

binding sites opposite to that occupied by the polymer chains can be used to bind other biotinylated molecules, as was demonstrated for the iron storage protein ferritin. The giant amphiphiles can also be functionalized with enzymes as was shown with horse radish peroxidase. The resulting hybrids retained their catalytic activity. The precise control over the structure of the giant amphiphiles in principle allows for tuning of their aggregate morphologies. In this way well-defined structures analogous to those reported for low molecular weight surfactants and surfactants derived from block copolymers will become attainable.

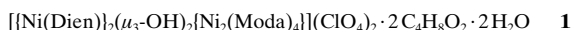
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## A Tetrameric Nickel(II) “Chair” with both Antiferromagnetic Internal Coupling and Ferromagnetic Spin Alignment\*\*

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Interest in polynuclear complexes of the 3d metals has been stimulated by the search for new magnetic materials<sup>[1, 2]</sup> and by demonstration of the occurrence of oligonuclear metal centers in proteins such as urease.<sup>[3]</sup> Of the relatively small number of reported tetranuclear complexes of  $S = 1$  nickel(II) of known structure, the majority have a hemicubane- or “butterfly-” rather than a squarelike core.<sup>[4]</sup> Of these molecules, just one is entirely antiferromagnetic,<sup>[5]</sup> while the remainder entail purely ferromagnetic interactions amongst the nickel(II) ions.<sup>[6–10]</sup> Oximes have shown promise as bridging ligands for the preparation of polynuclear complexes.<sup>[11, 12]</sup> The reaction of 1,4,7-triazaheptane (diethylenetriamine, Dien) with the monooxime of 2,3-butanedione (ModaH) in the presence of Ni<sup>II</sup> ions, instead of yielding the anticipated Schiff base derivative, gave the tetranuclear Ni<sup>II</sup> compound **1** (dark brown crystals;  $C_4H_8O_2 = 1,4$ -dioxane), containing uncondensed but coordinated ketone and amine groups. Figure 1a shows the structure of the the cation of **1**, while Figure 1b highlights its Ni<sup>II</sup> core.



The centrosymmetric  $[Ni(Dien)_2(\mu_3-OH)_2[Ni_2(Moda)_4]]^{2+}$  ion possesses an  $Ni_4O_2$  core based on a “chair” topology.<sup>[13]</sup> Two central Ni atoms ( $Ni_c$ ) with pseudo-octahedral  $N_2O_4$  donor ligand sets are bridged by hydroxyl ions to form a central  $Ni_2O_2$  parallelogram (Figure 1b) in which the  $Ni_c-O(\mu)$  distances are 2.038 Å, the Ni-O-Ni angles are 97.73°, and the  $Ni_c-Ni_c$  separation is 3.070 Å. The  $Moda^-$  ligands are coordinated to the  $Ni_c$  atoms through their ketone-O and oximate-N atoms. The  $Ni_c-O(ketone)$  bonds in **1** (2.113 and 2.114 Å) are akin to another recently described<sup>[14]</sup>

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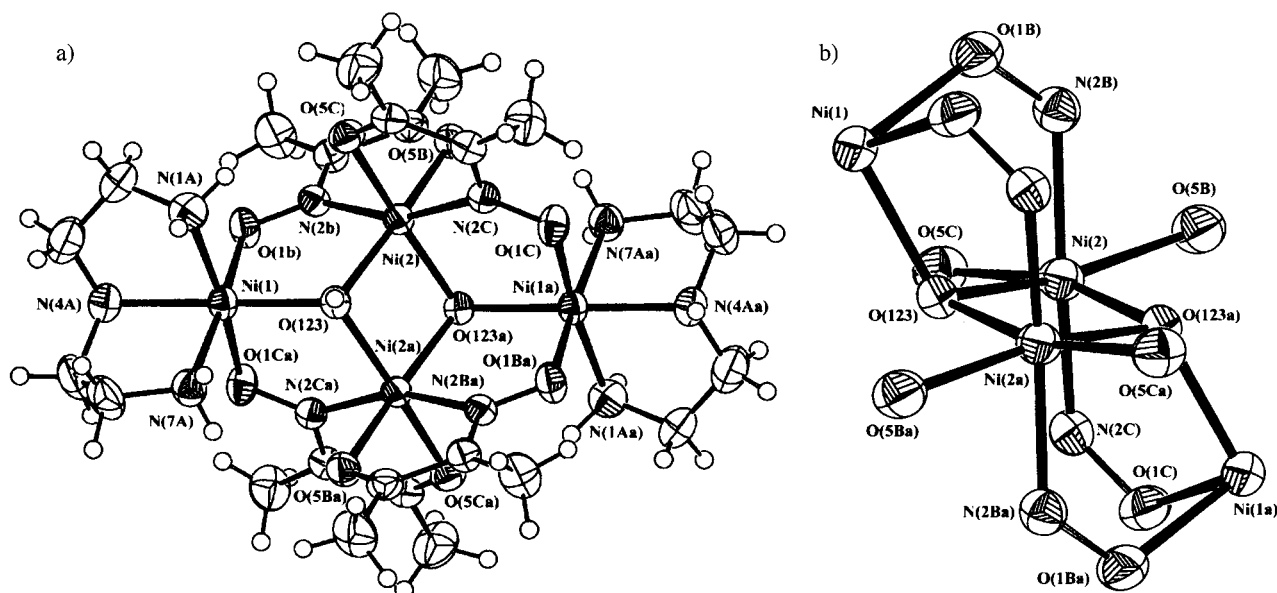
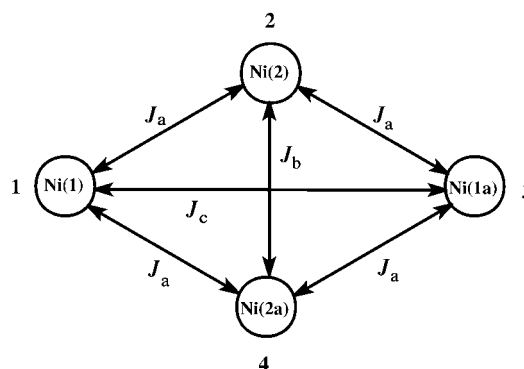


Figure 1. a) Structure of the tetranuclear cation of **1** (ORTEP diagram); b) structure of the coordination core of the tetranuclear complex (ORTEP diagram), displaying the displacement of the terminal nickel ions above and below the central  $\text{Ni}_2\text{O}_2$  plane. The diagrams are differently scaled.

example of a similarly rare Ni–O(ketone) bond (2.13 Å). The terminal  $\text{Ni}^{\text{II}}$  ions ( $\text{Ni}_t$ ) are bound to opposite sides of the  $\text{Ni}_{\text{c}2}\text{O}_2$  parallelogram, each one by a  $\mu_3\text{-OH}^-$  group and two oximate-O atoms (Figure 1b). The pseudo-octahedral  $\text{N}_3\text{O}_3$  coordination sphere around each  $\text{Ni}_t$  atom is completed by the three nitrogen donor atoms of a facially coordinated Dien molecule. The  $\text{Ni}_t\text{--Ni}_c$  distances are 3.412 and 3.397 Å, the  $\text{Ni}_t\text{--O--Ni}_c$  angles are 112.37 and 111.61°, and the  $\text{Ni}_t\text{--Ni}_t$  separation is 6.077 Å. The  $\text{Ni}_t$  atoms lie below and above the  $\text{Ni}_{\text{c}2}\text{O}_2$  plane, respectively, the  $\text{Ni}_t\text{--O(hydroxyl)}$  vectors being at 125° to this plane, though the four Ni atoms themselves lie in (another) common plane.

The magnetochemical behavior of a polycrystalline sample of **1** in the temperature range 2–300 K is displayed in Figure 2. The value of  $\chi_m T$  decreases with decreasing temperature, from 4.56 ( $\mu_{\text{eff}} = 3.0 \mu_{\text{B}}$  per Ni) at 300 K to 0.02  $\text{cm}^3 \text{K mol}^{-1}$  ( $0.2 \mu_{\text{B}}$  per Ni) at 2 K. As the value of  $\chi_m T$  for a tetranuclear unit of four noninteracting  $S = 1$   $\text{Ni}^{\text{II}}$  ions with  $g = 2.0$  would be 4.0  $\text{cm}^3 \text{mol}^{-1} \text{K}$  ( $\mu_{\text{eff}} = 2.83 \mu_{\text{B}}$  per Ni), it is clear that the major interactions within **1** are antiferromagnetic in nature. The three different types of Ni–Ni exchange interactions, namely between  $\text{Ni}_c\text{--Ni}_t$ ,  $\text{Ni}_c\text{--Ni}_c$ , and

$\text{Ni}_t\text{--Ni}_t$ , may be represented as  $J_a$ ,  $J_b$ , and  $J_c$ , respectively (Scheme 1).



Scheme 1. Magnetic coupling topology for the tetranuclear complex **1**.

According to Kambe's vector coupling scheme,<sup>[15]</sup> the total spin  $S_T$  steps integrally from 0 to 4 for this tetranickel(II) molecule, while the internal pairwise spin combinations  $S_{13}$  (devolving from  $J_c$ ) and  $S_{24}$  (devolving from  $J_b$ ) correspondingly vary integrally from 0 to 2 for each of these  $\text{Ni}^{\text{II}}$  pairs. Nineteen combinations of  $S_T$ ,  $S_{13}$ , and  $S_{24}$  result, designated by ( $S_T$ ,  $S_{13}$ ,  $S_{24}$ ), and at each energy Equation (1) is valid.<sup>[16]</sup>

$$E_{S_T} = -J_a S_T(S_T + 1) - S_{13}(S_{13} + 1)(J_c - J_a) - S_{24}(S_{24} + 1)(J_b - J_a) + 4J_b + 4J_c \quad (1)$$

Application of the van Vleck equation<sup>[17]</sup> to the corresponding isotropic exchange Hamiltonian [Eq. (2)]<sup>[16]</sup> yielded the susceptibility expression [Eqs. (3), (4)] to which the variable-temperature magnetic data were fitted.

$$\mathcal{H} = -2J_a(S_1 S_2 + S_2 S_3 + S_3 S_4 + S_1 S_4) - 2J_b(S_2 S_4) - 2J_c(S_1 S_3) \quad (2)$$

$$\chi'_m = \frac{Ng^2\beta^2}{3kT} \left[ \frac{(\sum S_T(S_T + 1)(2S_T + 1)e^{(-E_{S_T}/kT)})}{(\sum S_T(2S_T + 1)e^{(-E_{S_T}/kT)})} \right] \quad (3)$$

$$\chi_m = \chi'_m(1 - \rho) + \frac{2Ng^2\beta^2\rho}{3kT} + \text{tip} \quad (4)$$

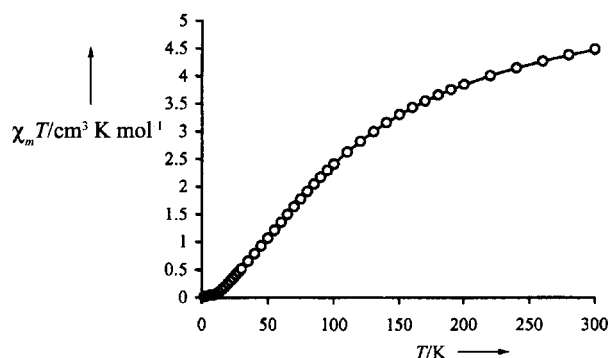


Figure 2. A plot of  $\chi T$  versus  $T$  for **1**. The points represent the experimental data, the line the least-squares fit as described in the text.

This yielded  $g = 2.32(2)$ ,  $2J_a = -40.6(5) \text{ cm}^{-1}$ ,  $2J_b = +20(5) \text{ cm}^{-1}$ ,  $\rho = 0.019$ ,  $\text{tip}(4\text{Ni}) = 1.00 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ ,  $R^2 = 1.7 \times 10^{-5}$ . No significant improvement in fit was effected by introduction of a nonzero value for the third  $J$  parameter ( $J_c$  or of intermolecular  $zJ'$ ); these are expected to be small in any case. As values of  $\chi_m T$  are much less responsive to  $J$  for ferromagnets ( $J > 0$ ) of low nuclearity than for analogous antiferromagnets ( $J < 0$ ), the dominating effect of  $J_a$  results in reduced precision for the estimate of  $J_b$  (or  $J_c$ ). Indeed, the trough for the dependence of  $R$  on  $J_a$  and  $J_b$  in Figure 3 shows

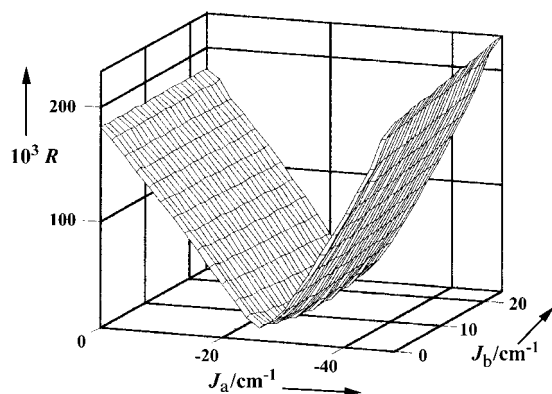


Figure 3. Variation of the residual fit error  $R$  (as  $\sqrt{R^2}$ ), as a function of the variation of  $J_a$  and  $J_b$  about the deduced values for **1**.

how a numerical outcome of the very weak dependence of  $\chi_m T$  on  $J_b > 0$  is that any estimate of  $J_b$  is rendered exceedingly imprecise. An analogous situation with  $-J_a \gg J_b$  has been observed for other tetranuclear iron(III) systems,<sup>[18, 19]</sup> for which spin frustration was proposed. The similar numerical properties of the  $\text{Ni}_4$  model render it difficult in such cases to distinguish between intrinsic ferromagnetic coupling between the  $\text{Ni}_c$  versus the obligatory alignment of their spins to parallel as a consequence of other couplings. However, more recent work<sup>[20, 21]</sup> appears to mitigate against the spin frustration interpretation and in favor of a *competing spin interaction* outcome. First, a classical spin-frustrated state

does not sensibly correspond to an  $S_T = 0$  state. A *degenerate frustrated* state may occur if the ground state is (or is at a crossing with) an  $S_T > 0$  state.<sup>[21]</sup> Figure 4a displays the spin ladder corresponding to the fitted parameters. This illustrates the relative isolation of the (0,2,2) ground state (e.g.,  $[\text{Ni}_1, \text{Ni}_2, \text{Ni}_3, \text{Ni}_4] = [\uparrow\uparrow, \downarrow\downarrow, \uparrow\uparrow; \downarrow\downarrow]$ ), while Figure 4b and c, which display the progress of the lowest state energies as a function of  $J_a$  and  $J_b$ , respectively, reinforce the finding<sup>[5]</sup> that there is no such crossover in this  $J_a < 0$  region. They also illustrate how the  $E_{S_T}$  themselves are much more strongly dependent on  $J_a$  than on  $J_b$ .

One particular aspect of the comparison of **1** with other reported tetranickel(II) systems is revealing with respect to the relationship between the  $J_a$  and  $J_b$  values. Correlations<sup>[22, 23]</sup> of  $J$  with the angle  $\theta$ , reinforced by other recent results,<sup>[5, 9, 10]</sup> quite clearly indicate that  $J$  decreases with  $\theta$ , crossing  $J = 0$  at a  $\theta$  value of about  $95-100^\circ$ . At  $112^\circ$ , this predicts a  $2J_a$  value of about  $-30$  to  $-60 \text{ cm}^{-1}$ , while the lesser angle predicts a  $2J_b$  value around zero. A value of  $2J_a = -40 \text{ cm}^{-1}$  fits this correlation well. We conclude that the larger ( $\text{Ni}_c\text{-O-Ni}_t$ ) angle is the core's fundamentally causative structural feature, which by setting the larger  $-2J$  value, thus drives all the  $\text{Ni}_c$  spins parallel.<sup>[5, 20]</sup>

### Experimental Section

**1**:  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.46 g, 4 mmol), followed by  $\text{Et}_3\text{N}$  (606 mg, 6 mmol) were added to  $\text{ModaH}$  (404 mg, 4 mmol) and  $\text{Dien}$  (206 mg, 2 mmol) in 96 % ethanol (5 mL) at room temperature. The brown solid obtained was recrystallized from  $\text{MeNO}_2/1,4\text{-dioxane}$  (1:1) to yield **1** as a crystalline product (yield: 1.09 g, 85 %). Elemental analysis (%) calcd for  $\text{C}_{32}\text{H}_{72}\text{Cl}_2\text{N}_{10}\text{Ni}_4\text{O}_{24}$ : C 29.9, H 5.60, N 10.9, Ni 18.3; found: C 29.8, H 5.55, N 10.9, Ni 18.3; FAB mass spectrum:  $m/z$  (%): 971 (49)  $[(\text{Ni}_4(\text{Dien})_2(\text{OH})_2(\text{Moda})_4)\text{ClO}_4]^+$ , 492 (100)  $[\text{Ni}_3\text{O}(\text{Moda})_2\text{ClO}_4]^+$ .

Crystal data for **1**:  $\text{C}_{32}\text{H}_{72}\text{Cl}_2\text{N}_{10}\text{Ni}_4\text{O}_{24}$ ,  $M_r = 1286.74$ , monoclinic,  $a = 10.4880(7)$ ,  $b = 16.1935(10)$ ,  $c = 16.2944(11) \text{ \AA}$ ,  $\beta = 106.9580(10)$ ,  $V = 2647.1(3) \text{ \AA}^3$ ,  $T = 295(2) \text{ K}$ , space group  $P2_1/c$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.614 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.71069 \text{ \AA}$ ,  $\mu = 1.589 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 56.58^\circ$ ; crystal dimensions  $0.18 \times 0.13 \times 0.05 \text{ mm}$ , 24155 reflections measured, 6524 unique reflections ( $R_{\text{int}} = 0.118$ ) used for solution (SIR-99) and refinement (SHELX-97) by full-matrix least-squares on  $F^2$ ; no absorption correction. Final  $R_w(F^2) =$

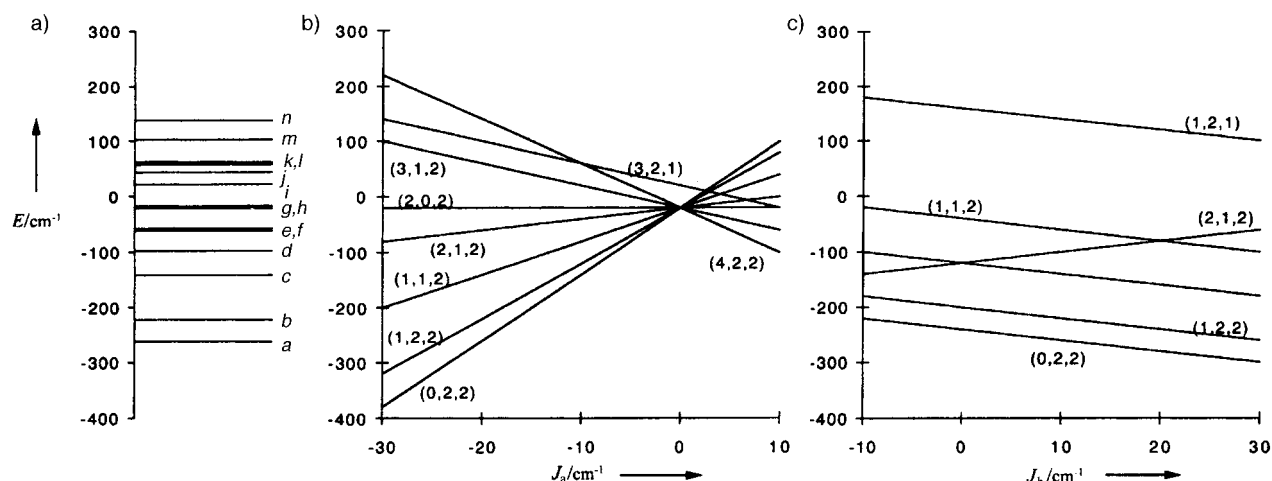


Figure 4. a) Spin ladder for  $[\text{Ni}(\text{Dien})]_2(\mu_3\text{-OH})_2[\text{Ni}_2(\text{Moda})_4]^{2+}$ . The levels are  $a = 0,2,2$ ;  $b = 1,2,2$ ;  $c = 2,2,2/1,1,2$ ;  $d = 1,2,1$ ;  $e = 2,1,2$ ;  $f = 0,1,1$ ;  $g = 3,2,2/2,0,2$ ;  $h = 0,1,1$ ;  $i = 2,2,2/1,1,1$ ;  $j = 2,2,0/1,1,0/0,0,0$ ;  $k = 3,1,2$ ;  $l = 2,1,1$ ;  $m = 3,2,1$ ;  $n = 4,2,2$ . The 0,2,2 ground state is separated from the next lowest state (1,2,2) by  $40 \text{ cm}^{-1}$ . b) Effect on the energies of the lowest states at  $2J_b = +20 \text{ cm}^{-1}$  as a result of the variation in  $J_a$  about the experimental value, and c) as a result of the variation in  $J_b$  about the experimental value at  $2J_a = -40 \text{ cm}^{-1}$ .

0.110; H atoms treated by a riding model; max. and min. residual electron densities were +0.550 and -0.453, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-55327. 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). Susceptibilities from a Pd-standard-calibrated Quantum Design MPMS5S SQUID, at a field of 0.1 T. The diamagnetic correction applied for **1** was  $-5.32 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ .

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## A Calix[4]arene Gd<sup>III</sup> Complex Endowed with High Stability, Relaxivity, and Binding Affinity to Serum Albumin\*\*

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Alessandro Casnati,\* Marco Fragai, Claudio Luchinat,  
and Rocco Ungaro

An interesting class of macrocyclic ligands uses calixarenes as a molecular platform. These ionophores<sup>[1]</sup> are characterized by high lipophilicity and have been mainly used as selective extractants or carriers of alkali,<sup>[2]</sup> alkaline earth,<sup>[3]</sup> lanthanide, and actinide metal ions.<sup>[4]</sup> The complexation of lanthanide ions by calix[4]arene ligands has also been studied with the purpose of developing new luminescent probes.<sup>[5]</sup> Very little is known on the use of calixarene lanthanide complexes as contrast agents for magnetic resonance imaging (MRI),<sup>[6]</sup> although this possibility has been envisaged<sup>[7]</sup> and a recent example has been reported.<sup>[8]</sup> To develop efficient systems for MRI the problem of water solubility and stability of the complexes has to be solved. Several years ago we reported the luminescent properties of lanthanide complexes of a calix[4]-arene tetraamide derivative in water.<sup>[9]</sup> However, the complexes were not very stable and after a short time the free ligand precipitated out of the solution. One efficient way to complex hard divalent and trivalent metal ions in water is to use aminopolycarboxylic acid derivatives.<sup>[10]</sup> Herein we report the synthesis of a new calix[4]arene-based ligand which presents two acetamide and two ethylenaminodicarboxy groups at the lower rim of the macrocycle, able to form complexes with Gd<sup>III</sup> in water, these complexes are characterized by high values of relaxivity.<sup>[6]</sup>

The diamide tetraacid derivative **1** was synthesized in 45 % overall yield, by alkylation of the diamide of calix[4]arene **2**<sup>[11]</sup> with Na<sub>2</sub>CO<sub>3</sub> and 2-[N,N-bis(tert-butyloxycarbonylmethyl)-amino]-1-bromo-ethane (**3**)<sup>[12]</sup> in acetonitrile, followed by hydrolysis of tert-butyl esters using trifluoroacetic acid (TFA) and triethyl silane (Scheme 1). The <sup>1</sup>H NMR spectrum of **1** in CD<sub>3</sub>OD, clearly show that the calixarene ligand is in the cone

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