



## The first 3D coordination polymer with *cis*-oxamidato-bridged and *trans*-oxamidato-bridged: Synthesis, crystal structure and magnetic properties

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### ABSTRACT

Using dissymmetrical copper(II) precursor,  $[\text{Cu}(\text{oxbe})]^{2-}$ , a novel coordination polymer, namely  $\{[\text{Cu}(\text{cis-oxbe})]_2[\text{Cu}(\text{trans-oxbe})]_2\text{CuNa}_2(\text{DMF})_2\}_n$  (**1**) (oxbe = *N*-benzoate-*N'*-(2-aminoethyl)oxamido) has been synthesized and characterized by IR, elemental analysis, X-ray crystal diffraction and magnetic properties. Single-crystal structural analysis shows that complex **1** consists of 3D framework containing both *cis*-oxamidato bridges and *trans*-oxamidato bridges, which is the first example that *cis*- and *trans*-oxamidato occur in the same structure. Its magnetic properties have also been investigated.

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The current interest in the coordination polymers is rapidly expanding because of their intriguing variety of topologies with inner cavities and channels [1], as well as their potential applications in catalysis [2], host–guest chemistry [3], and molecular electronics [4]. Self-assembly of suitably designed ligands with transition-metal ions allows the creation of inorganic architectures with defined geometry and special properties [5–7]. The shapes and the coordination behavior of the organic ligands are very important in the control of the frameworks [8–10].

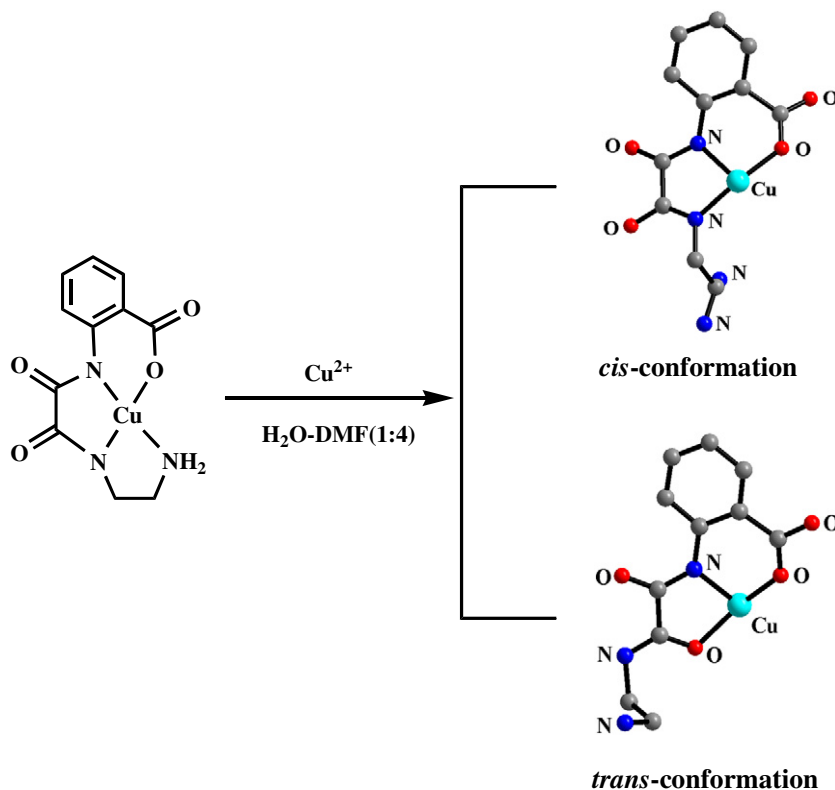
Oxamidate derivatives are known to be versatile organic ligands. One of the most outstanding characters of these ligands is the liable transformation between *cis*- and *trans*-conformations, which makes it advantageous to design tunable molecular materials with extended structures and desired properties. Although the flexibility can give rise to a rich variety of complexes and extended structures, it allows much less control over the final architecture of complex obtained [11].

In our previous work, we employed the dissymmetrical copper(II) precursor,  $[\text{Cu}(\text{oxbe})]^{2-}$ , to generate a 3D heterometallic supramolecular coordination polymer [12]. In this communication, we extend the use of the copper(II) complex  $[\text{Cu}(\text{oxbe})]^{2-}$  (oxbe = *N*-benzoate-*N'*-(2-aminoethyl)oxamido) as precursors for the preparation of homometallic complex. As a result, a novel 3D complex  $\{[\text{Cu}(\text{cis-oxbe})]_2[\text{Cu}(\text{trans-oxbe})]_2\text{CuNa}_2(\text{DMF})_2\}_n$  (**1**), was obtained. To the best of our knowledge, complex **1** is the first example that both *cis*-oxamidato bridges and *trans*-oxamidato bridges are contained in the same framework (Scheme 1). The magnetic properties have also been investigated.

Complex **1** was synthesized [13] by the reaction of  $\text{Na}_2[\text{Cu}(\text{oxbe})] \cdot x\text{H}_2\text{O}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in a mole ratio of 1:2. Single-crystal X-ray analyses [14] revealed that complex **1** is a novel 3D network containing both *cis*-oxamidato bridges and *trans*-oxamidato bridges for the first time. A perspective view of the asymmetry unit of complex **1** is shown in Fig. 1. The asymmetry unit of complex **1** contains two different mononuclear moieties Cu1(*trans*-oxbe) denoted as A and Cu2(*cis*-oxbe) denoted as B, which are united together by the dissymmetric *cis*-oxamidate bridge of B with the Cu1...Cu2 distance of 5.325 Å. The dihedral angle of A and B moieties is 107.1°. In the entity, the three copper ions have two kinds of coordination environments: square pyramidal and distorted octahedral geometry. The coordination polyhedron of Cu1 and Cu2 can be considered as a square pyramid with apical elongation (4 + 1). The basal plane of Cu1 is formed by one nitrogen atom (N1) and two oxygen atoms (O1 and O4) from the dissymmetric *trans*-oxamidate ligand, one oxygen atom (O8) from the dissymmetric *cis*-oxamidate ligand, Cu1 is displaced from least squares basal plane toward the apex by 0.2693 Å, and deviations of the basal donors from this plane are 0.2027 Å (O1), –0.2044 Å (O4), –0.1983 Å (O8), and –0.2088 Å (N1). The axial position is occupied by another oxygen atom (O7) from the dissymmetric *cis*-oxamidate ligand. The four bonds lengths in the plane range from 1.924 Å to 1.955 Å. The axial (Cu1–O7) bond length is 2.25(2) Å, which is elongated due to the Jahn–Teller effect of the  $d^9$  electronic configuration. The basal plane of Cu2 is formed by two nitrogen atoms (N3 and N4) and one oxygen atoms (O5) from the dissymmetric *cis*-oxamidate ligand, one oxygen atom (O2#1) from another dissymmetric *trans*-oxamidate ligand. Cu2 is displaced from least squares basal plane toward the apex by 0.1493 Å, and deviations of the basal donors from this plane are 0.1302 Å (N3), –0.1243 Å (N4), –0.1262 Å (O5), and 0.1203 Å (O2#1). The axial position is occupied by an oxygen atom (O1#1) from the dissymmetric *trans*-oxamidate ligand.

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**Scheme 1.** Formation of two conformations oxamidato-bridged in complex **1**.

The axial (Cu2–O1#1) bond length is 2.39(3) Å, which is elongated also due to the Jahn–Teller effect of the  $d^9$  electronic configuration. The Cu3 atom locates at an inversion center and has a distorted octahedral coordination environment. Two oxygen atoms (O3 and O3#3), and two nitrogen atoms (N2 and N2#3) from two dissymmetric *trans*-oxamidate groups occupy the equatorial sites. The axial positions are filled with two oxygen atoms (O6#7 and O6#8) with elongated Cu–O distances (2.593(4) Å).

From Fig. 2, we can find that the adjacent asymmetry units are bridged together by the carboxylic group (O1C11O2) of A, one oxygen atom (O8) of the carboxylic group (O5C22O6) of B and the *trans*-oxamidate bridge of A coordinates to Cu ions to form a 2D layer. The 2D layers are connected by pairs of Na ions, through one nitrogen atom

(N6A) of the *cis*-oxamidate bridge, one oxygen atom (O2) of the *trans*-oxamidate bridge and two DMF molecules acting as bridging ligands through O9 resulting in a novel 3D network, as shown in Fig. 3. The Na ions are hexacoordinated by three DMF molecules, one carboxylate oxygen atom, and two amido N atoms. The Na...Na distance is 3.722 Å.

The magnetic behavior of complex **1** is investigated in the 5–300 K temperature range and indicative of an overall anti-ferromagnetic coupling, as seen in Fig. 4. To our knowledge, no formula in literatures is available to reproduce the magnetic susceptibility of such a complex system. Therefore, its magnetic properties were preliminarily investigated. At room temperature, the  $\mu_{\text{eff}}$  (where  $\mu_{\text{eff}}$  is the effective magnetic moment) value of complex **1** is 4.38 B.M., which is larger than the spin-only value (3.87 B.M.) for the pentanuclear copper(II) system ( $S = 1/2$  with  $g = 2.0$ ). Upon cooling the  $\mu_{\text{eff}}$  values decrease regularly, approaching a minimum around 5 K with  $\mu_{\text{eff}} = 2.31$  B.M. Fitting the data to the Curie–Weiss law gave  $C = 1.684 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -30.3$  K. The large negative  $\theta$  values indicate the existence of strong anti-ferromagnetic interaction between copper(II) ions.

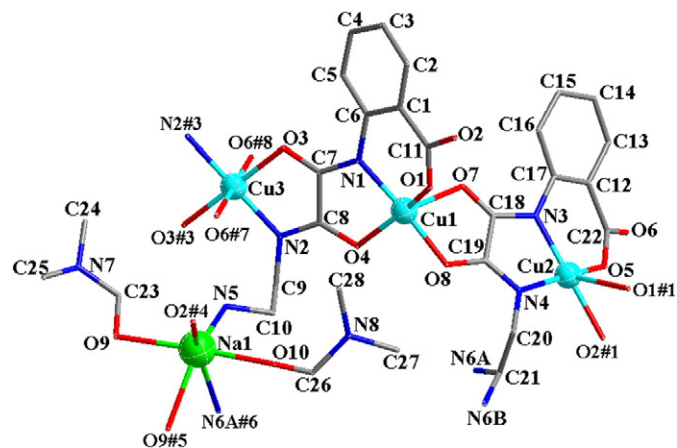
In summary, a novel 3D coordination polymer has been synthesized and characterized structurally and magnetically. This is the first time that the *cis*-oxamidato bridges and *trans*-oxamidato bridges units coexist in one complex. And the 3D supramolecular architecture linked through  $\text{Na}^+$  cations, has never been reported before in this system.

#### Acknowledgment

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#### Appendix A. Supplementary material

CCDC 706286 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif),



**Fig. 1.** The dissymmetrical unit of the complex **1**. Hydrogen atoms are omitted for clarity. Symmetry codes: #1  $-x+2, -y+1, -z+1$ . #2  $x,y,z-1$ . #3  $-x+1, -y+1, -z+2$ . #4  $-x+2, -y+1, -z+2$ . #5  $-x+2, -y, -z+3$ . #6  $-x+2, -y, -z+2$ . #7  $x,y,z+1$ . #8  $-x+1, -y+1, -z+1$ .

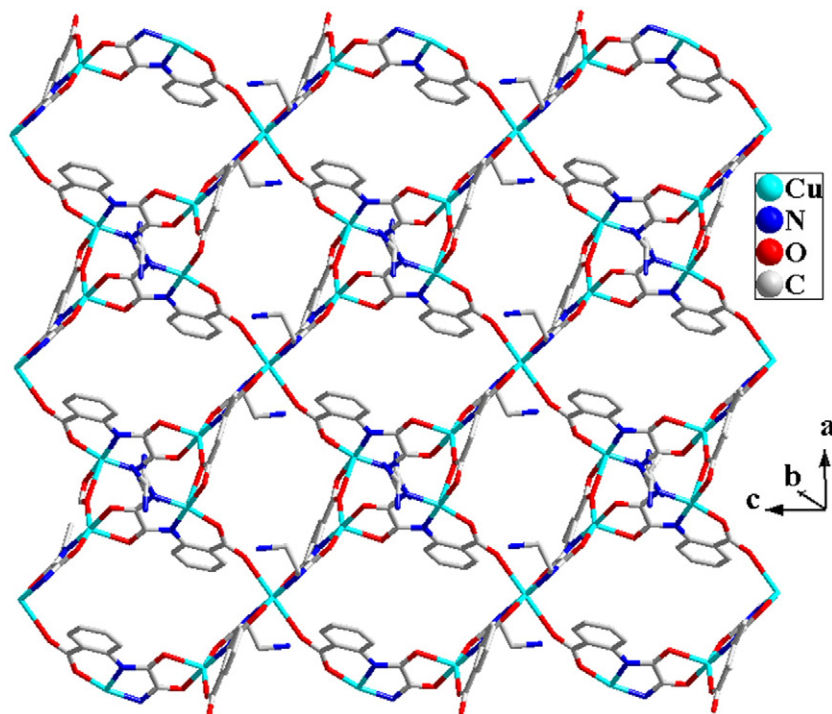


Fig. 2. The 2D layer structure of complex 1. The DMF molecules, sodium cations, and hydrogen atoms are omitted for clarity.

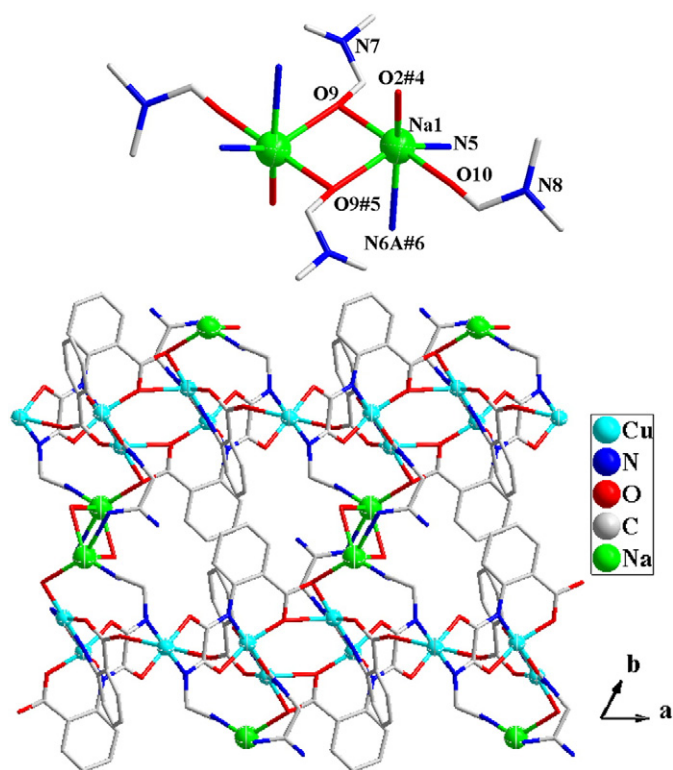


Fig. 3. Top: the  $\text{Na}_2$ -dimer formed between the layers. Other irrespective parts are omitted for clarity. Bottom: the formation of 3D structure through the bridges of O9 atom of DMF, NGA and O2 atoms of ligands between layers in complex 1. Hydrogen atoms and  $\text{CH}_2\text{N}(\text{CH}_3)_2$  groups of DMF molecule are omitted for clarity. Symmetry codes: #1  $-x+2, -y+1, -z+1$ . #2  $x, y, z-1$ . #3  $-x+1, -y+1, -z+2$ . #4  $-x+2, -y+1, -z+2$ . #5  $-x+2, -y, -z+3$ . #6  $-x+2, -y, -z+2$ .

12 Union Road, Cambridge CB21EZ, UK [Fax: int code +44(1223)336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]. Supplementary material to this article can be found online at [doi:10.1016/j.inoche.2010.09.022](https://doi.org/10.1016/j.inoche.2010.09.022).

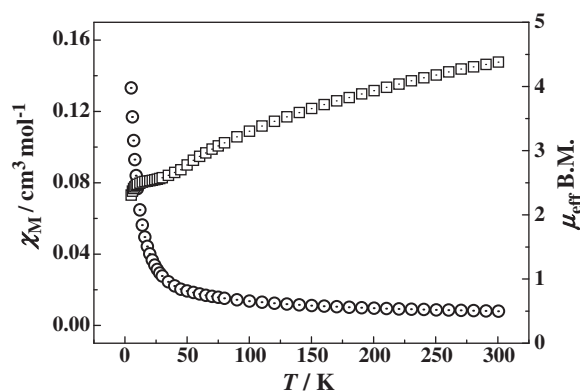


Fig. 4.  $\chi_M$  versus  $T$  and  $\mu_{\text{eff}}$  versus  $T$  plots for complex 1.

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- [13] Synthesis of **1**: Copper perchlorate (0.5 ml, 0.186 g) dissolved in water (10 ml) was added to a DMF solution (40 ml) of Na<sub>2</sub>[Cu(oxbe)]·xH<sub>2</sub>O (1 ml, 0.362 g). After heating to reflux for two hours, the resultant green solution was filtered; the filtrate was left to stand at room temperature. Green crystals of **1** were obtained in one month. Yield: 45% based on copper. Anal. Calcd for C<sub>50</sub>H<sub>56</sub>N<sub>14</sub>O<sub>18</sub>Cu<sub>5</sub>Na<sub>2</sub>: C 39.11; H 3.75; N 13.03. Found: C 38.97; H 3.78; N 13.11%. IR (KBr, cm<sup>-1</sup>): ν<sub>C=O</sub> 1635 cm<sup>-1</sup>, ν<sub>NH<sub>2</sub></sub> 3412 cm<sup>-1</sup>, ν<sub>as(coo<sup>-</sup>)</sub> 1409 cm<sup>-1</sup>, ν<sub>s(coo<sup>-</sup>)</sub> 1433 cm<sup>-1</sup>.
- [14] Crystallographic data: complex **1**, Formula: C<sub>50</sub>H<sub>56</sub>N<sub>14</sub>O<sub>18</sub>Cu<sub>5</sub>Na<sub>2</sub>, FW = 1504.77, Triclinic, *P*-1, *a* = 12.1479(12) Å, *b* = 13.0321(13) Å, *c* = 13.1281(13) Å, α = 64.689(2)°, β = 105.465(2)°, γ = 64.509(2)°, *V* = 1654.6(3) Å<sup>3</sup>, *T* = 293(2) K, *Z* = 1, μ(Mo Kα) = 1.668 mm<sup>-1</sup>, 8215 Reflections collected, 5729 unique [R(int) = 0.0372]. Final *R* indices [*I* > 2σ(*I*)] was R1 = 0.0934, wR2 = 0.2553.