

Magnetic canting or not? Two isomorphous 3D Co^{II} and Ni^{II} coordination polymers with the rare non-interpenetrated (10,3)-d topological network, showing spin-canted antiferromagnetism only in the Co^{II} system†

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The *in situ* solvothermal reaction of 3,4-dicyano-1,2,5-thiadiazole with MCl₂ (M = Co, Ni) and NaOH afforded two isomorphous complexes, [M₂(L)₂(H₂O)₂]_n (L = 2,1,3-thiadiazole-4,5-dicarboxylate), which exhibit a rare non-interpenetrated (10,3)-d (utp) network topology and interesting magnetic behaviors: spin-canted antiferromagnetism for the Co^{II} complex, but simple antiferromagnetic coupling for the Ni^{II}.

Construction of metal–organic coordination polymers has attracted intense attention, owing to their intriguing network topologies and peculiar properties.¹ Intelligent ligand design and the proper choice of a metal center are the main keys to the design of such coordination polymers. In this context, some progress has been achieved in the construction of magnetic materials with extended structures by using multi-functional organic carboxylic acid ligands to assemble paramagnetic metal ions; however it still remains difficult to predict their structures and magnetic behaviors due to the diversity of coordination and the complicated nature of magnetic interactions.² Thus, the search for magnetic metal–organic framework structures has become a major challenge. As an example, imidazole-4,5-dicarboxylic acid has been used in this field,³ whereas an analog of it, 2,1,3-thiadiazole-4,5-dicarboxylic acid (H₂L, Chart 1S, ESI†), is still unexplored to date. Herein, we report the first crystallographically characterized metal complexes of H₂L, [M₂(L)₂(H₂O)₂]_n (M = Co, **1**; Ni, **2**), which are isomorphous and exhibit a rare three-dimensional (3D) (10,3)-d (utp) network topology and unexpected magnetic behaviors: the Co^{II} complex shows spin-canting,⁴ whereas the Ni^{II} complex shows only simple antiferromagnetic coupling.

Complicated magnetic anisotropy has significant influence on the bulk magnetic properties. Indeed, Co^{II}, owing to its single-ion anisotropy, is a good candidate for giving a spin-canted system, although the number of Co^{II} complexes with this property is limited. It is known that α-CoSO₄ is a 3D canted antiferromagnet,⁵ as well as α-Co(dca)₂ (dca = dicyanamide).⁶ Recently, another 3D Co^{II} complex showing spin canting was reported by Chen and co-workers.⁷ With azide and 4,4'-bipyridine, a 2D network structure

has been reported with this behavior.⁸ In fact, very few low-dimensional framework complexes with this behavior have been reported.⁹ It is also worth mentioning that the first and extremely rare discrete molecule showing this magnetic ordering (3D by nature) was a Co^{II} complex, {K₂[CoO₃PCH₂N-(CH₂CO₂)₂]₆·xH₂O}.¹⁰

The *in situ* solvothermal reaction of 3,4-dicyano-1,2,5-thiadiazole (DCT) with CoCl₂·6H₂O and NaOH in H₂O–EtOH (1 : 1) gave brownish red crystals of **1** (Fig. 1),‡ which have high thermal stability (decomposes above 300 °C, Fig. 3S, ESI†). Its phase purity was confirmed by XRPD (Fig. 1S, ESI†) and EA. It should be pointed out that in the solvothermal process the two nitriles of DCT have been converted to carboxylate groups, giving the ligand L²⁻, which has been observed before.¹¹ Single-crystal X-ray diffraction§ of **1** indicates that it crystallizes in the chiral space group *P*2₁ and has a 3D framework structure. In the crystallographic asymmetric unit there each exist two unique but chemically similar Co^{II} ions and L²⁻ ligands, and two coordinated H₂O molecules (Fig. 1 and 4S, ESI†). Each Co^{II} lies on a general position and shows a distorted octahedral geometry formed by three O and two N atoms of three distinct L²⁻ ligands and one H₂O molecule. Two L²⁻ chelate one Co^{II} ion in a κ*N*,*O*-mode, while the third L²⁻ binds Co^{II} in a monodentate mode *via* one carboxylate O atom. Thus each L²⁻ adopts a μ₃-κ*N*,*O*:κ*N'*,*O'*:κ*O'*

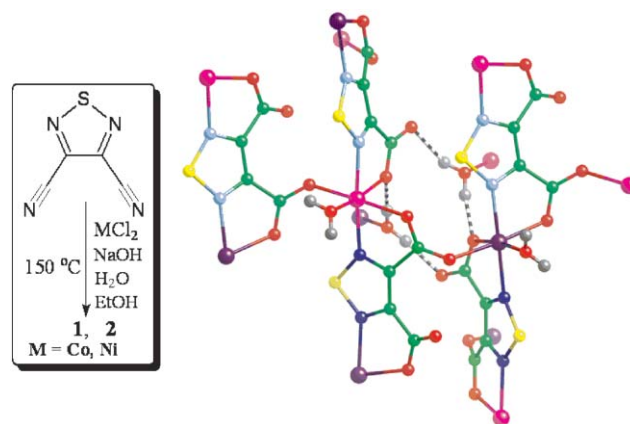


Fig. 1 Left: scheme showing the preparation of **1** and **2**; right: local coordination geometries and H-bonding interactions (striped bonds) in **1**. Co1 atoms are shown in light purple, Co2 as dark purple, and the two crystallographically distinct L have their N atoms depicted in different shades of blue. C are shown as green, O as red, S as yellow, and H as grey.

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coordination mode to bridge three Co^{II} ions: these firstly form a 1D chain (Fig. 5S, ESI†) through bis-*N,O*-chelating μ_2 bridging coordination of L^{2-} , and then form an unusual non-interpenetrated 3D framework (Fig. 4S, ESI†) by the monodentate coordination of O atoms bridging adjacent chains. In the *b* direction, several helices related by 2_1 axes can be defined; these are interconnected and possess opposite chirality. The uncoordinated and one of the coordinated carboxylate O atoms H-bond to the coordinated water molecule (Fig. 1, $\text{H}\cdots\text{O}$ 1.82(1)–1.93(2) Å), which may play an important role in directing the formation of this unusual network. Topologically, each Co^{II} and L^{2-} ligand act as 3-connecting nodes (non-planar *i.e.* pyramidal), to generate a non-interpenetrated (10,3)-d^{12a} (or **utp**^{12b}) network (Fig. 2). The extended Schläfli symbol for this network is $10^2\cdot 10^4\cdot 10^4$. It is different from the regular **utp** net in three aspects: (1) there exist two chemical (and four crystallographic) types of nodes, and the edges and angles are not equivalent; (2) the 4-fold screw axes in the regular **utp** net is lowered to 2-fold; (3) the space group $P2_1$ of **1**, being lower than the $Pnma$ for the most symmetrical configuration of the **utp** net (see Fig. 6S, ESI†). On the other hand, in the *b* direction the planar projection (4.8^2) net is comparable to that of nets (10,3)-a, d, f, although the nonequivalence between Co^{II} and L^{2-} as 3-connected nodes reduces the 4-fold screw axis to a 2-fold. The 3D (10,3) nets are particularly interesting because many of them possess helical channels or voids, and in some cases are chiral. Compared with (10,3)-a (**srs**) and (10,3)-b (**ths**),¹³ the (10,3)-d net is rare.¹⁴ To the best of our knowledge, **1** is only the third example of a metal–organic coordination polymer with a non-interpenetrated (10,3)-d topologic network.^{14g,h}

Interestingly, **1** shows unexpected long-range magnetic ordering. A plot of $\chi_m T$ vs. *T* for **1** is shown in Fig. 3(a) for two Co^{II} ions (given the two crystallographically different Co^{II} ions, Co1 and Co2). The $\chi_m T$ value at r.t., close to $5.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, is the typical value for two Co^{II} ions with spin–orbit coupling.¹⁵ From r.t. to 30 K there is a clear decrease due to the spin–orbit coupling of the Co^{II} ions as well as possible antiferromagnetic interactions between the Co^{II} ions. At lower temperatures there is a surprising feature, which has been studied in detail (see below). Furthermore, the plot (Fig. 3(a) (inset)) of the reduced magnetization vs. *H* at 2 K is not at all the typical plot for an isolated Co^{II} ion, which follows a Brillouin function with the appropriate *g* value. There is an abrupt increase of $M/N\beta$ at very low field, and then follows a sigmoidal curve of the reduced magnetization. This shape is clearly indicative

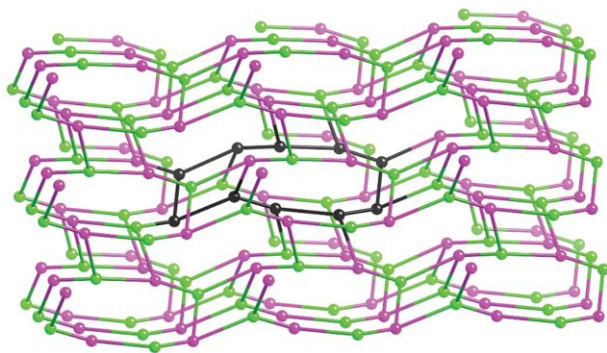


Fig. 2 Schematic representation of the (10,3)-d (**utp**) network in **1**. Ligands are represented by green spheres, Co^{II} by purple. All nodes are topologically identical, and a 10-membered ring is highlighted in black.

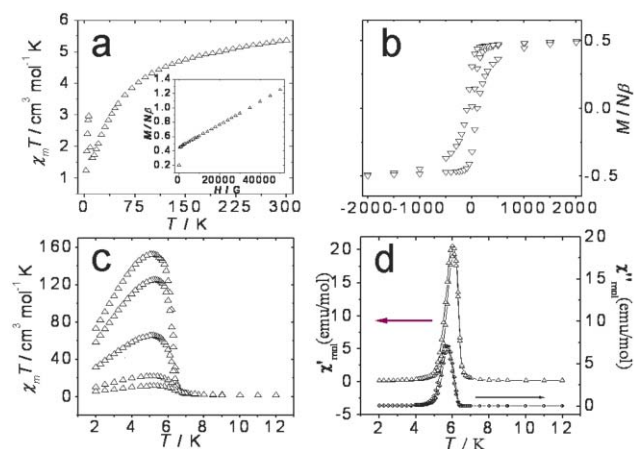


Fig. 3 (a) $\chi_m T$ vs. *T* plot for **1** (inset: plot of the reduced magnetization at 2 K). (b) Hysteresis loop for **1**. (c) $\chi_m T$ vs. *T* plots at different fields (from 1000 to 50 G) for **1** in the low temperature region. (d) Plot of the ac susceptibility for **1**.

of a hysteresis plot. Indeed, the hysteresis plot (Fig. 3(b)) reveals the existence of a behavior corresponding to a very soft magnet (small coercive field). This plot indicates, thus, long-range magnetic ordering in the 3D network of **1**. New proofs have corroborated this magnetic ordering. The plots of $\chi_m T$ vs. *T* at different fields (Fig. 3(c)) indicate that close to 6 K there is the starting point of this magnetic ordering. Finally, the definitive proof is the ac susceptibility measurement (Fig. 3(d)). The out-of-phase (χ'') signal is field independent and has a pronounced maximum close to 6 K, in agreement with the temperature in which the $\chi_m T$ values start to deviate from the normal behaviour.

Due to the shape of the $\chi_m T$ curve, at high temperatures ferromagnetic coupling between the Co^{II} ions does not seem likely. There are different magnetic pathways, Co1–Co2 (1D sub-net); Co1–Co1 and Co2–Co2 (which gives the overall 3D network). All these magnetic pathways have to be AF, unless the *syn-anti* carboxylate coordinate mode is ferromagnetic but very small. Thus, the origin of this magnetic order can be attributed to a weak magnetic ordering, the so-called *canting*.

Changing CoCl_2 to NiCl_2 under similar reaction conditions produced **2** as green crystals (thermal decomposes above 300 °C), which is isomorphous with **1** (Fig. 7S, ESI†), but show distinct magnetic properties. A plot of $\chi_m T$ vs. *T* for **2** is shown in Fig. 4(a). This plot is the typical for a simple antiferromagnetic system,

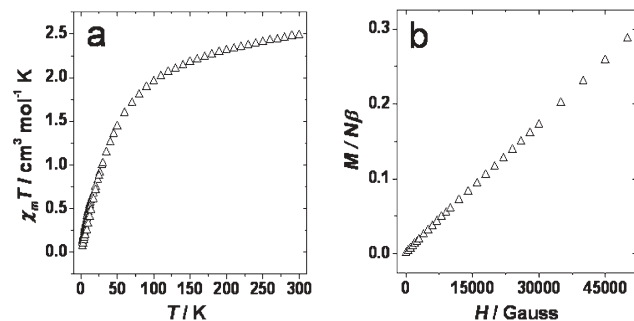


Fig. 4 (a) Plot of $\chi_m T$ vs. *T* for **2**. (b) Plot of the reduced magnetization at 2 K for **2**.

without any other important features. $\chi_m T$ value (for two Ni^{II} ions) is 2.5 cm³ mol⁻¹ K at r.t., a typical value for Ni^{II} ions with $g > 2.00$, and decreases in an unremarkable fashion to 0 cm³ mol⁻¹ K at 2 K. At low temperature the $\chi_m T$ values are independent of the field employed (in contrast with the Co^{II} system) and there is no signal in the ac susceptibility measurements. Due to the 3D structure it is impossible to fit the magnetic data. The pronounced slope of the curve indicates antiferromagnetic coupling. Furthermore, the plot of the reduced magnetization ($M/N\beta$ vs. H at 2 K (Fig. 4(b))) is clearly indicative of this antiferromagnetic coupling, because the value at 5 T is only of the order of 0.3 $N\beta$, when the theoretical value would be close to 2.1 $N\beta$ if the coupling was nil, corroborating the noticeable value of the J parameter.

Why does the Co^{II} system show canting phenomenon? Assuming necessarily that the magnetic ions in the unit cell are not related by a center of symmetry (such as occurs in **1** and **2**), there are two mechanisms by which weak ferromagnetism (canting) may occur.⁴ These are *single-ion anisotropy*, which results in a zero-field splitting (D tensor or parameter), such as occurs in NiF₂ (rutile-type structure), and *antisymmetric spin-spin coupling* ($H = \mathbf{d}_i[S_i \times S_j]$), which is an extra-term in the spin Hamiltonian that usually is taken as isotropic. The antisymmetric exchange is termed as the Dzyaloshinski-Moriya interaction and cants the spins because the coupling energy is minimized when the two spins are perpendicular to each other. It is very important to emphasize that for the two isomorphous systems, the isotropic exchange and the antisymmetric one should be of the same order, and therefore the local anisotropy is the dominant factor which determines the presence or not of the canting phenomenon. The local anisotropy of the Co^{II} ions is due to first-order spin-orbit coupling being, thus, greater than that for Ni^{II}, which is due only to the second order spin-orbit coupling. Therefore, Co^{II} ions are, inherently, much more anisotropic than Ni^{II} ions (for isomorphous complexes). From the structural point of view, the existence of two crystallographically independent Co^{II} ions in **1** may be the key to the canting. The similar situation has also been found in other Co^{II} systems.⁷ However, this magnetic difference in the two Co^{II} and Ni^{II} isomorphous complexes is still very rare in the literature.

In summary, the first use of a newly developed carboxylic acid ligand resulted in two isomorphous 3D Co^{II} and Ni^{II} coordination polymers with a rare (10,3)-d (**utp**) network topology and totally different magnetic properties. The former has an unexpected long-range magnetic ordering from spin-canted antiferromagnetic coupling, but the later displays normal antiferromagnetic coupling. This work probably provides the evidence for the origin of spin canting (at least, in the Co^{II} systems) and demonstrates the importance of engineering metal-organic coordination polymers in the field of molecular-based magnetic materials.

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Notes and references

† *Synthesis of [M₂(L)₂(H₂O)₂]_n (M = Co, **1**; Ni, **2**):* A mixture of DCT (27 mg, 0.2 mmol), NaOH (9 mg, 0.2 mmol) and MCl₂·6H₂O (0.3 mmol) in 12 mL of H₂O-EtOH (1 : 1) was sealed in a Teflon-lined autoclave and heated to 150 °C over 16 h, at this temperature the system was held for 36 h, and then cooled to r.t. over a period of 24 h. Block crystals were collected and washed sequentially by water and acetone. For **1**, brownish red, yield:

~60% based on DCT. EA (%): Calc. for C₈H₄Co₂N₄O₁₀S₂ (498.13): C 19.29, H 0.81, N 11.25. Found: C 19.04, H 0.95, N 11.41. For **2**, green, yield: ~20%. EA (%): Calc. for C₈H₄Ni₂N₄O₁₀S₂ (497.64): C 19.31, H 0.81, N 11.26. Found: C 19.11, H 0.78, N 11.10.

§ *Crystal data:* for **1**: C₈H₄Co₂N₄O₁₀S₂, $M_r = 498.13$; monoclinic; $P2_1$; $a = 7.1024(1)$, $b = 7.0967(1)$, $c = 13.380(3)$ Å, $\beta = 90.81(3)^\circ$; $V = 674.3(2)$ Å³; $Z = 2$; $D_c = 2.453$ g cm⁻³; $T = 293$ K; collected/unique = 6722/3068; $R_{int} = 0.0285$; $R_1 = 0.0226$, $wR_2 = 0.0515$ ($I > 2\sigma(I)$); $R_1 = 0.0247$, $wR_2 = 0.0523$ (all data) and GOF = 1.010; Flack parameter = $-0.002(1)$. For **2**: C₈H₄Ni₂N₄O₁₀S₂, $M_r = 497.69$; monoclinic; $P2_1$; $a = 7.1244(1)$, $b = 7.1131(1)$, $c = 13.153(3)$ Å, $\beta = 90.85(3)^\circ$; $V = 666.5(2)$ Å³; $Z = 2$; $D_c = 2.480$ g cm⁻³; $T = 293$ K; collected/unique = 6603/3009; $R_{int} = 0.0407$; $R_1 = 0.0280$, $wR_2 = 0.0617$ ($I > 2\sigma(I)$); $R_1 = 0.0308$, $wR_2 = 0.0631$ (all data) and GOF = 1.040; Flack parameter = 0.01(1). CCDC 626633 and 626634. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700569e.

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