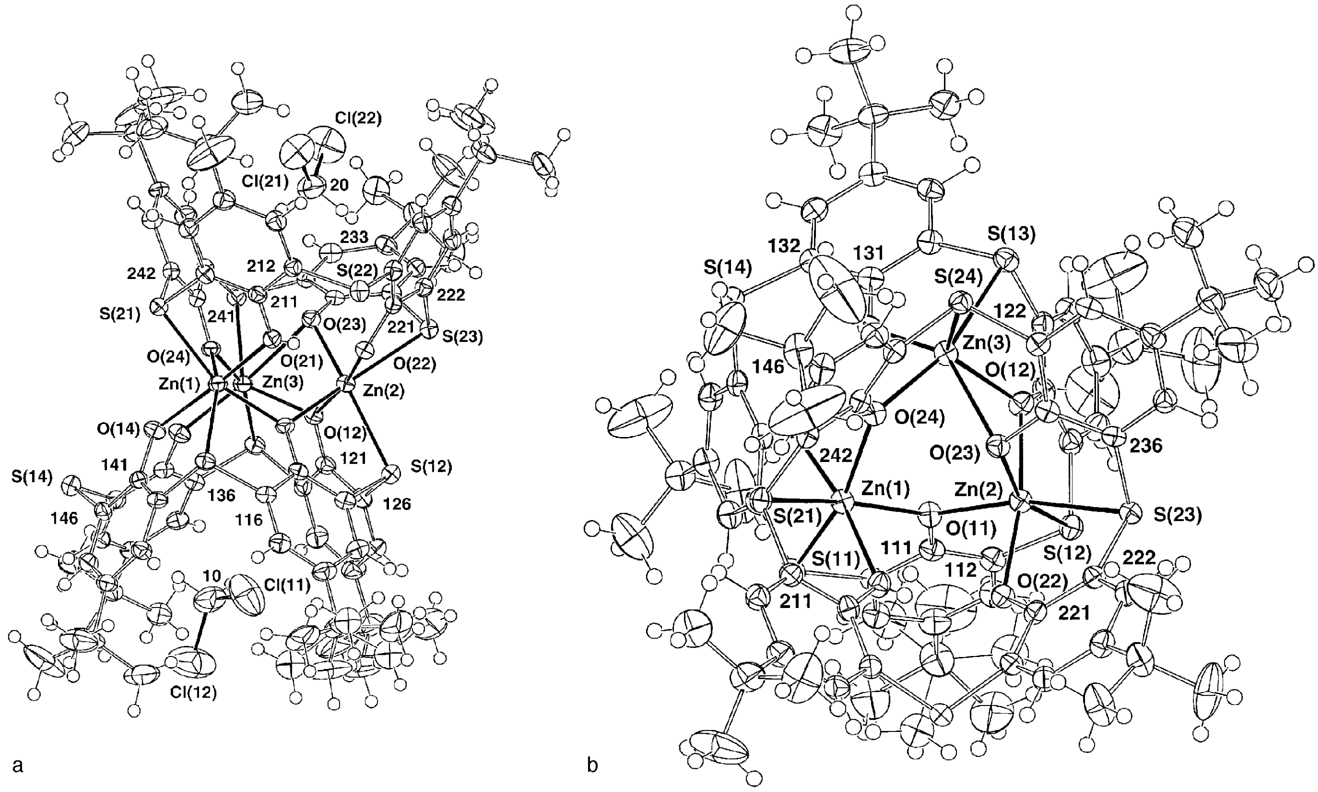

Figure 1. Projections of the zinc complex (a) through and (b) normal to the Zn_3 plane [included CH_2Cl_2 (x2) omitted in the latter]; thermal ellipsoids (50%) are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å; the chirality of the molecule is most readily appreciated from the relative dispositions of the oxygen pairs O(13,14) and O(21,22) which do not chelate a metal atom, and/or the sulfur atoms S(14,22) which do not bind a metal; note that Zn(2,3) are bridged by a pair of μ-oxo species [O(12,23)] whereas Zn(1,2), (1,3) are bridged by single oxygen atoms O(11), O(24), respectively; note also in (b) that whereas rings 12, 23 are eclipsed at the M(μ–O)$_2$M linkage, the other pairs do not superimpose in this manner. M(1)–M(2,3), M(2)–M(3) are 3.606(1), 3.649(1), 3.144(1) (M = Co) and 3.5092(7), 3.5623(8), 3.2648(7) Å (M = Zn); in (a) H(14) is hidden behind O(14)

lent. We have also found it possible to reproducibly obtain the same $Zn_3(calH)_2$ species by recrystallisation of a solvent extraction product from CH_2Cl_2. However the earlier report of a significantly different Zn complex with the stoichiometry, $Zn_4(cal)(calH_2)_2$,[8] prepared under similar conditions but recrystallised from toluene, highlights the ease with which different forms of the thiacalixarene complexes may be interconverted.

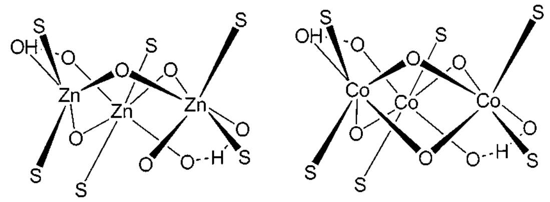

Figure 2. Representation of the coordination environments about the Zn and Co clusters; two of the Zn ions are six-coordinate, the other is five-coordinate, whilst the three Co atoms can be described as six-coordinate

In our isomorphous Co and Zn compounds, the repeating molecular unit in the solid (Figure 1) is a sandwich made up of three metal atoms between two calixarene cones arranged divergently about the metal cluster, each cone containing a dichloromethane molecule. In the case of the Co compound, each metal atom is in an approximately octahedral *cis*-MO_4S_2 environment (Figure 2), though with deviations of up to 20° from the ideal *cis* and *trans* bond angles of 90 and 180°, respectively. This is true for two of the metal atoms in the Zn compound but the third is perhaps better described as having a trigonal bipyramidal coordination environment (Figure 2), a potential sixth (O-donor) ligand atom, which in the Co compound is close enough [2.276(4) Å] to be considered bound, here lying at a distance of 2.652(3) Å. In addition, the Zn–S distances are very disparate for this atom [2.406(1), 2.674(1) Å], perhaps even indicating an approach to 4-coordination, and this disparity in M–S distances is also evident for the corresponding Co atom [Co–S 2.445(1), 2.729(2) Å]. As in the Cu^{II} compound, all donor atoms are derived from the calixarene units, one sulfur atom on each not being involved in coordination and solvent (dichloromethane) molecules only being included within the calixarene cavities and elsewhere within the lattice. The cluster sandwiches are chiral, the only approximate symmetry element being a near two-fold axis passing through one metal atom and bisecting the line joining the other two, true two-fold symmetry seemingly being lost as a result of the coordination sphere irregularities of M(3). The metal atom on the near-C_2 axis has the two phenoxide units bearing residual protons (detected and refined in the structure solution) coordinated to it in a *trans* arrangement [O–M–O 171.0(1)° (Zn), 173.8(1)° (Co)] and interacts with only two phenoxide oxygen atoms which bridge to the other metal atoms. In the Co compound, each of these has three bridging phenoxide donor atoms, although with Zn, again, only two phenoxide bridging atoms are bound to each. The residual protons on the ligand are probably involved in hydrogen bonding to adjacent phenoxide oxygen atoms [O···O 2.48, 2.49 Å (Zn), 2.44, 2.46 Å (Co)].

Magnetic susceptibility measurements by SQUID magnetometry 4–300 K do not indicate any strong magnetic interactions within the Co compound, with Curie-Weiss behaviour ($\theta = -30°$) being observed, though the room temperature magnetic moment of 8.2 BM is significantly lower than expected for three independent high-spin Co^{II} centres. The possibility exists, however, for the use of connector units in koilate structures which may allow extended interactions within such solids, and we are actively pursuing this hypothesis. The residual phenolic calixarene protons present in the Co and Zn compounds should be removable by base, generating anionic species capable of stronger, electrostatically-assisted association with linker molecules. Many other paramagnetic metal ions may also be readily substituted for Co^{II} in these complexes and we have already isolated rare earth derivatives, for example. It is clear that the strong coordinating properties of tetrathiacalix[4]arene provide a prospect for the far readier development of novel applications in metal ion chemistry than is true of the parent calix[4]arene, though it may be that development of this chemistry will provide insights into further uses of the more extensive class of calixarenes in general.

Experimental Section

General Remarks: All solvents were distilled prior to use except for AR grade DMF which was used as supplied. – ^{1}H NMR spectra were measured in $CDCl_3$ and calibrated to the residual solvent peak on a Bruker ARX500 spectrometer. – FAB mass spectra were recorded on a VG-Analytical ZAB HF spectrometer with 3-nitrobenzyl alcohol as the matrix and the electronic absorption spectra in CH_2Cl_2 solution on a Hewlett–Packard 8452A diode-array spectrometer. – Microanalyses were performed by the Microanalytical Unit at the Australian National University.

$[Zn_3(calH)_2(CH_2Cl_2)_2]\cdot 3CH_2Cl_2$: $CalH_4\cdot CHCl_3$ (200 mg, 240 mmol) was dissolved in DMSO (5 mL) containing NEt_3 (0.1 mL). A solution of $[Zn(DMSO)_6](ClO_4)_2$ (350 mg, 480 mmol) in DMSO (5 mL) was added. The clear solution was left overnight, filtered, and the resulting white powder (90 mg) washed with EtOH (5 mL) and dried in air. The solid was dissolved in CH_2Cl_2, filtered and an equal volume of ethanol carefully added to form a layer above the original solution. After 3 weeks of standing, colourless crystals suitable for structural determination were obtained. The remaining crystals were collected by vacuum filtration, washed with ethanol and dried under reduced pressure to give a white powder (65 mg, 40 μmol). – ^{1}H NMR (500 MHz): δ = 1.22 (s, 36 H, *tert*-butyl), 1.24 (s, 18 H, *tert*-butyl), 1.28(s, 18 H, *tert*-butyl), 7.568 (d, ^1J = 2.5 Hz, 2 H, ArH), 7.569 (d, ^1J = 2.5 Hz, 2 H, ArH), 7.59 (d, ^1J = 2.5 Hz, 2 H, ArH), 7.61 (d, ^1J = 2.5 Hz, 2 H, ArH), 7.65 (d, ^1J = 2.5 Hz, 2 H, ArH), 7.70 (d, ^1J = 2.5 Hz, 2 H, ArH), 7.77 (d, ^1J = 2.5 Hz, 2 H, ArH). – ^{13}C NMR (125.77 MHz): δ = 31.30, 31.36, 31.44, 31.47, 34.06, 34.14, 34.2, 117.8, 118.6, 120.7, 120.76, 120.87, 120.91, 122.2, 122.5, 132.4, 133.4, 134.0, 135.1, 135.26, 135.35, 136.6, 139.1, 140.4, 141.4, 142.5, 156.8, 158.9, 160.0, 161.8. – MS (FAB); *m/z*: 1631 (M^+). – $C_{80}H_{90}O_8S_8Zn_3$ (1632): calcd. C 58.87, H 5.56, S 15.2; found C 58.48, H 5.50, S 15.68. – Electronic spectrum: λ/nm (ε_{max}/M^{-1} cm^{-1}) = 314 (39100).

$[Co_3(calH)_2(CH_2Cl_2)_2]\cdot 3CH_2Cl_2$: $CalH_4\cdot CHCl_3$ (1.0 g, 1.19 mmol) was dissolved in DMF (8 mL) containing NEt_3 (0.5 mL). A solution of $[Co(DMF)_6](ClO_4)_2$ (2.12 g, 3.04 mmol) in DMF (5 mL) was added quickly and a light green precipitate formed immediately. After 2 hours the solid was collected by vacuum filtration, washed with ethanol (5 mL) and dried in air to give a light green powder (0.37 g). This solid was recrystallised by liquid diffusion of EtOH into a CH_2Cl_2 solution to give pale green crystals suitable for structural determination. The remaining crystals were collected by vacuum filtration and dried under reduced pressure to give a light green powder (0.26 g, 150 μmol). – MS (FAB); *m/z*: 1612 (M^+). – $C_{80}H_{90}Co_3O_8S_8$ (1613): calcd. C 55.25, H 5.31, S 14.39; found C 55.67, H 5.30, S 14.30. – Electronic spectrum: λ/nm (ε_{max}/M^{-1} cm^{-1}) = 316 (37400), 380 (sh.; 200), 574 (112), 602 (114).

X-ray Crystallographic Study

Co Compound: $[(CH_2Cl_2)_2(C_{40}H_{45}O_4S_4)_2Co_3]\cdot 3CH_2Cl_2$, $C_{85}H_{100}Cl_{10}Co_3O_8S_8$, M = 2037.6. monoclinic, space group $P2_1/n$, a = 13.294(2), b = 45.401(6), c = 17.510(2) Å, β = 111.034(3)°, V = 9863(4) Å^3, Z = 4, D_c = 1.372 g·cm^{-3}, T = 293(2) K, 109219 ($2\theta_{max}$ = 58° sphere) SAINT/SADABS processed CCD reflections ($T_{min,max}$ = 0.68, 0.89) merged to 24944 unique (R_{int} = 0.048), 11937 with $|F| > 4\sigma|F|$ refining to conventional R, R_w on $|F|$ 0.064, 0.064.

Zn Compound: $[(CH_2Cl_2)_2(C_{40}H_{45}O_4S_4)_2Zn_3]\cdot 2.8CH_2Cl_2$, $C_{84.8}H_{99.6}Cl_{9.6}O_8S_8Zn_3$, M 2040. monoclinic, space group $P2_1/n$, a = 13.085(1), b = 44.800(4), c = 17.503(2) Å, β = 111.934(2)°, V = 9517(3) Å^3, Z = 4, D_c = 1.423 g·cm^{-3}, T 153 K, 106685 ($2\theta_{max}$ = 55° sphere) SAINT/SADABS processed CCD reflections ($T_{min,max}$ = 0.78, 0.96) merged to 21818 unique (R_{int} = 0.048), 17210 with $|F| > 4\sigma|F|$ refining to conventional R, R_w on $|F|$ 0.062, 0.071.

Disorder was more widespread in the cobalt compound, involving *tert*-butyl groups 114, 214, 244 [rotated over two sets of sites, major component occupancies 0.662(7), 0.775(7), 0.743(7), 114 only being disordered in the zinc (0.701(5)], and the lattice dichloromethane molecules 4 (both) and 5 (Zn only). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication no CCDC-137200 (Co compound), CCDC-137201 (Zn compound). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] *Chem. Mater.* **1998**, *10*, Special Issue (Ed.: K. Poeppelmeier) devoted to *Frontiers in Inorganic Solid State Chemistry.*

[2] J. Martz, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, *J. Mater. Chem.* **1998**, *8*, 2331–2333 and references therein.

[3] D. M. Roundhill, *Progr. Inorg. Chem.* **1995**, *43*, 533.

[4] C. Wieser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93–162

[5] N. Iki, N. Morohashi, F. Narumi, S. Miyano, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1597.

[6] G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. M. Harrowfield, B. W. Skelton, A. H. White, *Chem. Commun.* **1999**, 373.

[7] *Xtal3.6.1 System* **1999**, (Eds.: S. R. Hall, D. J. du Boulay, R. Olthof-Hazekamp), University of Western Australia.

[8] N. Iki, M. Morohashi, C. Kabuto and S. Miyano, *Chem. Lett.* **1999**, 219.

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