

A new $[\text{Cu}(\text{ox})(\text{Im})_2]$ complex resulting from the oxidation of chelidonate to oxalate

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ABSTRACT

We report herein the solid state structure of a new complex $[\text{Cu}(\text{ox})(\text{Im})_2]$ (**II**) which adopts a mononuclear 0D form in contrast to the polymeric 1D form adopted by the previously described $[\text{Cu}(\text{ox})(\text{Im})_2]_{\infty}$ (**I**). Both compounds were obtained from an oxidative transformation of chelidonate to oxalate in the presence of Cu(II) and imidazole. The packing and weak interactions of **II** are analyzed and compared with those of **I**.

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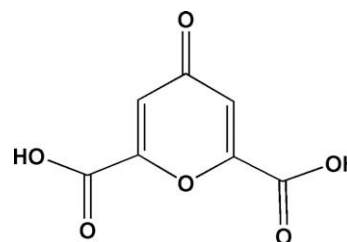
1. Introduction

One of the most interesting aspects of the field of crystal engineering is the structure prediction [1] which is further complicated by the frequent occurrence of polymorphism, supramolecular isomerism and multicomponent crystals such as co-crystals and solvates [2]. Another form of isomerism that can potentially be observed in coordination frameworks is structural isomerism in which the coordination sphere of the metal cation differs between the two isomers. This kind of isomerism has been observed, for example, in $[\text{Ni}(\text{DBM})_2]$, (DBM = dibenzoylmethanoate) which presents a monomer and a trimer forms [3]; in $[\text{M}(\text{dca})_2(\text{pyrazine})]_{\infty}$, (dca = dicyanamide), showing 2D and 3D polymeric forms [4] and in $[\text{Cu}(\text{SCN})(\text{dpt})]_{\infty}$, (dpt = 2,4-bis(4-pyridyl)1,3,5-triazine) with 1D and 3D isomers [5]. We report here the crystal structure of the molecular $[\text{Cu}(\text{ox})(\text{Im})_2]$ (**II**) complex which was obtained from an aerobic oxidation of chelidonate (see chemical diagram of the chelidonic acid in Scheme 1) to oxalate in presence of Cu(II) and imidazole. We also compare their crystal packing arrangement and weak interactions with that observed for the previously published polymeric isomer **I** [6].

2. Results and discussion

Compounds **I** and **II** have been serendipitously obtained in the attempt to obtain copper(II) coordination polymers with the

chelidonate ligand. Compound **I** was first obtained as sky blue single-crystals from a refluxed reaction of 1:1:4 mixture of copper(II) acetate, imidazole and chelidonic acid in MeOH:EtOH, after 15 d of slow evaporation of the resulting mother liquor [6]. Our first explanation for this result was that an aerial oxidation of the acetate precursor mediated by the presence of Cu(II) and imidazole occurred. Consequently, in order to prevent this oxidative process and with the aim to obtain a Cu(II) mixed-ligand complex with chelidonate and imidazole, we have changed the metal precursor to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. So, **II** was obtained by reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with imidazole, chelidonic acid and KOH in 1:4:1:2 molar ratio in MeOH solution. The resulting blue solution was concentrated in a sand bath for around 15 min and later was left to evaporate in air. After 4 months blue sapphire single-crystals of **II** were isolated. The conclusion is that both compounds come from an aerobic oxidation of chelidonate to oxalate in the presence of Cu(II) and imidazole. Similar processes of formation of oxalate from ligands containing car-



Scheme 1. Chemical diagram of chelidonic acid.

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boxylate groups has been described for isonicotinate in the formation of the mixed-ligand complex $[\text{Zn}_2(\text{ox})(\text{IN})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, (IN = isonicotinate) [7], and for orotic acid in the heterometallic coordination polymer $[\text{Sm}_2\text{Co}(\text{ox})_2(\text{Hdtpc})_2(\text{H}_2\text{O})_6]$ [8]. In situ formation of oxalate has been observed under hydrothermal conditions in both cases. However, to our knowledge this oxidative process has been never reported by traditional solution reactions for chelidonic acid. This in situ slow oxalate formation could contribute to the growth of single-crystals of enough quality for the two compounds. Compound **I** has been also recently reported as resulting from a copper(II) assisted decomposition of 1,1'-oxalyldimidazole to oxalate and imidazole [9].

The IR spectra of the two compounds exhibit many similar features with differences in some particular bands, which may provide distinctive markers for the characterization of the two forms. For example, in both spectra the $\nu(\text{NH})$ absorption shows two bands nearly in the same position but with changed intensities: the strong band at 3440 cm^{-1} in **I** appears as weak at 3438 cm^{-1} in **II** and the weak one at 3145 cm^{-1} in **I** appears as strong (3141 cm^{-1}) in **II**. This feature could be attributed to the different degree of involvement in hydrogen bonding of the NH groups in the two compounds. The characteristic bands of the oxalate ligand are at 1643 and 1413 cm^{-1} , corresponding to the $\nu_{\text{as}}(\text{O}-\text{CO})$ and $\nu_{\text{s}}(\text{OCO})$ modes, respectively.

2.1. Structural study

In Fig. 1 are shown the 1D coordination polymer **I** [6] and the molecular compound which is the building block of **II**. In Table 1 are compared the two compounds which crystallizes in the same crystal system but in different space groups.

Compound **I** is a polymeric neutral zig-zag chain with the oxalate ligand acting as bridge, such as in the related 1D polymeric compounds $[\text{Co}(\text{ox})(\text{im})_2]$ and $[\text{Fe}_2(\text{ox})_2(\text{im})_4]$ [10], showing a 4 + 2 type in the coordination environment around the copper(II) ion with the four oxygen atoms of the oxalate involved in coordination to Cu(II) ions. Compound **II** is a mononuclear neutral molecular compound similar to that found in the quasi-one-dimensional compound $[\text{Cu}(\text{ox})(\text{im})_2]_2[\text{Cu}(\text{im})_2(\text{H}_2\text{O})_2]$ [11]. In **II** the copper atom is surrounded by two N donors from two imidazole molecules and two oxygen atoms from one oxalate ligand in a square-planar geometry with the next close contact being one coordinated O_{ox} (O1) belonging to a neighbouring molecule ($x - 1, y, z$) at distance of $2.939(3)\text{ \AA}$.

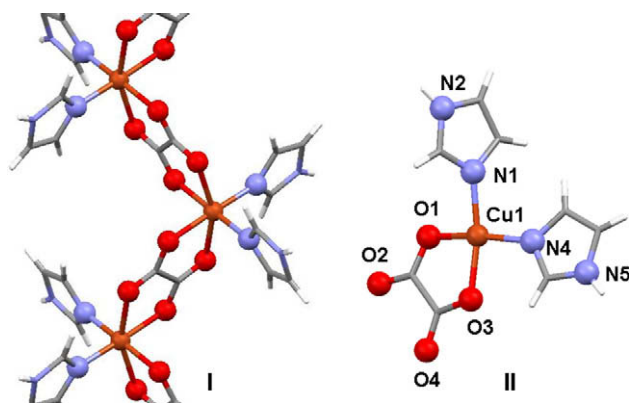


Fig. 1. (a) View of the 1D coordination polymer **I**. (b) View of the molecular structure of isomer **II** showing the atom labelling scheme. Selected bond distances (\AA) and angles ($^\circ$): Cu1–O1 1.954(2), Cu1–O3 1.962(2), Cu1–N1 1.966(3), Cu1–N4 1.976(3), O1–Cu1–O3 83.87(9), O1–Cu1–N1 90.01(10), O3–Cu1–N1 169.49(11), O1–Cu1–N4 169.23(11), O3–Cu1–N4 90.42(10), N1–Cu1–N4 96.92(11).

Table 1
Comparison between compounds **I** and **II**.

	I [6]	II
Dimensionality	1D	0D
Colour	Sky blue	Blue sapphire
Space group	C2/c	P2 ₁ /c
V_{cell} (\AA^3)	1216.6 ($Z = 4$)	1000.5 ($Z = 4$)
D_{calc} (g/cm^3)	1.571	1.910
KPI (%) [12]	61.8	77.1
Cu– O_{ox} (\AA)	2.005(2)/2.320(2)	1.954(2)/1.962(2)/2.939(3)
Cu–N (\AA)	1.979(2)	1.966(3)/1.976(3)
Cu–Cu (\AA)	5.591	3.785
Coordination type	$\text{N}_2\text{O}_4/\text{oct}$ (4 + 2)	$\text{N}_2\text{O}_2/\text{square-planar}$
Contacts type	NH... $\text{O}_{\text{coordinated}}$ $d(\text{N}\cdots\text{O}) = 2.780\text{ \AA}$	NH... $\text{O}_{\text{uncoordinated}}$ $d(\text{N}\cdots\text{O}) = 2.785\text{--}2.917\text{ \AA}$
IR: $\nu(\text{NH})$ (cm^{-1})	3440s, 3145w	3438w, 3141s

The coordinative situation in **II** allows the two uncoordinated oxygen atoms of oxalate, O2 and O4, to participate as acceptors in hydrogen bonding with the NH groups of two neighbouring molecules [$d(\text{N}\cdots\text{O}) = 2.785(4)$, $2.881(4)$ and $2.917(4)\text{ \AA}$ and $\angle(\text{NHO})$ between 138.2° and 176.2°]. So the two uncoordinated O_{ox} are involved in three hydrogen bonds leading to the formation of sheets (Fig. 2, left) which presents voids of approximate dimensions $11 \times 9\text{ \AA}$. These layers are stacked each other in an AB manner (Fig. 2, right) displaying a slipped geometry stabilized through π – π interactions between the imidazole rings along the a -axis (Fig. 2, center) giving rise to a dense 3D structure. The distance between the layers is 3.785 \AA and also the Cu–Cu distance between the packed molecules (Fig. 2, center) is 3.785 \AA , so is shorter than the Cu–Cu distance through the oxalate ligand in **I** (5.591 \AA). Another interesting structural feature in **II** is that as consequence of the slipped AB packing of the layers, the metal centre is at 3.444 \AA of the chelate ring centroid, suggesting the presence of weak metal–ring interaction.

In **I** all the O_{ox} are coordinated to the metal center and two of them are involved in hydrogen bonding to the NH groups of neighbouring chains [$d(\text{N}\cdots\text{O}) = 2.780(2)\text{ \AA}$, $\angle(\text{NHO}) = 165^\circ$] giving rise to a supramolecular 3D network without π – π interactions [6]. Compound **II** exhibits closer crystal packing than **I**. Compared to the dense form of isomer **II** which presents a value of density calculated (from XRD data) of 1.910 g/cm^3 and a packing index [12] KPI of 77.1%, the structure of **I** is expanded in volume by 21.6%, showing a density calculated value of 1.571 g/cm^3 and a KPI index of 61.8%.

A comparison of the structures of **I** and **II** suggest some questions about the nomenclature of crystal forms [13]. Since **I** and **II** have the same structural formula it is tempting to consider these forms to be polymorphs of one another. Polymorphism can be described as different arrangements of the same structural components. But the definition of a structural unit can be subjective [14]: when one considers interactions such as hydrogen bonds, coordination bonds and covalent bonds, the question of whether **I** and **II** are polymorphs depends on where is placed the line with regard to the formation of atomic or molecular networks. When one classify coordination bonds together with covalent bonds, the term of structural isomers seems to be more appropriate to describe the structures of **I** and **II** since the oxalate ligand act differently in the two cases: bidentate in **II** and bis-bidentate in **I**.

3. Experimental section

All chemicals and solvents were commercially available and were used as supplied. Analytical data (C, H, N) was obtained with a Fisons EA-1108 apparatus. Melting point (m.p.) was determined using a Gallenkamp MBF-595 apparatus. FT-IR spectrum was re-

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