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## Unique Single-Atom Binding of Pseudohalogeno Ligands to Four Metal Ions Induced by Their Trapping into High-Nuclearity Cages\*\*

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High-nuclearity transition metal clusters continue to attract a great deal of interest, partly because of their fascinating physical properties and partly for the beauty and complexity of their structures. An interesting subarea of transition metal cluster chemistry is the small but growing family of molecules that, in their ground states, have unusually large numbers of unpaired electrons. Molecular clusters with very high spin values have been prepared, often by one-pot synthesis, with the highest values to date being  $S_T = 51/2$  for the recently reported<sup>[1]</sup> Mn<sub>9</sub>,<sup>II</sup>Mo<sub>6</sub><sup>V</sup> cyano-bridged system and  $S_T \approx 33/2$  for one of the clusters in a compound containing cocrystallized Fe<sub>17</sub> and Fe<sub>19</sub> species.<sup>[2]</sup> The large-spin ground state results from either ferromagnetic (or ferrimagnetic) exchange interactions between the paramagnetic centers and/or topologically frustrated antiferromagnetic interactions.<sup>[3]</sup> In addition, it has recently become apparent that a fairly large  $S_T$  value is a necessary (but not sufficient) requirement for molecules to be able to exhibit the new phenomenon of single-molecule magnetism.<sup>[4]</sup> The synthesis of new high-spin molecules is thus of interest. However, it is difficult to predict in advance what type of topology and structure will lead to a high-spin cluster and even more difficult to then achieve a rational synthesis of such a species.

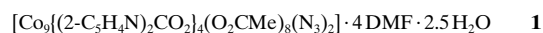
In most polynuclear clusters, magnetic exchange interactions are mainly propagated by bridging OH<sup>-</sup>, OR<sup>-</sup>, O<sup>2-</sup>, or RCO<sub>2</sub><sup>-</sup> ligands, or a combination of two or more of these groups; often these interactions lead to antiferromagnetic coupling. An alternative attractive approach to increase the  $S_T$  ground state would be the replacement of one or more of the above-mentioned bridging ligands with other groups that are more prone to ferromagnetic coupling. Herein we describe our preliminary results demonstrating the application of this approach.

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[\*\*] This work was supported by CICYT (Grant BP96/0163) and the Research Committee of the University of Patras (C. Caratheodory Programme, No 1941).

We have successfully applied a strategy to the antiferromagnetic cluster  $[\text{Co}_9\{(2\text{-C}_5\text{H}_4\text{N})_2\text{CO}_2\}_4(\text{O}_2\text{CMe})_8(\text{OH})_2]$  ( $(2\text{-C}_5\text{H}_4\text{N})_2\text{CO}_2^{2-}$  is the doubly deprotonated *gem*-diol form of di-2-pyridyl ketone,  $(2\text{-C}_5\text{H}_4\text{N})_2\text{CO}$ ),<sup>[5]</sup> in which, while maintaining the thermodynamically stable  $\text{Co}_9$  cage skeleton, we have been able to modulate the superexchange pathway by substitution of the  $\mu_4$ -hydroxides by unprecedented  $\mu_4$ -azide or  $\mu_4$ -cyanate ligands. The magnetic response changes from antiferromagnetic interactions for  $\text{NCO}^-$  to a ferrimagnetic high-spin anisotropic system in the  $\text{N}_3^-$  case.

Reaction of  $\text{Co}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$  with  $(2\text{-C}_5\text{H}_4\text{N})_2\text{CO}$  and  $\text{NaN}_3$  (9:4:2 molar ratio) in hot DMF led to a dark blue solution from which the nonanuclear cage **1** was isolated. The



X-ray crystal structure analysis<sup>[6]</sup> of **1** (Figure 1) reveals that the nine  $\text{Co}^{\text{II}}$  atoms adopt a topology of two square pyramids

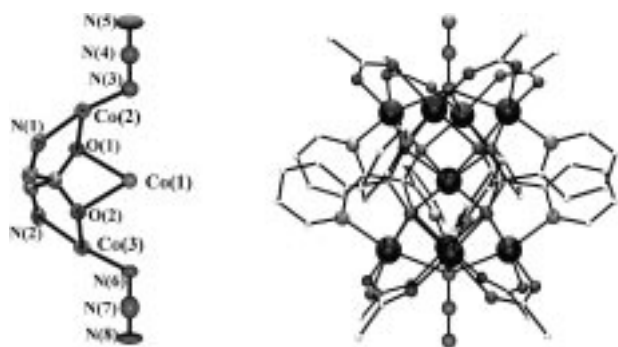
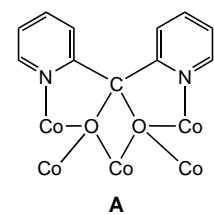
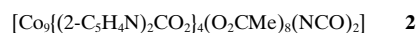


Figure 1. Left: Labeled asymmetric unit of **1**. Right: A view of cage **1**; the size of carbon atoms has been reduced for clarity and the solvate molecules are not shown. Selected bond lengths [Å] and angles [°]: Co(2)-N(3) 2.378(1), Co(3)-N(6) 2.362(1); Co(2)-N(3)-Co(2)' 83.06(6), 139.3(2)°, Co(3)-N(6)-Co(3)' 83.38(5), 140.3(2), O(1)-Co(1)-O(2) 75.85(4).

sharing a common apex (Co(1)). The oxygen atoms of the  $\mu_5:\eta^1:\eta^3:\eta^3:\eta^1$ -( $2\text{-C}_5\text{H}_4\text{N})_2\text{CO}_2^{2-}$  ligands (**A**) are placed in the center of the triangular faces of the pyramids, and bridge the central cobalt atom with two  $\text{Co}^{\text{II}}$  atoms of the base of each pyramid. A salient feature of the structure is the coordination number eight around Co(1), which is extremely rare in  $\text{Co}^{\text{II}}$  chemistry.<sup>[7]</sup> Each  $\text{Co} \cdots \text{Co}$  edge of the bases is further bridged by one *syn,syn*- $\mu_2:\eta^1:\eta^1$ -acetate group; each base is capped by one  $\mu_4$ -azido end-on ligand. The  $\text{MeCO}_2^-$  ligands create a concave cavity (the diameter of which is determined by the crown of the acetate ligands) on the base of each pyramid, into which the linear azido ligand is effectively trapped (Figure 2).



A similar reaction performed by using  $\text{NaOCN}$  instead of  $\text{NaN}_3$  allows easy isolation of the analogous cyanate cage **2**,



which has also been characterized by single-crystal X-ray crystallography.<sup>[6]</sup> Its structure is remarkably similar with the

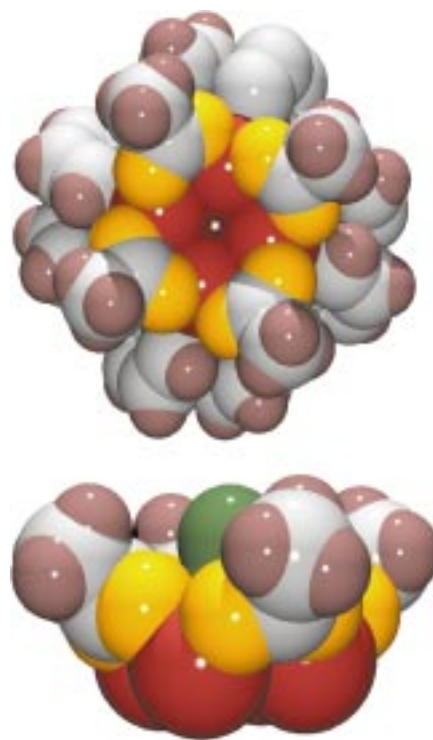


Figure 2. Axial view of the anion-trapping cavity (top) and a view showing one azide ligand in the cavity (bottom). Color code: Co: red, O: orange, N: green, C: gray, H: brown.

structure of **1** and contains  $\mu_4$  end-on (through the N atom) cyanate ligands.

As might be expected, the analogous nonanuclear clusters with angular monoanionic ligands, for example  $\text{NO}_2^-$ , or even with monoatomic but bigger anions such as  $\text{Cl}^-$  or  $\text{Br}^-$ , cannot be obtained. Our results indicate a good anion-trapping selectivity of the nonanuclear cage for small linear anions involving Lewis acid–base interactions. In fact, the  $\text{Co}_9^{\text{II}}$  cluster can be considered as a (preformed) host capable of accommodating external anionic ligands such as  $\text{N}_3^-$  and  $\text{OCN}^-$ .

For the azide ligand, the  $\mu_2$  coordination mode is common, while the  $\mu_3$  one is quite unusual.<sup>[8]</sup> For the cyanate ligand even the  $\mu_{1,1}$  end-on (through the N atom) coordination mode is rare. To the best of our knowledge, compounds **1** and **2** are unprecedented examples of  $\mu_4$  end-on coordination of pseudohalogeno ligands. They also extend the small number of structurally characterized polynuclear 3d metal complexes with mixed  $(2\text{-C}_5\text{H}_4\text{N})_2\text{CO}_2^{2-}/\text{RCO}_2^-$  ligation.<sup>[5, 9]</sup>

For complex **1** the product  $\chi_M T$  increases from  $23.38 \text{ cm}^3 \text{ K mol}^{-1}$  to a maximum of  $25.29 \text{ cm}^3 \text{ K mol}^{-1}$  at 16 K, and then decreases to  $19.73 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K, whereas on cooling,  $\chi_M T$  for **2** decreases continuously from 25.95 down to  $10.15 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K (Figure 3). The weak minimum  $\chi_M T$  at 116 K for **1** is the ferrimagnetic signature of the antiferromagnetic coupling between the central  $\text{Co}^{\text{II}}$  atom and the two ferromagnetically coupled squares in the bases of the cage. Magnetization measurements in the  $\pm 5 \text{ T}$  range of the external field do not show hysteresis, and ac measurements show neither an out-of-phase signal nor frequency dependence of the susceptibility, which excludes single-molecule magnet behavior for the two complexes. The strong aniso-

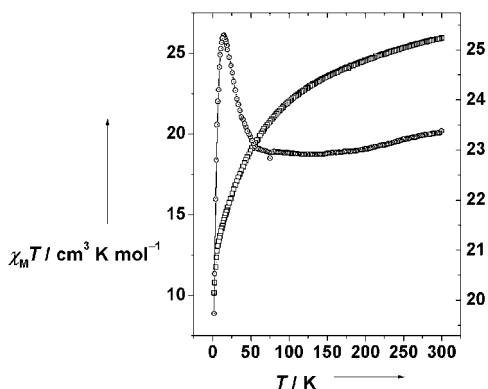
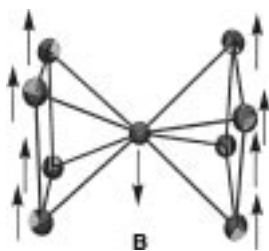


Figure 3. Plots of  $\chi_M T$  versus  $T$  for complexes **1** (right y axis, dot centered circles) and **2** (left y axis, open squares).

trophy of the  $\text{Co}^{\text{II}}$  ion does not permit us to quantify the magnitude of the coupling constants, but a qualitative approach to the interaction pattern may be deduced from the above data. Complex **2** shows an overall antiferromagnetic coupling, which may be associated to dominant antiferromagnetic coupling in the  $\text{Co}^{\text{II}}$  squares of the cage ( $\text{Co}_4$  partial  $S=0$ ) giving an  $S_T$  value equivalent to one isolated local spin. In contrast, the data for compound **1** should be associated to ferromagnetic coupling mediated by the  $\mu_4$ -azido bridges, giving an  $S_T$  value of seven times that of the local spins (assuming antiferromagnetic coupling between  $\text{Co}(1)$  and  $\text{Co}(2)$ , and between  $\text{Co}(1)$  and  $\text{Co}(3)$ ) and leading to a ferrimagnetic system **B**.



One of the main findings of this work is the experimental evidence that the end-on azide bridges introduce specifically ferromagnetic components in the superexchange scheme of a cage compound. The azide ligand in the end-on coordination mode is an effective bridging ligand which quasi-systematically affords ferromagnetic coupling between two, three, and now four metal ions for a large range of M-N-M bond angles.<sup>[10]</sup> Accordingly, the end-on azide ligand is a good substitute for hydroxo bridges in clusters to increase the  $S$  value of the ground state. However the most important result of this work is the novel coordination mode observed for  $\text{N}_3^-$  and  $\text{OCN}^-$ , which is induced by their effective trapping in the positively charged cavities of the  $\text{Co}_9$  cage.

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### Experimental Section

DMF (25 mL) was added to a mixture of  $\text{Co}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$  (0.15 g, 0.6 mmol),  $(2\text{-C}_3\text{H}_4\text{N})_2\text{CO}$  (0.06 g, 0.32 mmol), and  $\text{NaN}_3$  (0.02 g, 0.30 mmol). The solids dissolved on stirring under heating to give a dark blue solution, which was allowed to stand undisturbed at room temperature for 3 days. Well-formed, X-ray quality pink-red crystals of **1** appeared, which were isolated by filtration, washed with DMF and  $\text{Et}_2\text{O}$ , and dried in air. Yield 60%. A similar procedure was employed to isolate complex **2** using  $\text{NaOCN}$  instead of  $\text{NaN}_3$ . The two complexes gave satisfactory elemental analyses (C,H,N).

Magnetic susceptibility data were collected with a Quantum Design SQUID magnetometer in the temperature range 2–300 K. The output data

were corrected for the diamagnetism of the samples and the sample holder. Magnetization measurements were performed in the  $\pm 5$  T range of the magnetic field.

Received: August 3, 2000

Revised: November 29, 2000 [Z15576]

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