A covalently linked 2D CuII compound, \([\text{Cu}(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2]_n\), 1 (3-pyOH = 3-hydroxypyridine), when dissolved in thf, undergoes conversion to a hydrogen-bond linked 2D CuII compound, \([\text{Cu}(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2(\text{thf})_2]_n\), 2, which upon heating or standing at 23 °C for a few hours is converted back to compound 1 by losing the coordinated thf molecule; weak ferromagnetic interactions between CuII centres dominate in both compounds.

There has been an increasing interest in metal complexes containing paramagnetic metal ions and exhibiting extended structures because of their potential applications in molecular magnetic materials. One commonly used strategy in building metal complexes with extended structures is to employ appropriate bridging ligands which are capable of binding to several metal centres through direct bond formation and promoting magnetic interactions as well. The drawback of this strategy is that the complexes tend to have a poor solubility in common solvents which makes them difficult to characterize and fabricate. In contrast, compounds which have hydrogen-bond linked extended structures usually have a good solubility in common solvents. The shortcoming of hydrogen-bonded systems is that the magnetic interactions between the metal centres are usually weak and sometimes the compound undergoes irreversible dissociation when dissolved. It is conceivable that if one can use both covalent and hydrogen bonds in building the extended structures, the compounds may have the desired magnetic properties and solubility. In fact, such a strategy has been adapted either by serendipity or by design in a number of magnetic metal complexes where the extended structures are dictated by both covalent and hydrogen bonds. We have been interested in building extended structures by using bifunctional ligands (ligands that are capable of forming both metal–ligand bonds and hydrogen bonds). We report herein an unusual structural interconversion, facilitated by the bifunctional ligand, 3-hydroxypyridine (3-pyOH), between a novel CuII complex \([\text{Cu}(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2]_n\), 1, exhibiting a two-dimensional covalently linked extended structure and weak ferromagnetic exchange, and a hydrogen-bonded 2D CuII complex \([\text{Cu}_2(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2(\text{thf})_2]_n\), 2.

Compound 1 was obtained from the reaction of Cu(OMe)$_2$ with 2 equiv. of trifluoroacetic acid and 3-hydroxypyridine in either 1,4-dioxane or MeCN as a royal blue crystalline solid. The molecular structure of 1 (Fig. 1), established by single-crystal X-ray diffraction analysis, has an inversion centre. The 3-pyOH ligand acts as a bridging ligand to two CuII via the nitrogen and the oxygen atoms. The CuII centre in 1 is an elongated octahedron with two nitrogen atoms of the 3-pyOH ligands and two oxygen atoms of the trifluoroacetate ligands occupying the basal positions and two oxygen atoms of the 3-pyOH ligands from the neighbouring molecules occupying the axial positions. The H(5) atom of the 3-pyOH ligand forms a hydrogen bond with the non-coordinated oxygen atom of the trifluoroacetate ligand [O(1′)···O(3) 2.65(2) Å]. As a consequence of the 3-pyOH bridge, compound 1 has an extended 2D sheet structure as shown in Fig. 2. Each mononuclear CuII unit in the 2D sheet is linked to four other identical mononuclear CuII units by four 3-pyOH ligands, related by inversion centres with a Cu···Cu separation of 7.27 Å. The two pyridyl rings from two neighbouring mononuclear units are partially stacked with...
the shortest atomic separation distance being 3.67 Å. The 2D sheets of 1 stack along the a axis with the interlayer Cu–Cu distance being 8.99 Å. Compound 1 is closely related to [Cu(O2CCF3)2(3-py- OH)2(thf)2], 2 where the axial positions are occupied by two thf ligands and the mononuclear CuII units are linked together to form a 2D sheet through intermolecular hydrogen bonds between 3-pyOH and trifluoroacetate ligands (Fig. 3). The separation distance between two neighbouring CuII ions in the 2D sheet of 2 is 8.04 Å, much longer than that in 1. Compound 1 is insoluble in solvents such as CH2Cl2 and MeCN, but very soluble in thf. Upon dissolving in thf, the hydroxy groups at the axial positions in 1 are replaced by two thf molecules and compound 1 is converted to compound 2. Upon heating or standing at 23 °C for a few hours, compound 2 is converted back to compound 1 in the solid state, accompanied by the loss of thf, as confirmed by X-ray powder diffraction, TGA and DSC analyses. The thf ligand in 2 is replaced by the hydroxy group of the 3-pyOH ligand from a neighbouring CuII centre in the 2D sheet. The bifunctionality of the 3-pyOH ligand clearly facilitated the conversion process. In 2, the hydroxy group of the 3-pyOH ligand forms a hydrogen bond only to link the mononuclear units together while in 1 it forms a new weak Cu–O bond, retaining the hydrogen bond to link the mononuclear units together. It is conceivable that such a structural interconversion is common occurrence among complexes where the metal centres are bound by weak donor ligands and bifunctional ligands. However, to our knowledge, the reversible interconversion between a covalently bonded and a hydrogen-bonded inorganic 2D structure, as observed in 1 and 2, has not been reported previously. We believe that this interconversion process is important because it provides a mechanism for switching between a soluble and an insoluble phase.

Interestingly, despite the dramatic bonding difference between 1 and 2, both compounds display similar magnetic properties. For example, the EPR spectrum of the powder sample of 1 at 77 K has a broad signal with g∥ = 2.077 and g⊥ = 2.223, consistent with the elongated octahedral geometry, and a weak half-field transition band at g = 4.240, indicative of the presence of magnetic exchange between the CuII units. The EPR spectrum of the powder sample of 2 at 77 K resembles that of 1 with g∥ = 2.080 and g⊥ = 2.221 and a weak half-field transition peak at g = 4.200. The nature of magnetic exchange in 1 and 2 was established by magnetization and magnetic susceptibility measurements. The effective magnetic moment of 1 increases steadily with the decrease of temperature in the range of 2–10 K, suggesting the presence of ferromagnetic exchange. The magnetization of 1 at 2 K increases rapidly with increasing field strength and reaches 6105 emu G mol⁻¹ (1.095 μB) at 55 K, in good agreement with the theoretical magnetization saturation $M_s = 5950$ emu G mol⁻¹ (1.065 μB) for an S = 1/2 and $g_{av} = 2.13$ system. The magnetization curve at 2 K is above the curve of Brillouin function for an S = 1/2 and $g_{av} = 2.13$ system, consistent with the presence of weak ferromagnetic interactions. Because all the mononuclear CuII units in the 2D sheet of 1 are identical and related to each other by inversion centres, the ferromagnetic interaction is likely to be two dimensional. The low temperature susceptibility data $x_m$ and $T$ (2 K–10 K) were fitted successfully by using a 2D, spin = 1/2 Heisenberg model, yielding $g = 2.137$ and $J = 0.020(2)$ cm⁻¹ from the $x_m$ $T$ data and $g = 2.138$ and $J = 0.018(2)$ cm⁻¹ from the $x_m$ data, supporting the presence of weak 2D ferromagnetic exchange. Preliminary data indicated that 2 is also a weak ferromagnetic interaction dominated system, as evidenced by the positive intercept (θ = 1.25 K) on the $T$ axis obtained by the extrapolation of the $C/Tm$ data of 2 (5 K–280 K). We have not been able to obtain data below 5 K for 2 due to its poor stability under high vacuum.

The 3-pyOH ligand in 1 binds to a d2 and a d2−2 orbitals located at two CuII centres, respectively, thus makes the interaction of the two d2−2 orbitals magnetic orbitals via a σ pathway impossible. Therefore, if the σ orbital interaction dictates the spin exchange, one can predict that the magnetic interaction within the 2D sheet of 1 would be either paramagnetic or ferromagnetic:1,6,8 The π orbitals of the 3-pyOH ligand are essentially orthogonal to the d2−2 orbital. Consequently, the π superexchange pathway, which may yield antiferromagnetic exchange, also becomes impossible. We therefore believe that the weak ferromagnetic exchange observed in 1 is likely caused by orbital orthogonality imposed by the geometric constraint of the 3-pyOH ligand. Dipole–dipole interactions may also contribute since the magnitude of the spin interaction in 1 is very small.

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Footnotes

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† Crystal data for 1: monoclinic, $P2_1/c$, $a = 8.986(4), b = 9.620(6), c = 10.908(4) Å, β = 104.80(3)°$, $Z = 2, U = 911.7(7) Å^3$. Final residuals $R = 0.076$ and $R_w = 0.082$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/390.

References


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