Heteroleptic pyrimidine-2-olate and 4,4′-bipyridine copper(II) layered metal–organic frameworks with swelling properties†

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One-pot reaction of CuX, salts (X = NO3, Cl, ClO4, AcO, SO4/2), 2-Hydroxypyrimidine hydrochloride (2-Hpymo-HCl) and 4,4′-bipyridine (4,4′-bpy), in H2O : ethanol : ammonia (20 : 10 : 5) solution, leads to isomorphous extended layered materials of type [Cu4(μ-OH)2(μ-Cl)2(μ-2-pymo)(μ-4,4′-bpy)3]n, X·mH2O (X = NO3 (1a), Cl (1b), ClO4 (1c), AcO (1d), SO4/2 (1e)). The single crystal X-ray crystallographic analysis performed on species 1a exemplifies that it is built by 2D [Cu4(μ-OH)2(μ-Cl)2(μ-2-pymo)(μ-4,4′-bpy)3]n+ cationic sheets, which pack in a staggered fashion, with non coordinated NO3− anions and crystallisation water molecules included in the interlayer voids. XRPD studies performed on the 1a–e species show a swelling response along the crystallographic a axis concomitant to aliphatic alcohol inclusion. Additionally, we have also studied the magnetic properties of 1a, which show that its magnetic behaviour is dominated by the strong antiferromagnetic interactions taking place in the Cu4(μ-OH)2(μ-Cl)3 trinuclear cores.

Introduction

The wide range of applications of crystalline open framework aluminosilicates is closely related to their well defined porous nature with concomitant selective ion exchange, sorptive and catalytic processes.† However, these materials possess intrinsic limitations due to the rigid and anionic nature of the aluminosilicate framework, the difficulty in its functionalization and the absence of homochirality. Many such limitations have already been overcome by porous coordination polymers, which are based on metal ions and organic bridging ligands.‡ In principle, from the wide choice of metal ions and the infinite design possibilities of ligands, a broad range of structural, magnetic, electrical, optical, catalytic and ion exchange properties might be rationally incorporated into such materials.§ An illustrative example is the rod-like 4,4′-bipyridine (4,4′-bpy) organic ligand, which clearly shows the success of this strategy to build a wide variety of these materials.¶ The metal ion geometry, crystallisation conditions and the presence of templating agents are decisive in the formation process of extended open frameworks with novel structural features, sorptive and catalytic properties.† Moreover, fine tuning of cavities and channels of MOFs can be easily achieved in mixed ligand systems.¶ For this reason, in the present work, we have pursued the formation of mixed ligand coordination compounds by combining 4,4′-bpy with the bent 2-Hpymo ligand, which has also been shown to form a wide range of coordination polymers with rich structural, thermal, magnetic and sorptive properties.¶

† Electronic supplementary information (ESI) available: Table S1: Selected bond distances [Å] and angles [°] for 1a. Table S2: Selected H-bond distances [Å] for 1a. See http://www.rsc.org/suppdata/ dt/b5/b500942a/

Results and discussion

We have observed that one-pot reaction of Cu(II) salts with 2-hydroxypyrimidine hydrochloride (2-Hpymo-HCl) and 4,4′-bpy in H2O : ethanol : ammonia (20 : 10 : 5) solution leads to the formation of a series of isomorphous extended 2D layered frameworks of formula [Cu4(μ-OH)2(μ-Cl)2(μ-2-pymo)(μ-4,4′-bpy)3]n, X·mH2O, where X = NO3 (1a), Cl (1b), ClO4 (1c), AcO (1d), SO4·2 (1e) (Scheme 1a). Suitable single crystals for conventional X-ray diffraction were obtained only for compound 1a, nevertheless the isomorphous nature of the analogous complexes 1b, 1d, 1e was illustrated by X-ray powder diffraction methods. In addition, the isomorphous 1 series show swelling properties as they are able to host aliphatic alcohols between their layers (Scheme 1b).

Crystal structure of [Cu4(μ-OH)2(μ-Cl)2(μ-2-pymo)-(μ-4,4′-bpy)3]n(NO3)m·nH2O (1a)

The crystal structure of 1a reveals a layered structure built up of 2D [Cu4(μ-OH)2(μ-Cl)2(μ-2-pymo)(μ-4,4′-bpy)3]n+ cationic sheets (Fig. 1) and non coordinated NO3− ions and crystallisation water molecules included in the interlayer voids (Fig. 2). The basic structural blocks in 1a are the linear trinuclear copper(II) cores with 3.2–3.3 Å Cu···Cu separations, which are supported by asymmetric μ-hydroxo- and μ-chlorido- bridges (Fig. 1a). The central copper ions exhibit a distorted octahedral environment of CuO,N,Cl type in an all trans configuration whereas the two copper ions at the sides possess distorted square pyramidal environments of CuON,Cl type with the Cl− ion occupying the apical position. The extended structure results from the bridging mode of 2-pymo and 4,4′-bpy ligands. In the Cu–Cu direction, the 2-pymo ligands act in a N,N′-bridging mode connecting two different trinuclear cores 5.4 Å apart, whereas,

Scheme 1 (a) Synthesis of the 1 isomorphous series. (b) Swelling response to aliphatic alcohols.
in the perpendicular direction, the 4,4'-bpy ligands bridge trinuclear cores separated by 11.2 Å (Fig. 1b). The establishment of the four different bridges (µ-OH, µ-Cl, µ-4,4'-bpy and µ-2-pymo) leads to a rather compact bidimensional framework. The 2D [Cu₃(µ-OH)(µ-Cl)(µ-2-pymo)(µ-4,4'-bpy)]ₙ cationic sheets, separated by ~8.5 Å, pack in a staggered fashion (Fig. 2). The resulting interlayer space is filled by non-coordinated nitrate anions and water molecules. The crystallisation water molecules build an extensive H-bonding network with the OH, Cl, the exocyclic pyrimidine oxygens and nitrate anions stabilizing the whole structure.

Spectroscopic and thermal properties

IR spectra are indicative of the nature of the materials. For all the species, the ν(CO) band appears at a lower wavelength (1610 cm⁻¹) than that usually found for a N¹,N¹-exo-bidentate coordination mode of the 2-pymo ligand (~1630 cm⁻¹). This fact suggests a larger delocalization of the charge in the 2-pymo moity in comparison with the homoleptic extended systems containing 2-pymo bridges.⁸ On the other hand, in the case of 1a, 1c, 1d and 1e, additional absorption bands can be observed due to the presence of the different interlayer anions and water molecules (see below).⁷ The water content of 1 series has been confirmed by thermogravimetric and differential scanning calorimetric analyses: the water molecules are lost in a single-step endothermic process at about 60 °C (ΔH = 96 (1a), 69 (1b), 81 (1e), 178 (1d) and 70 (1e) kJ mol⁻¹). The low dehydration temperature as well as its corresponding endothermic effect (10–20 kJ mol⁻¹ per water molecule) agrees with the location of the crystal water molecules in the interlayer voids. In all cases, concomitant with dehydration i) slight colour changes, indicative of a small modification of the electronic nature of the trinuclear metal cores as a consequence of the loss of H-bonding interactions of hydration water molecules with the OH and Cl bridging ligands, are observed and ii) amorphous compounds of [Cu(µ-OH)(µ-Cl)(µ-2-pymo)(µ-4,4'-bpy)]ₙ X, formulation are recovered. On cooling these materials at room temperature and in humid air within 3 h, the original crystalline species are recovered in all cases, which is indicative of reversible dehydration–hydration processes. The crystalline 1 series can also be restored by stirring a suspension of the amorphous [Cu(µ-OH)(µ-Cl)(µ-2-pymo)(µ-4,4'-bpy)]ₙ X, species in water for a few minutes.

After dehydration, a dehalogenation event takes place in an endothermic process at 182 (1a), 142 (1b), 144 (1c), 133 (1d) and 143 °C (1e) (ΔH = 117 (1a), 81 (1b), 87 (1c), 91 (1d) and 99 (1e) kJ mol⁻¹). Further decomposition of the 1 species is responsible for large sharp weight loss effects on the TG diagrams taking place at about 278 (1a), 295 (1b), 277 (1c), 294 (1d) and 300 °C (1e). This event is similar to the one found for the decomposition process of the homoleptic [Cu(2-pymo)]ₙ and [Cu(4-pymo)]ₙ derivatives (Tm = 250 and 270 °C, respectively).

 Adsorption properties

The mineralomimetic nature of this system should be highlighted, particularly, to clay minerals which show rich sorption properties and possess poorly negatively charged aluminosilicate sheets separated by hydrated metal ions.⁶ In 1a, the reverse situation is observed: in this case, there are poorly charged cationic sheets with hydrated anions hosted in the interlayer voids. The possibility of formation of an isomorphous series with different interlayer anions Cl⁻ (1b), ClO₄⁻ (1c), AcO⁻ (1d), SO₄²⁻ / 2 (1e) further highlights its analogy to clays (Fig. 3a). Moreover, the XRD studies are also indicative of a preferential orientation of these compounds perpendicular to the c crystallographic axis, which agrees with an exfoliable material.

Clay minerals are well known as adsorbents of different guest molecules showing a swelling response upon guest inclusion in the interlayer voids. The related nature of our systems prompted us to study their adsorption properties towards different guest molecules. Thus, we have performed N₂ adsorption measurements on the evacuated materials at 77 K. The results do not show diffusion of N₂ molecules in the interlayer voids, which may be attributed to a shrinkage of the framework upon dehydration, which results in the formation of an amorphous phase with a porous framework unsuitable for N₂ diffusion at 77 K. At higher temperatures and pressures, we presume that N₂ sorption should take place.⁶ In addition, at room temperature, guest
molecules of higher polarity are readily included in the interlayer voids with a consequent restoration of the material crystallinity and a swelling response depending on the size of the guest molecule. This fact suggests a guest induced fit process upon inclusion. Thus, the XRPD studies clearly show increasing interlayer space along the crystallographic a direction as a result of the replacement of the crystallisation water molecules by alcohols of increasing size (Fig. 3b), namely +0.2 Å for MeOH, +0.3 Å for EtOH and +0.8 Å for ethylene glycol. The latter process corresponds with incorporation of four ethylene glycol molecules per unit formula. It should also be remarked that the dehydration, as well as the alcohol sorption processes, are reversible. These results contrast the situation found by Suh and Choi in a pillared system, which also shows alcohol adsorption but no significant swelling. Thus, in our case the spongelike behaviour similar to clay minerals should be noted.

**Magnetic properties**

Additionally, we have studied the magnetic properties of 1a. The thermal behaviour of magnetic molar susceptibility ($\chi_M$) and $\chi_M T$ are shown in Fig. 4. The complex nature of 1a should give rise to a great variety of possible magnetic exchange pathways. However, we think that the magnetic behaviour is dominated by the exchange inside the trinuclear copper(II) cores through the $\mu$-hydroxo- and $\mu$-chloro bridges. Thus, the observed steady decrease of $\chi_M T$ values at low temperatures agrees with a strong antiferromagnetic interaction taking place inside the trinuclear core. A pseudo-plateau at about 25 K is followed by a pronounced decrease in the $\chi_M T$ values. The pseudo-plateau results from a $S = 1/2$ state. The posterior decrease can be attributed to inter-trinuclear antiferromagnetic couplings probably taking place through the 2-pymo bridges. The magnetic susceptibility deduced from the Hamiltonian ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2 - J\hat{S}_2\cdot\hat{S}_3$) for a centrosymmetric trinuclear system is as in eqn. (1).

$$\chi_M = \frac{Ng^2\beta^2}{4k(T - J')} \times \left( \exp(-J/kT) + \exp(-J/kT) + 10 \exp(J/kT) \exp(-J/kT) + 2 \exp(J/kT) \right)$$

(1)

The fitting of the experimental data by eqn. (1) shows a satisfactory agreement between calculated and experimental data by assuming $J = 0$, $g = 2.03$, $J = -101(\pm3) \text{ cm}^{-1}$ and $J' = -2.20(\pm4) \text{ cm}^{-1}$. Thus, the magnetic behaviour of this material is dominated by the strong antiferromagnetic intra-trinuclear coupling $J$ transmitted through the hydroxo-bridges. The $J'$ value due to inter-trinuclear interactions can be clearly related to the pyrimidinolate bridges.

**Conclusions**

A series of isomorphous 2D layered materials containing four different kind of bridges has been reported. Additionally, we show swelling properties related to clay minerals upon alcohol adsorption. Finally, these materials also posses an interesting magnetic behaviour, which is dominated by the antiferromagnetic exchange taking place through the $\mu$-hydroxy, $\mu$-chloro and $\mu$-pymo bridges.

**Experimental**

**Materials**

2-Hydroxypyrimidine-HCl and 4,4'-bipyridine were purchased from Aldrich.

**Preparation of 1 [Cu$_3$($\mu$-OH)$_2$($\mu$-Cl)$_2$($\mu$-2-pymo)-($\mu$-4,4'-bpy)$_3$]$_n$·$n$H$_2$O ($X = NO_3$ (1a), Cl (1b), ClO$_4$ (1c), AcO (1d), SO$_4$/2 (1e))**

1 compounds were obtained from NH$_3$·H$_2$O : EtOH (5 : 20 : 10) solutions (25 mL) containing CuX$_2$ (2 mmol), 2-hydroxypyrimidine hydrochloride (2-Hpymo-HCl, 2 mmol) and 4,4'-bipyridine (4,4'-bpy, 2 mmol). Prior filtration of the homoleptic [Cu(2-pymo)$_2$)$_2$]$_2$ polymer after four days at room temperature and later addition of 2 mL of EtOH afforded [Cu$_3$($\mu$-OH)$_2$($\mu$-Cl)$_2$-($\mu$-2-pymo)($\mu$-4,4'-bpy)$_3$]$_n$·$n$H$_2$O (1) blue crystals four days later in approx. 50% yield based on CuX$_2$. 

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*Fig. 4*  Thermal behavior of $\chi_M$ (circles) and $\chi_M T$ (squares) for 1a. Solid lines are best fit to eqn. (1).
Elemental analyses

1a. Yield 54%. Anal. Calcd. For CuH2Cu3Cul4N5O12·8(H2O): C, 38.33; H, 4.26; N, 11.83. Found: C, 38.3; H, 4.1; N, 11.8. IR (ν, cm−1): 1384 vs (NO3).


1c. Yield 40%. Anal. Calcd. For CuH2Cu3Cul4N5O12·8(H2O): C, 38.7; H, 3.8; N, 10.4. IR (ν, cm−1): 1088 vs (ClO4).

1d. Yield 52%. Anal. Calcd. For CuH2Cu3Cul4N5O12·9(H2O): C, 40.02; H, 4.66; N, 10.37. Found: C, 39.8; H, 4.4; N, 10.6.

1e. Yield 53%. Anal. Calcd. For CuH2Cu3Cul4N5O12·8(H2O): C, 35.73; H, 3.8; N, 10.7. Found: C, 38.7; H, 4.7; N, 10.6. IR (ν, cm−1): 1099 m (SO3).

Characterisation and physical measurements

Elemental (C, H, N) analyses were obtained at a FISONS-MARKES equipment. Microcrystalline samples were ground and heated at 150 °C under vacuum (10−4 Torr) for 3 h to remove the crystallisation water molecules.

X-Ray powder diffraction characterisation

Analytical measurements. XRPD data of 1a to 1e (CuKα, λ = 1.5418 Å) were collected on a 0–θ BRUKER DS ADVANCE diffractometer equipped with an aluminium sample holder (Centre of Scientific Instrumentation of the University of Granada).

Aliphatic alcohol sorption. The effect of the addition of a drop of MeOH, EtOH or ethylene glycol aliphatic alcohols over 1a to 1e materials has been studied by XRPD. The XRPD studies show an immediate swelling along the a axis after alcohol addition which was evaluated on 2 0 0 and 4 0 0 reflections. The amount of sorbed ethylene glycol was determined by elemental analysis.

Single crystal X-ray analysis. Single crystal X-ray intensity data for 1a were collected with a BRUKER SMART APEX (MoKα, λ = 0.71069 Å, graphite monochromator) (University of Zaragoza). In all cases, the whole sphere reciprocal space was covered by measurements of 360 frames. Frames were integrated and corrected for Lorenz and polarization effects using DENZO. The scaling and the global refinement of crystal parameters were performed by SCALEPACK. The crystal was corrected for absorption by multiscan method. Crystal data for 1a, [Cu2Cl6(OH)(2-pyrom)-4.4-bpy]·2H2O: 6·2.5H2O: FW = 1033.78 g mol−1. Orthorhombic. Pmn21, a = 17.076(5) Å, b = 19.34(1) Å, c = 13.48(1) Å, Z = 4, μ(calcd) = 1.54 M g m−2, size (mm) 0.29 × 0.23 × 0.05, T = 100 K, Reflns. Obs 6423, R = 0.083, wR2 = 0.19, residuals 1.387–0.808 e Å−3. The single crystal structure was solved by standard direct methods and refined by full-matrix least squares methods based on F2 using the SHELXL-97 programs. All non disordered non-hydrogen atoms were refined anisotropically. The [Cu(μ-OH)(μ-Cl)(μ-2-pyrom)-4.4-bpy)]+ framework is well defined while the NO3 counter ions appear disordered in two positions with 1/2 occupancy.

CCDC reference number 232901. See http://www.rsc.org/suppdata/dt/b5/b500942a/ for crystallographic data in CIF or other electronic format.

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References

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16. J denotes the exchange between central and terminal copper(II) ions and j the parameter between the two terminal copper(II) centres. g Denotes the average g factor for the three copper(II) ions. The J′ term takes into account the inter-trinuclear interactions.