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A 2D Coordination Polymer with Canted Ferromagnetism Constructed from Ferromagnetic [$Ni^{II}Co^{II}$] Nodes

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A bimetallic coordination polymer, $_{\infty}^{2}[\{LNi^{II}Co^{II}\}(dca)_2]$, has been constructed from heterobinuclear [$Ni^{II}Co^{II}$] nodes and dicyanamido spacers [L^{2-} is the dianion of the Schiff base resulting from the 2:1 condensation of 3-methoxysalicyladehyde with 1,3-propanediamine; L^{2-} = *N*,*N*′-propylenebis(3-methoxysalycilideneiminato)]. The intranode $Co^{II}-Ni^{II}$ interaction was found to be ferromagnetic because of the orthogonality of the magnetic orbitals. Below 12 K, the onset of the canted ferromagnetic ordering is observed.

The node-and-spacer paradigm is largely employed for the construction of coordination polymers.[1] It relies upon the strong directionality of the coordination bonds established between the metal ions (nodes and connectors) and the exodentate ligands (spacers and linkers). Coordination polymers can be constructed from oligonuclear nodes as well.[2] The metal ions interact with the divergent ligand through their easily accessible coordination sites. The presence of two or more metal ions confers to the node a higher geometrical flexibility. Moreover, the metal−metal intra- and internode interactions can lead to new redox, electric, or magnetic properties.[2,3]

We have developed an alternative way to obtain heterometallic systems, by connecting preformed heterometallic nodes with various spacers.[4] The nuclearity of the nodes can be controlled by choosing appropriate compartmental ligands. For example, the dissymmetric side-off Schiff bases derived from *o*-vanillin were specially designed to generate 3d−4f complexes.[5] The second compartment, O_2O_2', is sufficiently large to accommodate 4f metal ions. Such complexes were successfully used as nodes in constructing 3d−4f coordination polymers with various dimensionalities and network topologies.[6] We have found that these ligands can also accommodate two different 3d metal ions (Cu^{II} and Co^{II}): the first metal ion is hosted into the N_2O_2 compartment, while the second one occupies the O_2O_2' compartment.[7] The disposition of the oxygen atoms defining the second compartment is favorable for coordination to 4f ions, allowing them to achieve high coordination numbers. On the other hand, when 3d metal ions are hosted into this compartment, their stereochemistry is strongly distorted, with four short and two long coordination bonds that involve the methoxy groups.[7] For example, the reaction between [LCu] and cobalt perchlorate followed by the addition of sodium dicyanamide led to a 1D coordination polymer, $[\{LCuCo\}(dca)_2]$ (**1**), with dicyanamido bridges connecting a copper ion from one node with the cobalt ion from another one (Chart 1a).[7b]

A terminal dicyanamido ligand is coordinated to the cobalt ion. The copper ion, occupying the N_2O_2 compartment, is pentacoordinated, with the bridging dca^- group coordinated into the apical position. The analysis of this structure raised

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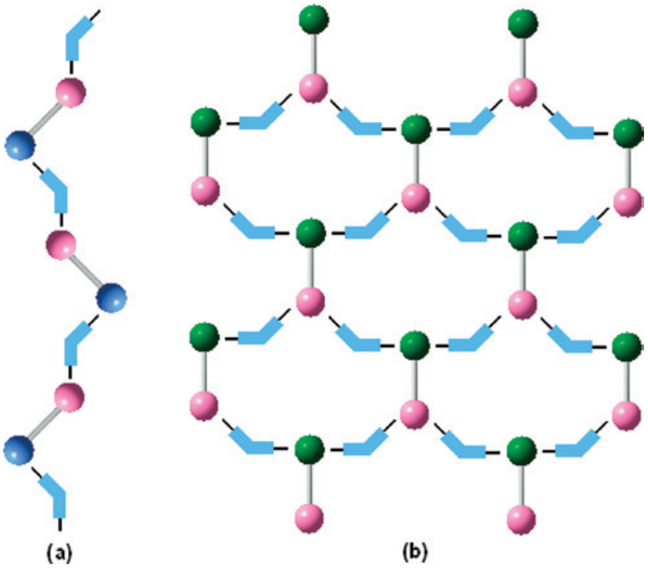
Chart 1



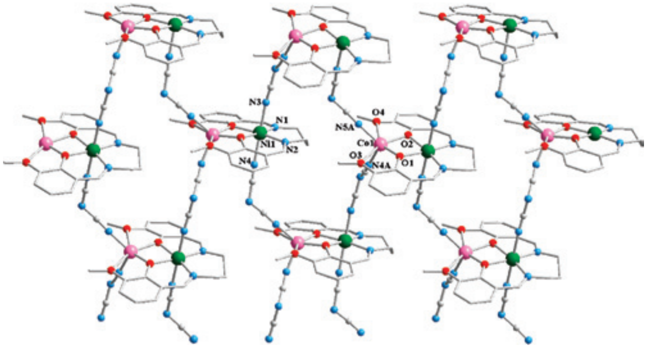


Figure 1. Perspective view of the 2D network of **2**.

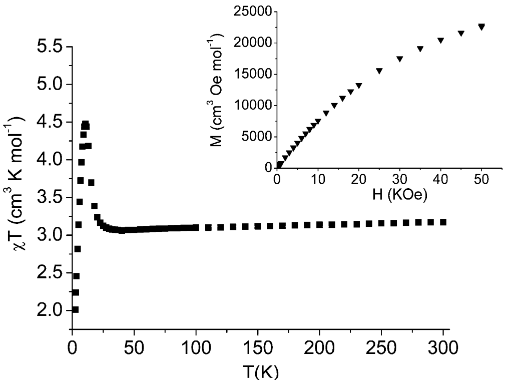


Figure 2. χT vs T plot for **2** measured at 1 kOe and M vs H at 1.9 K (inset).

the following question: is it possible to increase the dimensionality of the coordination polymer by replacing the Cu^{II} ion with a metal ion preferring a higher coordination number, let us say six (Chart 1b)? In order to answer this question, we synthesized the [NiL] precursor [L^{2-} is the dianion of the Schiff base resulting from the 2:1 condensation of 3-methoxysalicyladehyde with 1,3-propanediamine; L^{2-} = *N*,*N*′-propylenebis(3-methoxysalycilideneiminato)]. Indeed the reaction of [NiL] with cobalt(II) perchlorate and sodium dicyanamide leads to $_{\infty}^{2}$[{LNi^{II}Co^{II}}(dca)$_2$] (**2**),[8] whose crystal structure has been solved.[9] As expected, a 2D coordination polymer is assembled (Figure 1). The Ni^{II} ions exhibit a slightly elongated octahedral geometry [the basal plane is described by two nitrogen and two oxygen atoms from the compartmental ligand, with metal−ligand distances varying between 2.022(4) and 2.038(4) Å; the apical positions are occupied by the nitrogen atoms arising from the dicyanamido ligands: Ni1−N3 = 2.099(4), Ni1−N4 = 2.129(4) Å]. As far as the coordination geometry of the cobalt ion concerned, this is more delicate to state precisely. At first sight, a tetrahedral environment comprising two phenoxo oxygen atoms of the bridge [Co1−O1 = 1.992(3); Co1−O2 = 1.991(3) Å] and two nitrogen atoms from the two coordinated dicyanamido ions [Co1−N4A = 1.980(4); Co1−N5A = 2.004(4) Å] can be noticed. The values of the Co−O (methoxy oxygen atoms) distances [2.570(3) and 2.584(4) Å], longer than those in [{LCuCo}(dca)$_2$], indicate that they can be considered as weakly coordinated. The intranode Ni⋯Co distance is 3.085 Å.

A useful tool to diagnose the stereochemistry of the Co^{II} ion is the UV−vis spectroscopy. The diffuse-reflectance spectrum of **2** is a superposition of the absorption bands of the two chromophores (Figure S1 in the Supporting Information). The intense band located at ∼600 nm is similar to the one exhibited by cobalt(II) complexes with a tetrahedral geometry and can be assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition.[10] Another characteristic band for tetrahedral cobalt(II) complexes is located in the NIR region. This band is assigned to the $^4A_2 \rightarrow {}^4T_1(F)$ transition. When the symmetry of the Co^{II} ion decreases from T_d to C_{2v}, the $^4T_1$(F) level is split into $^4A_2 + {}^4B_1 + {}^4B_2$ levels and three bands are expected. Indeed, in the NIR region, compound **2** shows a large band with a maximum at 1350 nm and two shoulders at about 1100 and 1500 nm (Figure S1 in the Supporting Information). This is in agreement with the results of the χT vs T measurements (actually MT/H vs T; Figure 2), which show a room temperature value for **2** of 3.18 cm^3 K mol^{-1}. This value is in agreement with that expected from the sum of the independent contributions of a tetrahedral Co^{II} ($2.0 < \chi T < 2.6$ cm^3 K mol^{-1}) and an octahedral Ni^{II} ($\chi T \sim 1.1$ cm^3 K mol^{-1}), whereas it is too low to be compatible with a distorted octahedral Co^{II} center ($2.5 < \chi T < 3.1$ cm^3 K

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(8) A total of 2 mmol of *o*-vanillin in THF was deprotonated with 2 mmol of LiOH and then reacted with an aqueuos solution of Ni(CH$_3$COO)$_2$·4H$_2$O. To the resulting green suspension were added dropwise 2 mmol of 1,3-propanediamine, and the resulting mixture was stirred for 1 h, which led to the formation of [NiL] as a green precipitate, which was filtered off, washed with water and THF, and dried in air. Yield: 91%. To an acetonitrile/ethanol (20 mL, 1:1) solution of [NiL] (0.04 mmol) was added solid Co(ClO$_4$)$_2$·6H$_2$O (0.04 mmol), and the resulting mixture was stirred for 30 min. To the mixture was added an aqueous solution of NaN(CN)$_2$ (0.08 mmol), and the resulting mixture was stirred for other 10 min. Dark-mauve crystals were obtained upon slow evaporation.

(9) Crystallographic analysis of **2**: C$_{23}$H$_{20}$CoNiN$_8$O$_4$, $M = 590.11$ g mol^{-1}, monoclinic, space group $P21n$, $a = 9.400$ Å, $b = 15.340$ Å, $c = 17.637$ Å, $\beta = 100.00°$, $V = 2504.7$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 1.565$ g cm^{-3}, $\mu = 1.460$ mm^{-1}, R1 = 0.0507, wR2 = 0.0646, GOF = 0.786. CCDC reference number for **2**: 68815.

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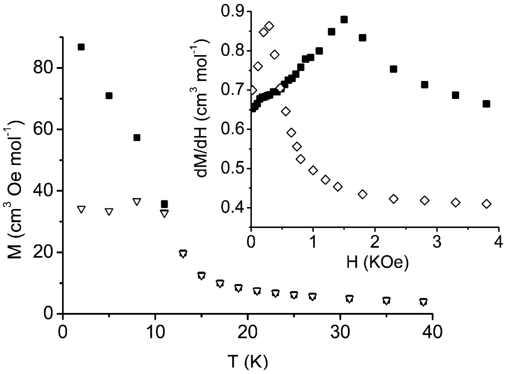

Figure 3. ZFC (empty triangles) and FC (full squares) magnetization curves for **2** in a field of 50 Oe. In the inset, d*M*/d*H* vs *H* curves at 5 K (empty diamonds) and 1.9 K (full squares) are reported, evidencing the occurrence of the metamagnetic transition.

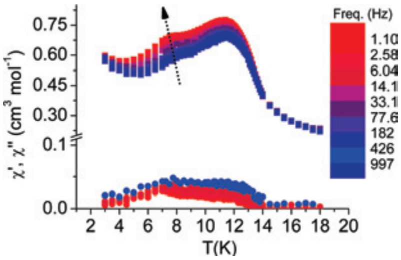

Figure 4. Plot of χ' (upper) and χ'' (lower) vs T for **2** at variable frequencies. The dotted arrow highlights the occurrence of a second, frequency-dependent feature around 8 K.

mol^{-1}).[11,12] Upon a decrease in the temperature, the χT product slowly decreases down to 40 K (3.06 cm^3 K mol^{-1}) and then rapidly increases up to a maximum of 4.5 cm^3 K mol^{-1} (in a field of 1 kOe) at 12 K, after which its value drops to 2.5 cm^3 K mol^{-1} at 2 K. The zero-field-cooled (ZFC)/field-cooled (FC) curve (Figure 3) clearly evidences that this behavior should be attributed to the onset of a magnetic ordering process below 12 K, where the two curves show a bifurcation. This is confirmed by the presence of a frequency-independent signal for the in-phase alternating current susceptibility (Figure 4). The existence of a small but detectable signal in χ'' further indicates that the magnetic ordering results in a magnetized state. The low-field M vs H curves (Figure S2 in the Supporting Information) at different temperatures indicate that the resulting state should be a weak ferromagnetic one, undergoing a metamagnetic transition at 1600 and 250 Oe at 2 and 5 K, respectively (inset of Figure 3). Below 8 K, the M vs H cycle shows an appreciable hysteresis (Figure S3 in the Supporting Information; $H_c = 100$ Oe and $M_r = 90$ cm^3 Oe mol^{-1} at 5 K; $H_c = 250$ Oe and $M_r = 250$ cm^3 Oe mol^{-1} at 1.9 K).

The detection of a weak ferromagnetic transition in **2** at 12 K should be compared with 9 K of the weak ferromagnetic transition observed with β-Co(dca)$_2$, containing tetrahedral Co^{II} centers connected through $\mu_{1,5}$-dca bridges, and with the absence of magnetic order in [Ni(dca)$_3$]$^-$ containing Ni^{II} ions only interacting through $\mu_{1,5}$-dca groups.[13] In **2**, both the high-field magnetization value at low temperatures and the value of a χT maximum in high field are consistent with each NiCo node being ferromagnetically coupled (a full population of the $S = {}^5/_2$ state would give $\chi T = 5.3$ cm^3 K mol^{-1} and $M = 30\,720$ cm^3 Oe mol^{-1} for $g_{ave} = 2.2$). This is reasonable if one considers the electronic configurations of the two ions ($t_{2g}^{6}e_g^{2}$ for Ni^{II} and $e^4t_2^3$ for Co^{II}), giving rise to orthogonal arrangements of the magnetic orbitals. On the other hand, there is no easy way to evaluate the interaction between adjacent Ni−Co nodes, which should, however, be quite weak, considering that observed in β-Co(dca)$_2$ and [Ni(dca)$_3$]$^-$ derivatives. However, the observation of the weak ferromagnetic transition suggests that this interaction should be weakly ferromagnetic, with the order occurring between ferromagnetic sheets, interacting antiferromagnetically through dipolar interactions. It has to be noted that, because the shortest interlayer interactions involve either the two different metal centers or noncentrosymmetric Co^{II} and Ni^{II} pairs, the proposed mechanism fulfills the symmetry requirements for the observation of a canted magnetic structure.[14]

Finally it has to be noted that the χ' vs T plot evidences another feature around 8 K, namely, a weakly frequency-dependent peak in χ'. The variation of the temperature at which the peak occurs as a function of the frequency strongly suggests that this second peak should be related to the introduction of glassiness in the system. Indeed, ϕ, defined as

$$\varphi = \frac{T_{peak}(\nu_{min}) - T_{peak}(\nu_{max})}{T_{peak}(\nu_{min})\log(\nu_{max}/\nu_{min})} \qquad (1)$$

takes a value of 0.03, which is in the expected range for spin-glass behavior.[15] This suggests a re-entrant spin-glass transition, with the coexistence of both glassy and ordered behavior below 8 K.[16] In conclusion, we have illustrated that the dimensionality of the coordination polymers, when constructed from heterobinuclear tectons, can be controlled by choosing the appropriate pair of metal ions. Moreover, such compounds exhibit interesting magnetic properties. Further work on other systems constructed from heterometallic nodes is in progress.

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Supporting Information Available: Solid-state UV−vis−NIR spectrum, M vs H, and magnetic hysteresis cycles at 1.9 and 5 K for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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