ChemComm

Ferromagnetic interactions in the first *dicubane-type* complex involving cyanate ligand: $[Co_4(dpk\text{-}OH)_2(dpk\text{-}OMe)_2(NCO)_4]$

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Received (in Cambridge, UK) 12th October 2000, Accepted 14th November 2000
First published as an Advance Article on the web 15th December 2000

The ligands cyanate and di-2-pyridyl ketone (dpk) are used to construct a tetranuclear cobalt(II) complex involving $\mu_{1,1}$-cyanate bridges: $[Co_4(dpk\text{-}OH)_2(dpk\text{-}OMe)_2(NCO)_4]$, which shows a dicubane-type structure, with two missing vertices, and having ferromagnetic interactions.

A considerable ongoing research has been directed at the preparation of molecule-based magnets over recent years. In this area, great activity has been focused on obtaining nanoscale magnets in which each microcrystal behaves as a single domain. A way to deal with the preparation of nanomagnets concerns single molecules having ground electronic states with a large number of unpaired electrons.[1] In relation to the ligands for the preparation of those clusters, a variety of blocking organic compounds has been used, most of them providing oxo-bridges between metallic centers.[2]

An efficient way for the generation of interactions between metallic centers concerns the use of pseudohalide ligands. Among these, azide has been undoubtedly one of the most interesting magnetic coupling species found so far in molecular magnetism.[3] One of the latest findings found for this ligand is its incorporation into *cubane-type* systems and those exhibiting $\mu_{1,1}$-azido bridges have been observed to be ferromagnetic.[4] The cyanate pseudohalide is a more unusual ligand, its chemistry and bonding properties have been the subject of several studies[5] which focussed upon its ability to coordinate to metals, and its ability and adaptability as a bridging ligand.[6] It shows preference for the end-on bridging mode, through the nitrogen atom. In this kind of bridging, the cyanate ligand has been shown to be able to mediate ferromagnetic interactions.[7]

As mentioned above, in most of the clusters for nanomagnets, the intermetallic connections take place through oxo-bridges. In this way, the coordination behavior of di-2-pyridyl ketone (dpk) as a ligand has also attracted much attention.[8] Its hydrolyzed derivatives, namely, the *gem*-diol[9] and its respective mono- and di-anions, are potential chelating or chelating-bridging ligands. In fact, a number of mononuclear[10] and oligomeric polynuclear[11] complexes derived from these ligands have been isolated and crystallographically characterized. Solvolysis reactions are also observed to occur in contact with other solvents thus widening the possibilities in structural arrangement.

For the indicated reasons above, the simultaneous use of dpk and cyanate ligands could be expected to enhance the formation of intermetallic bridges. Thus, taking into account these considerations, this work reports on a ferromagnetic tetranuclear cobalt(II) system of formula $[Co_2(dpkOH)(dpkOMe)(NCO)_2]_2$, the structural core of which can be described as that of a 'dicubane' having two missing vertices. Very few examples of cobalt(II) dicubanes are known[12] and no cobalt–$\mu_{1,1}$-cyanate polynuclear compound has been characterized structurally and magnetically to date. Furthermore, as far as we are aware, this is the first example of a 'cubane-type' system involving cyanate ligands.

Reaction of dpk, $Co(NO_3)_2\cdot 4H_2O$ and KNCO yielded,† after evaporation, a brown-red crystalline material, the composition of which was consistent with the formula $[Co_2(C_{23}H_{20}N_4O_4)(NCO)_2]$ **1**. The X-ray crystal structure determination of **1** (Fig. 1)‡ revealed that it consists of centrosymmetric tetranuclear units in which the cobalt(II) ions are connected through the ligands NCO, dpkOH, and dpkOMe (the latter tworesulting from solvolysis of the dpk ligand) to give a face-shared dicubane-like coordination core containing two missing vertices (Fig. 1).

The Co(II) ions exhibit slightly distorted octahedral $[CoN_3O_3]$ and $[CoN_4O_2]$ environments, with the Co–N distances ranging from 2.024(6) (dpk) to 2.146(4) Å (cyanate) and the Co–O distances ranging from 2.025(3) to 2.244(3). The EO cyanate bridges form an angle with the metal of 101.8(2)°, while the Co–O–Co angles range from 97.1(1) to 100.6(2)°. The Co···Co distance through the combined cyanate and oxo bridges is 3.283(2) Å, while those corresponding to the oxo-bridges alone are 3.144(1) and 3.238(2) Å.

The temperature dependence of the magnetic susceptibility χ_m of **1** has been investigated in the range 4–300 K. The product $\chi_m T$ continuously increases upon cooling and its value, per 4 Co atoms, at room temperature is 11.7 cm^3 K mol^{-1}, which is larger than the 7.5 cm^3 K mol^{-1} expected for four isolated spin-only $S = 3/2$ ions. This larger value is the result of contributions to the susceptibility from orbital angular momentum at high temperatures, which produces effective moments per cobalt atom in the range 4.7–5.2 μ_B.[13] A maximum of 18.3 cm^3 K mol^{-1} appears at 12 K. After this maximum, $\chi_m T$ decreases [Fig. 2(a)]. This behavior is characteristic of a system exhibiting intramolecular ferromagnetic interactions; while the sudden decrease must be associated to spin–orbit coupling and/or the existence of intermolecular interactions. It is not possible to fit the behavior of an array of four high-spin Co^{II} centers given current theory, even if the centers are orbitally degenerate. Besides, in the present compound the environment of the Co(II) centers which are in distorted octahedra, probably removes the degenereracy. Taking into account that, even for the simplest of the possible Co(II) tetranuclear systems (*i.e.* a square planar cluster with a single J value[14]), fitting has not been carried out, the extreme difficulty of modeling a four-J system (see Scheme 1) for this cation that should include aspects such as spin–orbit coupling, magnetic anisotropy, orbital degeneracy, *etc*, should be appreciated.

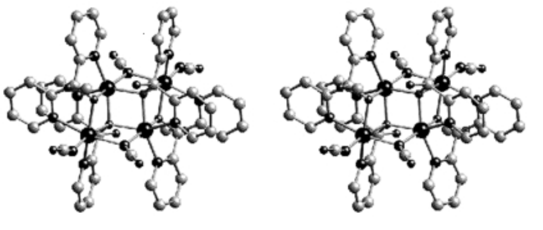


Fig. 1 Stereoview of the tetranuclear structure of compound **1**. Sizes of spheres is in the order Mn > C > N > O. Hydrogen atoms have been omitted for clarity.

DOI: 10.1039/b008256m

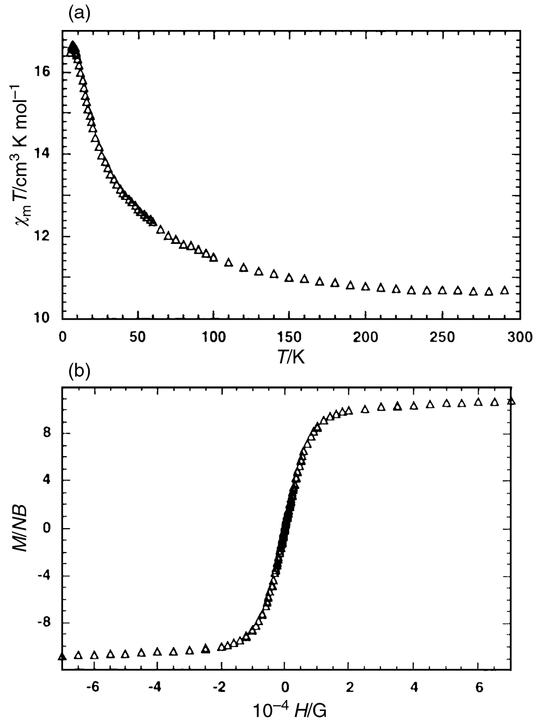
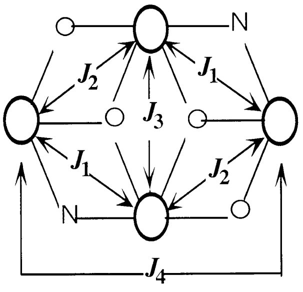


Fig. 2 (a) Thermal variation of $\chi_m T$ for **1**, per tetranuclear unit. (b) Representation of the magnetization *vs.* magnetic field at 5 K.



Scheme 1

In order to gain more information on **1**, we investigated the variation of the magnetization *M vs.* the applied magnetic field *H*, in the field range 0 < *H*/T < 7 at 5 K and results are shown in Fig. 2(b), where it can be observed that the magnetization reaches the saturation value expected for a tetranuclear ferromagnetic cobalt(II) compound, *i.e.* $N\beta g/2$ (≈ 12). Further studies are being undertaken to thoroughly characterize this system.

The ferromagnetic behavior of this compound can be explained by the existence of *end-on* cyanate bridges, with angles close to 100°, which gives rise to moderately strong ferromagnetic interactions.[7] In addition, the oxo bridges in the compound also promote ferromagnetic interactions, as has been observed in related cubane oxo-bridged compounds.[11b]

In conclusion, the combination of dpk and cyanate ligands has been shown to be a good strategy for obtaining 'cubane-like' systems and related nickel, cobalt and manganese systems are now under investigation. The resulting compound **1** shows a tetranuclear molecular structure of dicubane type which is unprecedented for cyanate ligand. The bridging ligands connecting the cobalt(II) ions provide global ferromagnetic exchange interactions.

Fundings by the Basque Government (grant PI 99/53), the University of the Basque Country (grant UPV 130310-EB201/1998), and the Dirección General de Enseñanza Superior-MEC (Spain) (grant PB97-0637) are gratefully acknowledged. Z. E. S. thanks the University of the Basque Country for a doctoral fellowship.

Notes and references

† *Experimental procedure*: reaction of a methanolic solution (10 cm³) containing dpk (1 mmol) with a aqueous solution (10 cm³) containing both $Co(NO_3)_2 \cdot 4H_2O$ (1 mmol) and KNCO (1 mmol) yielded, after two weeks evaporation, a brown crystalline material **1**. Yield 63%. Elemental analysis. Calc. for $C_{25}H_{20}N_6O_6Co_2$: C, 48.56; H, 3.26; N, 13.59; Co, 19.06. Found: C, 48.13; H, 3.15; N, 13.22; Co, 19.06%.

‡ *Crystal data*: $C_{25}H_{20}N_6O_6Co_2$, M = 618.33, monoclinic, space group $P2_1/c$ (no. 14), a = 13.039(1), b = 12.303(1), c = 19.365(1) Å, β = 122.57(1)°, V = 2618.0(4) Å³, Z = 4, D_c = 1.569 g cm⁻³, $2\theta_{max}$ = 60°, T = 293 K, ω–2θ scans; Lorentzian, polarization, and extinction corrections were made, μ(Mo-Kα) = 13.2 cm⁻¹, 14672 reflections measured, 6653 unique (R_{int} = 0.1483) all included in the refinement; structure solution by direct methods; 353 parameters refined $R1(F_o)$ = 0.058 [for 6653 reflections with $I > 2\sigma(I)$]; $wR2(F_o^2)$ = 0.098 (all data); quality of fit 0.80. Max./min. residual peaks in the final difference map 0.531/−0.605 e Å⁻³. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods and refined with SHELXL-97.[14] All non-H atoms were refined anisotropically. CCDC 182/1849. See http://www.rsc.org/suppdata/cc/b0/b008256m/ for crystallographic files in .cif format.

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