Unique self-assembled 2D metal-tetrazolate networks: crystal structure and magnetic properties of [M(pmtz)₂] (M = Co(II) and Fe(II); Hpmtz = 5-(pyrimidyl)tetrazole)†

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The title compounds, which have been prepared from M(II) salts (M = Co and Fe) and 5-(pyrimidyl)tetrazole under hydrothermal conditions, are isomorphous and exhibit a 2D square-grid-like structure; the cobalt complex is a spin-canted antiferromagnet with T_c = 15 K.

The design and preparation of multidimensional coordination polymers has attracted much attention during the last few years not only because of their structural and topological novelty but also because of their potential applications as functional materials in fields such as electrical conductivity, molecular magnetism, molecular absorption, catalysis, ion-exchange, *etc.*[1] Among them, molecular magnetic materials have been usually prepared through a building-block approach, combining paramagnetic transition metal ions with appropriate bridging ligands that allow for magnetic exchange coupling.[1e] The nature of the bridging ligand and metal ions mainly determines the sign and magnitude of the magnetic exchange coupling between the paramagnetic metal centers.[2] It should be noted that only a few polyatomic bridging ligands (cyanide, oxalate, dicyanamide, azide, pyrimidine, imidazol, carboxylate, *etc.*) have been shown to be able of mediating strong magnetic coupling between transition metal ions that, in some cases, leads to bulk magnetic ordering.[1e,3–5] Consequently, there exists still now a great interest in the search for new bridging ligands, which can produce new magnetic materials with intriguing structures and magnetic properties. 5-substituted-1*H*-tetrazole ligands have been shown to be excellent and versatile building blocks, with charge and multi-connectivity ability, to produce multidimensional coordination polymers with interesting optical properties.[6] In spite of this, as far as we know, no examples of magnetically characterized 5-substituted tetrazolate-bridged extended systems with paramagnetic metal ions have been reported so far. Herein we report the structural and magnetic properties of two coordination polymers[M(pmtz)₂] (M = Co[II] **1** and Fe[II] **2**) with the new multidentate ligand 5-(pyrimidyl)tetrazol (Hpmtz), which is given in chart 1. †

Hydrothermal reactions of the appropriate metal chloride (1.1 mmol) with Hpmtz (1.1 mmol) in water (10 ml) at 190 °C for 12 h followed by cooling to room temperature over 2 h yields prismatic yellow crystals of **1** (in 64% yield) and red crystals of **2**

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(in 83% yield). The crystal structures‡ were determined by single crystal X-ray crystallography and found to be isomorphous. The structures consist of neutral parallel sheets made of M[II] ions (Co[II] and Fe[II]) and pmtz⁻ bridging ligands in 1 : 2 ratio. In the structure, each M[II] ion is located on an inversion centre and exhibits a distorted octahedral MN₆ geometry with the six nitrogen atoms belonging to four deprotonated tridentate ligands (Fig. 1).

Four in-plane positions are occupied by two chelating pmtz⁻ ligands, which adopt a *trans* disposition. Each of these ligands is coordinated to the M[II] ion through one of the pyrimidyl nitrogen atoms (N₇) and the tetrazole nitrogen in *cis* position (N₁), giving rise to a stable five-membered chelate ring. Two N₃-tetrazolate nitrogen atoms belonging to two neighbouring [M(pmtz)₂] units complete the slightly compressed geometry, with the short axes defined by the two N₁ tetrazole nitrogens. This is the first time that the N₁, N₃, N₇ tridentate coordination mode of the ligand is observed in 5-substituted-tetrazolate bridged complexes. M–N
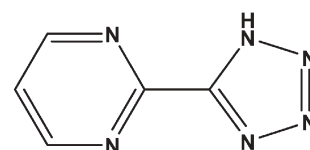
Hpmtz

Chart 1

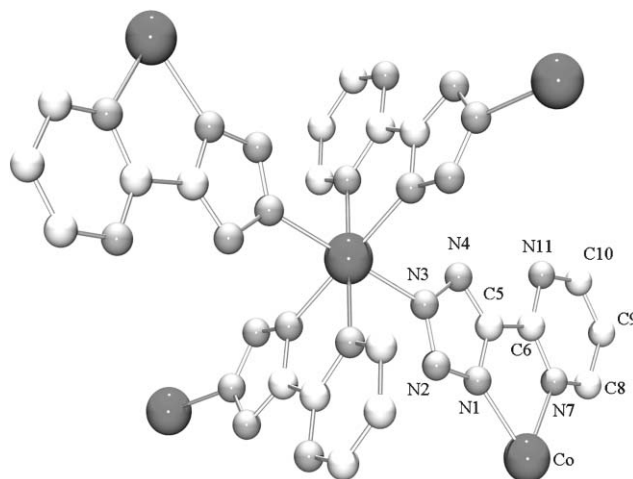
Fig. 1 A view of the metal environment and coordination mode of the ligand for **1** and **2**.

distances are in the ranges 2.0902(15)–2.1493(15) and 1.9578(11)–1.9946(11) Å for **1** and **2**, respectively, whereas *cis* N–M–N angles are in the ranges 77.70(6)–102.30(6) and 80.82(5)–99.18(5)° for **1** and **2**, respectively. The distortion of the M coordination polyhedron is mainly due to the small bite angle of the pmtz⁻ ligand.

Each tridentate bridging pmtz⁻ ligand is bound to two metal ions and each metal ion is linked to four other metal ions by four pmtz⁻ ligands, thus generating square-grid-like sheets paralell to the *ab* plane (Fig. 2). Within the M_4 units, the intralayer M···M separations through the tetrazolate ring are 6.2274(3) Å for **1** and 5.9469(3) Å for **2**, whereas the M···M distances through the diagonals, which correspond to *a* and *b* unit cell parameters, are 8.2299(6) Å and 9.3483(7) Å for **1**, and 8.0193(5) and 8.7837(5) Å for **2**. For **1**, the sheet plane forms a dihedral angle of 71.79(2)° with the mean plane of the coplanar pmtz⁻ ligand, while the corresponding angle for **2** is 72.13(2)°. The N_3MN_3 axes on two adjacent pmtz⁻-bridged M(II) ions are not collinear but form angles of 84.03° and 87.37° for **1** and **2**, respectively. Therefore, there is an alternation of the relative orientation of adjacent metal chromophores (see Fig. 2).

The M(II) ions form the core of the planar layers with the pyridyl groups pointing outwards. The space-filling is achieved by appropriate stacking of layers, interdigitating pyrimidyl groups in such a fashion as to align the pyrimidyl groups above and below one sheet with the cavities in neighbouring networks, leading to *c*/2 interlayer separation (8.950 Å for **1** and 9.019 Å for **2**).

The magnetic properties of **1**, in the form of $\chi_M T$ *vs. T* are represented for two values of the applied magnetic field in Fig. 3. The room-temperature $\chi_M T$ value of 2.58 cm³ mol⁻¹ K is larger than the spin-only value of 1.875 cm³ mol⁻¹ K for an uncoupled high-spin octahedral Co^{II} ion (S = 3/2, g = 2), in accordance with the well-documented orbital contribution of the octahedral Co^{II} ions. Upon lowering the temperature, $\chi_M T$ decreases, attains a minimum at 20 K ($\chi_M T$ = 0.95 cm³ mol⁻¹ K), then exhibits an abrupt increase to a maximum value (35 cm³ mol⁻¹ K at 300 G) before decreasing in the very low temperature region.
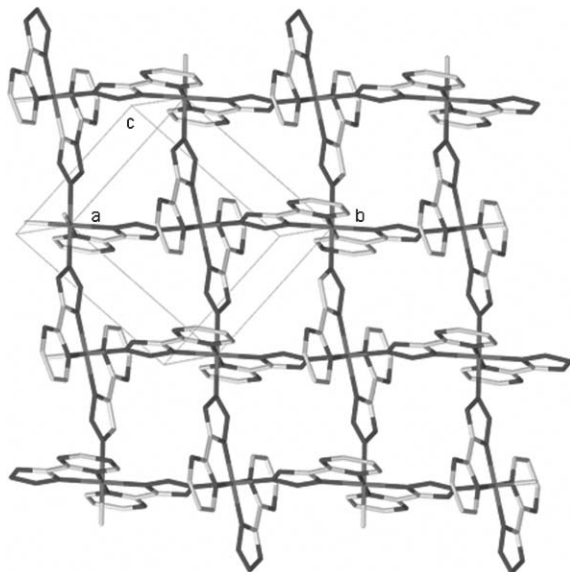

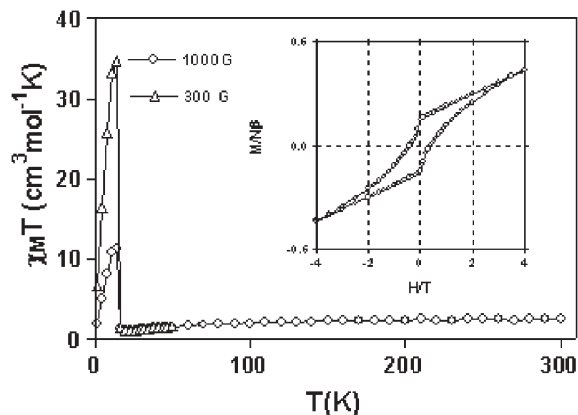**Fig. 2** A fragment of the layered structure of **1** and **2** in the *ab* plane.

Fig. 3 Temperature dependence of $\chi_M T$ at 300 G and 1000 G (the solid line is just an eye-guide). The inset shows the hysteresis loop of **1** at 2.0 K between ±4 *T*.

The magnetic susceptibility in the range 100–300 K obeys the Curie–Weiss law with a Curie constant C = 2.86 cm³ mol⁻¹ K and θ = −36 K. The continuous decrease in $\chi_M T$ from room-temperature to 20 K can be attributed to both the spin–orbit coupling of the octahedral Co^{II} ions with a $^4T_{1g}$ ground term and the moderate antiferromagnetic coupling between the Co^{II} centres through the tetrazolato bridging ligand. Below 20 K, where an abrupt increase in $\chi_M T$ is observed, the susceptibility becomes field dependent, thus suggesting a ferromagnetic phase transition. Both the in-phase (χ_M') and out-of-phase (χ_M'') ac susceptibility signals, which are frequency independent, show a sharp peak below a T_c = 15 K (T_c = Curie temperature), confirming the presence of net magnetization. At 2 K, **1** exhibits a magnetic hysteresis loop (Fig. 3, inset) with a large coercitive field of 0.4 T and a remnant magnetization of 0.024 Nβ. The isothermal magnetization shows linear dependence with field and attains a highest value at 2 K and 5 T of 2353 cm³ G mol⁻¹, which is significantly below the theoretical saturation magnetization of 16755 cm³ G mol⁻¹.

All these magnetic properties (negative Weiss constant, sharp signals in the ac susceptibilities, linear dependence of the isothermal magnetization in the ordered state and no saturation limit) are characteristics of spin canted antiferromagnetism, leading to weak ferromagnetism.[7] Two mechanism can lead to spin canting, namely the magnetic anisotropy and the antisymmetric magnetic exchange.[8] In this case, the canting is not derived from the antisymmetric exchange mechanism as the space group of **1** is centrosymmetric.[9] Consequently, the observed spin canting may be attributed to the single ion magnetic anisotropy of the octahedral Co^{II} ion and to the systematic alternation of the relative orientation of adjacent metal chromophores (see above); this latter being a typical feature of some of these canted systems.[7b] The 3D long-range order in **1** is only possible through dipolar and other weak interlayer interactions and this is the reason why T_c is relatively low.

In complex **2**, octahedral Fe(II) ions are in the low-spin state (S = 0) and therefore this compound exhibits diamagnetic behaviour.

These results show that new and interesting magnetic materials can be assembled from paramagnetic metal ions and tetrazolato-bridging ligands. Work along this line using other paramagnetic metal and tetrazolate ligands is in progress in our lab.

Notes and references

† This new ligand was prepared according to the method proposed by Sharpless and Demko.[10]

‡ *Crystal Data.* **1**: [Co(C$_5$H$_3$N$_6$)$_2$], M = 353.20, orthorhombic, space group *Pbca*, a = 8.2299(6), b = 9.3483(7), c = 17.8999(14) Å, V = 1377.14(18) Å^3, Z = 4, ρ_{calcd} = 1.704 g cm^{-3}, μ(Mo-$K\alpha$) = 1.268 mm^{-1}, T = 293 K $F(000)$ = 708, $R1(F_o)$ = 0.0326 ($wR2(F_o^2)$ = 0.0752) for 1603 unique reflections (R_{int} = 0.0314) with a goodness-of-fit on F^2 1.051. **2**: [Fe(C$_5$H$_3$N$_6$)$_2$], M = 350.12, orthorhombic, space group *Pbca*, a = 8.0193(5), b = 8.7837(5), c = 18.0385(11) Å, V = 1270.62(13) Å^3, Z = 4, ρ_{calcd} = 1.830 g cm^{-3}, μ(Mo-$K\alpha$) = 1.210 mm^{-1}, T = 100 K. $F(000)$ = 704, $R1(F_o)$ = 0.0279 ($wR2(F_o^2)$ = 0.0790) for 1484 unique reflections (R_{int} = 0.0184) with a goodness-of-fit of 1.092. For both structures, data were collected by $\omega/2\theta$ scans ($2\theta_{max}$ =56°) on a Bruker SMART CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by the SHELX-97 program.[11] CCDC 277210 & 277211. See http://dx.doi.org/10.1039/b509069e for crystallographic data in CIF or other electronic format.

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