Initial use of 1,1′-oxalylldiimidazole for inorganic synthesis: Decomposition of the ligand as a means to the preparation of an imidazole- and oxalate(-2)-containing, 1D copper(II) complex

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The use of 1,1′-oxalylldiimidazole, (im)COCO(im), for the synthesis of coordination complexes is explored for the first time. The [Cu2(O2CMe)4(H2O)2]/(im)COCO(im) reaction system in 96% EtOH yields the new, 1D coordination polymer [Cu(ox)(Him)2]n [1], where Him is the neutral imidazole and ox2− is the oxalate(-2) ligand. A mechanism for the hydrolytic decomposition of the ligand is proposed. Complex 1 comprises neutral, zigzag chains with the n2–n2–n2–µ3–µ2 (2.1111 using Harris notation) ox2− ligand bridging two neighboring CuII centers; two cis Him groups complete a Jahn–Teller distorted octahedral geometry at the metal. The dc, variable-temperature magnetic susceptibility data for the complex reveal antiferromagnetic CuII...CuII exchange interactions.

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Molecular clusters [1] and coordination polymers [2] of 3d transition metals continue to be a major research theme of many groups around the world. Among the diverse reasons for the interest for new clusters are the search for models of metal-containing biological sites [3] and single-molecule magnets [4] with improved properties. The current great interest in the synthesis of coordination polymers (also known as metal-organic coordination networks, metal-organic frameworks or organic–inorganic hybrid materials) is due to their potential applications as functional molecular materials in many fields and areas, such as catalysis, electrical conductivity, luminescence, non-linear optics, magnetism, molecular electronics, medicine, sensing and zeolitic behaviour [2,5]. Their properties originate from the metal centers or/and the organic components.

The chances of identifying new clusters and metal-containing polymeric species will benefit from the development of new reaction systems with suitable organic ligands. Our groups have had a strong interest over the last 10 years in the coordination chemistry of ligands of the general types X–CO–X, X–CO–CO–X and X–CO–X–CO–X. Examples of three thoroughly studied such ligands are di-2-pyridyl ketone [6,7], (py)2CO, 2,2'-pyridil [8], (py)COCO(py), and 2,6-di(2-pyridylcarbonyl)pyridine [9], (py'CO(py))COCO(py), see Scheme 1. There is a chemical characteristic that makes these molecules special as ligands: this is the carbonyl group. Water and alcohols, among other nucleophiles, have been shown to add to the carbonyl group(s) upon coordination of the carbonyl oxygen(s) and/or the 2-pyridyl rings forming the gem-diol (in the case of H2O) and hemiacetal (in the case of ROH) derivatives. The deprotonated forms of those derivatives are versatile and can adopt a plethora of bridging modes, allowing the synthesis of a variety of 3d-metal clusters [6–9], and occasionally of coordination polymers [10]. More recently, our efforts have been turned toward the use of 1,1′-carboxyldiimidazole ([im]2CO, Scheme 1) and 1,1′-oxalylldiimidazole ([im]COCO(im), Scheme 1), which present structural similarities to (py)2CO and (py)COCO(py), respectively, but contain N-imidazolyl instead of 2-pyridyl groups. Our goal has been to see how incorporation of these ligand types might affect the chemical and structural identity of the products. We have just reported [11] that the reaction of [im]2CO and [Cu2(O2CMe)4(H2O)2] in EtOH yields the novel 1D polymeric species [Cu(O2CMe)(im)(Him)–(EtOH)]n containing bridging imidazolate (im−, Scheme 1) and neutral imidazole (Him, Scheme 1) groups, both derived from the alcoholysis/hydrolysis of (im)2CO.

This Communication describes the initial use of (im)COCO(im) for inorganic synthesis. 1,1′-Oxalylldiimidazole is a known reagent in organic [12] and analytical [13] chemistry. At the outset of our efforts we were aware that the ligand might exhibit metal-ion as-
sisted reactivity toward nucleophilic reagents, because of the electron attraction exerted from each carbonyl group by the neighboring heterocycle. Thus, we expected that (im)COCO(im) could not be incorporated intact in metal complexes in aqueous or alcoholic reaction media. However, we hoped that such reactions would likely give cluster or polymeric metal complexes containing decomposition “fragments” of (im)COCO(im), different from those obtained with the use of the simpler “fragments” as starting ligands. This has, indeed, turned out to be the case. We herein report that the Cu(II)-assisted decomposition of (im)COCO(im) leads to an interesting Him- and oxalate(-2) (ox2-, Scheme 1) -containing 1D coordination polymer.

Reaction of a solution of [Cu₂(O₂CMe)₄(H₂O)₂] (0.50 mmol) in 96% EtOH (20 mL) with a slurry of (im)COCO(im) (1.00 mmol) in the same solvent (10 mL) yielded a green solution, which upon layering with n-hexane gave pale green crystals of [Cu(ox)(Him)₂]₂ in 77% yield [14]. In Eqs. 1 and 2 we propose a simplistic reaction scheme that may explain the observed decomposition of the starting ligand to Him and oxalate(-2). A detailed mechanistic perspective is beyond our intention

\[
\text{(im)COCO(im) + 2H₂O \text{Cu}^{II} \text{Him} + \text{HOOC} \text{COOH}} \quad (1) \\
\text{HOOC} \text{COOH} + 2\text{MeCO}_2\text{H} \rightarrow \text{OOC-COO}^- + 2\text{MeCO}_2\text{H} \quad (2)
\]

According to the above equations, the first step of this decomposition involves the hydrolysis (from the water present in the solvent and in the starting Cu(II) material) of (im)COCO(im) to oxalic acid and two equivalents of imidazole, followed by the deprotonation of the former by the more basic acetate. Overall, the formation of 1 can be represented by Eq. 3

\[
n\text{[Cu}_2\text{O}_2\text{CMe}_4\text{H}_2\text{O}_2]_2 + 2n\text{(im)COCO(im)} + 2n\text{H}_2\text{O} \rightarrow 2\text{[Cu(OOC-COO)(Him)]}_2 + 4n\text{MeCO}_2\text{H} \quad (3)
\]

The step described by Eq. 1 seems to be metal-ion assisted as proven by the limited reactivity of (im)COCO(im) with 96% EtOH; in fact, the ligand has limited solubility in EtOH. Slow evaporation of a dilute solution of (im)COCO(im) in 96% EtOH at room temperature gave a mixture of the intact complex, free imidazole and oxalic acid (IR, ¹H NMR evidences). Coordination of the carbonyl oxygen atoms in solution is likely to increase the reactivity of those groups [15]. The Cu(II) centre polarizes the carbonyl group and H₂O can attack the carbonyl carbons more easily to generate the bis-tetrahedral intermediate before the cleavage of the N=C bonds. Mechanisms requiring elevated temperatures were not considered.

The reaction represented by Eq. 3 does not seem particularly alcohol dependent; complex 1 was obtained cleanly in a not optimized yield of ~50% from commercially available (i.e., non-absolute) MeOH. In an attempt to prepare a Cu(II) compound with both ox₂⁻ and im⁻ bridging ligands, we explored reaction systems with various concentrations of external hydroxide sources (the cations of the bases were Me₄N⁺, Et₄N⁺ and Bu₄N⁺ to favour anionic cluster or polymeric species), but those led to 1 in low yields, contaminated with amorphous Cu(II) hydroxo species of uncertain nature. A perspective view of 1 is shown in Fig. 1. The complex crystallizes in the monoclinic space group C2/c. Its structure [16] consists of cis-[Cu(II)(Him)₂]₂⁻ units bridged sequentially by bis-bidentate, centrosymmetric oxalate(-2) ligands to form zigzag polymeric chains. The Cu(II)–Cu(II) separation across the bridging ox₂⁻ group is 5.594(3) Å, typical for bis-bidentate, ox₂⁻-bridged copper(II) complexes [17]. The Cu(II) centre, based on a crystallographic 2-fold axis, is coordinated to four oxygen atoms from two symmetry related bridging oxalate ligands and the pyridine-type nitrogen atoms of two symmetry related, cis-arranged imidazole ligands. The two ox₂⁻ groups around the metal ion are twisted by 85.9°.

The metal coordination geometry is well described as Jahn–Teller distorted octahedral with four short bonds formed by the imine nitrogen atoms, from two crystallographically related Him molecules [Cu(1)–N(1) 1.969(4) Å], and two oxygen atoms from two asymmetrically ligated ox₂⁻ ions [Cu(1)–O(1) 2.000(3) Å]. The axial coordination sites are occupied by the two remaining ox₂⁻ oxygen atoms, with a Cu–O bond length (2.323(3) Å) that is significantly shorter than the Cu–O(im) bond length (2.552(2) Å).
longer than the equatorial ones. The ox2− and the Him ligands form dihedral angles of 83.4° and 86.6°, respectively, with the equatorial coordination plane.

The 1D chains of 1 are hydrogen-bonded into 2D frameworks (Figs. 2 and 3) through O(ox2−)⋯N(Him) interactions [N(2)⋯O(1′) 2.754(3) Å].

Complex 1 joins a family of 1D coordination polymers of the general type [Cu(ox)(L)2]n [17,18], where L is a monodentate ligand. It is only the third example of any CuII complex containing both ox2− and imidazole ligands, the two previous examples being the already mentioned compound [Cu(ox)(Him)2][Cu(ox)(Him)2(H2O)]2 [19] and the 1D polymer [Cu(ox)[(2-Me)Him]2]n [18a], where (2-Me)Him is 2-methylimidazole; in the latter, however, the ox2− ion behaves as a 2.1110 ligand and consequently the CuII centre is 5-coordinate.

The presence of neutral Him ligands in 1 is manifested by a broad IR band at ~3160 cm−1, assigned to (NH) [19]. The broad character and the relatively low wavenumber of this band are both indicative of hydrogen bonding. The spectrum of the complex does not exhibit a band in the region for the carbonyl stretching band, as expected from the absence of intact (im)COCO(im) ligands. The strong bands at ~1630 and 1415 cm−1 are assigned to the (as)(CO2) and (ms)(CO2) modes of the ox2− ligand, respectively [20].

Variable-temperature dc magnetic susceptibility studies were performed on a powdered sample of compound 1 in the 5.0–300 K range (Fig. 4). Previous studies have demonstrated the remarkable capability of the bis-bidentate ox2− ligand to mediate electronic effects between paramagnetic metal ions. For oxalate-bridged CuII complexes, it has been found that the type and value of the exchange coupling is mainly governed by the magnitude of the overlap between the symmetry adapted HOMOs (σ symmetry) of the ox2− ligand and the metal-centered magnetic orbitals (mainly of dx2−y2 type in square planar, square pyramidal and tetragonally elongated octahedral stereochemistries) which are defined by the short equatorial (or basal) copper(II)-ligand bonds [17,18d]. The strongest antiferromagnetic couplings (2J = −260 to −400 cm−1) appear when the ox2− group is symmetrically coordinated with two short bond lengths at each CuII, i.e., it is coplanar with the magnetic orbitals. When one copper(II)-bridge distance is long, the two metal-centered magnetic orbitals are parallel to each other and perpendicular to the ox2− ligand, and the magnetic coupling through the bridge is substantially reduced. In the latter case, the overlap can be zero (accidental orthogonality) and a weak ferromagnetic coupling may be observed.

The χM(T) product for 1 (0.5 T) is 0.27 cm3 mol−1 K at 300 K, significantly below the value theoretically predicted for an isolated S = 1/2 spin (0.41 cm3 mol−1 K, g = 2.1), suggesting strong antiferromagnetic interactions. This is corroborated by the continuous decrease of χM(T) upon cooling, down to a plateau of 0.030 cm3 mol−1 K at 2 K, indicative of a significant amount of paramagnetic impurity. The magnetic susceptibility shows an increase from its 300 K value (8.9 × 10−4 cm3 mol−1) to a broad maximum around 230 K (9.4 × 10−4 cm3 mol−1). Based on the relation proposed by Bonner and Fisher [21] between the position of this maximum and the exchange coupling (kTmax|J| = 1.282, −2JSiSj
Hamiltonian formalism) we may derive a value of $-125 \text{ cm}^{-1}$ for $J$. A number of attempts to fit the data using the Bonner–Fisher model were performed, however we were unable to obtain a good quality fit. Nevertheless, the estimated value is in agreement with an oxalate bridge asymmetrically coordinated through one long and one short bond to each Cu$^{II}$ ion \[17,18d\].

In summary, the initial use of (im)COCO(im) in metal chemistry has led to a 1D Cu$^{II}$ coordination polymer containing hydrolysis "fragments" of the ligand. It is important to note that we could not prepare this compound from reaction systems containing the imidazole and oxalate(-2) ligands. The reactions of the activated ligand (im)COCO(im) with a host of other 3d transition elements not prepare this compound from reaction systems containing the "fragments" of the ligand. It is important to note that we could not prepare this compound from reaction systems containing the imidazole and oxalate(-2) ligands.

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**Appendix A. Supplementary material**

CCDC 716949 contains the supplementary crystallographic data for 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.02.024.

**References**

[14] Analytical data: Calc for C$_{8}$H$_{8}$CuN$_{4}$O$_{4}$: C, 33.39; H, 2.81; N, 14.48. Found: C, 33.56; H, 2.73; N, 14.20. IR data (KBr, cm$^{-1}$): 3160m, 3079w, 2974w, 2879w, 1630s, 1615s, 1546sh, 1423m, 1415s, 1360s, 1333m, 1302s, 1265w, 1192w, 1142m, 1075s, 920m, 800s, 762m, 655s, 619m, 496m.
[16] Crystallographic data for 1: C$_{6}$H$_{8}$Na$_{2}$Cu. M = 287.72, monoclinic, C2/c, a = 13.124(9) Å, b = 10.098(7) Å, c = 9.085(6) Å, $\beta = 97.56(2)$. V = 1193.5(14) Å$^{3}$, Z = 4, D$_{m}$ = 1.601 g cm$^{-3}$, $\mu$(CuK$\alpha$) = 2.715 mm$^{-1}$. T = 298 K. 1478 reflections collected, 862 unique ($R_{int} = 0.068$). $R_{1}$ on $F$ (wR$_{2}$ on $F^2$) = 0.0449 (0.1239) for 782 observed ($I > 2\sigma(I)$) reflections.