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Syntheses, structures and magnetic properties of two-dimensional chiral coordination polymers based on a tetradentate chiral ligand†

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Two chiral coordination polymers, Δ-[M^{II}(*S*-pabn)]$_2$[$Mo^{IV}(CN)_8$]$\cdot 3H_2O$ (M = Cu and Co, *S*-pabn = (*S*)-*N*2,*N*2′-bis(pyridin-2-ylmethyl-1,1′-binaphthyl-2,2′-diamine)), with two-dimensional network structures, were synthesized by the reaction of $MCl_2\cdot 6H_2O$, *S*-pabn and $K_4[Mo(CN)_8]$. The compounds show paramagnetic behavior originating from the unpaired electrons of the Cu(II) or Co(II) centers.

Chiral network compounds have great potential as multifunctional materials as their chirality-dependent physical properties such as optical activity and permittivity can be controlled by molecular design. Coordination polymers derived from metal ions and organic ligands have magnetic and electronic interactions between neighboring metal ions through their bridging ligands. If a paramagnetic metal center exists in a chiral coordination environment, physical properties resulting from the chirality can propagate entire molecules and enhance their functionality through the generation of a chiral spin structure. For example, if a chiral moiety is located on the magnetic center of a molecular magnet, the chirality can be transferred to the local spins of the material leading to unusual magneto-optical characteristics such as magneto-chiral dichroism (MChD).[1,2] Consequently, chiral molecular magnets continue to draw the attention of synthetic chemists. It is generally considered that the best way to synthesize chiral molecular magnets is through the use of chiral ligands or counter ions due to the relative ease of the synthetic approach.

A number of magnetic chiral network materials have been reported in recent years. M. Verdaguer *et al.* reported the discovery of two-dimensional chiral molecular magnets, $[N(CH_3)(n\text{-}C_3H_7)_2((S)\text{-}s\text{-}C_4H_9)][(\Lambda)\text{-}Mn(\Delta)\text{-}Cr(ox)_3]$ and $[N(CH_3)(n\text{-}C_3H_7)_2((R)\text{-}s\text{-}C_4H_9)][(\Delta)\text{-}Mn(\Lambda)\text{-}Cr(ox)_3]$, which showed strong magneto-chiral effects,[1] and M. Ohba and K. Inoue *et al.* synthesized two-dimensional chiral molecular-magnets, $[Mn^{II}(HL)(H_2O)][M^{III}(CN)_6]\cdot 2H_2O$ (M = Mn, Cr; L = *S*- or *R*-1,2-diaminopropane), using a chiral amine ligand.[3,4] Extending such chiral networks to form three-dimensional framework materials E. Coronado *et al.* used the chiral carboxylate, L-tartrate, to generate three dimensional chiral magnetic compounds.[5]

From a physical viewpoint, the toroidal moment derived from chiral spin moieties has attracted a great deal of research. Dzyaloshinskii–Moriya interactions were investigated in V_3 and Cu_3 magnetic clusters,[6–8] while M. Mito *et al.* investigated the giant nonlinear magnetic response in a chiral molecular magnet,[9] and Kishine *et al.* studied physical phenomena related to chiral spin systems.[10,11]

Underpinning the research into the physical nature of such materials is the need to be able to generate paramagnetic chiral compounds through a rational molecular design. The development of enhanced magneto-chiral molecular materials relies on the generation of molecular species with chiral spin centers, as the magneto-optical effect and permittivity depend upon the spin chirality of the paramagnetic centers. In the present research we used chiral ligands to introduce the desired chirality in paramagnetic transition metal ions, due to the predictability of their coordination behavior.

Previously, we reported a study on optically-active decanuclear nickel–iron cage compounds with bidentate chiral ligands which showed ferromagnetic interactions between nickel and iron ions.[12] Additionally, we reported the synthesis and physical properties of one-dimensional chiral magnetic networks with tetradentate chiral ligands.[13,14] In this work, we synthesized two new two-dimensional chiral network compounds, Δ-[M^{II}(*S*-pabn)]$_2$[$Mo^{IV}(CN)_8$]$\cdot 3H_2O$ (M = Cu and Co, *S*-pabn = (*S*)-*N*2,*N*2′-bis(pyridin-2-ylmethyl-1,1′-binaphthyl-2,2′-diamine)) and investigated their crystallographically-determined structures and their optical and magnetic properties.

Δ-[M^{II}(*S*-pabn)]$_2$[$Mo^{IV}(CN)_8$]$\cdot 3H_2O$ (M = Cu^{II} (**1**) and Co^{II} (**2**)) have similar two-dimensional network structures, both crystallizing in the monoclinic space group *C*2. The asymmetric units include

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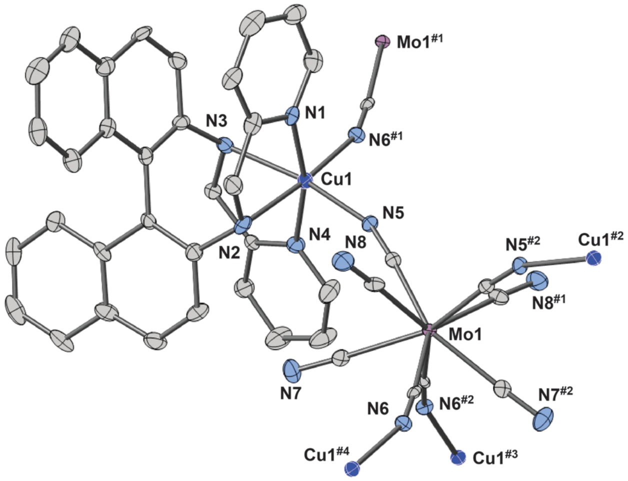

Fig. 1 Structure of compound Δ-$[Cu^{II}(S\text{-pabn})]_2[Mo^{IV}(CN)_8]\cdot 3H_2O$ (**1**·$3H_2O$), with thermal ellipsoids shown at 30% probability. Hydrogen atoms have been omitted for clarity. Symmetry code: #1 $+x - 1/2$, $+y - 1/2$, $+z$ #2 $-x + 2$, $+y$, $-z + 2$, #3 $-x + 3/2$, $+y$, $-z + 2$, #4 $+x + 1/2$, $+y + 1/2$, $+z$.

one $[M^{II}(S\text{-pabn})]^{2+}$ unit and half of one $[Mo^{IV}(CN)_8]^{4-}$ unit (Fig. 1). The Mo^{IV} ion (Mo1) is located on a two-fold axis, while the M^{II} ion is bound to the N_4 site of the chiral tetradentate ligand *S*-pabn and two nitrogen atoms from the cyanide groups of neighboring octamolybdate ions in an octahedral coordination environment. Four cyanide groups of each octacyanomolybdate unit are involved in bridging coordination behavior, resulting in a two-dimensional framework structure (Fig. 2). In the case of **1** (M = Cu), there are elongated coordination bonds due to Jahn–Teller distortion effects. Lying on the elongation axis, one of the $Cu–N_{amine}$ bonds, Cu1–N3, has a bonding distance of 2.406(9) Å, while in the case of **2** (M = Co), the same degree of stretching is not seen (2.31(2) Å). Selected bond lengths are summarized in Table 1. In the two-dimensional network structure, the copper and cobalt ions have homochiral coordination geometries in the Δ-form, which are defined by the orientation of the two pyridylamine bidentate units and the two cyanide groups.

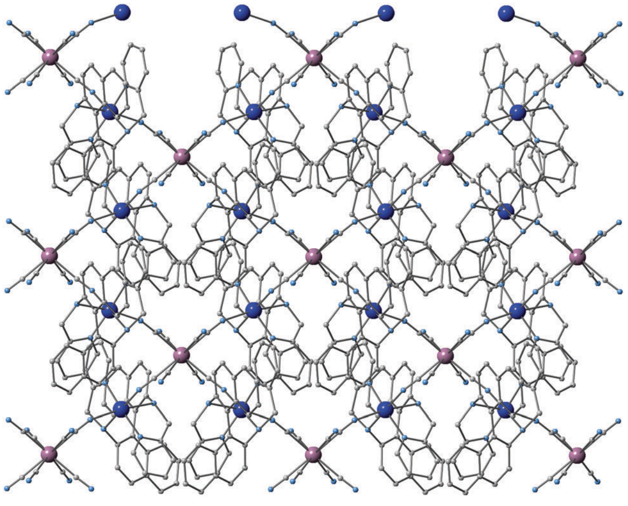

Fig. 2 Network structure of compound **1**·$3H_2O$.

Table 1 Selected bond lengths of **1** and **2**

	1·$3H_2O$		**2**·$3H_2O$
Cu(1)–N(1)	1.980(9)	Co(1)–N(1)	2.08(2)
Cu(1)–N(2)	2.209(11)	Co(1)–N(2)	2.29(2)
Cu(1)–N(3)	2.406(9)	Co(1)–N(3)	2.31(2)
Cu(1)–N(4)	1.980(9)	Co(1)–N(4)	2.07(2)
Cu(1)–N(5)	2.213(9)	Co(1)–N(5)	2.07(2)
Cu(1)–N(6)[a]	2.029(9)	Co(1)–N(6)[b]	2.05(2)
Mo(1)–C(33)	2.131(11)	Mo(1)–C(33)	2.13(3)
Mo(1)–C(34)	2.147(12)	Mo(1)–C(34)	2.14(2)
Mo(1)–C(35)	2.155(11)	Mo(1)–C(35)	2.18(3)
Mo(1)–C(36)	2.173(13)	Mo(1)–C(36)	2.14(4)

[a] $+x - 1/2$, $+y - 1/2$, $+z$. [b] $+x + 1/2$, $+y + 1/2$, $+z$.

Considering the charge balance and coordination bond lengths, the heterometal ion M is understood to be divalent and the Mo ion of the octacyanomolybdate is tetravalent in both compounds. Therefore, the bridging $[Mo(CN)_8]^{4-}$ unit is diamagnetic.

The crystallographically determined Flack parameters converged to zero, indicating that the structures were homochiral. Circular dichroism (CD) measurements were conducted on a solid sample of **1**·$3H_2O$ compressed into a KBr pellet and measured in transmission mode at room temperature using a JASCO J-820 spectrometer. The optical activity confirmed the chirality of the compound. The absorbance bands in the range of 300–400 nm can be attributed to ligand-based $\pi–\pi^*$ transitions, and display the positive Cotton effect. The peak at 601 nm corresponds to the low intensity absorption band associated with Cu^{II} d–d transitions (Fig. 3).

Magnetic susceptibility measurements for **1**·$3H_2O$ and **2**·$6H_2O$ were performed in the temperature range of 1.8–300 K. Temperature dependencies of the magnetic susceptibilities for **1**·$3H_2O$ and **2**·$6H_2O$ are shown in Fig. 4. The $\chi_m T$ value of **1**·$3H_2O$ at 300 K is 0.996 emu mol^{-1} K, larger than the value expected for two magnetically isolated copper ions (0.75 emu mol^{-1} K, $S = 1/2 + 1/2$, $g = 2.00$). The $\chi_m T$ value decreased in a linear fashion as the temperature was lowered, reaching a value of 0.78 emu mol^{-1} K at 1.8 K, which corresponds to the value expected for two isolated copper ions ($S = 1/2 + 1/2$, $g = 2.04$). This magnetic behavior might be derived from the second-order Zeeman effects of the Mo(IV) ions. On the other hand, the $\chi_m T$ value of **2**·$6H_2O$ at 300 K is 4.07 emu mol^{-1} K, corresponding to the value expected for two magnetically isolated cobalt ions ($S = 3/2$, $g = 2.08$).

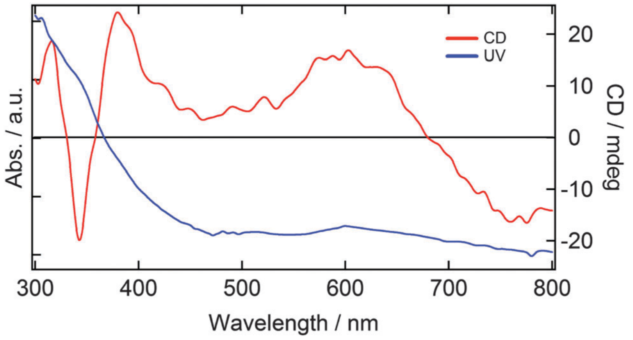

Fig. 3 Overlaid spectra (UV-vis = blue, and CD = red) for **1**·$3H_2O$.

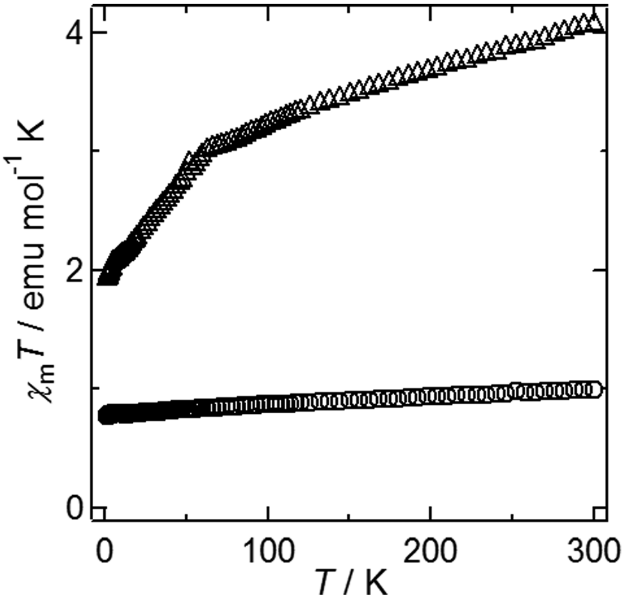

Fig. 4 Temperature dependence of the magnetic susceptibilities of $\mathbf{1}\cdot 3H_2O$ (circles) and $\mathbf{2}\cdot 6H_2O$ (triangles).

The $\chi_m T$ value gradually decreased as the temperature was lowered, and reached a value of 1.93 emu mol^{-1} K at 1.8 K. This magnetic behavior can be understood by the contributions of the spin–orbit coupling inherent to Co(II) ions. Light irradiation experiments for both compounds were performed at 5 K, however, no change in magnetic moment was observed for either compound. The absence of any photo-chemical response may be due to the rigidity of the metal ion coordination sites.

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Experimental

Materials and physical measurements

All of the reagents were obtained from commercial suppliers. All of the solutions were used without any purification. The building unit K$_4$[Mo(CN)$_8$] and the tetradentate ligand, *S*-pabn (*S*-pabn = (*S*)-*N*2,*N*2′-bis(pyridin-2-ylmethyl-1,1′-binaphthyl-2,2′-diamine)), were prepared according to the literature procedures.[15,16]

Syntheses of the compounds

Synthesis of Δ-[Cu^{II}(*S*-pabn)]$_2$[Mo^{IV}(CN)$_8$]·3H$_2$O (1·3H$_2$O). A powder sample of Cu^{II}Cl$_2$·6H$_2$O (1.7 mg, 0.01 mmol) was added to an acetonitrile solution of *S*-pabn (4.6 mg, 0.01 mmol) and the mixture was stirred. K$_4$[Mo(CN)$_8$] (2.5 mg, 0.005 mmol) in water (2 mL) was then added dropwise to the reaction solution. After storing the sample at room temperature overnight, green square plates of Δ-[Cu^{II}(*S*-pabn)]$_2$[Mo^{IV}(CN)$_8$]·3H$_2$O (**1**·3H$_2$O) were obtained. The crystals were collected by suction filtration and dried in air. Anal. calcd for $C_{72}H_{54}N_{16}O_3Cu_2Mo_1$ (**1**·3H$_2$O): C, 61.14; H, 3.85; N, 15.85%; found: C, 61.04; H, 4.06; N, 15.77%. IR (KBr pellet, cm^{-1}): 2110.0 (*vs.*), 1612.4 (m), 1510.2 (s), 1431.1 (m), 1361.7 (m), 1292.2 (m), 1155.3 (m).

Synthesis of Δ-[Co^{II}(*S*-pabn)]$_2$[Mo^{IV}(CN)$_8$]·3H$_2$O (2·3H$_2$O). Δ-[Co^{II}(*S*-pabn)]$_2$[Mo^{IV}(CN)$_8$]·3H$_2$O (2·3H$_2$O) was obtained by the same synthetic approach as that utilized in the preparation of **1**, but using Co^{II}Cl$_2$·6H$_2$O as the metal source. The crystals were collected by suction filtration and dried in air. Air dried samples tend to be moisture sensitive, leading to differences in the number of lattice water molecules observed in fresh crystals and samples that have been dried. Anal. calcd for $C_{72}H_{60}N_{16}O_6Co_2Mo_1$ (**2**·6H$_2$O): C, 59.27; H, 4.14; N, 15.36%; found: C, 59.28; H, 4.16; N, 15.47%. IR (KBr pellet, cm^{-1}): 2111.9 (*vs.*), 1612.4 (m), 1510.2 (s), 1431.1 (m), 1359.7 (m), 1203.5 (m), 1155.3 (m).

X-ray crystallography

The crystallographic parameters are summarized in ref. 17. Diffraction data were collected using a Bruker SMART APEX diffractometer equipped with a CCD type area detector. A hemisphere of data was collected with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). At the end of the data collection, the first 50 frames of data were recollected to establish that the crystal had not deteriorated during the data collection. The data frames were integrated using the SAINT program and merged to give a unique data set for structure determination. An absorption correction was performed using SADABS. The structure was solved by directed methods and refined by the full-matrix least-squares method based on all F2 data using the SHELXTL package (Bruker Analytical X-ray Systems). Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined using isotropic thermal parameters riding on those of the parent atoms.

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Notes and references

1 C. Train, R. Gheorghe, V. Krstic, L.-M. Chamoreau, N. S. Ovanesyan, G. L. J. A. Rikken, M. Gruselle and M. Verdaguer, *Nat. Mater.*, 2008, **7**, 729.
2 G. L. J. A. Rikken and E. Raupach, *Nature*, 1997, **390**, 493.
3 K. Inoue, K. Kikuchi, M. Ohba and H. Ōkawa, *Angew. Chem., Int. Ed.*, 2003, **42**, 4810.
4 W. Kaneko, S. Kitagawa and M. Ohba, *J. Am. Chem. Soc.*, 2007, **129**, 248.
5 E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García and A. Murcia-Martínez, *Chem.–Eur. J.*, 2006, **12**, 3484.

6 M. I. Belinsky, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 064425.

7 K.-Y. Choi, Y. H. Matsuda, H. Nojiri, U. Kortz, F. Hussain, A. C. Stowe, C. Ramsey and N. S. Dalal, *Phys. Rev. Lett.*, 2006, **96**, 107202.

8 K.-Y. Choi, N. S. Dalal, A. P. Reyes, P. L. Kuhns, Y. H. Matsuda, H. Nojiri, S. S. Mal and U. Kortz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 024406.

9 M. Mito, K. Iriguchi, H. Deguchi, J. Kishine, K. Kikuchi, H. Osumi, Y. Yoshida and K. Inoue, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 012406.

10 J. Kishine, K. Inoue and Y. Yoshida, *Prog. Theor. Phys.*, 2005, **159**, 82.

11 J. Kishine, I. V. Proskurin and A. S. Ovchinnikov, *Phys. Rev. Lett.*, 2011, **107**, 017205.

12 T. Shiga, G. N. Newton, J. S. Mathieson, T. Tetsuka, M. Nihei, L. Cronin and H. Oshio, *Dalton Trans.*, 2010, **39**, 4730.

13 N. Hoshino, Y. Sekine, M. Nihei and H. Oshio, *Chem. Commun.*, 2010, **46**, 6117.

14 N. Hoshino, F. Iijima, G. N. Newton, N. Yoshida, T. Shiga, H. Nojiri, A. Nakao, R. Kumai, Y. Murakami and H. Oshio, *Nat. Chem.*, 2012, **4**, 921.

15 (*a*) J. G. Leipoldt, L. D. C. Bok and P. J. Cilliers, *Z. Anorg. Allg. Chem.*, 1974, **409**, 343; (*b*) L. D. C. Bok, J. G. Leipoldt and S. S. Basson, *Z. Anorg. Allg. Chem.*, 1975, **415**, 81.

16 H. Huang, T. Okuno, K. Tsuda, M. Yoshimura and M. Kitamura, *J. Am. Chem. Soc.*, 2006, **128**, 8716.

17 Crystallographic data collected for **1**·3H$_2$O: $C_{72}H_{58}Cu_2MoN_{16}O_3$, 1418.36 g mol^{-1}, monoclinic $C2$, a = 15.2194(18), b = 11.4434(18), c = 19.218(3) Å, β = 90.342(4)°, V = 3346.9(8) Å^3, Z = 2. A total of 10 164 reflections were collected ($2.12^\circ < 2\theta < 55.0^\circ$) of which 5528 were unique (R_{int} = 0.0820). Final R_1 = 0.0564, wR_2 = 0.1061 ($I > 2\sigma(I)$). **2**·3H$_2$O: $C_{72}H_{58}Co_2MoN_{16}O_3$, 1409.14 g mol^{-1}, monoclinic $C2$, a = 14.943(7), b = 11.568(7), c = 19.366(10) Å, β = 90.045(19)°, V = 3348.3(8) Å^3, Z = 2. A total of 9245 reflections were collected ($2.1^\circ < 2\theta < 51.0^\circ$) of which 5627 were unique (R_{int} = 0.2008). Final R_1 = 0.0807, wR_2 = 0.1558 ($I > 2\sigma(I)$).