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Communication

Formation of a novel ferromagnetic end-to-end cyanate bridged homochiral helical copper(II) Schiff base complex via spontaneous symmetry breaking

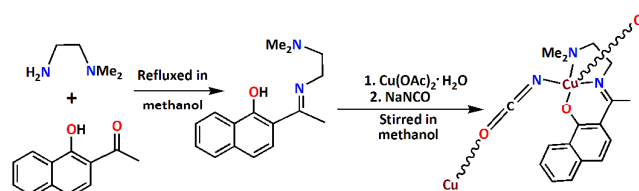
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Formation of a homochiral helical coordination polymer of copper(II) has been synthesized using achiral precursors via spontaneous chiral resolution has been confirmed by single crystal X-ray diffraction and solid-state CD spectroscopy. The variable temperature magnetic measurement indicates the presence of weak ferromagnetic exchange interactions mediated by end-to-end cyanate bridges ($J = +0.12 \text{ cm}^{-1}$).

Exploration of the structural and magnetic properties of polynuclear transition metal complexes is an attracting research area in the field of coordination chemistry, materials chemistry, and condensed matter physics for long.¹ Copper(II)-pseudohalide systems are very popular for the construction of such species because of their potential application in magnetic materials.² Different types of magnetic behaviors, e.g., ferromagnetic, antiferromagnetic, metamagnetic, spin flop, etc. have been observed in such systems.³ However, copper(II) pseudo-halide systems have not been utilized to prepare helical coordination polymers till date. It is to be mentioned here that dicyanamide, a bent pseudohalide,⁴ was used to prepare copper(II) helices, but these helical coordination polymers are usually optically inactive due to the presence of both P and M helices in them.⁵ The essential condition for a helical compound to be chiral as well as optically active is crystallizing in a chiral space group. Chirality in solids may be developed either by the presence of chiral building blocks, or in a better way by the chiral arrangement of achiral precursors through spontaneous chiral resolution.⁶



Scheme 1: Synthetic route to the complex.

In the present work, we used a N_2O donor tridentate achiral Schiff base, (1-(2-(dimethylamino)ethylimino)ethyl)-naphthalen-1-ol (HL) and cyanate to prepare a homochiral copper(II) helix,

$[\text{Cu}(\mu_{1,3}\text{-NCO})(\text{L})]_n$ (Scheme 1) via spontaneous chiral resolution (see the Supplementary Information for details). The ligand was prepared following the literature method.⁷ The structure is confirmed by single crystal X-ray diffraction. Variable temperature magnetic measurement indicates ferromagnetic coupling among the copper(II) centres within the helix. Herein, we report the synthesis and characterization of a new ferromagnetic homochiral helix obtained by spontaneous chiral resolution.

The absolute configuration (the left- or right-handedness) of any chiral crystal is usually determined by the Flack parameter.⁸ If the value is near 0, with a small standard uncertainty, the absolute structure given by the structure refinement is likely correct and if the value is near 0.5, the crystal may be racemic or twinned. The value of Flack parameter of the present crystal is only 0.016(14), which supports the enantiopurity of the single crystal. These chiral crystals often form racemic conglomerate containing both the left- and right-handed helices in the bulk solid. However, formation of crystals of a particular handedness leads to chiral symmetry breaking thereby produces homochiral materials.⁹ Such chiral symmetry breaking is not very uncommon for stirred crystallization.¹⁰ In this process, new crystals are generated by the surface of a crystal in contact with fluid in motion. The chirality of these secondary crystals is the same as that of the 'parent' crystals.¹¹ The process may sometimes be termed as 'secondary nucleation'. If the solution is stirred constantly during crystallization, almost all crystals have the same handedness.^{11b} In the present case, stirred crystallization favours the propagation of crystals of a particular handedness, leading to chiral symmetry breaking. Solid-state circular dichroism spectroscopy may be indicative of symmetry breaking, only if measured on a KBr pellet made with powder obtained upon grinding and mixing many single crystals. On the other hand, the enantiomeric excess of the product may also be amplified by the use of chiral catalyst which involves enantioselective catalytic step.¹²

In the present case, the stirred crystallization leads to the formation of homochiral material via the method of secondary nucleation. The complex crystallizes in the chiral monoclinic space group $P2_12_12_1$. The X-ray crystal structure analysis reveals that the copper(II) centres are bridged singly by end-to-end cyanates with the formation of a chiral helix. Perspective view of the complex with the selective atom-numbering scheme is shown in Fig. 1. Selected angles are listed in Table S1 (Supplementary

Information). Each copper(II) centre is coordinated equatorially by one imine nitrogen atom, N(1), amine nitrogen atom, N(2), and one oxygen atom, O(1), of the tridentate deprotonated Schiff base (L⁻) and a nitrogen atom, N(3), of the EE bridged cyanate; this defines the basal plane. An oxygen atom, O(2)^{*}, from a symmetry related (-x, -1/2+y, 1-z) bridging cyanate coordinates axially at a rather long distance furnishing an elongated square-pyramidal (4 + 1) geometry for each copper(II) center. The Addison parameter¹³ (0.0008) also indicates the square pyramidal geometry. The Cu–N_{imine} distance [1.961(3) Å] is shorter than the Cu–N_{amine} [2.056(2) Å] distance, as was also observed in similar systems.¹⁴ The deviations of N(1), N(2), O(1) and N(3) from the least square mean plane through them are 0.001(3), -0.001(2), -0.001(2) and 0.001(3) Å respectively and that of copper(II) from the same plane is -0.180(3) Å. The closest conformation of the five-membered chelate ring, Cu(1)–N(1)–C(13)–C(14)–N(2), is envelope with puckering parameters Q(2) = 0.428(3) Å and Φ(2) = 114.0(3)°. The bridging cyanates are quasi-linear; the N–C–O angle is 176.4(3)°. The shortest Cu···Cu distance is 5.8850(6) Å in the helix. The hydrogen atom, H(15B), attached with C(15), is involved in C–H···π interaction with a symmetry related (-1/2+x, -1/2-y, -1-z) phenyl ring R⁴ [C(5)–C(6)–C(7)–C(8)–C(9)–C(10)] from a neighbouring helix to form a supra-molecular 2D sheet as shown in Fig. S1 (Supplementary Information).

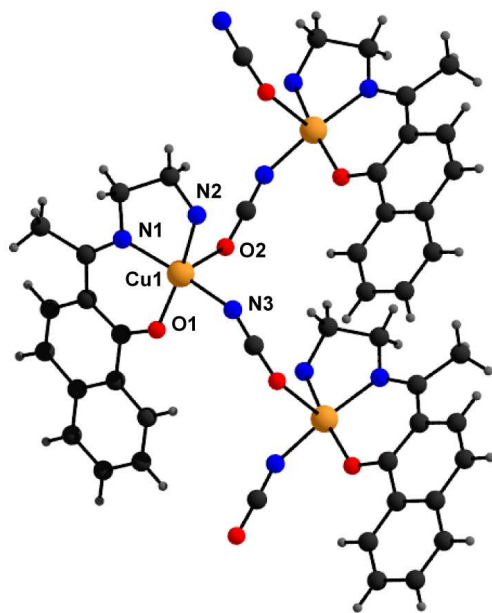


Fig. 1: Perspective view of the complex with selective atom numbering scheme. Methyl groups of the amine nitrogen atoms have been omitted for clarity. Selected bond lengths: Cu(1)–O(1) = 1.8987(17); Cu(1)–N(1) = 1.961(3); Cu(1)–N(2) = 2.0565(19); Cu(1)–N(3) = 1.951(2); Cu(1)–O(2)^{*} = 2.5174(19). Symmetry transformation ^{*} = -x, -1/2+y, 1-z.

In the IR spectrum, a distinct band at 1579 cm⁻¹ confirms azomethine (C=N) group¹⁶ and intense bands at 2186 and 1414 cm⁻¹ indicate the presence of EE bridged cyanate.¹⁷ The absorption spectrum in acetonitrile shows a *d-d* transition band at 603 nm.¹⁸ The intense absorption bands at 272 and 390 nm may be assigned to LMCT.¹⁸ The complex exhibits luminescence in acetonitrile medium at 440 nm on exciting at 380 nm and may be assigned to intra-ligand (π – π^*) fluorescence.¹⁹ The mean lifetime

(τ_{av}) of the excited state is 2.83 ns at room temperature.

The homochirality of the bulk material was evidenced from its solid state CD spectrum in which, two positive Cotton effects at 272 and 603 nm and a negative one at 390 nm are observed (Fig. 2). The CD was measured on a KBr pellet made with a powder obtained upon grinding and mixing many single crystals.

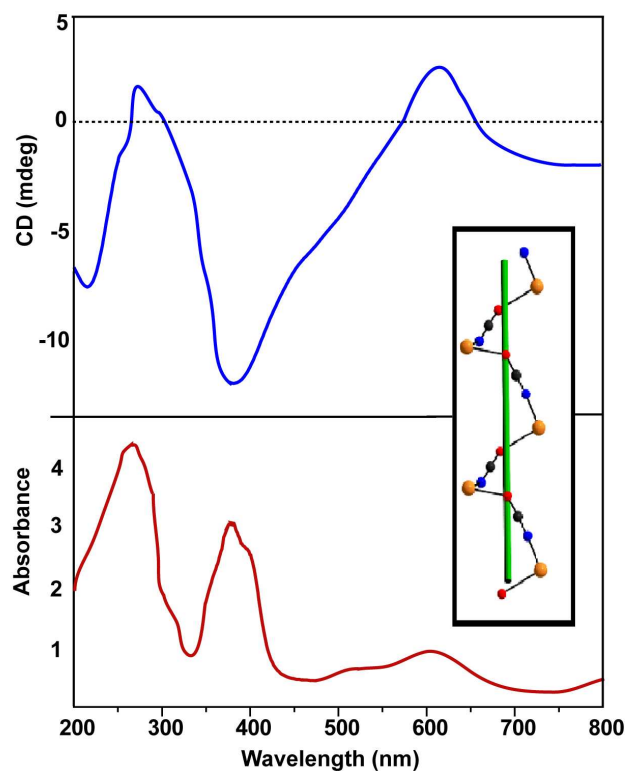


Fig. 2: Solid state CD spectrum of the complex (top). UV-VIS spectrum of the complex (bottom). A closer look at the M-helical chain (inset).

The temperature dependence of magnetic susceptibility of the complex has been measured at 1 T between 2 and 300 K. The representation of the magnetic susceptibility toward temperature of the complex shows a continuous increase with lowering temperature, typical of paramagnetic compounds (Fig. 3). The magnetic moment at room temperature of the complex is 1.87 μ_B , close to the expected for the presence of one unpaired electron per copper(II) ion. The $\chi_M T$ versus temperature representation shows an almost constant value of 0.43 $\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ until at around 12 K and then increases until 0.50 at 2 K (Fig. 3). This behaviour suggests the existence of non-interacting $S = 1/2$ spin per Cu(II) ion in most of the temperature range except at very low temperatures where weak ferromagnetic interactions are present. The representation of magnetization measurements at 2 K (Fig. S2, Supplementary Information) carried out between -5 and 5 T do not show hysteresis loop, which is not unusual in soft magnetic materials.²⁰

The variation of the isothermal magnetization M versus magnetic field measured at 2 K shows a linear relation between both magnitudes until 1.2 T. The experimental curve presents slightly higher values than those predicted by the Brillouin's function until 5 T (Fig. 4). This deviation indicates ferromagnetic interaction in the complex. Moreover, in the representation of the

reduced magnetization versus magnetic field (Fig. 4), the curve tends to 1.0 $M/N\mu_B$ at high fields, which confirms the presence of one unpaired electron in the copper(II) centers.

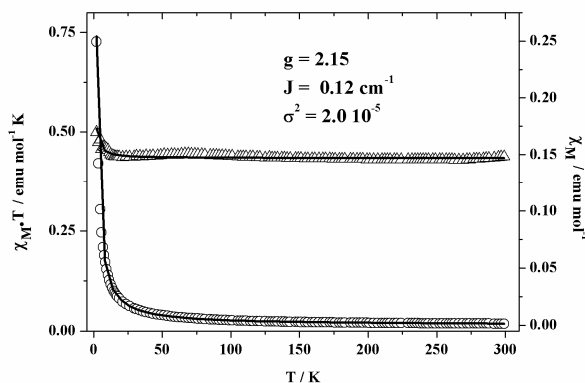


Fig. 3: Plot of magnetic susceptibility (\circ) and $\chi_M T$ (Δ) vs temperature for the complex. The solid lines are the result of fitting the experimental data with Eq. 1.

According to the structure of the complex the Hamiltonian corresponding to a uniform one-dimensional chain formed by equally spaced copper(II) ions (with $S = 1/2$) has been considered to fit the magnetic data of this complex:

$$H = -2J \sum_i S_{Cu_i} \cdot S_{Cu_{i+1}}$$

The more usual equation derived by Bonner and Fisher²¹ to fit the magnetic data of numerous one-dimensional complexes of Cu(II) is only valid for antiferromagnetic interactions ($J < 0$) and, therefore, is not accurate for the complex. For this reason, the fit of the experimental data was analysed by a high-temperature expansion, valid for ferro and antiferromagnetic compounds, developed by Baker and col.^{21a, 22} (equation 1)

$$\chi T = \frac{N\beta^2 g^2}{4k} (N/D)^{2/3} \quad \text{Eq.1}$$

where $D = 1 + 2.798x + 7.009x^2 + 8.654x^3 + 4.574x^4$,
 $N = 1 + 5.798x + 16.903x^2 + 29.377x^3 + 29.833x^4 + 14.037x^5$,
 and $x = J/kT$

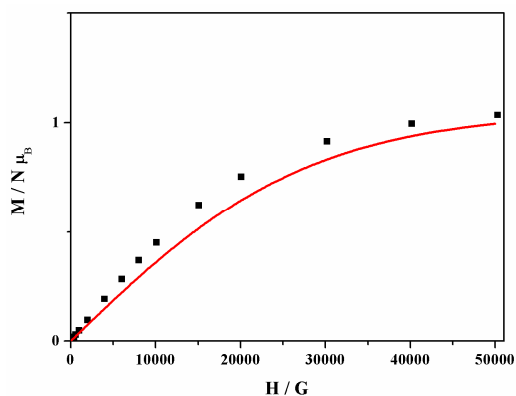


Fig. 4: Plot of the reduced magnetization ($M/N\mu_B$) versus H measured at 2.0 K for compound 1. The solid line correspond to the Brillouin equation

for $S = 1/2$ and $g = 2$, and black squares represent the experimental values.

The fit using this equation gives the following parameters: $g = 2.15$, $J = +0.12 \text{ cm}^{-1}$, and $\sigma^2 = 2.0 \cdot 10^{-5}$. The g value is very usual in copper(II) complexes and the agreement factor defined as: $\sum_i [(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2 / \sum_i [(\chi_M T)_{\text{obs}}(i)]^2$ indicates a very good agreement between experimental and calculated parameters. The positive sign of the coupling exchange confirms the existence of ferromagnetic interactions in the complex. Actually, the values obtained are very close to those found for $[\text{CuL}^1(\mu_{1,3}\text{-NCO})]_n \cdot 2n\text{H}_2\text{O}$ ($L^1 =$ tridentate Schiff base), the only previously reported²³ cyanate-bridged copper(II) polymer exhibiting ferromagnetic interactions: $g = 2.15$, $J = +0.19 \text{ cm}^{-1}$, and $\sigma^2 = 1.4 \cdot 10^{-5}$. Other copper polymers with pseudohalide ligands such as $[\text{Cu}(4\text{-apy})(\text{SCN})_2]_n$ (4-apy = 4-aminopyridine)²⁴ also shows ferromagnetic interactions ($J = +0.3 \text{ cm}^{-1}$). The symmetrical pseudohalide azide favours the magnetic exchange and, therefore, $[\text{CuL}^1(\mu_{1,3}\text{-N}_3)]_n \cdot 2n\text{H}_2\text{O}$ presents a $J = 0.79 \text{ cm}^{-1}$.²³ This phenomenon has been ascribed²⁵ to the larger Cu-O distance with respect to the Cu-N. Curiously, antiferromagnetic interactions though cyanate ligands in copper(II) polymers are observed when the Cu-N-C and Cu-O-C angles are very different as in $\{[\text{CuL}^2(\text{NCO})][\text{ClO}_4]\}_n$ ($L^2 = N,N,N',N'',N'''$ -pentamethyl-1,5-diamine)²⁶ or $[\text{CuL}^3(\mu_{1,3}\text{-NCO})]_n$ ($L^3 =$ tridentate Schiff base).²⁷ However, in the two examples of copper(II) pseudohalide polymers with ferromagnetic interactions the difference between the Cu-N-C and Cu-O-C angles is smaller (Table S2, Supplementary Information). Thus, although more examples are necessary to confirm this hypothesis, the crystallographic data of the one-dimensional cyanate-copper(II) complexes suggest that compounds with small differences between the Cu-N-C and Cu-O-C angles show ferromagnetic interactions while complexes with large differences exhibit antiferromagnetic coupling.

The synthesis of chiral compounds from achiral precursors by spontaneous resolution is an interesting research topic because of the limitation of the chiral pool and the high cost of chiral ligands. On the other hand, formation of homochiral helices of copper(II) amino acid building blocks by spontaneous chiral resolution has already been reported by several groups.²⁸ In the present work, an achiral tridentate N_2O donor Schiff base was used to prepare a single end-to-end cyanate bridged, ferromagnetic, homochiral, helical copper(II) complex. Work is in progress to improve the yield of the reaction and to develop more systems based on this strategy to generalize the concept.

Notes and references

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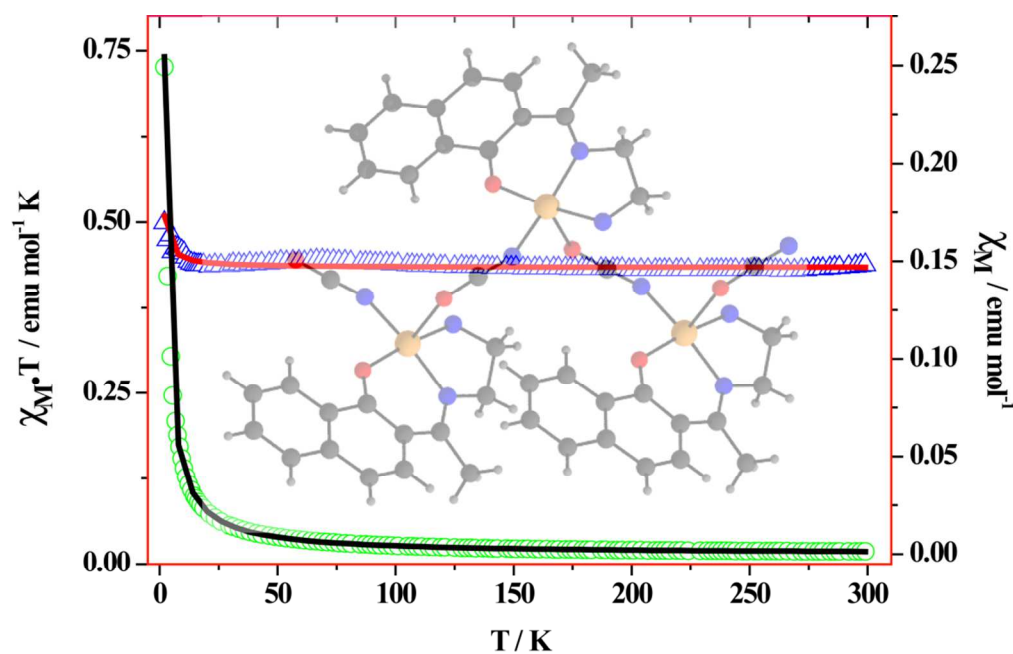
⁸⁰ † Electronic Supplementary Information (ESI) available: [Experimental details, X-ray crystallographic data and Instrumentation details]. See DOI: 10.1039/b000000x/

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Formation of a novel ferromagnetic end-to-end cyanate bridged homochiral helical copper(II) Schiff base complex via spontaneous symmetry breaking

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A homochiral helical coordination polymer has been synthesized using achiral precursors via spontaneous chiral resolution. The variable temperature magnetic measurement indicates the presence of weak ferromagnetic exchange interactions mediated by end-to-end cyanate bridges.