A Tetrmeric Nickel(n) “Chair” with both Antiferromagnetic Internal Coupling and Ferromagnetic Spin Alignment**

Vitaly P. Pavlishchuk,* Sergey V. Kolotilov, Anthony W. Addison,* Michael J. Prushan, Dieter Schollmeyer, Laurence K. Thompson, and Eugeny A. Goreshnik

Interest in polynuclear complexes of the 3d metals has been stimulated by the search for new magnetic materials[1, 2] and by demonstration of the occurrence of oligonuclear metal centers in proteins such as urease.[3] Of the relatively small number of reported tetranuclear complexes of \( S = 1 \) nickel(n) of known structure, the majority have a hemicubane- or “butterfly”- rather than a tetrasquarelike core.[4] Of these molecules, just one is entirely antiferromagnetic,[5] while the remainder entail purely ferromagnetic interactions amongst the nickel(n) ions.[6-10] Oximes have shown promise as bridging ligands for the preparation of polynuclear complexes.[11, 12] The reaction of 1,4,7-triazaheptane (diethylenetriamine, Dien) with the monoxoime of 2,3-butandione (ModaH) in the presence of Ni(n) ions, instead of yielding the anticipated Schiff base derivative, gave the tetranuclear Ni(n) compound 1 (dark brown crystals; \( \text{C}_4\text{H}_8\text{O}_2 \), 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(n) core.

\[ \text{Ni} \text{(Dien)}_2(\text{OH})\text{Ni} \text{(Moda)}_2[\text{ClO}_4]_2 \cdot 2\text{C}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O} \quad 1 \]

The centro symmetric \([\text{Ni} \text{(Dien)}_2(\text{OH})\text{Ni} \text{(Moda)}_2][\text{ClO}_4]_2\) ion possesses an \( \text{Ni}_4\text{O}_2 \) core based on a “chair” topology[13] Two central Ni(n) atoms (Nic) with pseudo-octahedral \( \text{N}_2\text{O}_4 \) ligand sets are bridged by hydroxyl ions to form a central \( \text{Ni}_4\text{O}_2 \) parallelogram (Figure 1b) in which the \( \text{Ni} - \text{O} (\mu) \) distances are 2.038 Å, the \( \text{Ni}-\text{O} - \text{Ni} \) angles are 97.73°, and the \( \text{Ni}_1 - \text{Ni}_2 \) separation is 3.070 Å. The Moda-ligands are coordinated to the Ni(n) atoms through their ketone-O and oximate-N atoms. The Ni(n)-O(ketone) bonds in 1 (2.113 and 2.114 Å) are akin to another recently described[14]

---

[**] A.W.A. and M.J.P. thank Drexel University for support.
example of a similarly rare Ni–O(ketone) bond (2.13 Å). The terminal NiII ions (Nit) are bound to opposite sides of the Ni2O2 parallelogram, each one by a μ2-OH– group and two oximate-O atoms (Figure 1b). The pseudo-octahedral NiO3 coordination sphere around each NiII atom is completed by the three nitrogen donor atoms of a facially coordinated Dien molecule. The Nit–NiII distances are 3.412 and 3.397 Å, the Nit-O-Nit angles are 112.37 and 111.61°, and the Nit–NiII separation is 6.077 Å. The Nit atoms lie below and above the Ni2O2 plane, respectively, the Nit-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 μT decreases with decreasing temperature, from 4.56 (μeff = 3.0 μB per Ni) at 300 K to 0.02 cm3Kmol−1 (0.2 μB per Ni) at 2 K. As the value of μT for a tetranuclear unit of four noninteracting S = 1 NiII ions with g = 2.0 would be 4.0 cm3mol−1 K (μeff = 2.83 μB 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 Ni2–Ni1, Ni3–Ni4, and Ni1–Ni4, may be represented as Jα, Jβ, and Jγ, respectively (Scheme 1).

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

According to Kambe’s vector coupling scheme,[15] the total spin ST steps integrally from 0 to 4 for this tetranickel(II) molecule, while the internal pairwise spin combinations S13 (devolving from Jγ) and S24 (devolving from Jβ) correspondingly vary integrally from 0 to 2 for each of these NiII pairs. Nineteen combinations of ST, S13, and S24 result, designated by (ST, S13, S24), and at each energy Equation (1) is valid.[16]

\[ E_{\alpha} = -J_{\beta}(S_2(S_2+1) - S_1(S_1+1)(J_1-J_2) - S_4(S_4+1)(J_2-J_4) + 4J_4+4J_6) \]  

(1)

Application of the van Vleck equation[17] to the corresponding isotropic exchange Hamiltonian [Eq. (2)][18] yielded the susceptibility expression [Eqs. (3), (4)] to which the variable-temperature magnetic data were fitted.

\[ \chi' = -2J_{\beta}(S_2S_2 + S_1S_1 + S_3S_3 - J_1S_1S_1 - 2J_2S_2S_2) \]  

(2)

\[ \chi_{\alpha} = \frac{3kT}{2\pi^2}\left[\left(S_1S_1 + S_2S_2 + S_3S_3 + S_4S_4\right) - 2J_1\left(S_1S_1 + 1\right)e^{-J_1/\epsilon} - 2J_2\left(S_2S_2 + 1\right)e^{-J_2/\epsilon} - 2J_3\left(S_3S_3 + 1\right)e^{-J_3/\epsilon} - 2J_4\left(S_4S_4 + 1\right)e^{-J_4/\epsilon}\right] \]  

(3)

\[ \chi_{\alpha} = \chi_{\alpha}(1 - \rho) + \frac{3kT}{2\pi^2}\rho \]  

(4)
Figure 3. Variation of the residual fit error $R$ (as $\sqrt{R^2}$), as a function of the variation of $J_b$ and $J_a$ about the deduced values for $J_a$ and $J_b$. How a numerical outcome of the very weak dependence of $\chi_mT$ on $J_b > 0$ is that any estimate of $J_b$ is rendered exceedingly imprecise. An analogous situation with $-J_b > J_a$ has been observed for other tetranuclear iron(II) systems\,[16, 17], for which spin frustration was proposed. The similar numerical properties of the Ni$_4$ model render it difficult in such cases to distinguish between intrinsic ferromagnetic coupling between the Ni$_4$ versus the obligatory alignment of their spins to parallel as a consequence of other couplings. However, more recent work\,[20, 21] 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) an $S_T > 0$ state.\,[21]

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., $[\text{Ni}, \text{Ni}_2, \text{Ni}_3, \text{Ni}_4] = [\uparrow \uparrow, \downarrow, \uparrow, \uparrow \uparrow]$), 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\,[20] that there is no such crossover in this $J_b$ region. They also illustrate how the $E_b$ themselves are much more strongly dependent on $J_b$ than on $J_a$.

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\,[22, 23] of $J$ with the angle $\theta$, reinforced by other recent results\,[5, 9, 10] 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 $J_a$ value of about $30–60$ cm$^{-1}$, while the lesser angle predicts a $2J_b$ value around zero. A value of $2J_b = -40$ cm$^{-1}$ fits this correlation well. We conclude that the larger (Ni$_4$-O-Ni$_4$) angle is the core’s fundamentally causative structural feature, which by setting the larger $-2J$ value, thus drives all the Ni$_4$ spins parallel\,[5, 20].

**Experimental Section**

1. Ni(ClO$_4$)$_2$ ¥ 6H$_2$O (1.46 g, 4 mmol), followed by Et$_3$N (606 mg, 6 mmol) were added to ModaH (404 mg, 4 mmol) and Dien (206 mg, 2 mmol) in 96% ethanol (5 mL) at room temperature. The brown solid obtained was recrystallized from MeNO$_2$/1,4-dioxane (1:1) to yield I as a crystalline product (yield: 1.09 g, 85%). Elemental analysis (%) calcd for C$_{20}$H$_{32}$Cl$_2$N$_{10}$Ni$_4$O$_{24}$: C 50.0, H 5.4, N 10.9, Ni 18.3; found: C 55.5, H 5.0, N 18.3; FAB mass spectrum: $m/z$: 971 (49) $[\text{Ni}_4\text{Cl}_2\text{OH}_2\text{H}_2\text{O}]^{+}$, 492 (100) $[\text{Ni}_4\text{O}4\text{Ni}_4\text{ClO}_4]^{2-}$.

Crystal data for 1: C$_{20}$H$_{32}$Cl$_2$N$_{10}$Ni$_4$O$_{24}$, $M_r = 1286.74$, monoclinic, $a = 10.4880(7)$, $b = 16.1935(10)$, $c = 16.2944(11)$ Å, $\beta = 90.038(10)$, $V = 2647.1(3)$ Å$^3$, $T = 295(2)$ K, space group $P2_1/c$, $Z = 2$, $\rho_{\text{calc}} = 1.614$ g cm$^{-3}$, $\mu$ (MoK$\alpha$) = 0.71069 Å, $\mu$ = 1.589 mm$^{-1}, 2\theta_{\text{max}} = 56.58^\circ$; crystal dimensions 0.18 x 0.13 x 0.05 mm, 24155 reflections measured, 6524 unique reflections ($R_{int} = 0.118$) used for solution (SIR-99) and refinement (SHELX-97) by full-matrix least-squares on $F^2$; no absorption correction. Final $R(F^2) = 0.054$ and $wR(F^2) = 0.132$.

Silvio Aime, Alessandro Barge, Mauro Botta,* Alessandro Casnati,* Marco Ffragi, Claudio Luchinat, and Rocco Ungaro

An interesting class of macrocyclic ligands uses calixarenes as a molecular platform. These ionophores[1] are characterized by high lipophilicity and have been mainly used as selective extractants or carriers of alkali,[2] alkaline earth,[3] lanthanide, and actinide metal ions.[4] The complexation of lanthanide ions by calix[4]arene ligands has also been studied with the purpose of developing new luminescent probes.[5] Very little is known on the use of calixarene lanthanide complexes as contrast agents for magnetic resonance imaging (MRI),[6] although this possibility has been envisaged[7] and a recent example has been reported.[8] 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.[9] 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.[10] Herein we report the synthesis of a new calix[4]arene-based ligand which presents two acetamide and two ethylenediaminodicarboxyl groups at the lower rim of the macrocycle, able to form complexes with Gd"III in water, these complexes are characterized by high values of relaxivity.[6]

The diamide tetraacetic derivative 1 was synthesized in 45% overall yield, by alkylation of the diamide of calix[4]arene 2[11] with Na₂CO₃ and 2-[N,N-bis(tert-butyloxycarbonylmethyl)-amino]-1-bromo-ethane (3)[8] in acetonitrile, followed by hydrolysis of tert-butyloxycarbonyl esters using trifluoroacetic acid (TFA) and triethyl silane (Scheme 1). The 1'H NMR spectrum of 1 in CD₃OD, clearly show that the calixarene ligand is in the cone

**[1] This work was supported by CNR (Programma M.U.R.S.T. - Chimica Legge 95/95) “Agenti di contrasto, di shift e sonde luminescenti”. We thank C.I.M. (Centro Interdipartimentale Misure) dell’Università di Parma for the NMR and mass spectroscopy facilities.