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# Copper(II) complexes with a flexible oxamato ligand

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## Abstract:

We report on a convenient synthesis of the ligand precursor; diethylethylene-1,2-bis(oxamate), ( $\text{Et}_2\text{H}_2\text{o eo}$ , **1**) and show how a partial and preferential hydrolysis of the ester group can give rise to the dianionic ligand,  $(\text{H}_2\text{o eo})^{2-}$ . Reaction of this ligand with Cu(II) affords the neutral dimeric species;  $[\text{Cu}_2(\text{H}_2\text{o eo})_2]$  which has a low aqueous solubility. We describe the crystal structure of the hydrate;  $\text{Cu}_2(\text{H}_2\text{o eo})_2(\text{H}_2\text{O})_4$  (**2**) and report magnetic studies that show a weak exchange interaction in the solid. Under more basic conditions and in the presence of Cu(II) ions, we are able to avoid amide cleavage and yet deprotonate the amide group, resulting in the formation of the highly soluble  $[\text{Cu}(\text{Hoeo})_2]^{4-}$  complex anion. The structure of  $(\text{NBu}_4)_4[\text{Cu}(\text{Hoeo})_2](\text{H}_2\text{O})_4$  (**3**) is described and compared with the recently reported anhydrous phase.

**Keywords:** Copper, oxamate, crystal structure, magnetism

## Introduction

Over 30 year ago Nonoyama first reported the use of the propylene-1,3-bis(oxamate) as a chelating ligand.[1] Coordination with copper(II) through the oxamato N and O atoms results in a very stable anionic copper complex, **a** (Scheme 1). This paramagnetic molecule was exploited by Kahn,[2] who realised that it would interact with other transition metal ions in a structurally and magnetically predictable manner. This predictability allowed Kahn to develop a very successful approach to "molecular magnetism".[3] More recently others[4] expanded this chemistry through

derivatisation and functionalisation of the polyamide ligand. Of particular interest is the elegant dimeric structure **b** (Scheme 1), in which a central spiro atom links two equivalent copper complexes.[5] Interestingly a survey of related structures reveals a striking absence of perhaps the simplest derivative, in which the propylene group of **a** is replaced by an ethylene group to give the hypothetical complex **c** (Scheme 1). We have embarked on a study of the coordination chemistry of this ligand (ethylene-1,2-bis(oxamate)) and report here on two related copper complexes.

## Experimental Section

All reagents were used as received without further purification. C, H and N analysis was determined using a EAI Exeter Analytical Inc. CE-440 Elemental Analyser. Infrared spectra were obtained either as KBr discs using a Jasco FT/IR-410 spectrophotometer, or as neat samples using a Jasco FT/IR-4100 equipped with a Pike Technologies MIRacle ATR.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured using a Bruker DPX/400 spectrometer operating at 400 MHz. Mass spectra were recorded on a Jeol JMS700 (MStation) spectrometer. Powder X-ray diffraction were measured in the range;  $5 < 2\theta < 75^\circ$  on a Siemens D5000, using Cu  $K\alpha$  radiation.

## Synthesis

### *Diethyl ethylene-1,2-bis(oxamate) (Et<sub>2</sub>H<sub>2</sub>oeo); 1*

A solution of ethylenediamine (4.40 ml, 65.2 mmol) in absolute ethanol (10 ml) was added to diethyloxalate (100 ml, 729 mmol) at 45 °C and stirred for 8 hours. The pale yellow mixture was left to cool down to room temperature. The white solid collected by filtration and washed several times with ethanol and dried in air (yield 15.7 g; 93 %).

C<sub>10</sub>H<sub>16</sub>O<sub>6</sub>N<sub>2</sub> requires: C, 46.1; H, 6.1; N, 10.7. Found: C, 44.8; H, 6.0; N, 10.4 %.

$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 7.60 (s, 1H, NH), 4.38 (quart, 2H,  $J = 6.8$  Hz, CH<sub>2</sub>O), 3.60 (m, 2H, CH<sub>2</sub>N), 1.42 (t, 3H,  $J = 6.8$  Hz, CH<sub>3</sub>).  $^{13}\text{C}$  NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 160.39 (C=O), 157.47 (CON), 63.96 (CH<sub>2</sub>O), 39.43 (CH<sub>2</sub>N), 13.96 (CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  3305 s, 3069 w, 2999 w, 2967 w, 2928 w, 2907 w 2866 w, 1747 m, 1735 m, 1673 s, 1543 s, 1474 w, 1459 m, 1394 w, 1363 m, 1324 m, 1300 m, 1236 s, 1215 s, 1163 m, 1110 m, 1055 m, 1013 m, 930 m, 866 m, 829 w, 818 m, 748 m, 708 s. MS (CI)  $m/z = 261.2$  ([C<sub>10</sub>H<sub>17</sub>O<sub>6</sub>N<sub>2</sub>]<sup>+</sup>).

### *Solutions of the ethylene-1,2-bis(oxamate) dianion*

The ethylene-1,2-dioxamate dianion, [(CH<sub>2</sub>NHCOCO<sub>2</sub>)<sub>2</sub>]<sup>2-</sup>, can be prepared as a aqueous solution directly by combining 2 equivalents of an alkali metal hydroxide with an aqueous suspension containing 1 equivalent of **1**. While **1** has a low solubility on water, the dianion is very soluble, and ester cleavage is achieved quickly by gently heating until the reaction mixture becomes a

monophasic, clear solution. In general we can isolate the salts as solid phases by adding ethanol to the reaction, in which **1** is more soluble while the salts of the dicarboxylate are generally insoluble.

*Bis(cis-O,O'-1,2-ethanediyl-bis(oxamato-O,O)copper(II)) tetrahydrate, Cu<sub>2</sub>(H<sub>2</sub>oeo)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>, **2**.*

To a stirring suspension of **1** (1.59 g, 6.11 mmol) in water (10 ml) at 75 °C, a solution of NaOH (0.60 g, 14.6 mmol) in water (5 ml) was added in a dropwise fashion. The solution was stirred for 1 hour, and allowed to cool to room temperature [This solution contains the compound Na<sub>2</sub>(H<sub>2</sub>oeo) which may be obtained as a solid if the solution is made more concentrated]. At this stage the solution of (H<sub>2</sub>oeo)<sup>2-</sup> was filtered to remove any particulate impurities. A solution of CuCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (1.00 g, 6.1 mmol) was then added and the mixture was stirred for a further hour. A turquoise solid that formed was collected by filtration, washed with water, and dried in air (yeild, 1.16 g, 58 %). Anal. Calc. for CuC<sub>6</sub>H<sub>10</sub>O<sub>8</sub>N<sub>2</sub>: C, 23.89; H, 3.34; N, 9.29. Found: C, 23.52; H, 2.52; N, 8.20%. IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  3473 m, 3432 m, 3261 m, 3098 w, 1684 m, 1631 s, 1563 m, 1467 w, 1362 s, 1317 m, 1263 m, 1225 m, 1050 w, 929 m, 823 m, 768 br.

For PXRD see Fig. S1 in supplementary information.

Crystals of **2** suitable for X-ray structure determination were obtained by slow diffusion of Cu<sup>2+</sup> into a gel containing the (H<sub>2</sub>oeo)<sup>2-</sup> anion. A solution of (H<sub>2</sub>oeo)<sup>2-</sup> is obtained by adding NaOH (80 mg, 2.0 mmol), to a suspension of **1** (0.26 g, 1.0 mmol) in water (18 ml). Addition of Si(OMe)<sub>4</sub> (2 ml) to the this solution, was followed by vigorous stirring until a single liquid phase was obtained. This mixture was allowed to set as a gel overnight. A solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.17 g, 1.0 mmol) in water (3 ml) was layered upon the gel and allowed to diffuse undisturbed. After some time well shaped turquoise prismatic crystals of **2** were formed (Fig. S2 – supplementary information).

*Tetrakis(tetra(n-butyl)ammonium) bis(trans-N,N'-1,2-ethanediyl-bis(oxamato-N,O))-copper(II) tetrahydrate, (Bu<sub>4</sub>N)<sub>4</sub>[Cu(oeoH)<sub>2</sub>](H<sub>2</sub>O)<sub>4</sub>, **3***

A solution of tetra(n-butyl)ammonium hydroxide (11 ml, 40 % w/w in water, 17 mmol) was added to **1** (1.00 g, 3.84 mmol) at room temperature. The mixture was stirred until the solid was dissolved. A solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.64 g, 3.6 mmol) in water (2 ml) was added to the reaction in a dropwise fashion to give a deep blue solution. The reaction was stirred overnight and then filtered to remove the green solid that formed. Slow solvent evaporation gave deep blue crystals suitable for X-ray analysis. IR (ATR, cm<sup>-1</sup>):  $\bar{\nu}$  3484 w, 3397 m, 3383 m, 3290 w, 2959 s, 2933 w, 2872 m, 1688 w, 1667 m, 1644 s, 1601 s, 1491 s, 1477 m, 1429 m, 1407 m, 1380 m, 1360 m, 1323 m, 1287 s, 1226 s, 1179 s, 1150 s, 1108 s, 1063 m, 1029 w, 980 s, 889 s, 844 w, 807 m, 775 s, 740 s, 642 s.

There is a tendency for the product to oil out of solution. Analysis of the oil is consistent with the fact that it contains the product seen in the X-ray crystallography, and some additional tetra(n-

butyl)ammonium cations, probably due to unreacted hydroxide. Thus, the proton NMR is characterised by broad peaks, in part due to the paramagnetic nature of **3** and partially due to the presence of impurity. In the  $^{13}\text{C}$  NMR a second type of butyl group is apparent, it is characterised by a smaller peak height, and is marked by \* below.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 2.71 (8H,  $^+\text{NCH}_2$ ), 1.77 ( $\text{CH}_2\text{N}$ ), 1.06 (8H,  $^+\text{NCH}_2\text{CH}_2$ ), 0.83 (8H,  $\text{CH}_2\text{CH}_3$ ), 0.39 (12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 165.31 ( $\text{CO}_2$ ), 163.35 ( $\text{CON}$ ), 58.06 (\*), 53.32 ( $^+\text{NC}$ ), 38.34 ( $\text{CH}_2\text{N}$ ), 28.71 ( $^+\text{NCH}_2\text{CH}_2$ ), 23.41 (\*), 20.17 ( $\text{CH}_2\text{CH}_3$ ), 19.11 (\*), 13.57 ( $\text{CH}_3$ ), 13.13 (\*). UV:  $\lambda_{\text{max}}$ , 629 nm.

### *X-ray crystallography*

Single crystal X-ray diffraction experiments were performed on a Bruker APEX II CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation. Data was collected at 100 K. All initial structures were found by direct methods [6] and were refined by a full-matrix least-squares refinement on  $F^2$  [7] in the WinGX environment.[8]

### *Special details for the refinement of 2*

All atoms (except H and O3w) were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealised geometries; methylene and amide protons were refined in riding mode, while the protons of the water molecule had their OH bond lengths and HOH bond angles restrained. All isotropic thermal parameter for H atoms were fixed at  $1.2 \times U_{\text{eq}}$  of the parent atom. We note some disorder in the water of crystallization with two nearby sites having occupancies that were constrained to sum to 100 %. Thus O2w is found with a 90 % occupancy while O3w has a 10 % occupancy. H atoms for O3w were neither found or include in calculate positions.

### *Special details for the refinement of 3.*

In view of the limited data quality and given the large number of atoms in the asymmetric unit, and consequently the large number of potential parameters, care was taken to apply sensible constraints and restraints to the model. All non-hydrogen atoms were refined anisotropically. One of the butyl groups is disordered over two sites, which refine with 51(1) and 49(1) % occupancies. Chemically equivalent carbon atoms in this disordered group have their anisotropic displacement parameters constrained to be equal. Within the  $[n\text{-Bu}_4\text{N}]^+$  cations corresponding pairs of chemically equivalents bond lengths were restrained to be equal. These bonds were also, refined subject to a 'rigid bond' restraint for each  $[n\text{-Bu}_4\text{N}]^+$  cation, which has the effect to restrain the values of the anisotropic thermal parameters in the bond direction. Hydrogen atoms of the ligand and the  $[n\text{-Bu}_4\text{N}]^+$  cations were placed in calculated positions and refined in riding mode. All H atom thermal parameters were fixed at  $1.2 \times U_{\text{eq}}$  of the parent atom. Hydrogen atoms of the water

molecule Ow1 were located on a difference Fourier map and refined with three restraints (O-H and H···H distances). Hydrogen atoms for Ow2 were neither found nor included in calculated geometries.

## Magnetism

Magnetic studies were performed on a Quantum Design MPMS SQUID magnetometer. A microcrystalline sample of **2** (15.21 mg) was contained in a gelatine capsule. Magnetisation measurements were made between 2 and 300 K in applied fields of 50 and 500 G. Field dependent measurements were recorded at 50 K while the field was swept between 0 and 50 kG. The diamagnetic correction of  $-1.31 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$  (per Cu atom) was calculated from Pascal's constants.[9]

## Results and discussion

### *Synthesis*

The reaction of 1,2-diaminoethane with an excess of diethyloxalate to give the diamide; diethyl ethylene-1,2-bis(oxamate) ( $\text{Et}_2\text{H}_2\text{oeo}$ , **1**) was first reported by Gaade [10]. The synthesis is subject to a number of technical difficulties, not least that in reactions where the diamine:oxalate stoichiometry approaches unity we observe the formation of complex oligomeric mixtures, which are difficult to separate, purify and even characterise, due to the low solubility of these compounds. Using ethanol as a solvent allows us to isolate **1** in both a high yield and reasonable purity. A partial hydrolysis of **1** can be achieved by the careful addition of an aqueous hydroxide solution (Scheme 2). The preferred cleavage of the ester linkage under mild conditions allows formation of the dicarboxylic salts of the amide. A trans-metallation reaction is achieved directly (without the need to isolate the alkali metal carboxylate) by the addition of copper(II) chloride solution (Scheme 3). The light green powder that is formed has a  $\text{Cu}(\text{H}_2\text{oeo})(\text{H}_2\text{O})_x$  composition. Depending upon the precise conditions of the reaction, we observe varying degrees of crystallinity. Rapid addition of high concentration solutions results in an amorphous solid, with no distinct Bragg peaks in powder X-ray diffraction pattern. Microanalysis is consistent with a composition:  $\text{Cu}(\text{H}_2\text{oeo})(\text{H}_2\text{O})_x$  where  $x = 2-3$ . At lower concentrations and slower addition rates, we see the emergence of a microcrystalline product, **2**, which while showing an identical infrared spectra to the amorphous phase, now shows distinct Bragg peaks in the powder X-ray diffraction. Very slow reactions where the components come together under conditions of slow diffusion produce crystals of that are sufficiently large for X-ray structure determination. These confirm that **2** has a  $[\text{Cu}_2(\text{H}_2\text{oeo})_2(\text{H}_2\text{O})_4]$  composition. The simulation of a powder diffractogram from the single crystal data showed a good match to the reflections positions and intensities recorded for the bulk sample of **2** (Fig. S1 – supplementary information).

Given that the amide proton has a  $pK_a \sim 15$  [11], the further addition of base to an aqueous solution of  $H_2oeo^{2-}$  anion should not result in any significant deprotonation, but would increase the likelihood of amide cleavage. In the presence of copper(II) the amide can be deprotonated and the oxamide group chelates the copper ion, through N and O atoms resulting in an intense deep blue solution. When the base is tetra(*n*-butyl)ammonium hydroxide, we form crystals of  $[(n\text{-Bu})_4N]_4[Cu(Hoeo)_2](H_2O)_4$  (**3**), in which deprotonation of one amide gives the ligand  $(Hoeo)^{3-}$ , and two such ligands coordinate the Cu(II) ion in a *trans* geometry.

#### *The structure of $Cu_2(H_2oeo)_2(H_2O)_4$ **2***

Copper(II) complex **2** crystallises in the monoclinic space group  $P2_1/c$  (Table 1). The asymmetric unit is comprised of one copper atom, one molecule of the dianionic ligand,  $(H_2oeo)^{2-}$  and two molecules of water. The oxamide group at each end of the ligand chelates a copper atom, through two oxygen atoms. Thus, the resulting neutral dimeric  $[Cu_2(H_2oeo)_2]$  species that lies on a crystallographic inversion centre (Fig. 1). The copper atom has a Jahn-Teller distorted (4 + 2) coordination sphere (Table 2), with one of the axial sites being coordinated by water, O1w, and the other site by an oxygen atom from a neighbouring  $[Cu_2(H_2oeo)_2]$  unit. This bridging of Cu atoms provides the shortest Cu...Cu separation of 5.267(2) Å, and connects the dimeric unit into a 2-D network in the *bc*-plane (Figure 2). Of the six potential D-H hydrogen bond donor groups, five form simple linear H-bonds (Table 3). One of the amide groups (N2-H2) hydrogen bonds to an oxamide oxygen in a neighbouring molecule forming a cyclic  $R_2^2(10)$  motif.[12] The other amide (N1-H1) is hydrogen bonded to water of crystallisation, (O2w) which in turn forms a hydrogen bond to another oxamide molecule. We note some disorder in the position of the water of crystallisation, with the O2w site having an occupancy of 90 %, and a nearby site O3w having a 10 % occupancy. The unfeasibly short inter-atomic distance (2.078(13) Å), ensures a mutually exclusive occupancies. We note that when present, a water molecule on the O3w site is ideally situated to hydrogen bond with the symmetry equivalent atom  $O2w^i\text{-}H2wa^i$  ( $i = 3-x, y-1/2, z-1/2$ ). However, in the main, when O3w is vacant, the proton H2wa is not involved in hydrogen bonding.

#### *Magnetism of **2***

Magnetisation measurements of **2** gives a room temperature moment of 1.94(2)  $\mu_B$ , which is virtually independent of temperature (Fig. 3). The reciprocal susceptibility was fitted to Curie-Weiss law and gave a Curie constant;  $C = 0.471(1) \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and a Weiss constant;  $\theta = -3.6(3) \text{ K}$ . We can equate this with an isolated  $S = 1/2$  ion and an average value of the *g*-tensor of 2.24. The field-induced magnetisation at 50 K is essentially linear and shows no sign of saturation up to 50 kG (Fig. S3 – supplementary information). Within the dimer unit the Cu ions are linked by a



tortuous Cu-OCNCCNCO-Cu bridge, and have a through space separation of 6.400(5) Å. For such a pathway we expect negligible coupling interactions. However, the shortest Cu...Cu separation of 5.267(5) Å corresponds to a carboxylate bridged inter-dimer contact, and is a likely super-exchange pathway. Although the carboxylate bridge is in a *syn-anti* geometry which under the right circumstances can mediate a significant exchange coupling, in this case the local Jahn-Teller axis of neighbouring Cu ions are almost perpendicular. By considering the likely orientations of the magnetic  $d_{x^2-y^2}$  orbitals on each ion, and the geometry of the carboxylate bridge, it is easy to envisage that in this case the carboxylate mediates a very poor exchange interaction. Thus it seems most likely that we can equate the small negative Weiss constant with a very small antiferromagnetic coupling interaction between neighbouring dimers.

#### *Structure of [n-Bu<sub>4</sub>N]<sub>4</sub>[Cu(Hoeo)<sub>2</sub>](H<sub>2</sub>O)<sub>4</sub> **3***

We obtain the tetra(*n*-butyl)ammonia salt of the mononuclear complex, [Cu(Hoeo)<sub>2</sub>]<sup>4-</sup>, as a tetrahydrate, **3**. The compound crystallises in the triclinic space group  $P\bar{1}$  (Table 1). The asymmetric unit is comprised of half of the coordination complex (the copper(II) ion lies on an inversion centre), two tetra(*n*-butyl)ammonia cations and two molecules of water (Fig. 4, Table 4). One of the *n*-butyl groups in one of the cations is disordered over two sites with approximately equal probabilities. The water of crystallisation is H-bonded to the ligand; O1w forming two interactions and linking the amide carbonyl O atoms within a ligand (Fig. 4), while O2w forms a single H-bond with the terminal carboxylate group (Table 5). Thus there are no significant hydrogen bond interactions for one of the protons on O2w or for the amide proton. Interestingly, the anhydrous form of this compound (**4**) has been reported previously [13] and a number of useful comparisons can be drawn. Both anhydride (**4**) and tetrahydrate (**3**) crystallise in the same space groups with very similar cell lengths and cell volumes. In both cases the Cu atom lies on an inversion centre, and in both cases conformational disorder in the cations is evident. The greatest difference in the structures is in the conformation of the oxamate ligand. The hydrogen bonding from the water of crystallisation in the tetrahydrate stabilises a conformation in which the non-coordinated oxamate group is almost parallel to the planar Cu coordination environment, whereas in the anhydride these groups are aligned perpendicular (Fig. 5).

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**Table 1.** Crystallographic data and structure refinement details for **2** and **3**.

	<b>2</b>	<b>3</b>
Empirical formula	C <sub>6</sub> H <sub>10</sub> CuN <sub>2</sub> O <sub>8</sub>	C <sub>76</sub> H <sub>162</sub> CuN <sub>8</sub> O <sub>16</sub>
Formula weight	301.70	1507.68
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.7513(6)	12.587(5)
<i>b</i> (Å)	5.8042(3)	12.716(5)
<i>c</i> (Å)	16.4521(9)	15.088(6)
$\alpha$ (°)	90.00	99.45(3)
$\beta$ (°)	93.514(3)	90.62(3)
$\gamma$ (°)	90.00	114.07(2)
<i>V</i> (Å <sup>3</sup> )	1024.73(10)	2166.9(15)
T(K)	100(2)	100(2)
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.954	1.155
<i>Z</i>	4	1
<i>F</i> (000)	612	831
Reflections collected	11899	15451
Unique reflections(>2 $\sigma$ ( <i>I</i> ))	3116(2696)	4690(3766)
<i>R</i> <sub>int</sub>	0.0244	0.0374
Parameters refined	171	473
Restraints	6	191
$\mu$ (mm <sup>-1</sup> )	2.168	0.315
$\theta$ Range (°)	1.90-30.48	1.37-21.10
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.065	1.051
<i>R</i> all data / <i>I</i> >2 $\sigma$ ( <i>I</i> )	0.0366/0.0294	0.0799/0.0642
<i>wR</i> <sub>2</sub> all data / <i>I</i> >2 $\sigma$ ( <i>I</i> )	0.0786/0.0753	0.1780/0.1659
Largest peak and hole (e Å <sup>-3</sup> )	1.05 and -0.75	0.96 and -0.51

**Table 2.** Selected geometric parameters for **2**. Bond lengths in Å; bond and torsion angles in °.

C1 – O1	1.239(3)	C6 – O6	1.234(3)
C1 – O2	1.267(2)	C6 – O5	1.262(3)
C1 – C2	1.538(3)	C5 – O6	1.543(3)
C2 – O3	1.254(3)	C5 – O4	1.254(2)
C2 – N1	1.310(2)	C5 – N2	1.315(3)
N1 – C3	1.458(2)	N2 – C4	1.461(3)
C3 – C4	1.535(2)		
		O1 – Cu – O1w	174.46(5)
Cu1 – O1w	2.381(2)	O3 – Cu1 – O5	174.15(6)
Cu1 – O1	2.379(1)	O2 – Cu1 – O4	176.62(6)
Cu1 – O2	1.940(2)	O2 – Cu1 – O3	84.82(5)
Cu1 – O3	1.970(2)	O4 – Cu1 – Cu5	84.64(6)
Cu1 – O4	1.966(2)		
Cu1 – O5	1.962(2)	C2 – N1 – C3 – C4	-78.7(2)
		N1 – C3 – C4 – N2	176.6(2)
		C3 – C4 – N2 – C5	-82.9(2)

**Table 3.** Hydrogen bonding interactions in **2**. Bond lengths in Å, angles in °.

<i>D-H...A</i>	<i>d(D-H)</i>	<i>d(H...A)</i>	<i>d(D...A)</i>	$\angle DHA$
N1-H1...O2w	0.860	2.039	2.834(5)	153.1(1)
N2-H2...O6 <sup>i</sup>	0.860	1.997	2.814(3)	158.2(1)
O1w-H1wa...O3 <sup>ii</sup>	0.91(2)	2.09(2)	2.957(2)	160(2)
O1w-H1wb...O1 <sup>iii</sup>	0.92(2)	2.08(3)	2.917(3)	151(2)
O2w-H2wa...O3w <sup>iv</sup>	0.90(3)	1.97(3)	2.851(13)	167(3)
O2w-H2wb...O6 <sup>v</sup>	0.91(2)	2.04(3)	2.894(3)	157(2)

<sup>i</sup> = 3-x, 2-y, 1-z; <sup>ii</sup> = 2-x, -y, 1-z; <sup>iii</sup> = 2-x, y-1/2, 1/2-z; <sup>iv</sup> = 3-x, y+1/2, 1/2-z; <sup>v</sup> = x, 3/2-y, z-1/2.

**Table 4.** Selected geometric parameters for **3**. Bond lengths in Å; bond and torsion angles in °

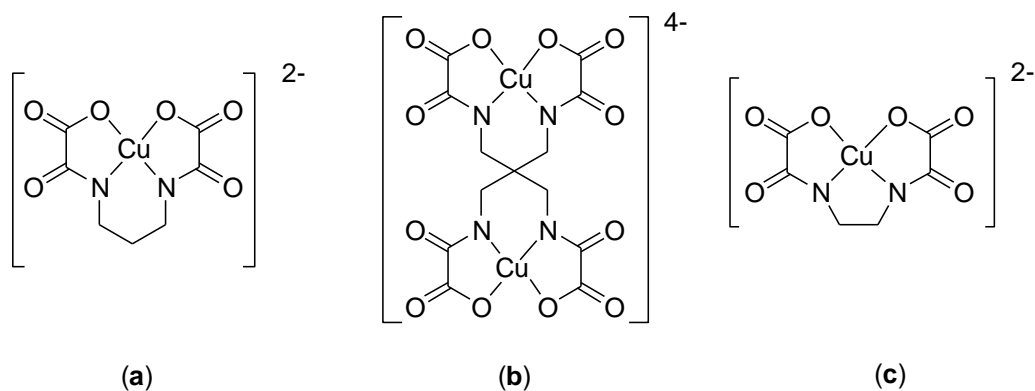
C1 – O1	1.219(7)	C6 – O6	1.235(7)
C1 – O2	1.231(7)	C6 – O5	1.256(8)
C1 – C2	1.556(9)	C6 – C5	1.565(9)
C2 – O3	1.254(6)	C5 – O4	1.234(7)
C2 – N1	1.325(7)	C5 – N2	1.329(7)
N1 – C3	1.463(8)	N2 – C4	1.545(8)
		C3 – C4	1.523(8)
O1 – Cu – O1i	180		
N1 – Cu1 – N1i	180	C2 – N1 – C3 – C4	93.0(5)
O1 – Cu1 – N1	84.4(1)	N1 – C3 – C4 – N2	168.6(4)
Cu1 – O1	1.964(5)	C3 – C4 – N2 – C5	93.3(6)
Cu1 – O2	1.920(6)		

**Table 5.** Hydrogen bonding interactions in **3**. Bond lengths in Å, angles in °.

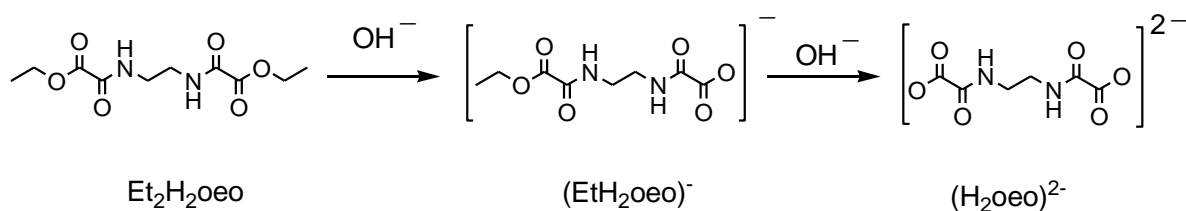
<i>D-H</i> ⋯ <i>A</i>	<i>d</i> ( <i>D-H</i> )	<i>d</i> ( <i>H</i> ⋯ <i>A</i> )	<i>d</i> ( <i>D</i> ⋯ <i>A</i> )	∠ <i>DHA</i>
O1w-H1wa⋯O3 <sup>i</sup>	0.93(6)	1.86(7)	2.78(1)	173(7)
O1w-H1wb⋯O4 <sup>i</sup>	0.94(9)	1.88(9)	2.82(1)	167(5)
O2w⋯O5 <sup>i</sup>	-	-	2.81(1)	-

<sup>i</sup> = x, 1+y, z.

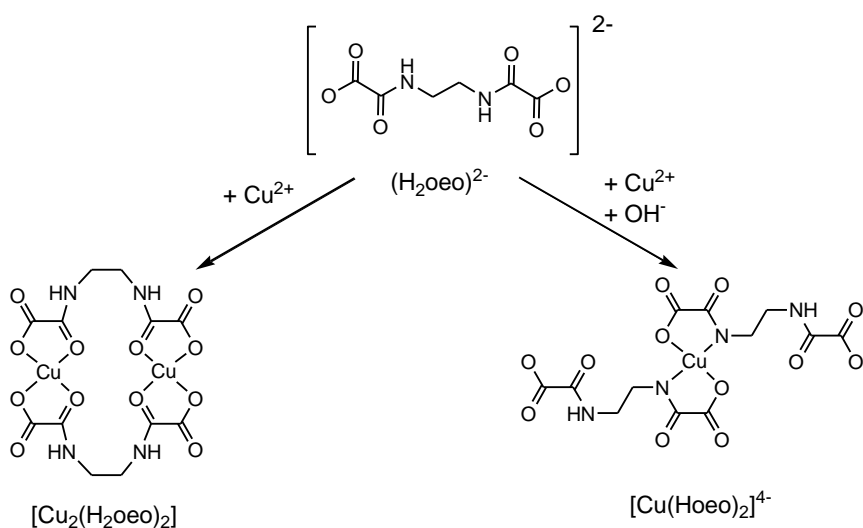
## Figures and Schemes



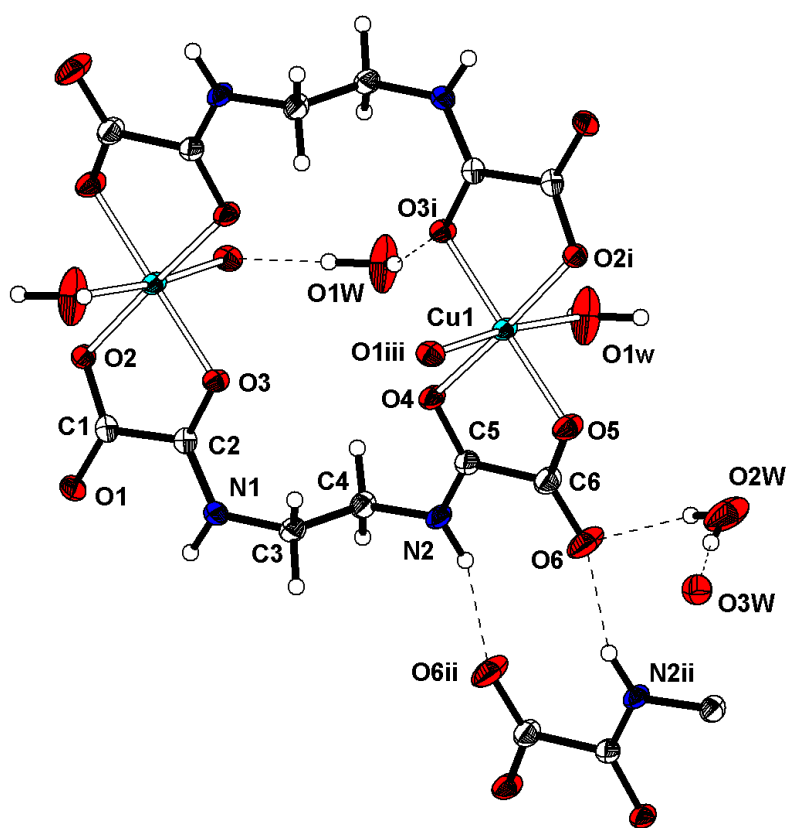
**Scheme 1.** Copper(II) oxamato complexes; (a) Originally reported by Nonoyama [1]. (b) A more recent derivative, which interestingly, tends to adopt a chiral ground state conformation [5]. (c) The as yet hypothetical analogue, that may have been anticipated from the ligand described in this work.



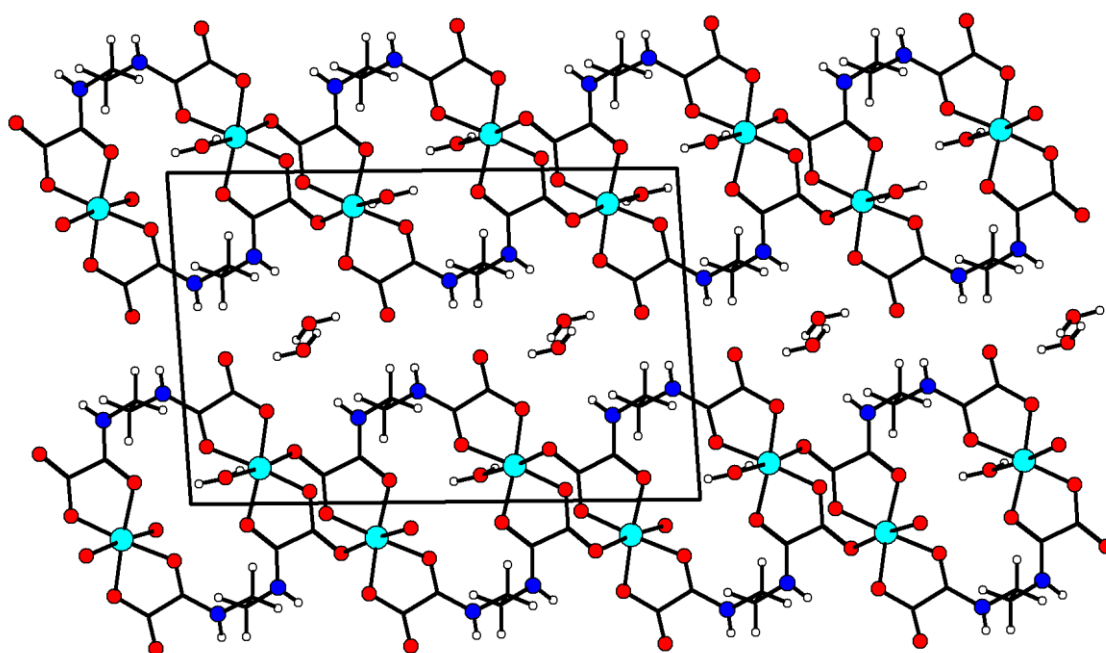
**Scheme 2:** Showing the sequential hydrolysis of the ligand precursor  $\text{Et}_2\text{H}_2\text{oeo}$  (**1**) under basic aqueous conditions and the corresponding abbreviation used in this text.



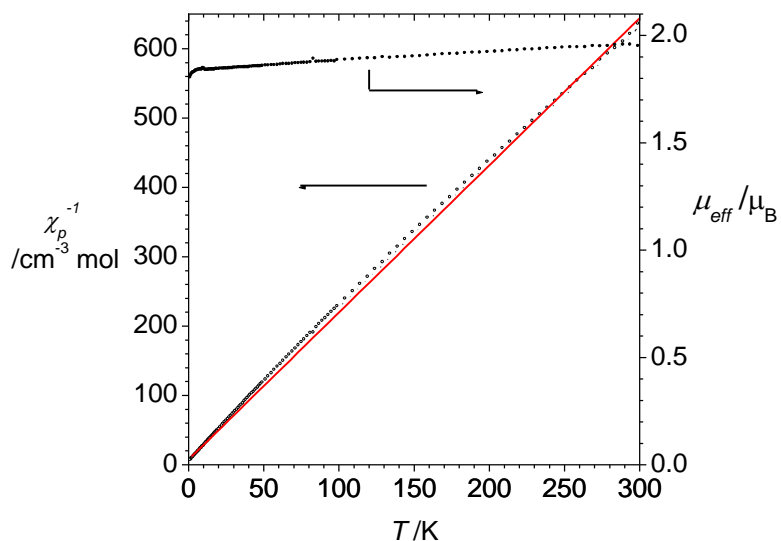
**Scheme 3:** The copper(II) coordination species formed under neutral  $[\text{Cu}_2(\text{H}_2\text{oeo})_2]$  (**2**) and basic  $[\text{Cu}(\text{Hoeo})_2]^{4-}$  (**3**) conditions.



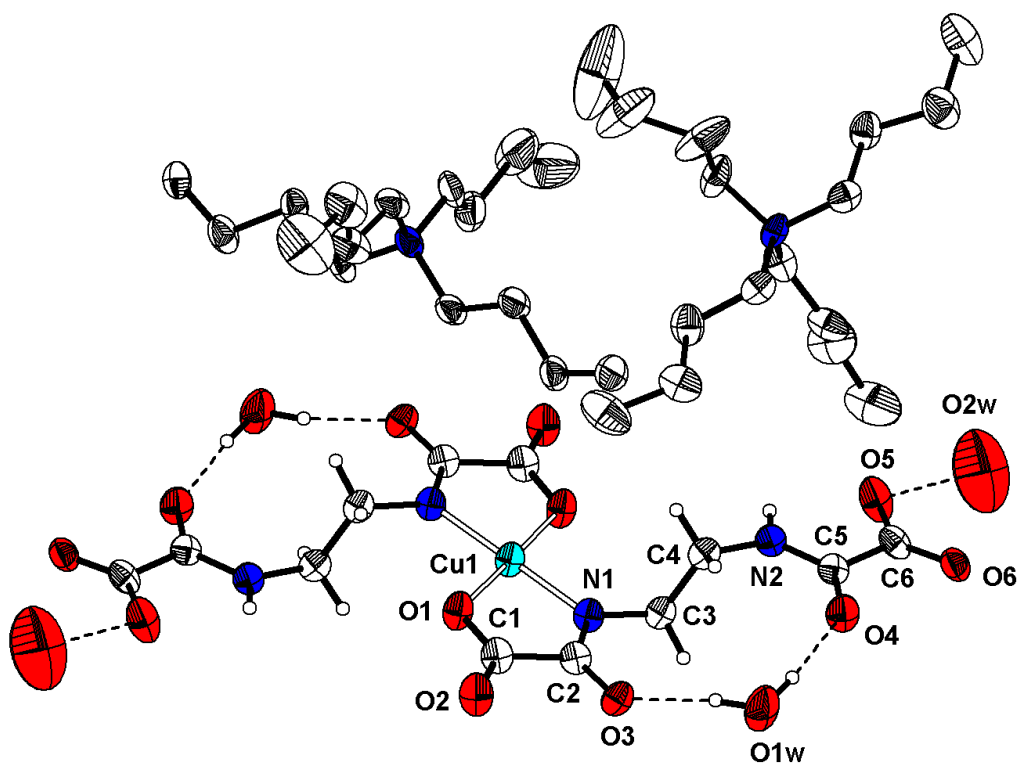
**Figure 1.** Asymmetric unit and selected symmetry equivalent atoms of **2**, showing key hydrogen bonds as well as the atom labelling scheme. Anisotropic thermal parameters are shown at the 70 % probability level.  $i = 2-x, 1-y, 1-z$ ;  $ii = 2-x, 1/2+y, 1/2-z$ ;  $iii = x, 1/2-y, 1/2+z$ .



**Figure 2.** Packing diagram of **2**, viewed along the  $b$  axis, showing the layered character of the material in the  $bc$ -plane.



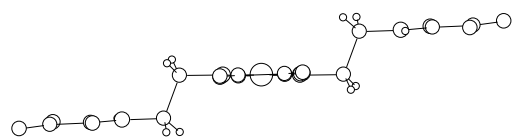
**Figure 3.** Thermal variation of the reciprocal susceptibility ( $\chi_p^{-1}$ ) and the corresponding microscopic molecular magnetic moment of **2**. The solid line shows the two-parameter Curie-Weiss fit to the data.



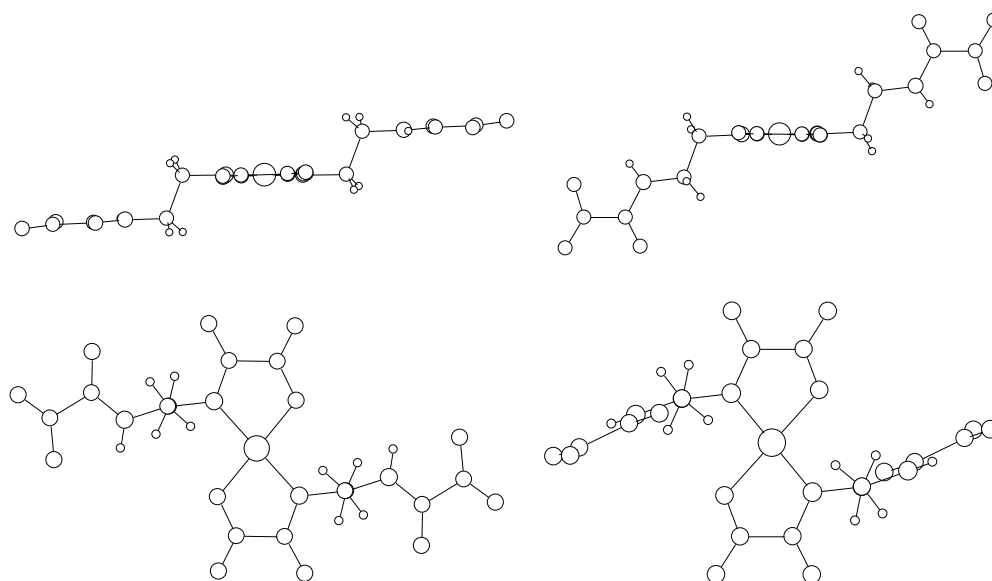
**Figure 4.** Asymmetric unit and selected symmetry equivalent atoms showing the molecular structure of **3**. Thermal ellipsoids at the 50 % probability level. Hydrogen bonding interactions are shown using dashed lines. A partial numbering scheme is shown, and for clarity H atoms on the cation and the conformational disorder is omitted.



**3** (*n*-Bu<sub>4</sub>N<sub>4</sub>)[Cu(Hoeo)<sub>2</sub>](H<sub>2</sub>O)<sub>4</sub>



**4** (*n*-Bu<sub>4</sub>N<sub>4</sub>)[Cu(Hoeo)<sub>2</sub>]

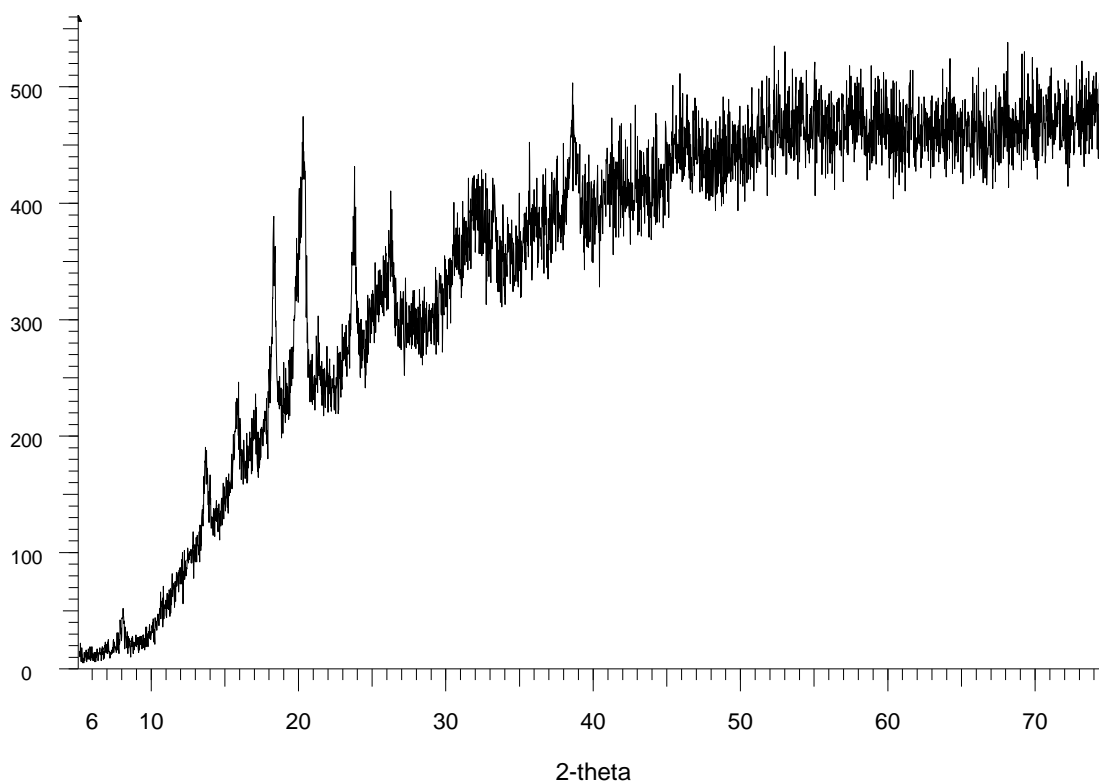


**Figure 5.** Comparison of the complex conformation in the tetrahydrate (**3**) and anhydrous phase (**4**).

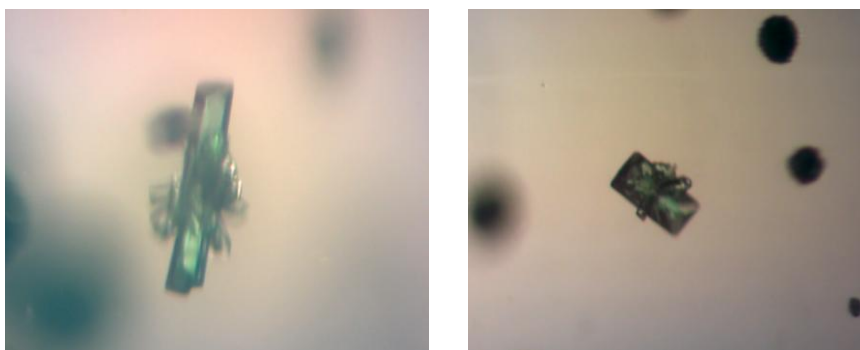
Supplementary information

**Copper(II) complexes with a flexible oxamato ligand**

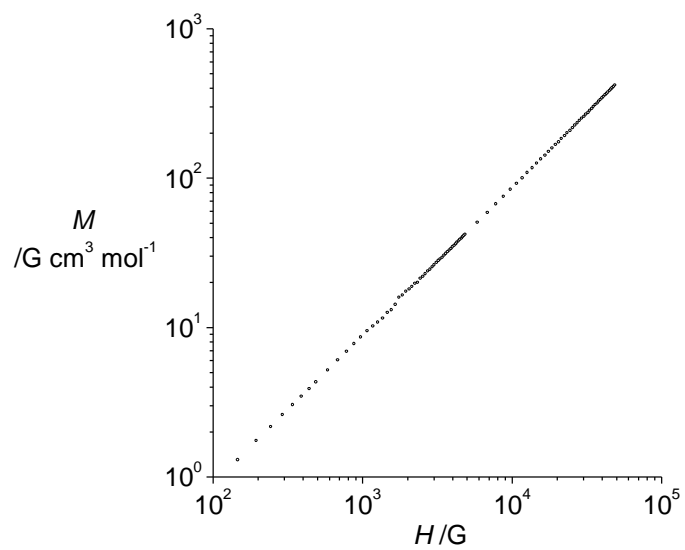
Marta Martinez Belmonte and Daniel J. Price



**Figure S1.** Powder X-ray diffraction of bulk sample of **2**, plotted as intensity (arbitrary scale) as a function of scattering angle  $2\theta$ .

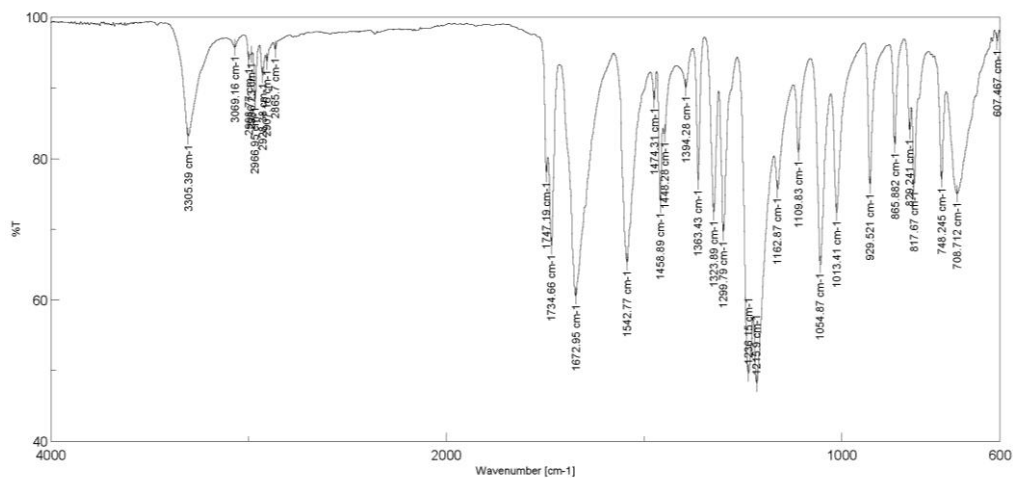


**Figure S2.** Photomicrograph of crystals of **2** growing in a gel medium, by slow diffusion. Image width is approximately 1 mm.

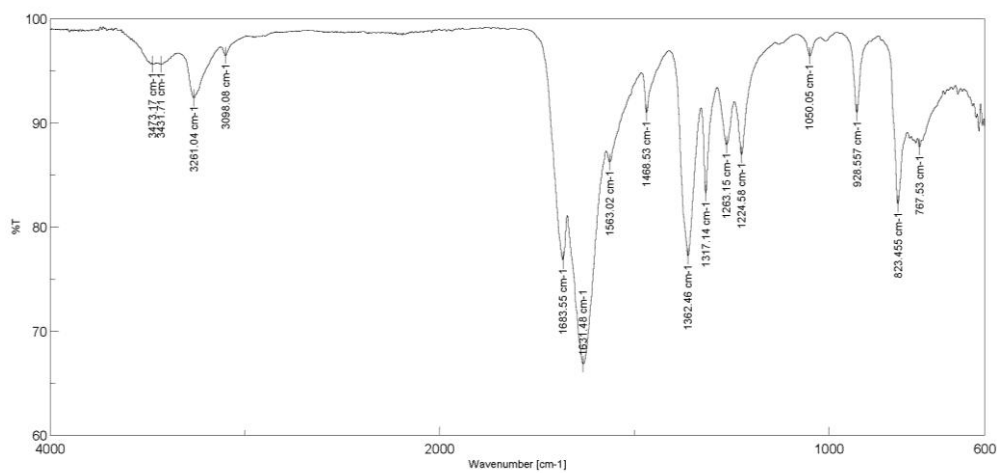


**Figure S3.** Field dependence of the magnetisation of **2** at  $50 \text{ K}$ .

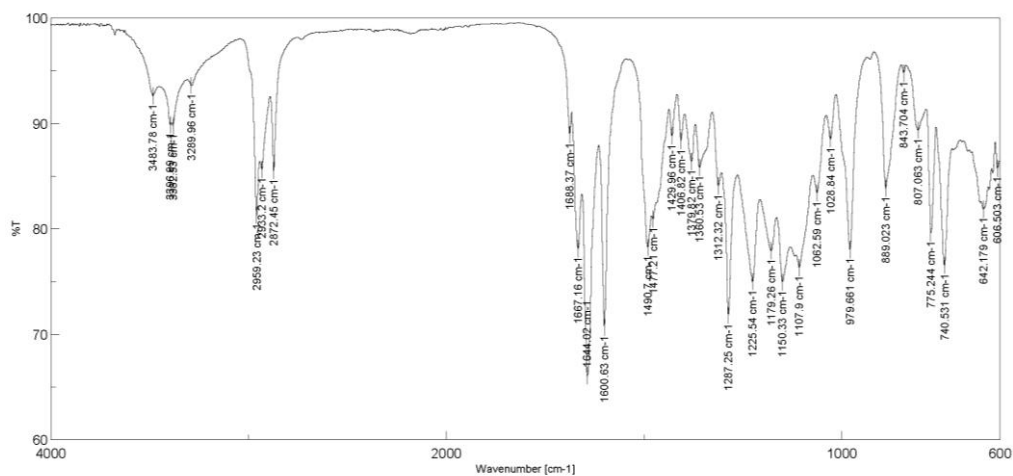
**Figure S4. Infrared spectra**



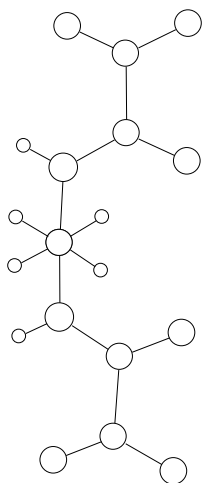
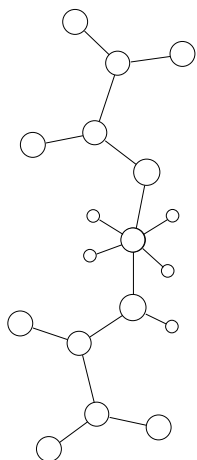
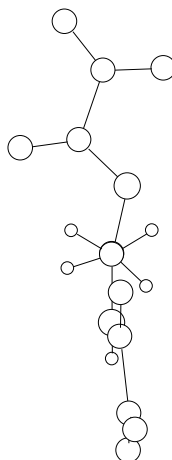
**$\text{Et}_2\text{H}_2(\text{oeo})$  (1)**



**$\text{Cu}_2(\text{H}_2\text{oeo})_2(\text{H}_2\text{O})_4$  (3)**



**$(n\text{-Bu}_4\text{N})_4[\text{Cu}(\text{oeo})_2](\text{H}_2\text{O})_4$  (4)**

**2****3****4**

**Figure S5.** Comparison of the ligand conformations in **2**, **3** and **4**. The torsion angles as defined by; C2-N1-C3-C4, N1-C3-C4-N2, C3-C4-N2-C5 uniquely define the ligand conformation, since the only unconstrained geometries is free rotation around the N1-C3, C3-C4 and C4-N5 bonds. Here we obtain  $-79$ ,  $176$ ,  $-83$  for **2**;  $93$ ,  $169$ ,  $93$  for **3**, and  $75$ ,  $176$ ,  $-175$  for **4**.