[1] R. R. Sinden, *DNA Structure and Function*, Academic Press, San Diego, **1994**.
[2] R. E. Dickerson, *Nucleic Acids Res.* **1998**, *26*, 1906–1926.
[3] B. C. Baguley, *Mol. Cell. Biochem.* **1982**, *43*, 167–181.
[4] W. A. Denny, *Anticancer Drug Des.* **1989**, *4*, 241–263.
[5] V. A. Bloomfield, *Biopolymers* **1991**, *31*, 1471–1481.
[6] M. Yuki, V. Grukhim, C. S. Lee, I. S. Haworth, *Arch. Biochem. Biophys.* **1996**, *325*, 39–46.
[7] J. E. Morgan, J. W. Blankenship, H. R. Matthews, *Biochemistry* **1987**, *26*, 3643–3649.
[8] S. E. Wellman, D. B. Sittman, J. B. Chaires, *Biochemistry* **1994**, *33*, 384–388.
[9] M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin, W. Errington, *Chem. Commun.* **1997**, 1807–1808.
[10] A. Rodger, K. J. Sanders, M. J. Hannon, I. Meistermann, A. Parkinson, D. S. Vidler, I. S. Haworth, *Chirality* **2000**, *12*, 221–236.
[11] A smaller *double*-helicate has been reported to bind to DNA but its mode of binding was not established. B. Schoentjes, J.-M. Lehn, *Helv. Chim. Acta* **1995**, *78*, 1–12.
[12] A. Rodger, B. Nordén, *Circular Dichroism and Linear Dichroism*, Oxford University Press, Oxford, **1997**.
[13] B. Nordén, M. Kubista, T. Kurucsev, *Q. Rev. Biophys.* **1992**, *25*, 51–170.
[14] P.-J. Chou, W. C. Johnson, *J. Am. Chem. Soc.* **1993**, *115*, 1205–1214.
[15] G. B. Onoa, G. Cervantes, V. Moreno, M. J. Prieto, *Nucleic Acids Res.* **1998**, *26*, 1473–1480.
[16] C. Hiort, B. Nordén, A. Rodger, *J. Am. Chem. Soc.* **1990**, *112*, 1971–1982.
[17] Z. Coggan, I. S. Haworth, P. J. Bates, A. Robinson, A. Rodger, *Inorg. Chem.* **1999**, *38*, 4486–4497.
[18] J. E. Coury, J. R. Anderson, L. McFail-Isom, L. D. Williams, L. A. Bottomley, *J. Am. Chem. Soc.* **1997**, *119*, 3792–3796.
[19] U.-M. Ohndorf, M. A. Rould, Q. He, C. O. Pabo, S. J. Lippard, *Nature* **1999**, *399*, 708–712.
[20] H. G. Hansma, K. J. Kim, D. E. Laney, R. A. Garcia, M. Argaman, M. J. Allen, S. M. Parsons, *J. Struct. Biol.* **1997**, *119*, 99–108.
[21] T. Simonson, M. Kubista, *Biopolymers* **1993**, *33*, 1225–1235.
[22] It should be noted that attempts to displace the ligand from DNA with ethidium bromide were unsuccessful indicating a binding constant in excess of $\sim 10^7\,\text{M}^{-1}$ under these conditions.
[23] The integrity of the metallo-cylindrical array and the maintenance of the Fe^{II} oxidation state are confirmed by both the NMR studies and the lack of perturbation to the visible chromophore (a metal to ligand charge transfer (MLCT) band in the UV/Vis spectrum).
[24] T. J. A. Ewing, I. D. Kuntz, *J. Comput. Chem.* **1997**, *18*, 1175–1189.
[25] M. Liu, X. Mao, C.Ye, H. Huang, J. K. Nicholson, J. C. Lindon, *J. Magn. Reson.* **1998**, *132*, 125–129.
[26] T.-L. Hwang, A. J. Shaka, *J. Magn. Reson. A* **1995**, *112*, 275–279.
[27] T. D. Goddard, D. G. Kneller, SPARKY3, University of California, San Francisco.
[28] A. Rodger, *Methods Enzymol.* **1993**, *226*, 232–258.

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

Giannis S. Papaefstathiou, Spyros P. Perlepes,
Albert Escuer,* Ramon Vicente, Mercé Font-Bardia,
and Xavier Solans

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[1] $\text{Mn}_9^{\text{II}}\text{Mo}_6^{\text{V}}$ cyano-bridged system and $S_T \approx 33/2$ for one of the clusters in a compound containing cocrystallized Fe_{17} and Fe_{19} species.[2] The large-spin ground state results from either ferromagnetic (or ferrimagnetic) exchange interactions between the paramagnetic centers and/or topologically frustrated antiferromagnetic interactions.[3] 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.[4] 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^-, OR^-, O^{2-}, or RCO_2^- 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.

---

[*] Dr. A. Escuer, Dr. R. Vicente
Departament de Química Inorgànica
Universitat de Barcelona
Av. Diagonal 647, 08028-Barcelona (Spain)
Fax: (+34) 93-4907725
E-mail: albert.escuer@qi.ub.es

G. S. Papaefstathiou, Prof. S. P. Perlepes
Department of Chemistry
University of Patras
GR-265 00 Patras (Greece)
Fax: (+30) 61-997118

M. Font-Bardia, Prof. X. Solans
Departament de Cristallografia i Mineralogia
Universitat de Barcelona
Marti Franqués s/n, 08028-Barcelona (Spain)

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

1433-7851/01/4005-0884 $ 17.50+.50/0

We have successfully applied a strategy to the antiferromagnetic cluster $[Co_9\{(2\text{-}C_5H_4N)_2CO_2\}_4(O_2CMe)_8(OH)_2]$ ($(2\text{-}C_5H_4N)_2CO_2^{2-}$ is the doubly deprotonated *gem*-diol form of di-2-pyridyl ketone, $(2\text{-}C_5H_4N)_2CO$),[5] in which, while maintaining the thermodynamically stable Co_9 cage skeleton, we have been able to modulate the superexchange pathway by substitution of the μ_4-hydroxides by unprecedented μ_4-azide or μ_4-cyanate ligands. The magnetic response changes from antiferromagnetic interactions for NCO^- to a ferrimagnetic high-spin anisotropic system in the N_3^- case.

Reaction of $Co(O_2CMe)_2 \cdot 4\,H_2O$ with $(2\text{-}C_5H_4N)_2CO$ and 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

$[Co_9\{(2\text{-}C_5H_4N)_2CO_2\}_4(O_2CMe)_8(N_3)_2] \cdot 4\,DMF \cdot 2.5\,H_2O$ **1**

X-ray crystal structure analysis[6] of **1** (Figure 1) reveals that the nine Co^{II} atoms adopt a topology of two square pyramids sharing a common apex (Co(1)). The oxygen atoms of the $\mu_5{:}\eta^1{:}\eta^3{:}\eta^3{:}\eta^1$-$(2\text{-}C_5H_4N)_2CO_2^{2-}$ ligands (**A**) are placed in the center of the triangular faces of the pyramids, and bridge the central cobalt atom with two Co^{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 Co^{II} chemistry.[7] Each Co ⋯ 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 μ_4-azido end-on ligand. The $MeCO_2^-$ 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).

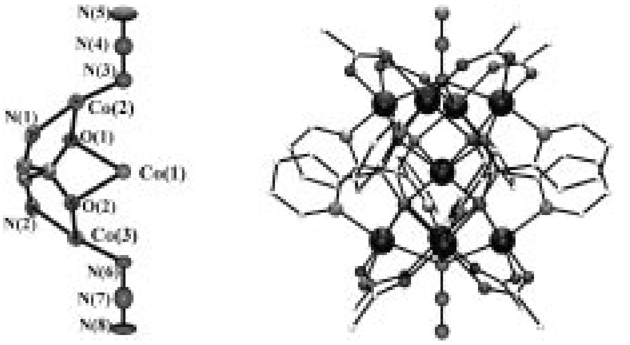
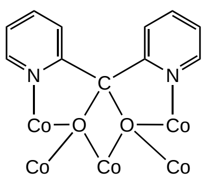


Figure 1. Left: Labeled asymmetric unit of **1**. Right: A view of cage **1**; the size of carbon atoms has been reduced for clarity and the solvate molecules are not shown. Selected bond lengths [Å] and angles [°]: Co(2)-N(3) 2.378(1), Co(3)-N(6) 2.362(1); Co(2)-N(3)-Co(2)′ 83.06(6), 139.3(2)°, Co(3)-N(6)-Co(3)′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



A

A similar reaction performed by using NaOCN instead of NaN_3 allows easy isolation of the analogous cyanate cage **2**,

$[Co_9\{(2\text{-}C_5H_4N)_2CO_2\}_4(O_2CMe)_8(NCO)_2]$ **2**

which has also been characterized by single-crystal X-ray crystallography.[6] Its structure is remarkably similar with the structure of **1** and contains μ_4 end-on (through the N atom) cyanate ligands.

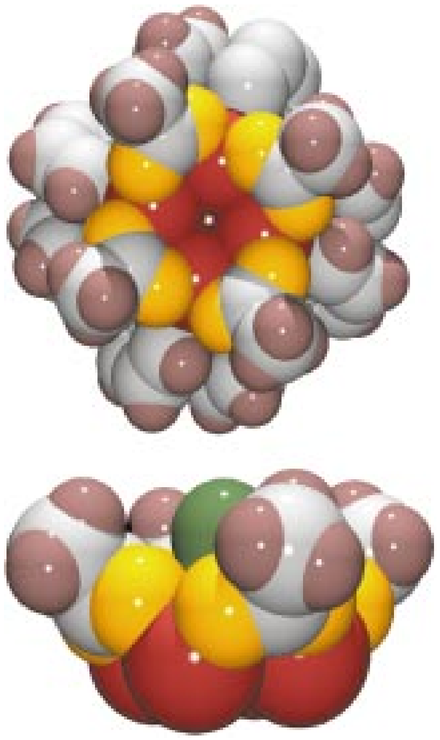


Figure 2. Axial view of the anion-trapping cavity (top) and a view showing one azide ligand in the cavity (bottom). Color code: Co: red, O: orange, N: green, C: gray, H: brown.

As might be expected, the analogous nonanuclear clusters with angular monoanionic ligands, for example NO_2^-, or even with monoatomic but bigger anions such as Cl^- or 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 Co_9^{II} cluster can be considered as a (preformed) host capable of accomodating external anionic ligands such as N_3^- and OCN^-.

For the azide ligand, the μ_2 coordination mode is common, while the μ_3 one is quite unusual.[8] 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 μ_4 end-on coordination of pseudohalogeno ligands. They also extend the small number of structurally characterized polynuclear 3d metal complexes with mixed $(2\text{-}C_5H_4N)_2CO_2^{2-}/RCO_2^-$ ligation.[5, 9]

For complex **1** the product $\chi_M T$ increases from $23.38\,cm^3\,K\,mol^{-1}$ to a maximum of $25.29\,cm^3\,K\,mol^{-1}$ at 16 K, and then decreases to $19.73\,cm^3\,K\,mol^{-1}$ at 2 K, whereas on cooling, $\chi_M T$ for **2** decreases continuously from 25.95 down to $10.15\,cm^3\,K\,mol^{-1}$ 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 Co^{II} atom and the two ferromagnetically coupled squares in the bases of the cage. Magnetization measurements in the ±5 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-

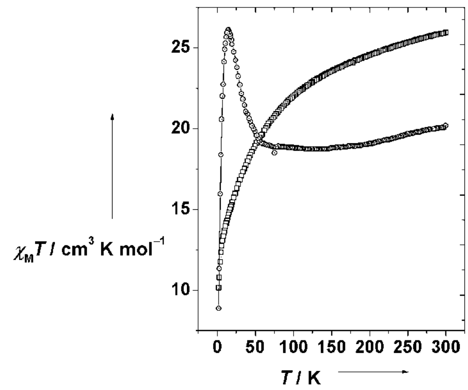
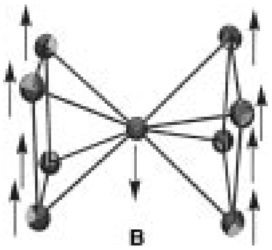


Figure 3. Plots of $\chi_M T$ versus T for complexes **1** (right y axis, dot centered circles) and **2** (left y axis, open squares).

tropy of the Co^{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 Co^{II} squares of the cage (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 μ_4-azido bridges, giving an S_T value of seven times that of the local spins (assuming antiferromagnetic coupling between Co(1) and Co(2), and between Co(1) and Co(3)) and leading to a ferrimagnetic system **B**.



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.[10] 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 N_3^- and OCN$^-$, which is induced by their effective trapping in the positively charged cavities of the Co$_9$ cage.

Experimental Section

DMF (25 mL) was added to a mixture of Co(O$_2$CMe)$_2\cdot$4H$_2$O (0.15 g, 0.6 mmol), (2-C$_5$H$_4$N)$_2$CO (0.06 g, 0.32 mmol), and NaN$_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 Et$_2$O, and dried in air. Yield 60%. A similar procedure was employed to isolate complex **2** using NaOCN instead of 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 ±5 T range of the magnetic field.

Received: August 3, 2000
Revised: November 29, 2000 [Z15576]

---

[1] J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem.* **2000**, *112*, 1579; *Angew. Chem. Int. Ed.* **2000**, *39*, 1605.

[2] A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo, F. Pieralli, *J. Am. Chem. Soc.* **1995**, *117*, 2491.

[3] G. Aromi, J.-P. Claude, M. J. Knapp, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1998**, *120*, 2977.

[4] a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141; b) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, *383*, 145; c) S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, D. N. Hedrickson, *J. Am. Chem. Soc.* **1996**, *118*, 7746; d) D. Gatteschi, R. Sessoli, A. Cornia, *Chem. Commun.* **2000**, 725; R. E. P. Winpenny, *Comments Inorg. Chem.* **1999**, *20*, 283.

[5] A. Tsohos, S. Dionyssopoulou, C. P. Raptopoulou, A. Terzis, E. G. Bakalbassis, S. P. Perlepes, *Angew. Chem.* **1999**, *111*, 1036; *Angew. Chem. Int. Ed.* **1999**, *38*, 983.

[6] Crystal data for **1**: C$_{72}$H$_{89}$Co$_9$N$_{18}$O$_{30.5}$, crystal dimensions 0.10 × 0.10 × 0.20 mm, tetragonal, space group $P4/n$, $a = b = 17.762(1)$, $c = 14.203(1)$ Å, $V = 4480.9(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.652$ g cm^{-3}, $2\theta_{max} = 31.55°$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71069$ Å, $T = 298$ K, 18191 measured reflections, 4761 independent reflections ($R_{int} = 0.0531$). Lorentz polarization and absorption corrections were applied, $\mu = 1.710$ mm^{-1}, 300 parameters refined, $R1 = 0.0365$ (for 2950 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1037$ (on $|F^2|$). Max./min. residual peaks in the final difference map 0.442/ -0.345 e Å^{-3}. Crystals of **1** were mounted in air. The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were computed and refined with an isotropic temperature factor equal to 1.2 times the equivalent isotropic temperature factor of the atom to which they are linked and by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147542. 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). Compound **2** crystallizes in the same $P4/n$ space group. Cell parameters: $a = b = 17.887(8)$, $c = 13.964(3)$ Å, measured on single crystals; full crystallographic data for this compound will appear in a subsequent full paper.

[7] a) W. O. Koch, J. T. Kaiser, H.-J. Krüger, *Chem. Commun.* **1997**, 2237; b) J. G. Bergman, F. A. Cotton, *Inorg. Chem.* **1966**, *5*, 1208.

[8] M. A. S. Goher, J. Cano, Y. Journaux, M. A. M. Abu-Youssef, F. A. Mautner, A. Escuer, R. Vicente, *Chem. Eur. J.* **2000**, *6*, 778.

[9] a) V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes, A. Terzis, *Angew. Chem.* **1997**, *109*, 1165; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1083; b) N. Lalioti, C. P. Raptopoulou, A. Terzis, A. E. Aliev, I. P. Gerothanassis, E. Manessi-Zoupa, S. P. Perlepes, unpublished results.

[10] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–5*, 1027.