Dicubane-like Tetrameric Cobalt(II)−Pseudohalide Ferromagnetic Clusters

Zurine E. Serna,[†] M. Karmele Urtiaga,[‡] M. Gotzone Barandika,[#] Roberto Cortés,*[,#]
Susana Martin,[#] Luis Lezama,[†] M. Isabel Arriortua,[‡] and Teófilo Rojo*[,†,§]

Departamento de Química Inorgánica and Departamento de Mineralogía y Petrología, Facultad de
Ciencias, Universidad del País Vasco (UPV./EHU), Apdo. 644, 48080 Bilbao, Spain, and
Departamento de Química Inorgánica, Facultad de Farmacia, Universidad del País Vasco (UPV./EHU),
Apdo. 450, 01080 Vitoria, Spain

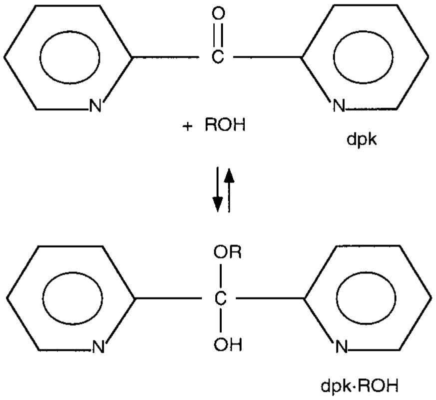
Received November 29, 2000

Three tetrameric cobalt(II)−pseudohalide complexes have been structurally and magnetically characterized. Compounds **1** and **2** are isomorphous and exhibit the general formula $[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(L)(H_2O)]_2A_2{\cdot}4H_2O$ where dpk = di-2-pyridyl ketone, L = N_3^- and A = BF_4^- for **1**, and L = NCO^- and A = ClO_4^- for **2**. The ligands $dpk{\cdot}OH^-$ and $dpk{\cdot}CH_3O^-$ result from solvolysis and ulterior deprotonation of dpk in water and methanol, respectively. Both compounds exhibit cationic tetramers consisting of a dicubane-like core with two missing vertexes where the Co(II) ions are connected through *end-on* pseudohalide and oxo-bridges. A similar tetranuclear core has been found for **3** whose formula is $[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(NCO)_2]_2$. In this case, the tetramers are neutral and exhibit a terminal cyanate in place of the coordinated molecule of water for **1** and **2**. The tetrameric units for **2** and **3** represent the first examples of any kind of cubanes exhibiting cyanate bridges as well as the first Co(II) compounds exhibiting intermetallic bridges through these pseudohalide groups. Measurements of the magnetic susceptibility indicated the presence of ferromagnetic $Co^{II}-Co^{II}$ interactions in the three compounds.

Introduction

Over the last few years, the preparation of clusters for single-molecule magnets has been the focus of attention of various works in coordination chemistry. In this context, di-2-pyridylketone (dpk) can be considered a good candidate for an organic ligand. Thus, dpk easily gets accommodated to the coordination sphere by chelating in different ways.[1] In fact, dpk can coordinate as a ketone or as a derivative from solvolysis both as a neutral ligand or as an anionic one (Scheme 1). In this way, the presence of four potential donors in the dpk derivatives provides a great efficiency in congregating metallic ions to form clusters.[2−4] For instance, Tsohos et al.[2] have reported a nonanuclear Co(II) specimen where each dpk derivative is chelated to five metallic cations.

Scheme 1



Following the well-known strategy of combining the use of *N,N′*-type organic blockers with magnetic couplers such as azide, cyanate, or thiocyanate to obtain extended systems, we have been investigating on the simultaneous use of dpk with these pseudohalides. We have already prepared various dpk−

---

* To whom correspondence should be addressed.

[§] Fax: 00 34 944648500. E-mail: QIPROAPT@lg.ehu.es.

[†] Departamento de Química Inorgánica, Facultad de Ciencias.

[‡] Departamento de Mineralogía y Petrología.

[#] Departamento de Química Inorgánica, Facultad de Farmacia.

(1) (a) Deveson, A. C.; Heath, S. L.; Harding, C. J.; Powell, A. K. *J. Chem. Soc., Dalton Trans.* **1996**, 3173. (b) Basu, A.; Kasar, T. G.; Sapre, N. Y. *Inorg. Chem.* **1988**, *27*, 4539. (c) Papadopoulos, A. N.; Tangoulis, V.; Raptopoulou, C. P.; Terzis, A.; Kessissoglou, D. P. *Inorg. Chem.* **1996**, *35*, 559. (d) Tong, M. L.; Lee, H. K.; Zheng, S. L.; Chen, X. M. *Chem. Lett.* **1999**, 1087. (e) Sommerer, O. S.; Jensen, W. P.; Jacobson, R. A. *Inorg. Chim. Acta* **1990**, *172*, 3. (f) Alonzo, G.; Bertazzi, N.; Maggio, F.; Benetollo, F.; Bombieri, G. *Polyhedron* **1996**, *15*, 4269. (g) Wang, S. L.; Richardson, J. W.; Brigg, S. J.; Jacobson, R. A.; Jensen, W. P. *Inorg. Chim. Acta* **1986**, *111*, 67. (h) Kavounis, C. A.; Tsiamis, C.; Cardin, C. J.; Zubavichus, Y. *Polyhedron* **1996**, *15*, 385. (i) Serna, Z.; Barandika, M. G.; Cortés, R.; Urtiaga, M. K.; Arriortua, M. I. *Polyhedron* **1998**, *18*, 249. (j) Ferreira, A. D. Q.; Bino, A.; Gibson, D. *Inorg. Chim. Acta* **1997**, *265*, 155. (k) Sommerer, S. O.; Westcott, B. L.; Jircitano, A. J.; Abboud, K. A. *Acta Crystallogr.* **1996**, *C52*, 1426. (l) Breeze, S. R.; Wang, S. N.; Greedan, J. E.; Raju, N. P. *Inorg. Chem.* **1996**, *35*, 6944. (m) Goher, M. A. S.; Mautner, F. A. *Polyhedron* **2000**, *19*, 601.

(2) Tshosos, A.; Dionyssopoulou, S.; Raptopoulou, C. P.; Terzis, A.; Bakalbassis, E. G.; Perlepes, S. P. *Angew. Chem., Int. Ed.* **1999**, *38*, 983.

(3) (a) Serna, Z.; Barandika, M. G.; Cortés, R.; Urtiaga, M. K.; Barberis, G. E.; Rojo T. *J. Chem. Soc., Dalton Trans.* **2000**, 29. (b) Serna, Z.; Lezama, L.; Urtiaga, M. K.; Arriortua, M. I.; Barandika, M. G.; Cortés, R.; Rojo, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 344. (c) Unpublished results.

(4) (a) Tangoulis, V.; Raptopoulou, C. P.; Paschalidou, S.; Bakalbassis, E. G.; Perlepes, S. P.; Terzis, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1083. (b) Tangoulis, V.; Raptopoulou, C. P.; Terzis, A.; Paschalidou, S.; Perlepes, S. P.; Bakalbassis, E. G *Inorg. Chem.* **1997**, *36*, 3966. (c) Tangoulis, V.; Raptopoulou, C. P.; Paschalidou, S.; Tsohos, A. E.; Bakalbassis, E. G.; Terzis, A.; Perlepes, S. P. *Inorg. Chem.* **1997**, *36*, 5270.

10.1021/ic0013476 CCC: $20.00

pseudohalide polynuclear arrays with Ni(II) and Cu(II). It is worth mentioning that all the Ni^{II}−dpk−azide compounds characterized[3] are isomorphous and consist of ferromagnetic tetramers where the four metallic ions are disposed in a dicubane core that is common for all the compounds. This uniformity in structural arrangements does not exist for Cu^{II}−dpk−pseudohalide systems. Instead, a variety of arrangements has been found for these systems, including extended polymers.[5]

Our further research in this area has been devoted to Co(II) systems. Thus, in this work, we report on the synthesis and magnetostructural characterization of three Co(II) compounds. Two of them exhibit the general formula $[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(L)(H_2O)]_2(A)_2{\cdot}4H_2O$ (where L = N_3, A = BF_4 for **1**; L = NCO and A = ClO_4 for **2**) while the third tetramer shows the formula $[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(NCO)_2]_2$ (**3**). Obviously, the anionic ligands dpk·OH and dpk·CH_3O are the products of solvolysis, in water and methanol, respectively, and ulterior deprotonation of the original dpk. The three compounds exhibit tetrameric units consisting in dicubane cores with two missing vertexes. It should be pointed out that these compounds join the very scarce family of Co(II) dicubanes characterized so far.[6] However, the main novelty of compounds **2** and **3** lies on the following. These polynuclear compounds represent the very first examples of any kind of cubanes exhibiting cyanate bridges as well as the first Co(II) compounds, structurally characterized, exhibiting this type of pseudohalide bridges.[7]

Experimental Section

Caution! Azide and perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared and it should be handled with caution.

Synthesis. $[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(N_3)(H_2O)]_2(BF_4)_2{\cdot}4H_2O$ (**1**) was synthesized by slow addition of a methanolic solution (10 mL) containing dpk ligand (1 mmol) to an aqueous solution (10 mL) containing $CoCl_2{\cdot}6H_2O$ (1 mmol) and NaN_3 (0.5 mmol). The reaction was carried out under continuous stirring at 45 °C. Afterward, an aqueous solution of $NaBF_4$ (0.5 mmol) was added. The resulting solution was stirred for several hours, filtered, and left to stand. Pink prismatic crystals appeared after several days. Yield: 41% (based on cobalt). Elemental Analysis ($Co_2C_{23}H_{26}N_7BF_4O_7$, 717.18) Calcd (Found): Co, 16.4 (16.1); N, 13.7 (14.1); C, 38.5 (38.3); H, 3.6 (3.5)%.

Synthesis of $[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(NCO)(H_2O)]_2(ClO_4)_2{\cdot}4H_2O$ (**2**) was similar with the difference of the addition of KNCO (1 mmol) in place of NaN_3 and $KClO_4$ (0.5 mmol), in place of $NaBF_4$. After the addition of $KClO_4$, a pink precipitate is obtained. Further attempts to recrystallize this precipitate were unfruitful. Yield: 63% (based on cobalt). Elemental Analysis ($Co_2C_{24}H_{26}N_5ClO_{12}$, 729.8) Calcd (Found): Co, 15.9 (14.0); N, 14.2 (14.6); C, 42.5 (41.7); H, 3.1 (3.2)%.

$[Co_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(NCO)_2]_2$ (**3**)[8] was synthesized by slow addition of a methanolic solution (10 mL) containing dpk ligand (1 mmol) to an aqueous solution (10 mL) containing $CoCl_2{\cdot}6H_2O$ (1 mmol) and KNCO (1 mmol). The reaction was carried out under continuous stirring at 45 °C. Pink prismatic crystals appeared after several days. Yield: 35% (based on cobalt). Elemental Analysis ($Co_2C_{25}H_{20}N_6O$, 618.33) Calcd (Found): Co, 16.4 (16.1); N, 15.6 (15.6); C, 50.4 (50.6); H, 2.9 (3.0)%.

Table 1. Selected IR Bands (cm^{-1}) for Free dpk and Compounds **1**−**3**, Together with Their Assignments

	free dpk	compound **1**	compound **2**	compound **3**
azide, υ_{as}		2059 split		
cyanate, υ(C-N)			2177 split	2179 split
diol, υ(CO)	1680	1602	1602	1605
pyridyl ring stretching	1578	1438	1471	421
pyridyl ring breathing	998	1020	1064	1068
pyridyl C−H out of plane bending	753	777	777	760
BF_4, υ_3		1062		
BF_4, υ_4		662		
ClO_4, υ_3			1064	
ClO_4, υ_4			682	
H_2O_{cryst}		3500	3470	

IR Spectroscopy. A summary of the most important IR bands corresponding to compounds **1**−**3** together with their tentative assignment are given in Table 1. As can be seen, the three compounds exhibit a split absorption at about 2125 cm^{-1} that corresponds to the asymmetric stretching mode of bridging azide (**1**) and cyanate (**2** and **3**).

In relation to the absorptions caused by the organic ligand, it is worth mentioning that the band at 1680 cm^{-1} attributed to the C═O bond in conjugation with the pyridyl rings in dpk is shifted to lower frequencies in **1**−**3** as corresponds to single C−O bond after solvolysis. The bands attributed to the pyridyl ring stretching are also remarkably shifted in **1**−**3** in relation to the free dpk due to the loss of coplanarity between pyridil rings after rehybridation of the ketocarbonyl group from sp^2 to sp^3.

The IR spectra also show the bands attributed to the crystallization molecules of water and the counteranions BF_4^- (**1**) and ClO_4^- (**2**).

UV−Vis Diffuse Reflectance. The three compounds exhibit similar UV−vis diffuse reflectance spectra. In fact, compounds **1** and **2** are not distinguishable by this technique. The three of them show two main absorptions that have been attributed to the spin allowed transitions from $^4T_{1g}$ to $^4T_{2g}$ (ν_1) and $^4T_{1g}(P)$ (ν_2), respectively. Additionally, in the three cases there is a third absorption that appears as a shoulder of the second transition corresponding to the spin allowed transitions from $^4T_{1g}$ to $^4A_{2g}$ (ν_3). Compounds **1** and **2** (ν [cm^{-1}]): 8500 (ν_1), 15 600 (ν_2), 20 400 (ν_3), $D_q = 750$ cm^{-1}, $B = 857$ cm^{-1}. Compound **3** (ν [cm^{-1}]): 8300 (ν_1), 15 900 (ν_2), 20 400 (ν_3), $D_q = 710$ cm^{-1}, $B = 918$ cm^{-1}.

The values of D_q and B which have been estimated from these transitions are typical for high-spin Co(II) complexes. The values of B are indicative of 88% and 94% covalency of the Co bonds **1** (and **2**) and **3**, respectively.

Physical Measurements. Microanalyses were performed with a LECO CHNS-932 analyzer. Analytical measurements were carried out in an ARL 3410 + ICP with a Minitorch equipment. IR spectroscopy was performed on a Nicolet 520 FTIR spectrophotometer in the 400−4000 cm^{-1} region. Diffuse reflectance spectra were registered at room temperature on a CARY 2415 spectrometer in the 5000−45000 cm^{-1} region. Magnetic susceptibilities and magnetization of powdered samples were carried out in the temperature range 5−300 K at values of the magnetic field up to 10 000 G, using a Quantum Design Squid magnetometer, equipped with a helium continuous-flow cryostat. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal tables).

X-ray Crystallography. Single-crystal X-ray measurements for compounds **1** and **3** were taken at room temperature on an STOE IPDS (Imaging Plate Diffraction System). Corrections for Lorentz and polarization factors were applied to the intensity values. The structures were solved by heavy-atoms Patterson methods using the program SHELXS97[9] and refined by a full-matrix least-squares procedure on F^2 using SHELXL97.[10] Non-hydrogen atomic scattering factors were taken from International Tables of X-ray Crystallography.[11] Owing to

---

(5) (a) Serna, Z. E.; Cortés, R.; Urtiaga, M. K.; Barandika, M. G.; Lezama, L.; Arriortua, M. I.; Rojo, T. *Eur. J. Inorg. Chem*., in press (b) Unpublished results.

(6) (a) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439. (b) Bertrand, J. A.; Fujita, E.; VanDerVeer, D. G. *Inorg. Chem.* **1979**, *18*, 230. (c) Coronado, E.; Gómez-García, C. J. *Comments Inorg. Chem.* **1995**, *17*, 255 (and refs 11 to 15 therein). (d) Clemente-Juan, J. M.; Coronado, E. *Coord. Chem. Rev.* 1999, 193−195, 361 (and refs 14−19 therein)

(7) Drew, M. G. B.; Harding, C. J.; Nelson, J. *Inorg. Chim. Acta*, **1996**, *246*, 73−79. A Co(II) compound exhibiting cyanate bridges is mentioned in this paper but no structural characterization has been carried out.

(8) Barandika, M. G.; Serna, Z.; Cortés, R.; Lezama, L.; Urtiaga, M. K.; Arriortua, M. I.; Rojo, T. *Chem. Commun.* **2001**, 45.

Table 2. Crystal Data and Structure Refinement for **1** and **3**

	1	**3**
formula	$Co_2C_{23}H_{26}N_7BF_4O_7$	$Co_2C_{25}H_{20}N_6O_6$
fw	717.18	618.33
space group	$P2_1/c$	$P2_1/c$
a, Å	13.537(3)	13.039(1)
b, Å	11.077(2)	12.303(1)
c, Å	19.941(7)	19.365(1)
β, deg	90.19(3)	122.575(9)
V, Å^3	2990(1)	2618.0(4)
Z	4	4
ρ_{cald}, g·cm^{-3}	1.593	1.569
μ(M*o* Kα), mm^{-1}	1.188	1.319
T, °C	20(2)	20(2)
λ (Mo Kα), Å	0.71070	0.71070
R1[a]	0.0634	0.0581
wR2[b]	0.1559	0.0981

[a] $R1\ (F_o) = (\sum||F_o| - |F_c||)/(\sum |F_o|)$ [b] $wR2\ (F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Table 3. Crystallographic Data for **2**

formula	$Co_2C_{24}H_{26}N_5ClO_{12}$	*V*, Å^3	3002(3)
fw	729.8	*Z*	4
space group	$P2_1/c$	*T*, °C	20
a, Å	13.572(1)	*λ*(Mo Kα), Å	1.54
b, Å	11.111(1)	R_b[a]	4.47
c, Å	19.915(2)	R_p[b]	7.85
β, deg	91.227(7)	R_{wp}[c]	10.1

[a] $R_b = 100[\sum|I_o - I_c|]/\sum|I_o|$. [b] $R_p = 100[\sum|y_o - y_c|]/\sum|y_o|$. [c] $R_{wp} = [\sum[w|y_o - y_c|^2]/\sum[w|y_o|^2]]^{1/2}$.

the large number of faces shown by the crystals, no ideal method could have been used for absorption corrections and the program DIFABS[12] was applied. In Table 2, crystallographic data and processing parameters for compounds **1** and **3** are shown.

X-ray powder diffraction data for compound **2** were collected on a PHILIPS X′PERT powder diffractometer with Cu Kα radiation in steps of 0.02° (2*θ*) over the 5−60° (2*θ*) angular range and a fixed-time counting of 4 s at 25 °C. The powder diffraction patterns were indexed with the FULLPROF[13] program based on the Rietveld method[14,15] using the *Profile Matching* option. Crystallographic data and processing parameters for compound **2** are given in Table 3.

Results and Discussion

Description of the Structures. Compound **1** consists of tetrameric cationic units where two *end-on* azides, two *N,O,N′*-chelating dpk·OH, two *N,O,N′*-chelating dpk·CH_3O, and two water molecules can be found (Figure 1). As mentioned above, dpk·OH and dpk·CH_3O are the anionic products resulting from solvolysis (with water and methanol, respectively) and ulterior deprotonation of the original dpk. There are also two BF_4^- counteranions and four molecules of crystallization water per tetrameric unit in the lattice. The four Co(II) cations are octahedrally coordinated.

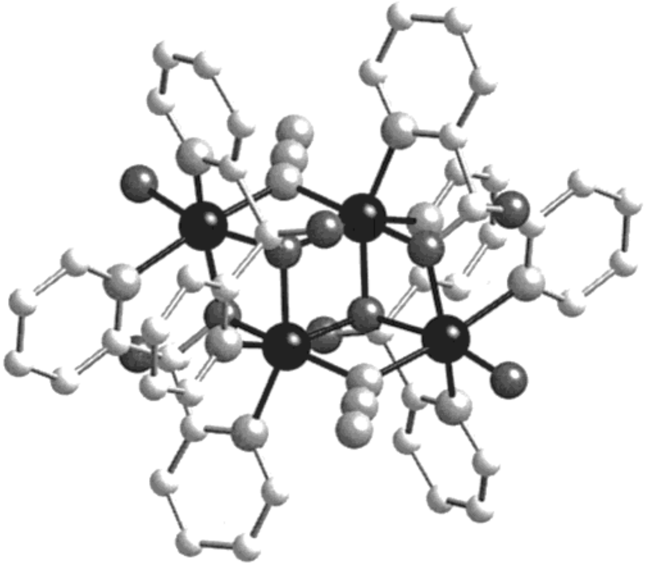


Figure 1. View of the cationic tetramer for **1**.

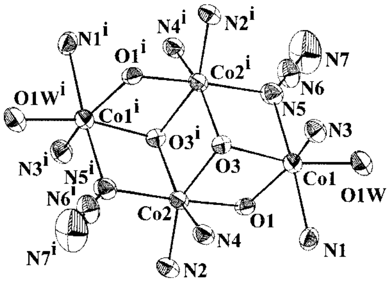


Figure 2. ATOMS view (50% probability) of the dicubane-like core structure showing the coordination polyhedra in the tetrameric unit for **1**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Co(1)−O(1)	2.027(5)	Co(2)−O(3)−Co(2i)	98.7(2)
Co(1)−O(1W)	2.094(6)	Co(2)−O(3)−Co(1)	96.7(2)
Co(1)−O(3)	2.189(5)	Co(2i)−O(3)−Co(1)	98.9(2)
Co(1)−N(3)	2.127(6)	Co(2)−N(5)−Co(1i)	102.3(3)
Co(1)−N(5i)	2.132(7)	Co(1)−O(1)−Co(2)	97.9(2)
Co(1)−N(1)	2.162(7)	O(1)−Co(1)−O(3)	81.2(2)
Co(2)−O(1)	2.156(5)	O(3)−Co(2)−O(3i)	81.3(2)
Co(2)−O(3i)	2.142(5)	N(5)−Co(2)−O(3i)	79.6(2)
Co(2)−O(3)	2.034(5)	O(3)−Co(2)−O(1)	81.8(2)
Co(2)−N(4)	2.151(6)	N(6)−N(5)−Co(1i)	130.6(6)
Co(2)−N(5)	2.093(7)	N(6)−N(5)−Co(2)	124.1(6)
Co(2)−N(2)	2.087(7)	N(7)−N(6)−N(5)	177(1)

[a] Symmetry transformations used to generate equivalent atoms: *i* = −*x*, −*y*, −*z*.

The tetramers are centrosymmetric and exhibit a central core (Figure 2) that can be described as a dicubane-unit with two missing vertexes. As observed, the connections take place through double bridges and three different types can be distinguished: Co1−($O1_{dpk\cdot CH_3O}$,$O3_{dpk\cdot OH}$)−Co2, Co1−($O3_{dpk\cdot OH}$,$N5_{azide}$)−Co2, and Co2−($O3_{dpk\cdot OH}$,$O3_{dpk\cdot OH}$)−Co2. The rest of the coordination sites are occupied by the N-atoms belonging to the dpk derivatives ((N1,O1,N2)-dpk·CH_3O and (N3,O3,-N4)-dpk·OH) and the coordinated molecules of water (O1w).

The intermetallic distances are 3.169(2) Å (Co2···Co2i), 3.156(2) Å (Co1···Co2), 3.291(2) Å (Co1···Co2i), and 5.616(3) Å (Co1···Co1i). The bond distances and angles are displayed in Table 4. As observed, the Co−O distances range from 2.034(5) to 2.189(5) Å while the Co−N ones vary from 2.027(5) to 2.162(7) Å. The bond angles are quite far from the ideal ones due to the tridentate coordination of the dpk derivatives that imposes an important distortion on the coordination sphere.

Compound **2** has been determined to be isomorphous to compound **1** on the basis of X-ray powdered diffraction pattern

---

(9) Sheldrick, G. M. *SHELXS97. Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.

(10) Sheldrick, G. M. *SHELXS97. Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974.; Vol. IV.

(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A.* **1983**, *39*, 158.

(13) Rodriguez Carvajal, J. *FULLPROOF, Program Rietveld Pattern Matching Analysis of Powder Patterns*; 1997.

(14) Rietveld, H. M. *Acta Crystallogr.* **1967**, *12*, 151−152.

(15) Rietveld, H. M. *J. Appl. Cryst.* **1969**, *6*, 65−67.

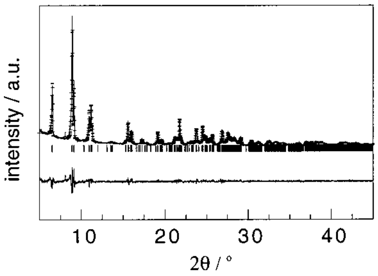


Figure 3. Observed, calculated, and difference X-ray diffraction patterns for **2**.

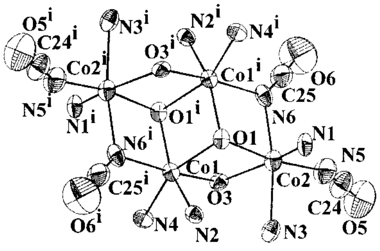


Figure 4. ATOMS view (50% probability) of the dicubane-like core structure showing the coordination polyhedra in the tetrameric units for **3**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

Co(1)−O(1)	2.025(3)	Co(1)−O(1)−Co(1i)	98.3(1)
Co(1)−O(1i)	2.133(3)	Co(1)−O(1)−Co(2)	98.5(1)
Co(1)−O(3)	2.193(3)	Co(1i)−O(1)−Co(2)	97.2(1)
Co(1)−N(6i)	2.088(4)	Co(2)−O(3)−Co(1)	99.6(1)
Co(1)−N(4)	2.096(4)	Co(1i)−N(6)−Co(2)	101.7(2)
Co(1)−N(2)	2.162(4)	O(1)−Co(1)−O(3)	80.5(1)
Co(2)−N(5)	2.025(5)	O(1)−Co(1)−O(1i)	81.7(1)
Co(2)−O(1)	2.244(3)	O(3)−Co(2)−O(1)	78.9(1)
Co(2)−O(3)	2.046(3)	O(1)−Co(1)−N(6i)	106.9(1)
Co(2)−N(6)	2.146(5)	C(25)−N(6)−Co(1i)	128.2(5)
Co(2)−N(3)	2.217(5)	C(25)−N(6)−Co(2)	129.6(5)
Co(2)−N(1)	2.135(4)	N(6)−C(25)−O(6)	178.1(8)

[a] Symmetry transformations used to generate equivalent atoms: *i* = −*x* + 1, −*y* + 1, −*z*.

matching. Figure 3 shows the observed, calculated, and difference X-ray diffraction patterns for **2** (according to the data in Table 3). Thus, for compound **2** cyanate groups occupy the positions for azide in **1** and ClO_4^- counteranions should be found in place of BF_4^-. The isomorphism between **1** and **2** is also confirmed by the rest of the techniques used for this work.

Compound **3** also consists of dicubane-like units. However, the tetramers in this case (Figure 4) are neutral as a result of the presence of terminal cyanate groups in place of the coordinated water molecules for **1** and **2**. The rest of the structural features are similar. Thus, the intermetallic connections are Co1−(O1$_{\mathrm{dpk\cdot OH}}$,O3$_{\mathrm{dpk\cdot CH_3O}}$)−Co2, Co1−(O1$_{\mathrm{dpk\cdot OH}}$,N6)−Co2 (N6−C25−O6 is an *end-on* cyanate), and Co1−(O1$_{\mathrm{dpk\cdot OH}}$,O1$_{\mathrm{dpk\cdot OH}}$)−Co1. On the rest of the coordination sites, N-atoms can be found corresponding to the terminal cyanate groups (N5−C24−O5) and the dpk derivatives ((N1,O1,N2)-dpk·OHCH$_3$O and (N3,O3,N4)-dpk·CH$_3$O).

The intermetallic distances for **3** are 3.144(2) Å (Co1···Co1i), 3.238(2) Å (Co1···Co2), 3.283(2) Å (Co1···Co2i), and 5.712(3) Å (Co2···Co2i). Table 5 summarizes the bond distances and angles for **3**. As seen, the Co−N distances range from 2.025(5) to 2.217(5) Å while the Co−O distances vary from 2.025(3) to 2.244(3) Å. The bond angles are also in this case remarkably far from the ideal ones.

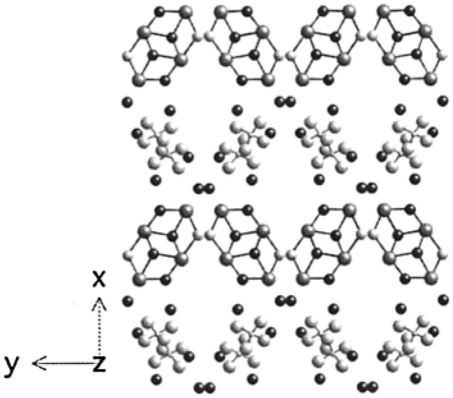


Figure 5. View of the packing for **1** showing the layered distribution of the charges in planes along the *x* direction. Only the dicubane cores in the clusters have been drawn for clarity.

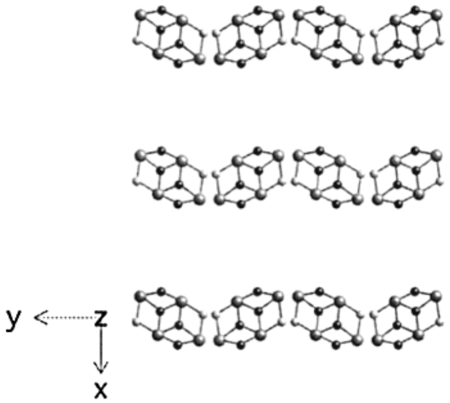


Figure 6. View of the packing for **3**. Only the dicubane cores in the clusters have been drawn for clarity.

The packing for **1** (Figure 5) exhibits a layered distribution of charges where the cationic tetramers and the counteranions lie on different *yz* planes. There are crystallization molecules of water on both the positively and negatively charged planes. For compound **3**, the packing of the tetramers is very similar (Figure 6) but in this case the layers are neutral. This indicates that the entrance of the counteranions to the lattice does not disturb the distribution of the dicubanes. The absence of counteranions and crystallization molecules of water provokes the volume of the unit cell to be more than 10% smaller for **3** (V = 2618.0(4) Å^3) than for **1** (V = 2990(1) Å^3) and **2** (V = 3002(2) Å3).

As mentioned above, compounds **2** and **3** represent the first examples of any kind of cubanes exhibiting cyanate bridges as well as the first Co(II) compounds with cyanate bridges.[7] On the other hand, compounds **1**−**3** join a short family of Co(II) dicubanes with two missing vertexes.[6] Another members of this family have been reported for other metals such as nickel(II),[16] copper(II),[17] manganese(II−III),[18] and iron(III).[19] Among these dicubanes, those exhibiting pseudohalides, reported just for nickel(II)[3a,3b] and cobalt(II),[8] are isomorphous. Table 6 shows some structural parameters for a family of [M$_2$(dpk·OH)(dpk·CH$_3$O)(L)(H$_2$O)]$_2$A$_2$.nH$_2$O compounds (where M = Ni, Co; L = N$_3$, NCO; A = NO$_3$, ClO$_4$, BF$_4$). As observed, the difference in the number of crystallization molecules of water for Ni(II)

---

(16) Clemente-Juan, J. M.; Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J. *Inorg. Chem.* **1999**, *38*, 55.

(17) Breeze, S. R.; Wang, S.; Creedan, J. E.; Raju, N. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2327.

(18) Sumatsuki, Y.; Shimada, H.; Matsuo, T.; Nakamura, M.; Kai, F.; Matsumoto, N.; Re, N. *Inorg. Chem.* **1998**, *37*, 5566.

(19) Li, H.; Zhong, Z. J.; Chen, W.; Tou, X.-Z. *J. Chem. Soc., Dalton Trans.* **1997**, 463.

Table 6. Cell Parameters for $[M_2(dpk{\cdot}OH)(dpk{\cdot}CH_3O)(L)(H_2O)]_2A_2.nH_2O$ Tetramers[a]

M(II)	L	A	*n*	*a* (Å)	*b* (Å)	*c* (Å)	β (deg)	*V* (Å^3)	ref
Ni(II)	N_3	ClO_4	2	13.456(3)	10.906(2)	19.990(7)	91.59(3)	2932(1)	3b
Ni(II)	N_3	NO_3	2	13.289(3)	10.972(2)	20.007(3)	91.07(2)	2916(6)	3c
Co(II)	N_3	BF_4	4	13.537(3)	11.007(2)	19.941(7)	90.19(3)	2990(1)	this work
Co(II)	NCO	ClO_4	4	13.572(1)	11.111(1)	19.915(2)	91.227(7)	3002(3)	this work

[a] All of them are monoclinic ($P2_1/c$, $Z = 4$).

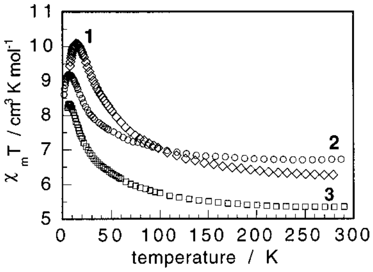


Figure 7. Thermal evolution of $\chi_m T$ (four Co(II)) for **1**−**3**.

and Co(II) compounds does not lead to any significant changes in the structural parameters.

Magnetic Studies. Susceptibility and magnetization measurements were performed for compounds **1**, **2**, and **3**. As seen in Figure 7 where the thermal variation of $\chi_m T$ for **1**−**3** is displayed, the three of them exhibit an analogous behavior. Thus, the $\chi_m T$ (cm^{3}mol^{-1}K)/μ_{eff} (μ_B) values increase from RT (12.0/9.8 (**1**), 13.4/10.3 (**2**) and 10.8/9.3 (**3**), per four Co(II) ions) reaching a maximum value (23.8/13.8 at 12 K for **1**, 18.4/12.1 at 9 K for **2**, and 16.6/11.5 at 8 K for **3**). Upon further cooling, $\chi_m T/\mu_{eff}$ values tend to zero. Thus, the Curie−Weiss law is obeyed down to 50 K for **1** with values of $C_m = 2.84$ cm^3 K mol^{-1} (per Co) and $\theta = +16.3$ K. For **2** and **3**, the Curie−Weiss law is obeyed down to 20 K with the following values: $C_m = 3.29$ cm^3 K mol^{-1} (per Co) and $\theta = +6.0$ K for **2** and $C_m = 2.63$ cm^3 K mol^{-1} (per Co) and $\theta = +6.0$ K for **3**. The different values of these parameters correspond to the typical range of values for Co(II).[20]

These results are indicative of the occurrence of moderate ferromagnetic interactions for **1**−**3**. The decrease of the magnetic moment observed at low temperatures should be attributed to the anisotropy of the cluster (as concluded by Inelastic Neutron Scattering studies on Co(II) dicubanes[6d,21]) and/or to the occurrence of intermolecular interactions. However, since the tetranuclear units are isolated in the three compounds (Figures 5 and 6), the intermolecular interactions are expected to be negligible.

The field dependence of the magnetization, *M*, was also recorded for **1**−**3** at different temperatures ($0 \leq H(T) \leq 7$). Figure 8, in which the results for **2** at 5 and 10 K are displayed, is illustrative of the three compounds. As observed, *M* reaches the saturation value expected for a tetranuclear ferromagnetic cobalt(II) compound, i.e., ≈12, in agreement with the parallel alignment of the spins deduced from the thermal variation of $\chi_m T$.

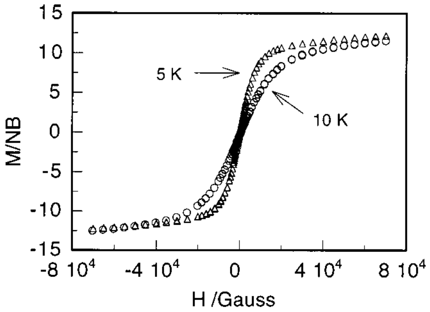
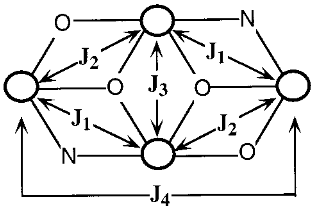


Figure 8. Field dependence of the magnetization for **2** at 5 K and 10 K.

Scheme 2



The presence of *end-on* azide/cyanate bridges in **1**−**3** with angles close to 100° is undoubtedly related to the occurrence of ferromagnetic coupling. Thus, as expected, these interactions are more intense for **1**, which exhibits intermetallic connections through azide in comparison to the coupling through cyanate in **2** and **3**. Additionally, there are three other pathways for exchange that do not involve pseudohalides as shown in the connectivity diagram in Scheme 2 (valid for centrosymmetric dicubanes with the ideal C_{2h} symmetry). This means that a four-*J* model would be used to evaluate the exchange coupling for **1**−**3**. According to this disposition, the coupling through the oxo-bridges must be necessarily ferromagnetic. Otherwise, the two ferromagnetically coupled μ-azido, μ-oxo Co_2 units would couple antiferromagnetically to $S = 0$, irrespective of the relative magnitude of the different *J* values. Evidence of the ferromagnetic coupling through the oxo bridges has been found for similar Co(II) clusters.[6c]

Unfortunately, if it is complicated to fit the behavior of an array of four orbitally degenerate Co(II) centers given current theory, proposing a four-J model for a Co(II) tetramer seems to be impossible. Even neglecting J_4, the anisotropy of the exchange constants and the *g* parameter makes it very difficult to modelize the magnetic behavior of the three compounds.

These type of calculations, though, have been carried out for isomorphous Ni(II) dicubanes.[3b,3c] For these compounds, positive *J* constants have been evaluated for the four pathways, in accordance with the theoretical predictions.

Concluding Comments. The simultaneous use of dpk and pseudohalides such as azide/cyanate gives rise to three Co(II) tetramers consisting of dicubane-like cores with two missing vertexes. The metallic ions in these tetramers are linked through *end-on* azide/cyanate groups and oxo-bridges belonging to the dpk derivatives. One of the compounds exhibits neutral dicubanes while in the other two the tetramers are cationic. The packing in these latter cases consists of alternative cationic and anionic planes providing a layered distribution of charges. These compounds are new examples of the scarce family of tetrameric dicubanes in coordination chemistry. The tetrameric units for

---

(20) Mabbs, F. E.; Machin, D. J. *Magnetism and transition metal complexes*; Oxford University Press: Oxford, 1973.

(21) Andres, H.; Clemente-Juan, J. M.; Aebersold, M.; Güdel, H. U.; Coronado, E.; Bütner, H.; Kearly, G.; Melero, J.; Burriel, R. *J. Am. Chem. Soc.* **1999**, *121*, 10028.

the NCO tetramers represent the first examples of any kind of cubanes exhibiting cyanate bridges. Additionally, these clusters are the first Co(II) compounds with cyanate bridges. The three compounds are moderately ferromagnetic, the interaction being, as expected, more important for the azide dicubane than for the cyanate tetramers.

Acknowledgment. This work has been carried out with the financial support of the Universidad del País Vasco/Euskal Herriko Unibertsitatea (Grant UPV 130310-EB201/1998), the Gobierno Vasco/Eusko Jaurlaritza (Project PI99/53), and the Ministerio de Educación y Cultura (Project PB97-0637). Z.E.S. also thanks the Ministerio de Educación y Ciencia for the grant AP96 20174323. The authors thank Dr. V. Esteve of the University Jaume I (Castellón, Spain) for the X-ray data collection for compound **3**.

Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0013476