

# A square array of metal ions from the full metallation of calix[4]resorcinarenes

Euro Solari,<sup>a</sup> William Lesueur,<sup>a</sup> Alain Klose,<sup>a</sup> Kurt Schenk,<sup>b</sup> Carlo Floriani,<sup>\*a</sup> Angiola Chiesi-Villa<sup>c</sup> and Corrado Rizzoli<sup>c</sup>

<sup>a</sup> Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne, CH-1015 Lausanne, Switzerland

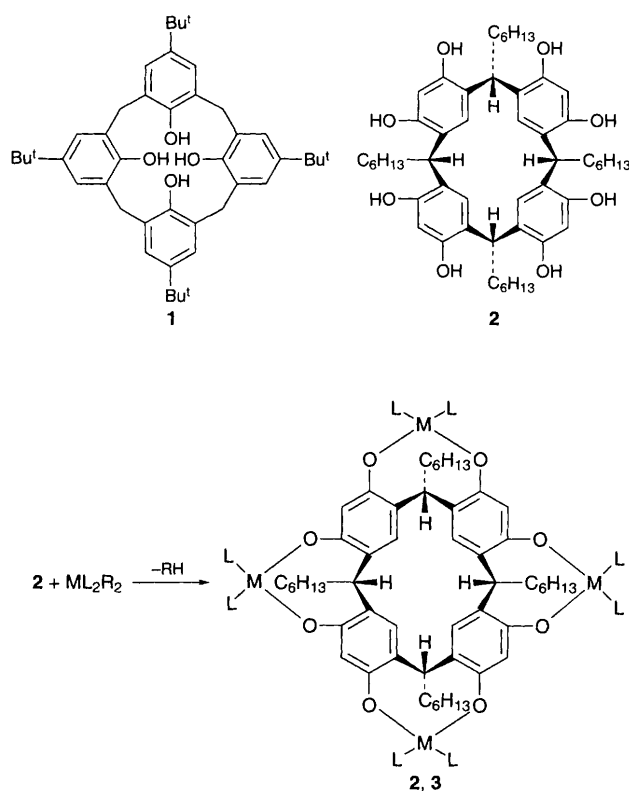
<sup>b</sup> Section de Physique, Université de Lausanne, CH-1015 Lausanne, Switzerland

<sup>c</sup> Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy

A square array of zirconium(IV) and iron(II) ions bound to a polyoxo matrix is achieved in the metallation of calix[4]resorcinarene (R = C<sub>6</sub>H<sub>13</sub>, H) using [Zr(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Me<sub>2</sub>] and [Fe(phen)(mes)<sub>2</sub>], respectively.

The two related classes of macrocycle, the calix[4]arenes *e.g.* **1**,<sup>1</sup> and the calix[4]resorcinarene **2**,<sup>1</sup> have different perspective uses as polyoxo binding sites for transition-metal ions, as a result of their different topologies.

However, the systematic and methodological approach to such metallated molecules is almost nonexistent, with only a few reported examples of metallacalix[4]arenes.<sup>2</sup> Two major metallated forms of these molecules can be anticipated if one considers the oxygen atom set and how it adapts to a transition-metal ion. In the case of calix[4]arene, the O<sub>4</sub> set in the cone conformation usually coordinates a single metal atom, rarely a pair, while in the case of calix[4]resorcinarene the eight oxygen atoms can function as four bidentate units,<sup>3</sup> giving rise to a polymetallic skeleton. The full metallation of **2** has been successfully achieved using a methodology which involves the use of dialkyl or diaryl derivatives of transition metals (Scheme 1).



Scheme 1 ML<sub>2</sub>R<sub>2</sub> = [Zr(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Me<sub>2</sub>] or [Fe(phen)(mes)<sub>2</sub>]; **3** (M = Zr, L = C<sub>5</sub>H<sub>5</sub>); **4** (M = Fe, L<sub>2</sub> = phen)

The structures of **3**<sup>†</sup> and **4**<sup>‡</sup> that we propose are supported by the X-ray analysis on **3** (Fig. 1). The ligand has a bowl conformation close to that reported on some calix[4]resorcinarene derivatives.<sup>4</sup> Following the suggestions of Cram<sup>4</sup> we can express the size of the cavity by way of the C...C diagonal distances within the reference planes B [C(4) C(10) C(17) C(28)] and C [C(1) C(3) C(20) C(27)] averaging to 8.92(3) and 5.07(3) Å, respectively. The two reference planes are parallel, the dihedral angle they form being 0.5(4)°. The calix[4]resorcinarene assumes a cone conformation, similar to a calix[4]arene skeleton possessing an imposed C<sub>4</sub> symmetry. This is supported by the equal diagonal C...C distances within each plane and by the dihedral angles between the aromatic rings and the reference planes: 46.3(4), 45.6(5), 47.7(5) and 46.5(4)° for C(1)...C(6), C(8)...C(13), C(15)...C(20) and C(22)...C(27), respectively.

The curvature of the cavity in the case of diether derivatization of cavitands<sup>4</sup> is a function of the length of the bridges across each pair of oxygens. In an analogous way to Cram's organic bridges, we showed how transition-metal fragments, ML<sub>n</sub>, can be used for shaping the cavity of the cavitand skeleton. The four zirconium cations define an almost square framework anchored to the upper rim of the macrocycle. The intermetallic distances between adjacent metal atoms average to 7.763(3) Å. The displacement of the Zr atoms from the Zr<sub>4</sub> mean planes ranges

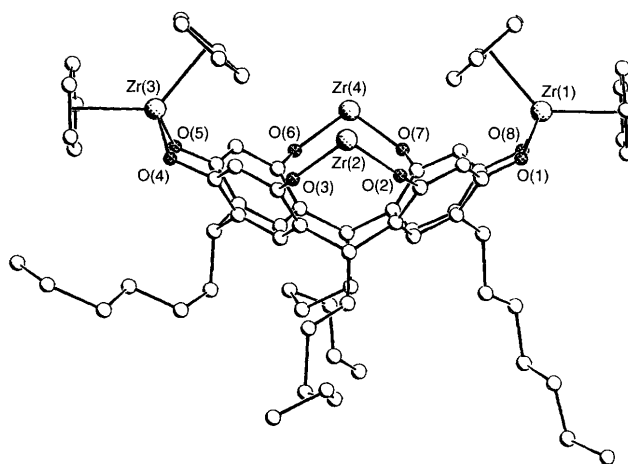


Fig. 1 SCHAKAL view of complex **3**. Selected bond distances (Å) and angles (°): Zr(1)–Cp(1) 2.27(2), Zr(1)–Cp(2) 2.22(3), Zr(1)–O(1) 2.02(3), Zr(1)–O(8) 2.02(2), Zr(2)–Cp(3) 2.24(3), Zr(2)–Cp(4) 2.18(3), Zr(2)–O(2) 2.02(2), Zr(2)–O(3) 1.95(2), Zr(3)–Cp(5) 2.24(4), Zr(3)–Cp(6) 2.19(4), Zr(3)–O(4) 1.99(3), Zr(3)–O(5) 1.99(2), Zr(4)–Cp(7) 2.24(3), Zr(4)–Cp(8) 2.26(3), Zr(4)–O(6) 1.90(2), Zr(4)–O(7) 1.95(2); O(1)–Zr(1)–O(8) 98.8(8), Cp(1)–Zr(1)–Cp(2) 129.9(9), O(2)–Zr(2)–O(3) 97.2(9), Cp(3)–Zr(2)–Cp(4) 129.9(10), O(4)–Zr(3)–O(5) 99.9(9), Cp(5)–Zr(3)–Cp(6) 128.7(14), O(6)–Zr(4)–O(7) 99.1(9), Cp(7)–Zr(4)–Cp(8) 132.1(11). The cyclopentadienyl rings bonded to Zr(2) and Zr(4) are omitted for clarity. Cp(1), Cp(2); Cp(3), Cp(4); Cp(5), Cp(6); Cp(7), Cp(8) refer to the centroids of the cyclopentadienyl rings bonded to Zr(1), Zr(2), Zr(3), Zr(4) respectively.

from  $-0.251(4)$  to  $0.297(4)$  Å. All the other structural parameters are those expected for the  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{OR})_2]$  fragment.<sup>5</sup> In the case of paramagnetic complex **4** one might expect a magnetic interaction within the tetrametallic unit. We found, on the contrary, that the magnetic moment per iron is essentially constant down to about 80 K, with a value of  $5.1 \mu_{\text{B}}$ , in the typical range for iron(II) complexes, and a  $J$  antiferromagnetic value of  $+0.4 \text{ cm}^{-1}$ . We should mention that a unique example of partial metallation of a calix[4]resorcinarene has been reported with a single copper ion bridging two cavitand units.<sup>6</sup> Some polymetallated forms of phosphinito and phosphonito calix[4]resorcinarene derivatives have also been reported.<sup>7</sup> We are currently pursuing the following objectives: (i) the obtention of a polymetallic functionalizable skeleton, to enter a polynuclear organometallic chemistry; (ii) the use of transition metals for shaping the cavity and the consequence of its binding properties.

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### Footnotes

† *Synthesis and spectroscopic data* of **3**:  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$  (3.60 g, 14.34 mmol) was added to an  $\text{Et}_2\text{O}$  (50  $\text{cm}^3$ ) solution of **2** (2.97 g, 3.58 mmol). A fast evolution of  $\text{CH}_4$  was observed and in 4 h a light-pink powder was obtained (79%). Crystals suitable for X-ray analysis were obtained from *n*-hexane.  $^1\text{H}$  NMR ( $\delta$ , 200 MHz,  $\text{CDCl}_3$ ): 0.91 (t, 12 H,  $\text{CCH}_3$ ), 1.27 (m, 32 H,  $\text{CH}_2$ ), 2.08 (br q, 8 H,  $\text{CCH}_2$ ), 4.44 (t, 4 H, CH), 5.77 (s, 4 H, Ar), 6.05 (s, 20 H,  $\text{C}_5\text{H}_5$ ), 6.47 (s, 20 H,  $\text{C}_5\text{H}_5$ ), 7.36 (s, 4 H, Ar). Satisfactory elemental analysis was obtained.

‡ *Crystal data* for complex **3**:  $\text{C}_{92}\text{H}_{104}\text{O}_8\text{Zr}_4$ ,  $M = 1702.7$ , monoclinic, space group  $C2/c$  or  $Cc$ , the latter confirmed by structural analysis,  $a = 18.320(6)$ ,  $b = 20.050(6)$ ,  $c = 21.849(8)$  Å,  $\beta = 100.45(3)^\circ$ ,  $U = 7892(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.433 \text{ g cm}^{-3}$ ,  $F(000) = 3520$ , Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å),  $\mu(\text{Cu-K}\alpha) = 47.13 \text{ cm}^{-1}$ , crystal dimensions  $0.20 \times 0.20 \times 0.30$  mm. The structure was solved by direct methods (MULTAN) and anisotropically refined only for the zirconium atoms. The hydrogen atoms were ignored. During the refinement the phenyl and cyclopentadienyl rings were constrained to be regular hexagons ( $\text{C-C} = 1.39$  Å) and pentagons ( $\text{C-C} = 1.42$  Å) respectively. The compound decomposes at room temperature. The low accuracy of the present analysis is reflected in the high standard deviations of the structural parameters. This could be mainly due to the low percentage of the observed reflections related to an intrinsic low scattering power of the crystal. For 2019 unique observed reflections [ $I > 2\sigma(I)$ ] collected at 103 K ( $5 < 2\theta < 120^\circ$ ) and corrected for absorption, the

current  $R$  was 0.076 (unit weights). All calculations were carried out with use of SHELX-76 on an Encore 91 computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/6.

§ *Synthesis* of **4**: A  $\text{thf}$  (50  $\text{cm}^3$ ) solution of **2** (0.652 g, 0.79 mmol) was added to a violet solution of  $[\text{Fe}(\text{phen})(\text{mes})_2]$  ( $\text{phen} = 1,10\text{-phenanthroline}$ ,  $\text{mes} = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ )<sup>8</sup> (1.52 g, 3.19 mmol), cooled to  $-30^\circ\text{C}$ . The solution then became deep green on reaching room temperature. The solution gave, on standing overnight, a green solid (97%) which was only slightly soluble in organic solvents. Satisfactory elemental analysis was obtained.

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