A Novel Bis(*N*,*N*′-dimethyl-1,4,7-triazacyclononane)calix[4]arene Ligand that forms a Ferromagnetic Dinuclear Nickel(II) Complex with Three End-on Azide Bridging Ligands

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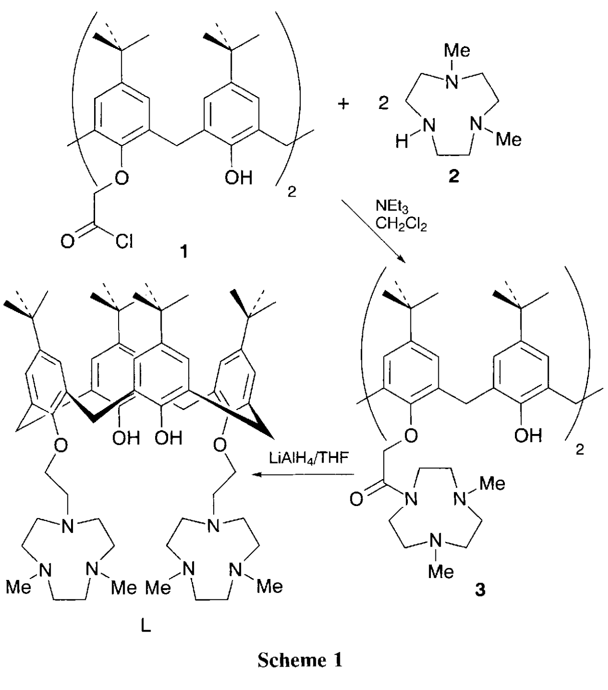
A new bis(*N*,*N*′-dimethyl-1,4,7-triazacyclononane)calix[4]arene ligand L has been prepared and a single-crystal structure determination of a novel ferromagnetic dinuclear nickel(II)–L complex containing three 1,1 end-on azide bridging ligands is described.

The calixarene macrocyclic structural framework[1,2] has been shown to be an attractive building block on which to append at the hydroxy lower rim additional hard donor groups such as esters,[2,3] amides,[2,3] carboxylic acids[2,4] and crown ethers[5] for the recognition of main group,[2,3] lanthanoid[2,4,6] and actinoid[2,7] metals. Surprisingly, in comparison there are relatively few examples of modified calixarene-based ligand systems designed specifically to coordinate transition metals. Pendant phosphino-,[8] bipyridyl-[9] and thioether-substituted[2,9] calixarenes are the main classes reported to date. As part of a research programme aimed at producing poly(transition metal–calixarene) complexes for bioinorganic modelling and catalysis, we describe here the synthesis of a novel bis(*N*,*N*′-dimethyl-1,4,7-triazacyclononane)calix[4]arene ligand L that, by virtue of the calix linking unit, forms a unique ferromagnetic dinuclear nickel(II) complex bridged by three azide ligands coordinating in the 1,1 end-on mode.

The reaction of *p*-*tert*-butylcalix[4]arenebis(acid chloride) **1**[10] with *N*,*N*′-dimethyl-1,4,7-triazacyclononane **2**[11] in the presence of triethylamine gave the diamide **3**, which on reduction with $LiAlH_4$ in dry THF gave the new ligand L as a glassy white solid in an overall yield of 40% (Scheme 1).

The addition of 2 equiv. of $Ni(ClO_4)_2{\cdot}6H_2O$ in acetonitrile to a solution of L in dichloromethane gave a pale blue solution. Addition of excess NaN_3 in methanol resulted in a slight darkening of the blue colour, and upon slow evaporation, a pale blue microcrystalline solid precipitated, which was recrystallised from dichloromethane–acetonitrile. Microanalytical results were consistent with the formulation $Ni_2L(N_3)_3(ClO_4)$ **4**, and the FAB-MS spectrum revealed a molecular ion at 1259, consistent with $[Ni_2L(N_3)_3]^+$. An analogous synthetic procedure using nickel(II) acetate resulted in the formation of large blue crystals of **5** suitable for a X-ray crystallographic structure determination.



Scheme 1

The results of the structure determination of **5**† are in agreement with the formulation $[Ni_2(L - H)(N_3)_3]{\cdot}MeCN$ (excluding lattice solvent molecules except for the MeCN molecule included in the cavity of the calixarene). The structure is shown in Fig. 1. The calix[4]arene moiety takes up the common cone conformation. At the 1,3-positions are substituted $-CH_2CH_2-(9aneN_3Me_2)$ groups. These are then connected by $Ni(N_3)_3Ni$ moieties. Both nickel atoms are six-coordinate with distorted octahedral environments being bonded to three nitrogen atoms of the $9aneN_3$ macrocycle and three azides bridging in the end-on-1,1 mode. There is no significant distinction between the Ni–N(macrocycle) and Ni–N(azide) distances, all being within the range 2.04–2.11 Å. The N(macrocycle)–Ni–N(macrocycle) angles average to 84.9°, while the average N(azide)–Ni–N(azide) angle is 78.4°. The bridging azide groups are approximately linear. The conformations of the nine-membered rings are as expected with approximate threefold symmetry, but two sets of ring torsion angles show opposite signs, indicating that they are mirror images of each other.

There are no examples in the Cambridge Crystallographic Database of three 1,1 end-on azide bridges between an isolated pair of nickel atoms. Recently, however, the crystal structure of $[Ni(N_3)_2(tmeda)]_n$ has been described, where $-Ni(1,1\text{-}N_3)Ni-$ dimers are linked by end-to-end 1,3-azide bridges to form a polymeric system.[12] The geometry of the triple bridge is similar to the present structure, with an average Ni–N(azide)–Ni angle of 84.2° (86.2° in **5**), and Ni···Ni distance of 2.8692(7) Å [2.852(2) in **5**]. Nickel complexes involving two 1,1-azide bridges are well established,[12,13] as are systems involving one,[14] two [15] and three[16] 1,3-azide bridges.

The IR spectra of **4** and **5** are identical in the azide stretching frequency region (2101, 2072, 2060 cm^{-1}), but show differences in the –OH stretching frequency (**4**, 3307; **5**, 3391 cm^{-1}). These results suggest that **4** and **5** are similar in structure, containing the $[Ni_2L(N_3)_3]^+$ moiety, with the fourth anion being a perchlorate anion in **4**, and a deprotonated phenol group in **5**. It is pertinent to compare these complexes with the related nickel complexes of *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane

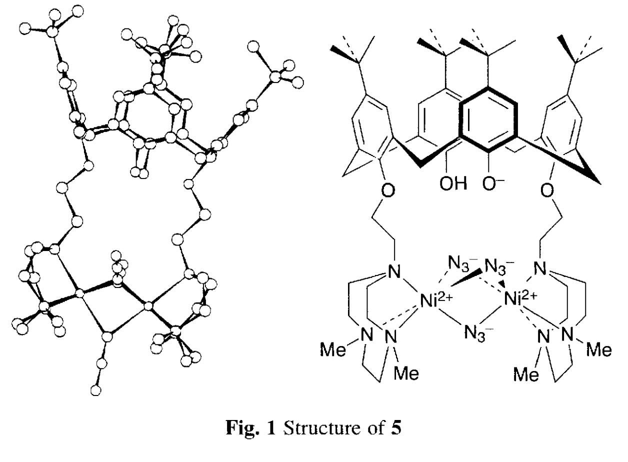


Fig. 1 Structure of **5**

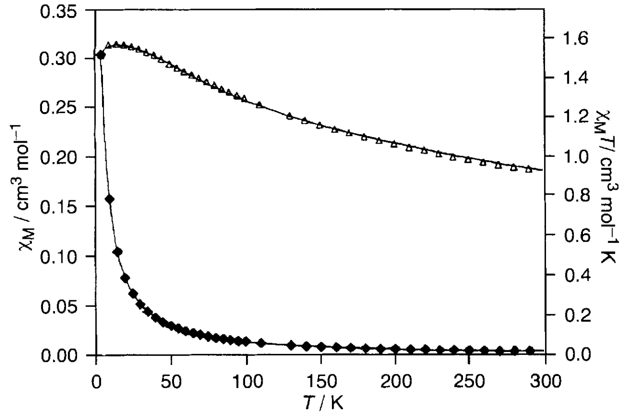


Fig. 2 Experimental and calculated (solid line) temperature dependence of the molar magnetic susceptibility, χ_m, (◆) and $\chi_m T$ (△) for **5**

where the use of nickel perchlorate and sodium azide gives rise to a dimeric complex with three 1,3-azide bridges, whereas nickel acetate produces a dimer with two 1,3-azide bridges, and one terminal azide ligand per nickel atom.[16]

Of particular interest in these azide-bridged nickel complexes are the magnetic properties. It has generally been found that 1,1-bridges between nickel atoms result in ferromagnetic coupling, whilst 1,3-bridges result in antiferromagnetic interactions.[13,14] However, studies of the triple 1,1-bridged system $[Ni(N_3)_2(tmeda)]_n$, mentioned above, indicate that 1,1-bridges can produce antiferromagnetic coupling.[12] Ribas *et al.* suggest that the Ni–N–Ni angle is important in determining the nature of the coupling; thus the average Ni–N–Ni angle in $[Ni(N_3)_2(tmeda)]_n$ of 84.2° is significantly lower than those observed previously in ferromagnetically coupled systems (100–105°). Since the study of $[Ni(N_3)_2(tmeda)]_n$ is complicated by the presence of 1,3-azide bridges, in addition to the 1,1-bridges, it was of interest to examine the magnetic properties of the present system, which has a similar structure with an isolated dimer. Variable-temperature solid-state magnetic susceptibility studies were performed on **4** from 290 to 5 K. The results clearly indicate ferromagnetic behaviour (Fig. 2). The data were analysed using the Ginsberg model,[17] with D (the single-ion zero-field splitting) set to zero, as it has been shown that this does not significantly alter the calculated J and g values,[13] to give $J = 17.2 \pm 0.5$ cm^{-1} ($g = 2.1$). There is an indication of some weak antiferromagnetic coupling at low temperature, which may be because of interdimer exchange.[13] Clearly there is a discrepancy between the magnetic properties of the present system, and those found for $[Ni(N_3)_2(tmeda)]_n$. Further work will be required to determine whether the underlying reasons for these differences are owing to slight differences in structure, or to complications introduced by the polymeric nature of the latter complex.

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Footnote

† *Crystal data* for **5** $[Ni_2(L - H)(N_3)_3]\cdot1.5MeCN\cdot1.5MeOH\cdot2H_2O$, $C_{68.5}H_{108}N_{16.5}Ni_2O_{7.5}$, $M = 1400.13$, Mo-Kα radiation, $\lambda = 0.7107$ Å, monoclinic, space group $P2_1/c$, $a = 20.632(6)$, $b = 15.221(6)$, $c = 26\,996(8)$ Å, $\beta = 92.40(1)°$, $U = 8740(5)$ Å^3, $Z = 4$, $D_m = 1.10$ Mg m^{-3}, $\mu = 0.50$ mm^{-1}, $F(000) = 3002$. 11557 Reflections, 6595 observed, $R = 0.087$. The structure was solved using direct methods with the SHELX86 program.[18] The structure contains a $[Ni_2(L - H)(N_3)]$ complex and solvent molecules identified as one MeCN with 100% occupancy (enclosed within the calixarene cone), one MeCN with 50% occupancy, two MeOH each with 50% occupancy, and four water molecules each with 50% occupancy. In the complex, the non-hydrogen atoms were refined with anisotropic thermal parameters apart from the *tert*-butyl groups where there were signs of disorder. For one group, two orientations were included each with 50% occupancy. All solvent molecules were included with isotropic thermal parameters. The structure was then refined using SHELXL.[19]

There is some ambiguity in the crystallographic evidence for the exact formulation of the complex. We considered two possibilities: firstly, that the complex was neutral with one of the hydroxide groups at the bottom of the cone being deprotonated and that the solvent was MeCN; and secondly, that the complex had a charge of +1 and that the solvent MeCN (there was only one with 100% occupancy) could be reclassified as N_3^-. This second possibility seemed unlikely to us, particularly as this molecule was to be found within the cone. This position within the hydrophobic cavity is well known to be occupied by neutral solvent molecules (and indeed MeCN has been observed often therein) but not by anions. The structure was therefore refined with solvent MeCN. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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