Chiral azide-bridged two-dimensional Cu(II) compounds showing a field-induced spin–flop transition†

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Two azide-bridged chiral Cu(II) compounds, [Cu(*R*,*R*-dacy)-$(N_3)_2]_n$ (1) (*R*,*R*-dacy = *trans*-(1*R*,2*R*)-diaminocyclohexane) and [Cu(*S*,*S*-dacy)$(N_3)_2]_n$ (2) (*S*,*S*-dacy = *trans*-(1*S*,2*S*)-diaminocyclohexane), with two-dimensional layer structures exhibiting end-to-end and end-on azide bridging patterns, were prepared and among them 1 was examined to show a field-induced spin–flop transition.

Multifunctional materials with properties including magnetism and a second physical characteristic such as electrical conductivity and second-order nonlinear optics have been actively investigated owing to their potential applications.[1] The recent discovery of magnetochiral dichroism (MChD), linking magnetism and chirality in a chiral paramagnetic compound, has encouraged many efforts to construct materials with such properties.[2] To control the molecular structure and magnetic nature of chiral coordination materials the adoption of appropriate bridging ligands is of importance. In this respect, for instance, hexacyanometalates and oxalate ligands have been successfully applied, forming chiral systems with dual functionality.[3,4] Azide is one of the good candidates for this purpose because its magnetic properties can be predicted based on its binding modes. The design of chiral materials has been attempted employing either achiral auxiliaries generating spontaneous resolution upon crystallization or chiral species as a source of optical activity. Homochiral Mn(II) azido compounds, prepared using achiral diazine ligands in a spontaneous resolution process, were reported.[5] Examples of chiral materials, especially bridged by azide ligands, are still lacking and we have attempted to utilize chiral ligands for the construction of chiral azide-bridged coordination polymers. Herein we report the structures, magnetic and optical properties of unprecedented 2D layered compounds, [Cu(*R*,*R*-dacy)$(N_3)_2]_n$ (**1**) (*R*,*R*-dacy = *trans*-(1*R*,2*R*)-diaminocyclohexane) and [Cu(*S*,*S*-dacy)$(N_3)_2]_n$ (**2**) (*S*,*S*-dacy = *trans*-(1*S*,2*S*)-diaminocyclohexane), which represent the first examples of a chiral azide-bridged system chelated with a chiral ancillary ligand.

1 and **2** were prepared by a stoichiometric mixing of $Cu(ClO_4)_2 \cdot 6H_2O$, *R*,*R*-dacy or *S*,*S*-dacy, and NaN_3 in MeOH–H_2O solvent.‡ Both complexes crystallize in the noncentrosymmetric monoclinic $P2_1$ space group.§ A structural disparity between them is found only in the absolute configuration of dacy as illustrated in Figs. 1 and S1.† For **1**, the Cu(II) ion in a distorted octahedral geometry is bridged by azide groups in μ-1,1,3 mode, leading to a two-dimensional layer structure. The overall structure is reminiscent of that of Ni azido complexes.[6] The Cu–N distances in the basal plane composed of four nitrogen atoms from *R*,*R*-dacy, one terminal and bridging azide groups range from 1.994 to 2.024 Å whereas the apical sites are significantly elongated (Cu1–N8 = 2.452(2) Å, Cu1–N11 = 2.615(2) Å, Cu2–N13b = 2.485(2) Å, and Cu2–N6 = 2.591(2) Å; $b = 1 - x, -0.5 + y, 1 - z$) which are in the range of a tetragonal distortion on an octahedral Cu(II) ion, characteristic of the Jahn–Teller effect. In end-on (EO) bridging mode, the average angle of Cu1–N(azido)–Cu2 is 90.8(5)°. In end-to-end (EE) mode the

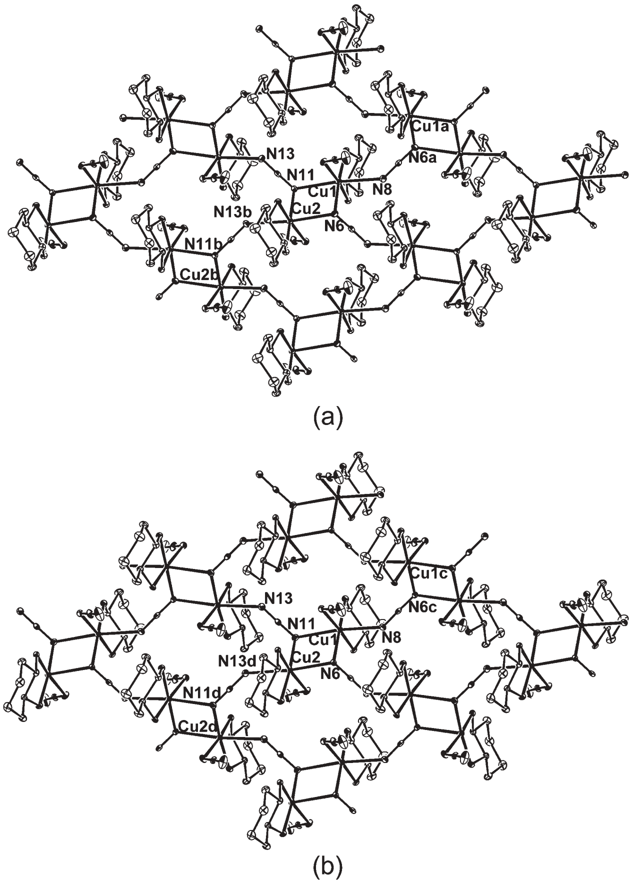

Fig. 1 Two-dimensional extended layer structures of (a) **1** and (b) **2**. Symmetry code: $a = 1 - x, 0.5 + y, -z$; $b = 1 - x, -0.5 + y, 1 - z$; $c = 1 - x, -0.5 + y, -z$; $d = 1 - x, 0.5 + y, 1 - z$.

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† Electronic Supplementary Information (ESI) available: Structures and magnetic data for **1** and **2** (Figs. S1–S6). See http://dx.doi.org/10.1039/b507051a

torsion angles are 69.2(1)° for Cu1–N8···N6a–Cu1a and 69.9(1)° for Cu2–N13b···N11b–Cu2b ($a = 1 - x, 0.5 + y, -z$). Another important parameter is the angle of Cu–N–N(azido): 117.0(1)° for Cu1a–N6a–N7a, 134.1(2)° for Cu1–N8–N7a, 117.0(1)° for Cu2–N11–N12, and 132.9(2)° for Cu2–N13b–N12b. The intradimer Cu···Cu distance *via* the EO azide bridge is 3.3180(3) Å while the shortest interdimer Cu···Cu distance through the EE bridge corresponds to 5.3773(3) Å. The overall structure can be viewed as a 2D sheet with the shortest interlayer Cu–Cu distance of 11.989(1) Å.

The cryomagnetic properties of **1** are shown in Fig. 2. The χ_mT value of 0.385 cm^3 K mol^{-1} at 300 K is slightly larger than the spin-only one (0.375 cm^3 K mol^{-1}) expected for a noninteracting Cu(II) center. As temperature decreases χ_mT rises gradually and reaches a maximum value of 0.404 cm^3 K mol^{-1} at 20 K, indicating that ferromagnetic couplings between spin centers are operating. Further cooling causes an abrupt drop, which signals dominant antiferromagnetic interactions at low temperatures.

To probe the magnetic nature in **1** we examined the structural parameters related with magnetic properties. There exist two magnetic pathways: one is *via* the EO azide bridge and the other through the EE one. In the dinuclear unit doubly bridged by EO azide groups, the interaction is expected to be ferromagnetic when the Cu–N(azido)–Cu angle falls in the range 96–104°.[7] The observed angle of 90.8(5)° is positioned far away from the range, accordingly antiferromagnetic couplings being anticipated as reported for a EO double azide-bridged Cu(II) dimer with an angle of 89.1° exhibiting antiferromagnetic interactions.[8] The average bond distance along the apical directions is longer, 2.60(2) Å, compared to that of the Cu(II) dimer with an apical bond length of 2.505 Å.[8] Therefore, weaker magnetic interactions in the EO mode for **1** than those for the reported Cu dimer case are predicted.[8] On the other hand, provided the torsion angle of Cu–N$_3$–Cu is close to 90°, ferromagnetic interactions *via* the EE route tend to occur as found in one-dimensional EE azide-bridged Cu(II), Co(II), Ni(II) complexes in which the torsion angles are equal to 91.6°, 71.6°, and 75.6°, respectively.[9] As a consequence, the average torsion angle of 69.6(5)° for **1** suggests the occurrence of ferromagnetic interactions through the EE azide linkage. From this structural point of view, a possible magnetic exchange pathway is thus schematized in Scheme 1.

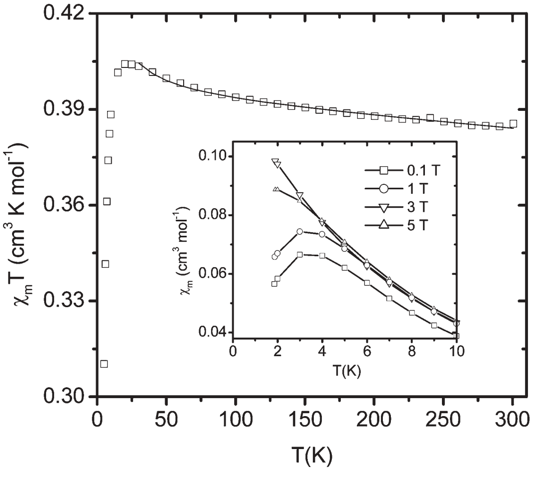
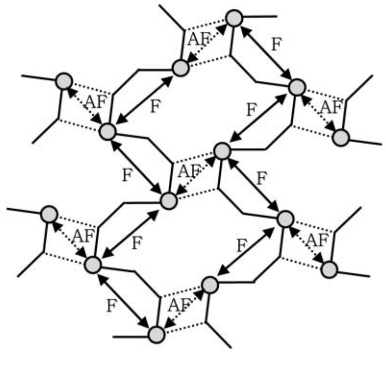


Fig. 2 Plot of χ_mT *vs.* T at 0.1 T for **1**. The solid line shows the best theoretical fit. The inset, in which the solid lines are guides, presents the temperature dependence of magnetic susceptibility at various fields.

Based on the aforementioned aspects the magnetic data were fitted with a high-temperature series expansion with the spin Hamiltonian $H = -J\Sigma_iS_i{\cdot}S_{i+1}$.[10] A best fit in the temperature range 30–300 K, where ferromagnetic interactions through the EE azide bridge are prevalent, affords parameters of $g = 2.05(1)$ (2.09 from EPR), $J = 0.63(4)$ cm^{-1} for **1** and $g = 2.09(1)$ (2.09 from EPR), $J = 0.48(3)$ cm^{-1} for **2** (Figs. S2–S4).† It is only possible to fit the experimental data at $T > 30$ K because below this temperature antiferromagnetic interactions transmitted by the EO azide bridges and between layers are present. The ferromagnetic interactions arise from the quasi-orthogonality of the magnetic orbitals ($d_{x^2-y^2}$), residing in the basal planes, of the two adjacent Cu(II) centers[9] and the magnitude of the ferromagnetic exchange coupling constant (J) is in line with that (1.36 cm^{-1}) of the EE azide-bridged Cu(II) system exhibiting the large torsion angle.[9a]

The ac susceptibility data for **1** demonstrate that an antiferromagnetic ordering[11] is present at 3.4 K and no shift of maxima with increasing frequency takes place (Fig. S5).† The magnetic order can be understood by taking into account that below this temperature the weak antiferromagnetic interactions *via* the EO azide groups and through space between layers may favor a long-range antiparallel arrangement among the ferromagnetic chains. The field dependence of the magnetization (Fig. 3) reveals that the magnetization curve at 20 K increases faster than the theoretical value calculated from the Brillouin function for a uncoupled Cu(II) spin. This behavior implies that ferromagnetic interactions subsist, which is consistent with the magnetic observation in the $\chi_mT(T)$ plot at the same temperature. The magnetization data at 1.9 K is smaller than the calculated Brillouin curve, indicative of global antiferromagnetic interactions. It is noted that the experimental curve is sigmoidal and arrives at a saturation value of 0.97 μ_B at 7 T, which is in good agreement with the theoretical value of 0.99 μ_B for an independent Cu(II) center. The observed magnetic phenomena are associated with a field-induced spin–flop transition as depicted in the inset of Fig. 2.[12] At fields up to 1 T, an antiferromagnetic phase is dominant as manifested from the existence of a peak in the $\chi_m(T)$ curve. Around 3 T, the antiferromagnetic state is almost diminished and a field-induced paramagnetic (or ferromagnetic-like) state eventually develops at 5 T. These features are confirmed by the field



Scheme 1 A possible magnetic exchange model in which the solid lines denote ferromagnetic interactions (J) through the EE azide bridge and the dotted ones are considered as weak antiferromagnetic couplings *via* the EO azide linkage.

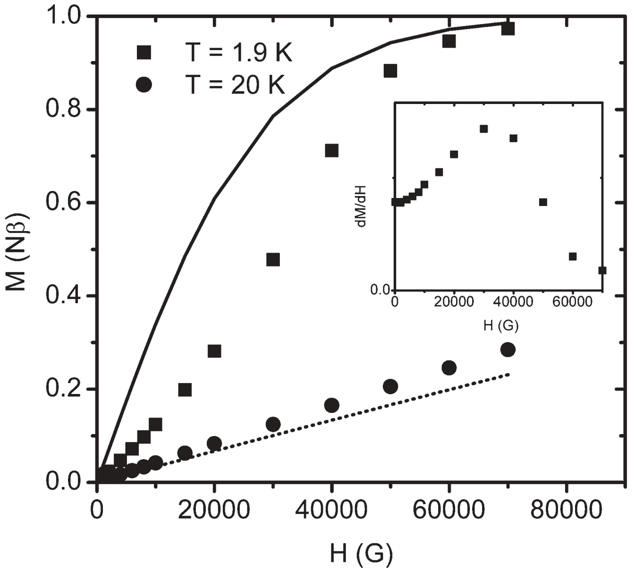


Fig. 3 Field dependence of the magnetization of **1** at 1.9 and 20 K. The solid and dotted lines illustrate the Brillouin curves for an independent Cu(II) ion at 1.9 and 20 K, respectively. The inset indicates the plot of d*M*/d*H* *vs.* *H* at 1.9 K.

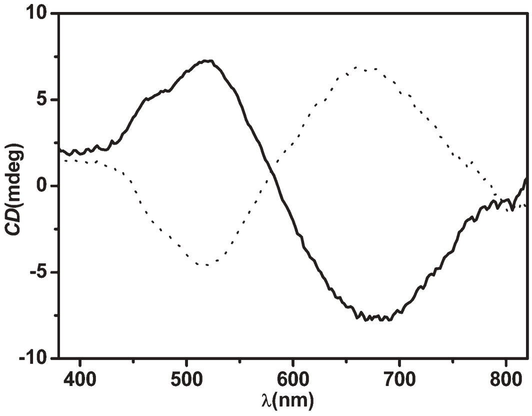


Fig. 4 Circular dichroism spectra in polycrystalline samples. The solid line stands for **1** and the dotted one for **2**.

dependence of real component of ac susceptibility $\chi_m'(H)$ (Fig. S6). The spin–flop field (H_{SF}) appears at about 0.4 T. The critical field (H_C) is not evident but a downturn in $\chi_m'(H)$ is observed at around 3.2 T,[13] which concurs with the advent of the inflection point of the $M(H)$ curve (Fig. 3, inset). The lack of sharp conversion in $\chi_m'(H)$ implies that the spin–flop transition to a paramagnetic (or ferromagnetic-like) state is rather gradual, which is also found in $(SPh_3)Mn(dicyanamide)_3$.[13] With these results, the anisotropy field $H_A \approx 0.05$ T and the exchange field $H_E \approx 1.6$ T are estimated. A similar spin–flop transition was reported in the low-dimensional Cu(II) compound, $Ba_3Cu_2O_4Cl_2$.[14]

Circular dichroism (CD) was measured to elucidate the enantiomeric properties of the optically active complexes (Fig. 4). For **1**, positive Cotton effects are evident at 466 nm and 520 nm, and a negative signal is observed at 670 nm while compound **2** possesses Cotton effects of the opposite sign at the same wavelengths. The CD bands can be attributed to d–d transitions whereas the electronic absorptions are centered at 617 nm for a d–d transition and at 372 nm for a charge-transfer transition.

In summary, we have prepared two novel 2D layered compounds displaying dual functionality of magnetism and chirality. Variation of chiral ancillary ligands is envisaged to build up new chiral magnetic materials with intriguing properties.

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Notes and references

‡ Preparations: **1**: Caution! Perchlorate and azide salts of metal compounds with organic ligands are potentially explosive. Only small amounts of material should be used, and cautiously handled. NaN_3 (0.2 mmol) in water (8 ml) was poured into a test tube. A methanol solution (8 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) and *R*,*R*-dacy (0.1 mmol) was layered on the aqueous solution. Deep green crystals (79%) were obtained after standing for a few weeks. **2**: The same procedure as for **1** was used to form deep green crystals (90%) except for the substitution of *S*,*S*-dacy. Satisfactory elemental analyses were obtained. Selected IR data (cm^{-1}, KBr pellet) for **1** and **2**: ν_{N3} = 2048s (sh), 2039s.

§ Crystal data: for **1**: $C_{12}H_{28}Cu_2N_{16}$, FW = 523.58, monoclinic, space group $P2_1$, a = 11.9892(2), b = 6.8589(2), c = 13.2287(4) Å, β = 93.281(1)°, V = 1087.06(6) Å^3, Z = 2, D_{calc} = 1.600 g cm^{-3}, T = 100 K, 9494 reflections collected, 4257 unique (R_{int} = 0.0151), $R1$ = 0.0163, $wR2$ = 0.0470, Final R indices [$I > 2\sigma(I)$]. For **2**: $C_{12}H_{28}Cu_2N_{16}$, FW = 523.58, monoclinic, space group $P2_1$, a = 12.0004(4), b = 6.8589(1), c = 13.2344(2) Å, β = 93.282(1)°, V = 1086.52(3) Å^3, Z = 2, D_{calc} = 1.600 g cm^{-3}, T = 100 K, 7763 reflections collected, 3709 unique (R_{int} = 0.0198), $R1$ = 0.0180, $wR2$ = 0.0483, Final R indices [$I > 2\sigma(I)$]. CCDC 264622 and 264623. See http://dx.doi.org/10.1039/b507051a for crystallographic data in CIF or other electronic format.

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