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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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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Formation of a homochiral helical coordination polymer of copper(II) has been synthesized using achiral precursors via spontaneous chiral resolution. The absolute configuration of the left- or right-handedness of any chiral crystal is usually determined by the Flack parameter. 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. The chirality of these secondary crystals is the same as that of the ‘parent’ crystals. The process may sometimes be termed as ‘secondary nucleation’. If the solution is stirred constantly during crystallization, almost all crystals have the same handedness. In the present case, stirred crystallization favours the propagation of crystals of a particular handedness, leading to chiral symmetry breaking thereby produces homochiral materials.

In the present work, we used a N\(_2\)O donor tridentate achiral Schiff base, (1-(2-(dimethylamino)ethylimino)ethyl)-naphthalene-1-carboxylic acid (HL) and cyanate to prepare a homochiral copper(II) helix.

Scheme 1: Synthetic route to the complex.

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\(_1\)2\(_1\)2\(_1\). 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,1/2-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 parameter (0.0008) also indicates the square pyramidal geometry. The Cu–N(3) distance [1.961(3) Å] is shorter than the Cu–N(1)* [2.056(2) Å] distance, as was also observed in similar systems. 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) = 0.42(3) Å and Φ(2) = 114.0(3)°. The deviations of N(1), N(2), O(1) and N(3) from the same plane are 0.000(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) = 0.42(3) Å and Φ(2) = 114.0(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 (kx,k1/2+y,1kz) phenyl ring.

In the IR spectrum, a distinct band at 1579 cm⁻¹ confirms azomethine (C=NH) group and intense bands at 2186 and 1414 cm⁻¹ indicate the presence of EE bridged cyanate. The absorption spectrum in acetonitrile shows a d-d transition band at 603 nm. The intense absorption bands at 272 and 390 nm may be assigned to LMCT. 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. The mean lifetime (τ₀) of the exited state is 2.83 ns at room temperature.

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 to 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 μ₀ B, close to the expected for the presence of one unpaired electron per copper(II) ion. The χM · T versus temperature representation shows an almost constant value of 0.43 emu·mol⁻¹·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.

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
The reduced magnetization versus magnetic field (Fig. 4), the curve tends to 1.0 M/Nμ₀ at high fields, which confirms the presence of one unpaired electron in the copper(II) centers.

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 cm⁻¹, and σ² = 2.0 × 10⁻⁵. The g value is very usual in copper(II) complexes and the agreement factor defined as: Σ[(χ²/T)obs(i)−(χ²/T)calc(i)]²/Σ[(χ²/T)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 [CuL¹(µ₁,3-NCO)]ₙ·2nH₂O (L¹ = tridentate Schiff base), the only previously reported cyanate-bridged copper(II) polymer exhibiting ferromagnetic interactions: g = 2.15, J = +0.19 cm⁻¹, and σ² = 1.4 × 10⁻⁵. Other copper polymers with pseudohalide ligands such as [Cu(4-apy)(SCN)]ₙ (4-apy = 4-aminopyridine) also shows ferromagnetic interactions (J > +0.3 cm⁻¹). The symmetrical pseudohalide azide favours the magnetic exchange and, therefore, [CuL¹(µ₁,3-N₃)]ₙ·2nH₂O presents a J = 0.79 cm⁻¹. This phenomenon has been ascribed 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 [(CuL²(NCO)][ClO₄]ₙ (L² = N,N,N',N'',N''-pentamethyl-1,5-diamine) or [CuL²(µ₁,3-NCO)]ₙ (L³ = tridentate Schiff base). 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. In the present work, an achiral tridentate N₃O 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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4. † Electronic Supplementary Information (ESI) available: [Experimental details, X-ray crystallographic data and Instrumentation details]. See DOI: 10.1039/b000000x/


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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.