

[Ni(cyclam)($\mu_{1,3}$ -dca) $_2$ Cu($\mu_{1,5}$ -dca) $_2$]: A Genuine 3D Bimetallic Coordination Polymer Containing Both $\mu_{1,3}$ - and $\mu_{1,5}$ -Bidentate Dicyanamide Bridges and a Ferromagnetic Interaction between Copper(II) and Nickel(II) Ions

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The structure of [Ni(cyclam)($\mu_{1,3}$ -dca) $_2$ Cu($\mu_{1,5}$ -dca) $_2$], a genuine 3D dicyanamide-bridged bimetallic coordination polymer, is made up of 2D [Cu($\mu_{1,5}$ -dca) $_2$] $_n$ layers connected by [Ni(cyclam)($\mu_{1,3}$ -dca) $_2$] bridging moieties; it exhibits a ferromagnetic exchange interaction between copper(II) and nickel(II) ions through the $\mu_{1,3}$ -bidentate dicyanamide bridges.

Dicyanamide-bridged extended systems are attracting much attention because of their fascinating structures and interesting magnetic properties. In this regard, binary metal–dicyanamide complexes, α -[M(dca) $_2$] (dca = dicyanamide), built from metal-ion nodes and the bifunctional dca ligand as a spacer, exhibit a 3D rutile-type architectures and magnetically order as ferro- or antiferromagnetic spin-canted systems at T_c lower than 47 K.¹ To modify metal–dca assemblies, monodentate and bridging ligands have been used as coligands, leading to a wide variety of 1D to 3D systems, some of them exhibiting magnetic order.² An alternative route

to dicyanamide-bridged systems consists of the cation templation of [M(dca) $_3$] $^-$ and [M(dca) $_4$] $^{2-}$ networks.^{2b,2g,2h,3} In this case, the topology of the final assembly strongly depends on the size, shape, and charge of the countercation used in the templation process. Significantly, paramagnetic metal complexes can be used as countercations, leading to heterometallic systems.^{2g,2h,3d,3e} In this context, we have recently reported a series of polymeric anionic metal–dicyanamide complexes containing $\mu_{1,5}$ -bidentate dicyanamide bridges, whose structures consist of (4,4) 2D [M(dca) $_4$] $_n^{2n-}$ [M = Co(II) and Mn(II)] layers and [Cu(pCTH)] $^{2+}$ template cations intercalated between the layers.^{2h} In these compounds, copper atoms of the template cations [Cu(pCTH)] $^{2+}$ are further semicoordinated at the axial positions by two nitrile nitrogen atoms of the axial nonbridging dca ligands of the [M(dca) $_4$] $_n^{2n-}$ sheets; the long Cu–N distance of 2.7 Å is mainly due to the great in-plane bond strength of the N4-pCTH ligand and the Jahn–Teller effect on the Cu(II) ion. Following the same strategy but using [Ni(cyclam)] $^{2+}$ as the template cation, we have succeeded in obtaining the dca-bridged bimetallic compound [Ni(cyclam)($\mu_{1,3}$ -dca) $_2$ Cu($\mu_{1,5}$ -dca) $_2$], **1** (see Chart 1). Herein, we report the synthesis,⁴ crystal structure,⁵ and magnetic properties of this compound.

The structure of **1** consists of (4,4) 2D [Cu($\mu_{1,5}$ -dca) $_2$] $_n$ layers joined by [Ni(cyclam)($\mu_{1,3}$ -dca) $_2$] units, leading to a 3D dicyanamide-bridged bimetallic system [Figures 1 and 1S (Supporting Information)]. The copper atom assumes a tetragonally elongated octahedral CuN $_6$ coordination envi-

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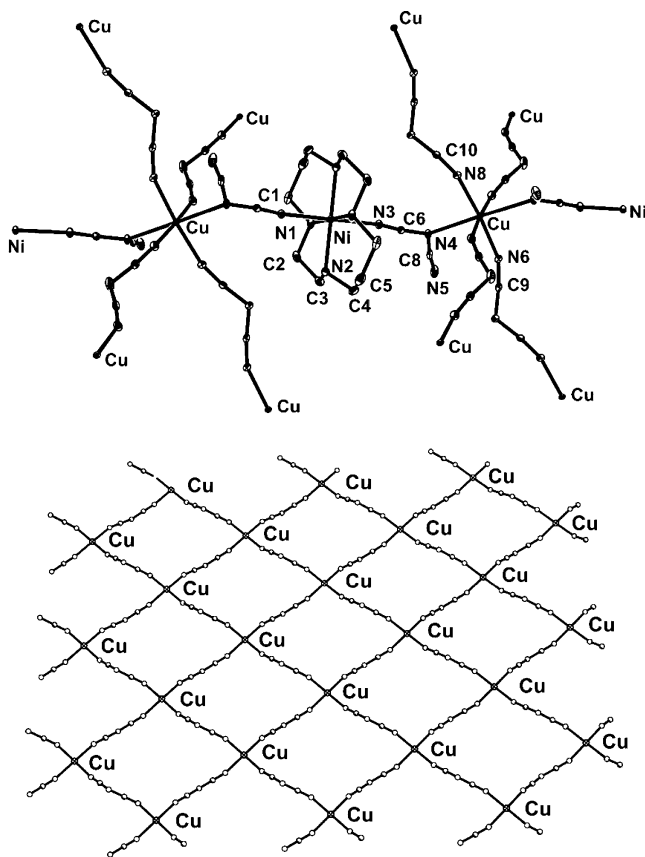
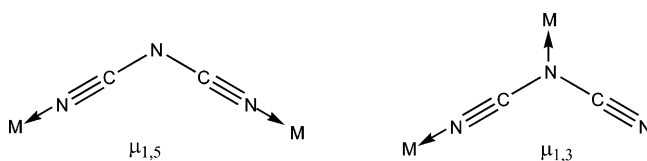


Figure 1. (Top) Perspective view of a fragment of the structure of **1** showing the $\mu_{1,5}$ - and $\mu_{1,3}$ -dca bridging modes. Hydrogen atoms are omitted for clarity. (Bottom) $[\text{Cu}(\mu_{1,5}\text{-dca})_2]$ rhombus-grid-like sheets of **1**.

Chart 1. dca Coordination Modes Observed in **1**



ronment, in which the nitrile nitrogen atoms of four $\mu_{1,5}$ -dca bridging ligands occupy the equatorial positions with M–N distances of 1.979(1) and 1.994(1) Å, whereas the axial positions are occupied by the amide nitrogen atoms of two $\mu_{1,3}$ -bridging dca ligands at a greater Cu–N distance of 2.374(2) Å because of the Jahn–Teller effect of the Cu(II) atom. Compared to $[\text{Cu}(\text{pCTH})][\text{M}(\text{dca})_4]$, **1** exhibits a much

shorter Cu–N axial distance, in good accord with the fact that the in-plane bond strength provided by the nitrogen atoms of the N4-macrocyclic ligand in the former is greater than that provided by the nitrile nitrogen atoms of the dicyanamide ligands in the latter. The single $\mu_{1,5}$ -dca bridges connect each copper(II) atom to four neighboring ones, leading to distorted rhombus-grid-like sheets parallel to the *ab* plane (Figure 1). Within buckled rhombus M_4 units, the intralayer $M\cdots M$ separations through the dicyanamide bridge are 8.323(1) Å, whereas the $M\cdots M$ distances through the diagonals are 13.145(2) and 10.213(2) Å. The sheets are similar to those observed in the 2D compounds $[\text{Cu}(\text{pCTH})][\text{M}(\text{dca})_4]^{2\text{h}}$ [$M = \text{Co}(\text{II})$ and $\text{Mn}(\text{II})$]. Sheets are further linked into an α -Po network via axially bound $[\text{Ni}(\text{cyclam})(\mu_{1,3}\text{-dca})_2]$ “pillars”.

Ni(II) atoms, which lie on inversion centers, exhibit a slightly axially distorted octahedral NiN_6 coordination environment, which comprises four nitrogen atoms of the cyclam ligand in equatorial positions (Ni–N distances of 2.073(2) and 2.080(0) Å), and two nitrile nitrogen atoms of $\mu_{1,3}$ -dca bridging ligands with a Ni–N distance of 2.115(3) Å (Figure 1).

Within the 3D structure, there exist weak hydrogen-bonding interactions involving the noncoordinated nitrile nitrogen atom of the $\mu_{1,3}$ -dca bridges and the N1–H group of the cyclam ligand of a neighboring unit, with a N5–N1ⁱ distance of 3.011(2) Å ($i = 1 - x, 2 - y, 2 - z$).

Complex **1** represents the first example of a genuine 3D bimetallic system containing dca bridging ligands between two different paramagnetic metal ions. Although the bimetallic complex $[\text{Cu}(\text{pn})_2][\text{Mn}(\text{dca})_4]^{2\text{g}}$ (pn = 1,3-diaminopropane) also exhibits a 3D structure with $\mu_{1,3}$ -dca bridging ligands between Cu(II) and Mn(II) ions, the Cu–N_{amide} bond is no more than semicoordinated [N–Cu distance of 2.519(2) Å], and consequently, the compound can better be considered as made of $[\text{M}(\text{dca})_4]^{2-}$ anionic chains, with terminal dca ligands and double $\mu_{1,5}$ -dca bridges, and $[\text{Cu}(\text{pn})_2]^{2+}$ counterions. It should be noted that, very recently, a bimetallic complex containing $\mu_{1,5}$ -dca bridges between Gd(III) and Cu(II) ions was reported, but this compound exhibited a 2D structure.⁶

Complexes containing $\mu_{1,3}$ -dca bridging ligands are relatively scarce, and with the exception of $\text{Co}_2(\text{dca})_4(2,5\text{-dmpdo})_2^{2\text{h}}$ (2,5-dmpdo = 2,5-dimethyl-pyrazine-dioxide) and complex **1**, all of them have M–N_{amide} distances longer than 2.5 Å.^{2g,7}

The magnetic properties of **1** in the form of $\chi_M T$ vs *T* plots (χ_M being the molar susceptibility) are presented in Figure 2.

At room temperature, the product $\chi_M T$ is 1.63 cm³ mol^{−1} K, which agrees well with the value expected for an uncoupled system with one Cu(II) ion ($S = 1/2$) and one Ni(II) ion ($S = 1$), assuming an average value of $g = 2.18$. Upon

(4) The compound was prepared as follows: To a methanol solution (20 mL) containing $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (0.034 g, 0.1 mmol) and $\text{Na}(\text{dca})$ (0.036 g, 0.4 mmol) was slowly added an orange methanol solution (20 mL) of $[\text{Ni}(\text{cyclam})(\text{ClO}_4)_2]^{13}$ (0.046 g, 0.1 mmol). After the resulting solution had been filtered and allowed to evaporate slowly at room temperature for several weeks, blue crystals suitable for X-ray analysis were obtained. Yield: 30% based on nickel. IR (KBr, cm^{-1}): 2295, 2229, 2165 $\nu(\text{CN})$. Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_{16}\text{CuNi}$: C, 36.85; H, 4.12; N, 38.19%. Found: C, 36.90; H, 4.61; N, 38.54%.

(5) Crystal and structure refinement parameters for **1**: $\text{C}_{18}\text{H}_{24}\text{N}_{16}\text{CuNi}$, $M = 586.78$, monoclinic, space group $C2/c$, $a = 10.2128(16)$ Å, $b = 13.145(2)$ Å, $c = 18.350(3)$ Å, $\beta = 102.151(3)^\circ$, $V = 2408.2(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.618$ g cm^{−3}, $\mu(\text{Mo K}\alpha) = 1.708$ mm^{−1}, $T = 293$ K, $F(000) = 1204$, $R_1 = 0.0262$ ($wR_2 = 0.0689$) for 2728 unique reflections ($R_{\text{int}} = 0.0192$) with a goodness-of-fit of 1.067. Data were collected by $\omega/2\theta$ ($2\theta_{\text{max}} = 56.3^\circ$) on a Bruker SMART CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined on F^2 using the SHELX-97 program¹⁴ of the WINGX pack.¹⁵

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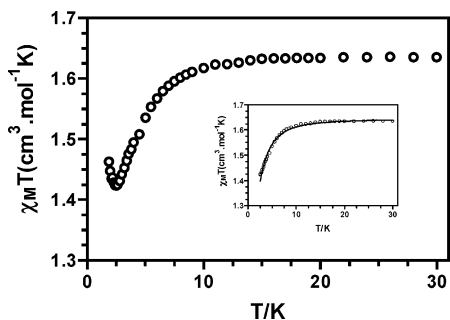


Figure 2. Plot of $\chi_M T$ vs T for **1**. The solid line (inset) represents the best fit to eq 1 (see text).

cooling of the compound, the $\chi_M T$ value remains almost constant until 20 K, then decreases sharply to reach a minimum value of $1.42 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.5 K, and finally increases to a value of $1.46 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 1.9 K. To understand the magnetic behavior of **1**, it is important to note the existence of two different exchange pathways in the 3D network: (i) the single long $\mu_{1,5}$ -dca bridge linking two neighboring copper(II) atoms through short Cu–N_{nitrile} equatorial bonds (ca. 1.98 \AA) and (ii) the single short $\mu_{1,3}$ -dca bridge connecting one axial position of a Cu(II) ion (ca. 2.37 \AA) with the adjacent Ni(II) ion. The first pathway is known to produce very weak antiferromagnetic interactions (hereafter AF) with $-J < 1 \text{ cm}^{-1}$.⁷ The magnetic interaction through the $\mu_{1,3}$ -dca pathway is expected to be weak as well because the N_{amide}–Cu distance is relatively long and the spin density on the axial positions is very small (the $d_{x^2-y^2}$ magnetic orbital is located in the equatorial plane). In principle, this latter interaction could be either ferromagnetic (hereafter F) or AF in nature. In summary, from a magnetic point of view, **1** contains AF copper(II) planes and alternating Cu–Ni chains with either F (ferromagnetic chains) or AF (ferrimagnetic chains) interactions. Although the shape of the $\chi_M T$ vs T curve resembles that of a ferrimagnetic chain, this can be ruled out because of the high $\chi_M T$ value at the minimum ($1.42 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). For such a ferrimagnetic chain, a much lower value (about $0.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) is expected at the minimum.⁸ Therefore, the increase of $\chi_M T$ at low temperature is indicative of F interactions between copper(II) and Ni(II) ions along the chain. This agrees well with the ferromagnetic behavior observed for the recently reported dinuclear complex $\text{Cu}_2\text{L}(\mu_{1,3}\text{-dca})$ ⁹ (L is a cryptand ligand), which, from spectroscopic data and the consideration of the steric requirements of the copper(II) cryptate, was assumed to exhibit a short $\mu_{1,3}$ -dicyanamide bridge between the copper(II) ions. In summary, from a magnetic point of view, we can describe **1** as ferromagnetic CuNi chains with very weak interchain Cu–Cu interactions (if any). These AF interactions must be weaker than the intrachain ferromagnetic CuNi ones. The opposite would produce a steady decrease in $\chi_M T$ at low temperature. In good accord with this result, some theoretical studies on the series of $\alpha\text{-M}(\text{dca})_2$ compounds, which contain $\mu_{1,3,5}$ -dca bridging ligands and so both

$\mu_{1,3}$ and $\mu_{1,5}$ superexchange pathways, have indicated that the magnetic exchange interaction mediated by the former superexchange pathway is stronger than that mediated by the latter.^{10,11}

The decrease in $\chi_M T$ between 20 and 2.5 K can only be ascribed to the zero-field splitting (ZFS) of the tetragonally elongated Ni(II) ions. In fact, the $\chi_M T$ data in the 30–2.5 K temperature range can be very well reproduced (inset of Figure 2) by using the following equations for an isolated Ni(II) ion with ZFS plus an isolated Cu(II) ion

$$\chi_M = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3} + \frac{Ng^2\beta^2}{4kT} \quad (1)$$

$$\chi_{\parallel} = \frac{2Ng_z^2\beta^2}{kT} \frac{\exp(-D/kT)}{1 + 2\exp(-D/kT)}$$

and

$$\chi_{\perp} = \frac{2Ng_x^2\beta^2}{kT} \frac{1 - \exp(-D/kT)}{1 + 2\exp(-D/kT)}$$

where D (axial zero-field splitting parameter) is the energy difference between $M_s = \pm 1$ and $M_s = 0$ levels. The best fit leads to the values $|D| = 5.1(6) \text{ cm}^{-1}$ (the sign of D cannot be determined from powder magnetic susceptibility data) and $g_{\text{mean}} = 2.184(1)$. The $|D|$ value is similar to that observed for other compounds containing Ni(II) ions with tetragonally elongated octahedral geometries.^{12,2h} The value of the magnetization at the maximum applied field (5 T) of $2.74 N\beta$ (Figure S1) is near the expected magnetization value $M_s = g(S_{\text{Ni}} + S_{\text{Cu}}) = 3.27 N\beta$.

In conclusion, complex **1** can be described as $\mu_{1,3}$ -dca bridged CuNi ferromagnetic chains with very weak antiferromagnetic interchain interactions through the $\mu_{1,5}$ -dca bridges that connect copper(II) ions. These weak AF interactions could ultimately lead to 3D antiferromagnetic order (Figure S2). However, this ordering would be observed below 1.9 K because of the small magnitude of the magnetic exchange interactions through the two types of dca bridges.

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Supporting Information Available: Crystallographic data in CIF format and a PDF file containing additional structural and magnetic figures (Figures S1 and S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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