

# Structural and spectral studies of *N*-alkyloxamates and their complexes: X-ray structures of MeHNCOCOOK and [Cu(EtHNCOCOO)<sub>2</sub>], and vibrational studies

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## Abstract

This work is devoted to structural and vibrational studies of *N*-alkyloxamates and their complexes. The structures of MeHNCOCOOK and [Cu(EtHNCOCOO)<sub>2</sub>] have been determined by single-crystal X-ray crystallography. The potassium salt crystallizes in the monoclinic space group  $P2_1/n$  and the copper(II) complex in the triclinic space group  $P\bar{1}$ . The lattice constants are  $a = 3.882(2)$ ,  $b = 10.175(1)$ ,  $c = 13.004(1)$ ,  $\beta = 97.04(1)^\circ$  for MeHNCOCOOK and  $a = 5.013(1)$ ,  $b = 6.996(1)$ ,  $c = 8.575(1)$  Å,  $\alpha = 73.54(1)$ ,  $\beta = 85.66(1)$ ,  $\gamma = 71.22(1)^\circ$  for [Cu(EtHNCOCOO)<sub>2</sub>]. The salt has a *trans* secondary amide group and the K<sup>+</sup> ion is surrounded by seven O atoms belonging to six different *N*-methyloxamate(-1) moieties. The ligand EtHNCOCOO<sup>-</sup> behaves as a bidentate chelate in the *trans* square planar copper(II) complex with ligated atoms being the amide and one of the carboxylate oxygens. The copper(II) complex was characterized by its room-temperature magnetic susceptibility and solid-state d–d spectrum. A detailed comparison of the vibrational spectra (FT-IR, FT-Raman) of [Cu(EtHNCOCOO)<sub>2</sub>] with the corresponding potassium salt, EtHNCOCOOK, is presented. The vibrational data are discussed in terms of the nature of bonding and the known structure of the copper(II) complex. Quantum-chemical calculations were performed to obtain the equilibrium geometries and torsional energies for an isolated oxamate(-1) ion (H<sub>2</sub>NCOCOO<sup>-</sup>) and its hypothetical square planar zinc(II) complex. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

It is becoming increasingly apparent that the coor-

dination chemistry of the mono and dianion of oxamic acid (H<sub>2</sub>NCOCOO<sup>-</sup>, HNCOCOO<sup>2-</sup>) and oxamate-based ligands with substituents bearing donor groups is a central theme in transition metal chemistry. Research in this area ranges from the solution of pure chemical [1–5] and spectroscopic [6,7] problems to the renaissance in the fields of heterometallic chemistry [8,9], molecular magnetism [10,11] and advanced materials [12]. The oxamate(-1) anion is

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also a flexible building block capable of generating extended hydrogen-bonded motifs for crystal engineering [13].

Single-crystal X-ray crystallography has revealed that the oxamic acid normally coordinates as a mono-anion, only after the ionization of the carboxylic hydrogen, through the amide and the one carboxylate oxygen atom forming five-membered chelate rings [1,14–17]. It also coordinates as a monodentate O-carboxylato ligand [1] or as a tridentate bridging ligand, using all of its oxygen atoms [18]. Oxamic acid also can coordinate as dianion since both the carboxylic and amidic hydrogens can be removed, and the oxamato(-2) complexes be prepared. In the only crystallographically characterized example, complex  $[\text{Pr}(\text{HNCOCOO})_{1.5}(\text{H}_2\text{O})_3]_n \cdot 2.75n\text{H}_2\text{O}$  [19], the oxamate(-2) anion behaves as a bis-bidentate O(carboxylate), O(amide)/N, O(carboxylate) bridging ligand. Other coordination modes of  $\text{H}_2\text{NCOCOO}^-$  [20,21] and  $\text{HNCOCOO}^{2-}$  [7,22–28] have also been proposed on the basis of vibrational spectroscopy.

For many years, our groups have been engaged in the development of chemistry, thermal properties and vibrational spectroscopy of transition metal complexes with oxamate anions as ligands [5–7,21,26–28]. In contrast to the obtained large body of knowledge, almost nothing is known about the corresponding complexes of alkyl-substituted oxamic acids ( $\text{RHNCOCOOH}$ ,  $\text{R}_2\text{NCOCOOH}$ ), although this class of compounds could offer interesting features in terms of structural and spectroscopic properties. The presence of an alkyl group instead of a hydrogen atom in the amide functional group is expected — due to different steric, electronic and hydrogen-bonding effects — to alter the coordinating behaviour of these ligands in comparison with the behaviour of simple oxamate anions and, hence, differences might be expected. From the vibrational spectroscopy point of view, the different spectral characteristics of the primary ( $-\text{NH}_2\text{CO}-$ ) and secondary ( $-\text{RHNCO}-$ ) or tertiary ( $-\text{R}_2\text{NCO}-$ ) amide groups [29] may give rise to interesting phenomena; the thorough study of the vibrational fundamentals of these functional groups should give valuable information regarding their coordination modes.

With the above considerations in mind we have begun a systematic study of the coordination chemistry of alkyl-substituted oxamic acids, with special

attention to vibrational spectra. Here we report on the X-ray structures of the potassium salt of *N*-methyloxamic acid ( $\text{MeHNCOCOOK}$ ) and complex bis(*N*-ethyloxamato(-1)-*O,O'*)copper(II),  $[\text{Cu}(\text{EtHNCOCOO})_2]$ , together with the spectroscopic characterization of the later. The vibrational analysis of  $\text{MeHNCOCOOK}$  has been given [30]. We also include in the present paper quantum-chemical calculations in order to obtain equilibrium geometries and torsional energies for an isolated  $\text{H}_2\text{NCOCOO}^-$  ion and its 1:2 zinc(II) complex.

## 2. Experimental

### 2.1. General

All manipulations were performed under aerobic conditions using materials (analytical grade) as-received;  $\text{H}_2\text{O}$  was distilled in-house. Microanalyses for C, H and N were performed by the University of Ioannina (Greece) Microanalytical Laboratory. Copper analysis was carried out by EDTA titration.

### 2.2. Compound preparation

The salts  $\text{RHNCOCOOK}$  ( $\text{R} = \text{Me}, \text{Et}$ ) were synthesized by reactions 1 and 2 as described elsewhere [30]. Their purity was checked by microanalyses and IR spectra.



For the preparation of the complex  $[\text{Cu}(\text{EtHNCOCOO})_2]$ , to a solution of  $\text{EtHNCOCOOK}$  (3.10 g, 20.0 mmol) in  $\text{H}_2\text{O}$  (20 ml) was added a solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.70 g, 10.0 mmol) in the same solvent (10 ml). A blue microcrystalline material formed within 1–2 min. The reaction mixture was stirred at room temperature for about 15 min after the precipitation was observed. The solid was collected by filtration, washed with  $\text{H}_2\text{O}$  ( $2 \times 3$  ml),  $\text{EtOH}$  ( $2 \times 5$  ml) and copious amounts of  $\text{Et}_2\text{O}$ , and dried in vacuo over  $\text{P}_4\text{O}_{10}$ . Yield: 2.10 g (71%). Anal. found (calcd.

Table 1

Summary of crystal data, data collection and structure refinement for X-ray diffraction study of MeHNCOCOOK and [Cu(EtHNCOCOO)<sub>2</sub>]

<i>Crystal data</i>		
Compound	MeHNCOCOOK	[Cu(EtHNCOCOO) <sub>2</sub> ]
Chemical formula	C <sub>3</sub> H <sub>4</sub> NO <sub>3</sub> K	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>6</sub> Cu
Formula weight	141.16	295.73
Colour, habit	Colourless prisms	Blue prisms
Crystal size (mm)	0.25 × 0.30 × 0.15	0.20 × 0.25 × 0.15
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	3.882(2)	5.013(1)
<i>b</i> (Å)	10.175(1)	6.996(1)
<i>c</i> (Å)	13.004(1)	8.575(1)
$\alpha$ (°)		73.54(1)
$\beta$ (°)	97.04(1)	85.66(1)
$\gamma$ (°)		71.22(1)
<i>V</i> (Å <sup>3</sup> )	509.8(4)	273.0(1)
<i>Z</i>	4	1
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.683	1.799
$\mu$ (mm <sup>-1</sup> )	0.93	2.02
Radiation (Å)	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
<i>Data collection</i>		
Temperature (K)	293	293
Monochromator	Graphite	Graphite
Collection method	$\omega/2\theta$ scan	$\omega/2\theta$ scan
Absorption	Numerical	Numerical
$\theta_{\max}$ (°)	27	27
Measured reflections	1097	1194
Observed reflections [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	918	1178
Index ranges	<i>h</i> , 0–4; <i>k</i> , 0–13; <i>l</i> , –16–16	<i>h</i> , 0–6; <i>k</i> , –8–8; <i>l</i> , –10–10
<i>Refinement on  F </i>		
Variables	85	97
$[\Delta/\sigma]_{\max}$	0.05	0.1
$ \Delta\rho _{\max}$ (e Å <sup>-3</sup> )	0.6	0.3
<i>R</i>	0.039	0.026
<i>R</i> <sub>w</sub>	0.047	0.039
GoF	2.17	2.24

for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>Cu): C, 32.5 (32.3); H, 4.1 (4.1); N, 9.5 (9.6); Cu, 21.5 (22.1)%.

The H/D substituted complex was prepared on a smaller synthetic scale as described for the normal complex using D<sub>2</sub>O as the solvent; the solid product was washed only with MeOD.

### 2.3. Physical measurements

The magnetic susceptibility was measured at room temperature by the Faraday method with a Cahn–Ventron RM-2 balance standardized with HgCo(SCN)<sub>4</sub>. The molar susceptibility was corrected for the diamagnetism of the constituent atoms using

Pascal's constants. The solid-state (diffuse reflectance, 850–350 nm) electronic spectrum of the copper(II) complex was recorded on a Varian 634 instrument. IR spectra (4000–500 cm<sup>-1</sup>) were recorded and averaged on a Bruker IFS 113v Fourier-transform (FT) spectrometer, using a liquid nitrogen-cooled MCT detector, with samples prepared as KBr pellets. FT far-IR spectra (500–50 cm<sup>-1</sup>) were recorded on a Bruker IFS 113v spectrometer with a DTGS detector using polyethylene pellets. FT Raman data have been collected on a Bruker IFS 66v interferometer equipped with a FRA 106 Raman accessory, a CW Nd-YAG laser source and a liquid nitrogen-cooled Ge detector.

Table 2

Interatomic distances, angles and dimensions of the hydrogen bonds (distances in Å and angles in °) for MeHNCOCOOK and [Cu(EtHNCOCOO)<sub>2</sub>]

<i>The potassium coordination in MeHNCOCOOK<sup>a</sup></i>				
K–O1 <sup>i</sup>	2.855(2)	O1 <sup>ii</sup> –K–O2 <sup>iii</sup>	71.4(1)	
K–O1 <sup>ii</sup>	2.713(2)	O1 <sup>ii</sup> –K–O5 <sup>ii</sup>	59.1(1)	
K–O2	2.996(2)	O1 <sup>ii</sup> –K–O5 <sup>iv</sup>	144.5(1)	
K–O2 <sup>iii</sup>	2.810(2)	O1 <sup>ii</sup> –K–O5 <sup>v</sup>	82.6(1)	
K–O5 <sup>ii</sup>	2.821(2)	O2–K–O2 <sup>iii</sup>	83.9(1)	
K–O5 <sup>iv</sup>	2.765(2)	O2–K–O5 <sup>ii</sup>	138.9(1)	
K–O5 <sup>v</sup>	2.962(2)	O2–K–O5 <sup>iv</sup>	82.6(1)	
O1 <sup>i</sup> –K–O1 <sup>ii</sup>	84.4(1)	O2–K–O5 <sup>v</sup>	142.2(1)	
O1 <sup>i</sup> –K–O2	66.9(1)	O2 <sup>iii</sup> –K–O5 <sup>ii</sup>	127.5(1)	
O1 <sup>i</sup> –K–O2 <sup>iii</sup>	124.7(1)	O2 <sup>iii</sup> –K–O5 <sup>iv</sup>	139.5(1)	
O1 <sup>i</sup> –K–O5 <sup>ii</sup>	72.8(1)	O2 <sup>iii</sup> –K–O5 <sup>v</sup>	82.5(1)	
O1 <sup>i</sup> –K–O5 <sup>iv</sup>	83.7(1)	O5 <sup>ii</sup> –K–O5 <sup>iv</sup>	85.5(1)	
O1 <sup>i</sup> –K–O5 <sup>v</sup>	146.6(1)	O5 <sup>ii</sup> –K–O5 <sup>v</sup>	75.0(1)	
O1 <sup>ii</sup> –K–O2	125.4(1)	O5 <sup>iv</sup> –K–O5 <sup>v</sup>	85.3(1)	
<i>The copper(II) coordination in [Cu(EtHNCOCOO)<sub>2</sub>]</i>				
Cu–O1	1.942(1)	O1–Cu–O5	84.7(1)	
Cu–O5	1.952(1)			
<i>The RHCOCOO<sup>-</sup> dimensions and geometry (R = Me, Et)</i>				
	MeHNCOCOOK	[Cu(EtHNCOCOO) <sub>2</sub> ]		
O1–C3	1.248(3)	1.269(2)		
O2–C3	1.245(3)	1.228(3)		
C3–C4	1.560(3)	1.544(3)		
C4–O5	1.237(3)	1.261(2)		
C4–N6	1.317(3)	1.299(2)		
N6–C7	1.447(3)	1.460(3)		
C7–C8		1.503(3)		
O1–C3–O2	128.9(2)	127.6(2)		
O1–C3–C4	114.5(2)	113.0(1)		
O2–C3–C4	116.6(2)	119.4(1)		
C3–C4–O5	121.6(2)	117.5(1)		
C3–C4–N6	115.0(2)	117.7(1)		
O5–C4–N6	123.3(2)	121.8(2)		
C4–N6–C7	122.6(2)	124.6(1)		
N6–C7–C8		111.4(2)		
O1–C3–C4–O5	8.5(3)	1.0(2)		
O1–C3–C4–N6	–171.3(2)	–179.5(2)		
C3–C4–N6–C7	179.2(2)	–174.2(2)		
C4–N6–C7–C8		114.2(2)		
<i>Hydrogen bonds<sup>a</sup></i>				
Compound	D <sup>b</sup> –H…A <sup>c</sup>	D <sup>b</sup> …A <sup>c</sup>	H…A <sup>c</sup>	<D <sup>b</sup> HA <sup>c</sup>
MeHNCOCOOK	N6–HN6…O2	2.681(3) +	2.42(3)	97(2)
MeHNCOCOOK	N6–HN6…O1 <sup>i</sup>	2.810(3)	1.94(3)	166(3)
[Cu(EtHNCOCOO) <sub>2</sub> ]	N6–HN6…O2	2.752(3)	2.39(3)	117(3)

<sup>a</sup> Symmetry transformations: (i)  $-0.5 - x, 0.5 + y, 1.5 - z$ ; (ii)  $0.5 - x, 0.5 + y, 1.5 - z$ ; (iii)  $1 + x, y, z$ ; (iv)  $-0.5 + x, 0.5 - y, -0.5 + z$ ; (v)  $0.5 + x, 0.5 - y, -0.5 + z$ .

<sup>b</sup> D = donor atom.

<sup>c</sup> A = acceptor atom.

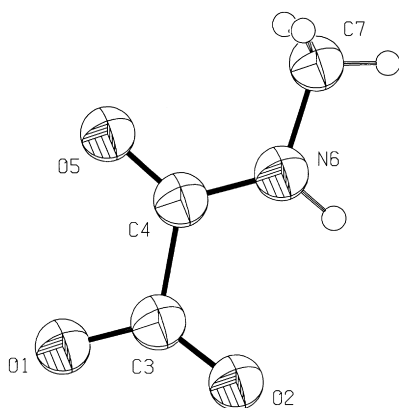


Fig. 1. PLATON view of the anion  $\text{MeHNCOCOO}^-$  showing the atom labeling scheme.

#### 2.4. X-ray crystallographic studies

Suitable crystals of  $\text{MeHNCOCOOK}$  were prepared by recrystallization from  $\text{H}_2\text{O}$ . Crystals of  $[\text{Cu}(\text{EtHNCOCOO})_2]$  suitable for diffractometry were obtained by layering of acetone into a dilute aqueous solution of the microcrystalline solid. Crystal data and full details of the data collection and data processing are listed in Table 1. The crystals were mounted in air on an Enraf–Nonius CAD-4 diffractometer. Unit cell dimensions were determined by using the angular settings of 25 reflections in the ranges  $4^\circ < \theta < 12^\circ$  for  $\text{MeHNCOCOOK}$  and  $6^\circ < \theta < 16^\circ$  for the copper(II) complex. Three intensity and orientation control reflections were measured every hour; they did not show significant fluctuations indicative of crystal decay or diffractometer instability.

The structures were solved by Patterson and Fourier

techniques. For both structures, all non-H atoms were readily located and refined with anisotropic thermal parameters. H atoms were clearly visible in difference electron density maps. Minimum and maximum transmissions were calculated using an absorption correction based on the work by De Meulenaer and Tompa [31]. The values of 0.72 and 0.78 were found for the potassium salt, and 0.64 and 0.74 for the copper(II) complex. In view of the size of the absorption errors, both measurements were corrected for X-ray absorption. Least-squares calculations on  $|F|$  were used to optimize the model parameters  $r$  and  $\beta$ . Reflections were weighted following their statistical errors. The temperature factors of the H atoms were kept fixed at  $4.0 \text{ \AA}^2$ . We stopped the refinement when the largest shift over the error ratio dropped below 0.05.

### 3. Results and discussion

#### 3.1. Description of structures

Interatomic distances, angles and details of the H-bonds for  $\text{MeHNCOCOOK}$  and  $[\text{Cu}(\text{EtHNCOCOO})_2]$  are given in Table 2. Figs. 1 and 2 show perspective views of  $\text{MeHNCOCOO}^-$  and the copper(II) complex, respectively.

The  $\text{K}^+$  ion is surrounded by seven O atoms (ca. 2.71–3.00  $\text{\AA}$ ). The environment of the potassium includes oxygens from six *N*-methyloxamate(-1) moieties, because O5<sup>ii</sup> and O1<sup>ii</sup> (for symmetry codes see Table 2) are part of the same anionic moiety. The ligands are in fact three translational pairs, in which the individual units are separated by the short *a*-axis of 3.882(2)  $\text{\AA}$ .

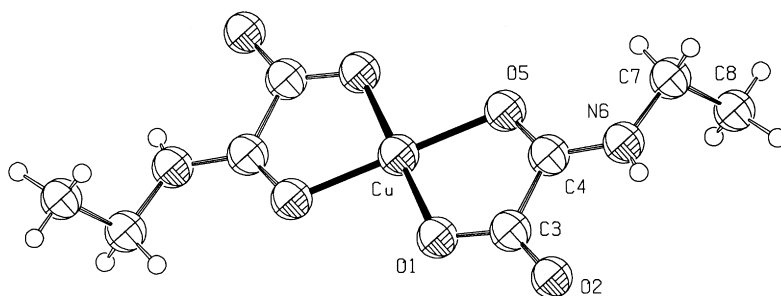
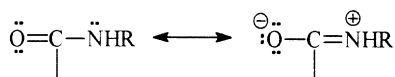


Fig. 2. PLATON view of complex  $[\text{Cu}(\text{EtHNCOCOO})_2]$  showing the atom labeling scheme. Atoms generated by the inversion centre have not been labelled.



Scheme 1.

The K–O distances may be compared with the corresponding distances in the seven-coordinate salt  $\text{H}_2\text{NCOCOOK}$  (2.74–2.84 Å) [13] and the five-coordinate salt  $\text{H}_2\text{NCSCOOK}$  (2.64–2.83 Å) [32].

The asymmetric unit of the copper(II) complex contains half of the  $[\text{Cu}(\text{EtHNCOCOO})_2]$  molecule; the  $\text{Cu}^{\text{II}}$  atom sits on an inversion centre. The mono-anionic ligand is coordinated to the copper(II) centre as bidentate chelate via the amide oxygen (O5) and one of the carboxylate oxygen (O1) atoms. Thus, the  $\text{Cu}^{\text{II}}$  atom shows a square planar coordination with a  $C_i$  symmetry. The Cu–O bond distances of 1.942(1) and 1.952(1) Å are very close to the corresponding distances [1.934(1) and 1.966(1), respectively] in the complex *trans*- $[\text{Cu}(\text{LH})_2(\text{H}_2\text{O})_2]$ , where  $\text{LH}^-$  is the malonamate(-1) ion ( $\text{H}_2\text{NCOCH}_2\text{COO}^-$ ), which contains the coordinated amide and carboxylate oxygens at the equatorial plane of the *trans*-elongated octahedron [33]. The formation of the five-membered chelate ring causes a 5° decrease in the O1–Cu–O5 angle [84.7(1)°]. Such a ring is also present in  $\text{MeHNCOCOOK}$ , but the corresponding angle (O1<sup>ii</sup>–K–O5<sup>ii</sup>) is reduced to 59.1(1)°. This great decrease is a consequence of the elongation in the metal–oxygen distances from ca. 1.95 Å in the copper(II) complex to ca. 2.75 Å in the potassium salt. For a fixed O1...O5 distance, the O–K–O angle should be equal to 55°; the slight increase to 59° is brought about by a increase in the O1...O5 distance caused by a change in the O1–C3–C4–O5 torsion angle from 1° in the complex to 8.5° in the salt.

The impact of complexation on the  $\text{RHNCOCOO}^-$  dimensions and geometry is clearly visible. The carboxylate O1–C3 and O2–C3 distances [1.248(3), 1.245(3) Å] are almost identical in  $\text{MeHNCOCOOK}$ . The observed equivalence is typical for salts and has also been seen in ammonium oxamate [34]. The monodentate coordination of the carboxylate group results in a significant difference between the length of the two carboxylate CO bonds, the O1–C3 distance [1.269(2) Å] involving the coordinated oxygen being longer than the O2–C3 distance [1.228(3) Å]. The formation of a strong bond between O5 and Cu has

also consequences in the dimensions of the secondary amide group. Although strictly speaking we compare different “free” and coordinated *N*-alkyloxamates ( $\text{MeHNCOCOO}^-$  vs.  $\text{EtHNCOCOO}^-$ ), the comparison between the  $\text{MeHNCOCOOK}$  and  $[\text{Cu}(\text{EtHNCOCOO})_2]$  structures shows that there is a lengthening of the C4–O5 [1.237(3) vs. 1.261(2) Å] and a shortening of the C4–N6 bond [1.317(3) vs. 1.299(2) Å] in the copper(II) complex. This can be explained by the fact that the partial double-bond character of the C–O and C–N bonds of the amide group, due to the resonance configurations shown in Scheme 1, is influenced by the copper(II) binding of the group. Upon coordination via oxygen, the doubly positively charged copper(II) ion stabilizes the negative charge on the oxygen atom. The amide function now occurs in its polar resonance form and, thus, the double-bond character of the C–N bond increases, while the double-bond character of the C–O bond decreases. Complex  $[\text{Cu}(\text{EtHNCOCOO})_2]$  is not extreme in the deformation of the *N*-alkyloxamate(-1) moiety. Its flexibility due to coordination effects can be demonstrated by tetrachloro(*N*-methyl-oxamato(-2)-*O,O'*)antimony(V),  $[\text{SbCl}_4(\text{MeHNCOCOO})]$ , which shows [35] a large difference between the carboxylate C–O distances [1.31, 1.22 Å]; the carbon–nitrogen and carbon–oxygen bond lengths of the secondary amide function are 1.27 and 1.29 Å, respectively, with the former being shorter than the latter!

As mentioned above, the O1–C3–C4–O5 torsion angle is 8.5(3)° in  $\text{MeHNCOCOOK}$  and 1.0(2)° in  $[\text{Cu}(\text{EtHNCOCOO})_2]$  indicating that “free” and coordinated  $\text{RHNCOCOO}^-$  ions are slightly non-planar and planar, respectively. The  $\text{Cu}^{\text{II}}$  atom is situated ~0.1 Å outside the least-squares plane through the ligand fragment O1O2C3C4O5N6, the dihedral angle between this plane and the plane defined by atoms Cu, O1, O5 being 4.1(5)°. The virtual planarity of the  $\text{RHNCOCOO}^-$  ions in the potassium salt and the copper(II) complex was rather unexpected, because, in theory, rotation can take place around the central C–C bond. This planarity of the anions can partly be attributed to the presence of an intramolecular hydrogen bond, N6...O2. Due to the geometry of anions, the NH...O angle is very steep (97, 117°). This intramolecular hydrogen bond is also an invariable characteristic feature in the crystal structures of

Table 3

Most characteristic and diagnostic vibrational fundamentals ( $\text{cm}^{-1}$ ) of EtHNCOCOOK and  $[\text{Cu}(\text{EtHNCOCOO})_2]$  (b = broad; m = medium; s = strong; sh = shoulder; v = very)

EtHNCOCOOK		$[\text{Cu}(\text{EtHNCOCOO})_2]$		Assignments
IR	Raman	IR	Raman	
3290 m	3290 [4]	3288 s	3293 [2]	$\nu(\text{NH})$
1669 vs	1661 [6]	1667 sh	1673 [2]	$\nu(\text{CO})$ [Amide I]
1630 vs	1633 [3]	1638 vsb	1649 [5]	$\nu_{\text{as}}(\text{CO}_2)$
1510 s	1514 [4]	1548 m	1544 [10]	$\delta(\text{NH}) + \nu(\text{CN})$ [Amide II]
1398 s	1403 [10]	1374 s	1372 [8]	$\nu_{\text{s}}(\text{CO}_2)$
1215 m	1216 [6]	1259 s	1258 [5]	$\nu(\text{CN}) + \delta(\text{NH})$ [Amide III]
1163 m	1158 [4]	1156 s	1153 [4]	$\nu(\text{NEt})$
850 m	850 [4]	835 m	835 [4]	$\nu(\text{CC})$
803 mb	803 [2]	791 mb	790 [1]	$\pi(\text{NH})$ [Amide V]
334 m	337 [4]	407 m	385 [3]	$\delta(\text{NEt})$
		349 s	265 [1]	$\nu(\text{CuO}_{\text{carboxylate}})$
		308 m	237 [10]	$\nu(\text{CuO}_{\text{amide}})$

six salts containing the unsubstituted oxamate anion ( $\text{H}_2\text{NCOCOO}^-$ ) and different organic or inorganic cations [13].

The crystal structure of MeHNCOCOOK is stabilized by the intermolecular  $\text{N6-H}\cdots\text{O1}$  ( $-0.5 - x, 0.5 + y, 1.5 - z$ ) hydrogen bond, which creates an infinite low-dimensional motif.

Up to this point we have directly analysed the geometrical evidence of the structures. Their dynamic behaviour, observed via the atomic displacement parameters, is also interesting. Hirshfeld's rigid bond test [36] shows that the anion can be regarded as a 'rigid body' in the salt as well as in the complex. This makes a TLS-analysis [37] worthwhile. The analysis of atomic  $\beta$ 's in the potassium salt reveals rms-translational values of 0.16, 0.13 and 0.11 Å. This represents a trace T of  $0.0526 \text{ \AA}^2$ , which suggests a  $B_{\text{eq}}$  value of  $1.4 \text{ \AA}^2$ . So the N-methyloxamate translation is practically dictating the B values for C3 and C4 [1.70(4) and 1.60(4)  $\text{Å}^2$ , respectively]. The adp's of the other atoms deviate from this reference value via molecular libration. We calculated mean square librations of 51.8, 9.3 and 4.4 degrees<sup>2</sup>. Here  $L_{11}$  of 52 degrees<sup>2</sup> is a partial rotation around the inertia axis that practically coincides with C3–C4.

A similar analysis was made for the copper(II) complex. Here the rms-values for translation are 0.19, 0.14 and 0.10 Å. With a trace T of  $0.064 \text{ \AA}^2$  we arrive at a  $B_{\text{eq}}$  value of  $1.68 \text{ \AA}^2$ . This value is not only very close

to B(C3) and B(C4) [1.79(3) and  $1.81(3) \text{ \AA}^2$ , respectively], but also to B(Cu) [ $1.87(1) \text{ \AA}^2$ ]. In our opinion this points out a strong correlation in the dynamic behaviour of the  $\text{Cu}^{\text{II}}$  atom and the ligand entity. This equality in behaviour is absent in the potassium salt with its difference of 30% between  $B_{\text{ligand}}$  (translation) and  $B(\text{K}^+)$ .

Librations also show a strong interaction between copper(II) and ligand. Mean square librations for the ligand in the copper(II) complex are 10.7, 8.3 and 7.5 degrees<sup>2</sup>. The decrease in  $L_{11}$  from  $\sim 52$  to  $\sim 11$  degrees<sup>2</sup> shows a drastic decrease in the partial rotation around the C3–C4 bond due to extra bonding, which is absent in the salt.

### 3.2. Magnetic moment and visible spectrum of $[\text{Cu}(\text{EtHNCOCOO})_2]$

The room-temperature effective magnetic moment ( $\mu_{\text{eff}}$ ) of  $[\text{Cu}(\text{EtHNCOCOO})_2]$  is 1.99 B.M., indicating that the complex is magnetically dilute [38].

The solid-state (diffuse reflectance) d–d spectrum of the copper(II) complex exhibits two broad structured bands at about 15,000 and 17,800  $\text{cm}^{-1}$ , which involve the three expected transitions to  $d_{x^2-y^2}$  from  $d_{z^2}$ ,  $d_{xy}$  and  $d_{xz, yz}$  [39]. The d–d frequencies are fairly typical of square planar stereochemistries with a  $\text{Cu}^{\text{II}}\text{O}_4$  chromophore [39].

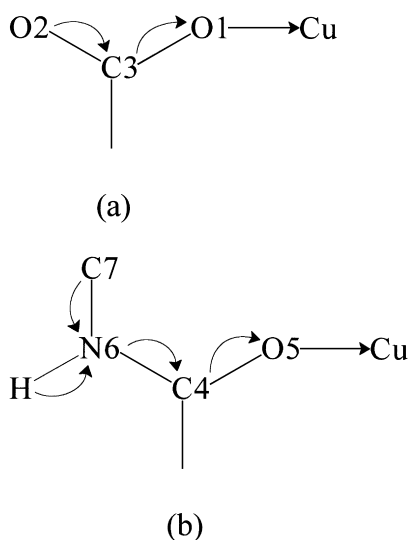


Fig. 3. The 'pile-up' effect for the coordinated carboxylate (a) and secondary amide (b) groups in  $[\text{Cu}(\text{EtHNCOCOO})_2]$ .

### 3.3. Vibrational spectra

Table 3 gives diagnostic IR and Raman bands for the anion  $\text{EtHNCOCOO}^-$  (present in its potassium salt) and its copper(II) complex. The full vibrational analysis of  $\text{MeHNCOCOOK}$ , considering a planar  $C_s$  configuration, has been published [30]. Assignments in Table 3 have been given in comparison with the data obtained for  $\text{MeHNCOCOOK}$  [30], for ligands containing carboxylate groups and their complexes [6,21,29,32,33,40,41] and for ligands with *trans* secondary amide groups and their complexes [29,42,43], and have been assisted by H/D isotopic substitution. The spectroscopic discussion will be confined only to the most important features in relation to the coordination mode of  $\text{EtHNCOCOO}^-$  and the structure of its copper(II) complex.

The frequency difference between some IR and Raman bands in  $[\text{Cu}(\text{EtHNCOCOO})_2]$ , especially in the  $\nu(\text{CuO})$  region ( $350\text{--}230\text{ cm}^{-1}$ ), clearly indicates the presence of an inversion centre.

The Amide V mode has a pure  $\pi(\text{NH})$  character and appears as a broad band of medium intensity in the IR spectra and as a weak Raman band in the  $800\text{ cm}^{-1}$  region. This mode is very sensitive to hydrogen bonding and its lower frequency in the copper(II) complex indicates that hydrogen bonds

are weaker in  $[\text{Cu}(\text{EtHNCOCOO})_2]$  than in  $\text{EtHNCOCOOK}$ .

The higher-frequency shift of the  $\nu_{\text{as}}(\text{CO}_2)$  mode and the lower-frequency shift of the  $\nu_{\text{s}}(\text{CO}_2)$  mode in the copper(II) complex are indicative of the monodentate carboxylate coordination [44]. The monodentate coordination removes the equivalence of the two CO bonds (present in the potassium salt) and a pseudo-ester configuration can be considered for the complex [29,44]. The spectroscopic behaviour of the carboxylate group is then no longer described by the  $\nu_{\text{as}}(\text{CO}_2)$  and  $\nu_{\text{s}}(\text{CO}_2)$  modes, but by an 'ester'  $\nu(\text{C}=\text{O}_{\text{uncoordinated}})$  mode situated at a higher frequency than  $\nu_{\text{as}}(\text{CO}_2)$  and a  $\nu(\text{C}=\text{O}_{\text{coordinated}})$  mode situated at a lower frequency than  $\nu_{\text{s}}(\text{CO}_2)$ .

Considering the *trans* secondary amide function, the Amide II and III bands — which involve the  $\nu(\text{CN})$  mode — are situated at higher frequencies in the spectra of  $[\text{Cu}(\text{EtHNCOCOO})_2]$  than for  $\text{EtHNCOCOOK}$ , whereas the Amide I band [ $\nu(\text{CO})$ ] shows a frequency decrease. These shifts are consistent with amide-O coordination [42,43].

The shifts of the carboxylate and amide fundamentals described above can very well be explained by considering the ligand–metal bonding as a donor–acceptor complex [45] as shown in Fig. 3. The 'pile-up' effect indicates a shortening of the O2–C3 and a lengthening of the O1–C3 bond for the coordinated carboxylate group, and a lengthening of the C4–O5, N6–H, N6–C7 bonds and a shortening of the C4–N6 bond for the coordinated amide group. This model also explains the lower frequency of  $\nu(\text{N}(\text{Et}))$  in the copper(II) complex. According to this model we should also observe lower and higher frequencies for the  $\nu(\text{NH})$  and  $\pi(\text{NH})$  modes, respectively, in the complex. As we do not observe the expected shifts, we can only conclude that the difference in hydrogen-bonding strength influences these fundamentals much more than the effect of coordination.

The fundamental with a high  $\nu(\text{CC})$  character is observed at a lower frequency in the copper(II) complex due to the ring system and the mass effect. The complicated character of  $\nu(\text{CC})$ , i.e. coupling with other vibrations in the ring, also influences this fundamental.

The presence of one  $\nu(\text{CuO}_{\text{carboxylate}})$  and one  $\nu(\text{CuO}_{\text{amide}})$  vibration in the low-frequency IR



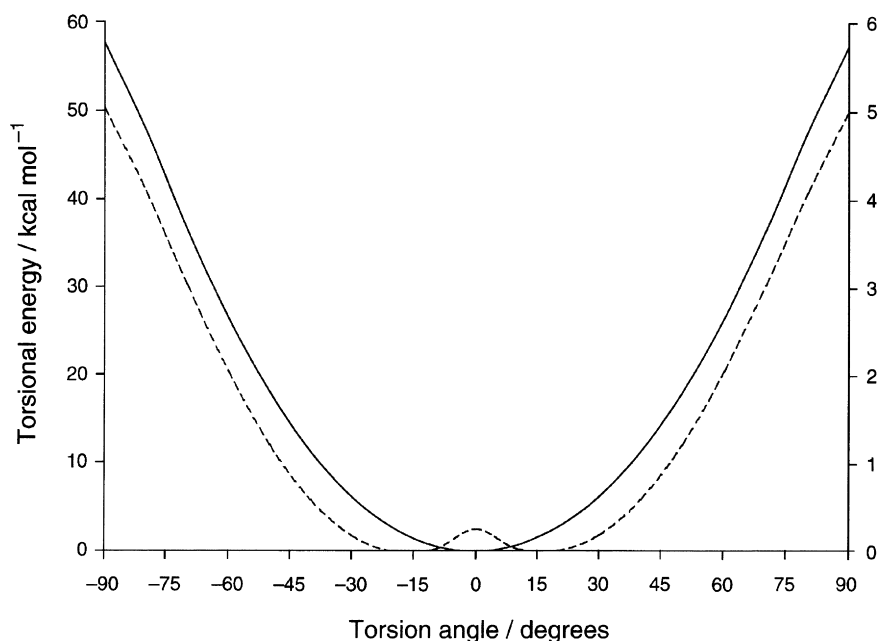


Fig. 4. The energy profile (Kcal/mol) for a torsion ( $^{\circ}$ ) around C3–C4. The energy scale on the left-hand side applies to the torsion in  $[\text{Zn}(\text{H}_2\text{NCOCOO})_2]$  (solid line). The scale on the right-hand side corresponds to the isolated  $\text{H}_2\text{NCOCOO}^-$  ion (dashed line).

( $B_u$ ) and Raman ( $A_g$ ) spectra of  $[\text{Cu}(\text{EtHN-COCOO})_2]$  reflects its *trans* square planar structure [46] established by single-crystal X-ray crystallography.

Table 4

Calculated bond distances, bond angles and torsional angles (distances in  $\text{\AA}$  and angles in  $^{\circ}$ ) for the oxamate(-1) ion and its square planar zinc(II) complex (The atomic labeling scheme for the oxamate(-1) is similar to that used in the structures of  $\text{MeHN-COCOOK}$  and  $[\text{Cu}(\text{EtHNCOCOO})_2]$  (see Figs. 1 and 2).)

	$\text{H}_2\text{NCOCOO}^-$	$[\text{Zn}(\text{H}_2\text{NCOCOO})_2]$
O1–C3	1.217	1.263
O2–C3	1.237	1.196
C3–C4	1.572	1.550
C4–O5	1.202	1.227
C4–N6	1.366	1.311
O1–C3–O2	131.3	130.6
O1–C3–C4	115.7	111.8
O2–C3–C4	113.0	117.6
C3–C4–O5	125.6	119.1
C3–C4–N6	112.3	116.3
O5–C4–N6	122.1	124.6
O1–C3–C4–O5	16.8	0.1
O1–C3–C4–N6	-162.8	-179.9

### 3.4. Quantum-chemical calculations

We decided to look at the molecular geometries and the variation in  $L_{11}$ -libration in more detail. Quantum-chemical calculations were performed at the RHF/6-31G\*\* level using the ab initio program BRABO [47]. We obtained equilibrium geometries and torsional energies for an isolated oxamate(-1) ion ( $\text{H}_2\text{NCOCOO}^-$ ) and for a hypothetical square planar Zn(II)/oxamate(-1) complex ( $[\text{Zn}(\text{H}_2\text{NCOCOO})_2]$ ). We selected the zinc(II) complex in order to avoid complications caused by open shell systems. The results of the calculations are presented in Fig. 4.

The equilibrium geometries of the oxamate(-1) moiety and its geometry in the Zn(II) complex are included in Table 4. The difference of 0.02  $\text{\AA}$  between the O1–C3 and O2–C3 bond distances in the structure of the free ion reflects the intramolecular N–H $\cdots$ O2 interaction. A very small barrier of 0.250 kcal/mol at  $\tau = 0^{\circ}$  separates the two energy minima at  $\tau = \pm 16^{\circ}$ . This leads at room temperature to an rms-torsional value of  $25^{\circ}$ . The crystalline packing clearly reduces this torsional variation to a maximum of  $7^{\circ}$ , i.e.  $L_{11}^{1/2}$ .

At the same time the molecular torsion of  $16^\circ$  for a free moiety shifts to  $8^\circ$  in the solid state.

Complexation has a direct impact on the oxamate(-1) geometry. The changes in the bond lengths and valence angles that were observed in the analysis of MeHNCOCOOK and [Cu(EtHNCOCOO)<sub>2</sub>] are matched by the calculated shifts. In the planar zinc(II) complex with the Zn<sup>II</sup> atom at the inversion centre, we arrived at Zn–O distances of 1.933 and 2.087 Å with an O–Zn–O angle of  $81.1^\circ$ . We calculated the torsional energy profile C3–C4 in [Zn(H<sub>2</sub>NCOCOO)<sub>2</sub>] while preserving the inversion centre at the Zn<sup>II</sup> position. The torsional energy changes practically as a parabolic function with the deformation in  $\tau$ , i.e. we observe an harmonic potential. With  $\Delta E = f(\tau - \langle \tau \rangle)^2$  we find  $\langle \tau \rangle = 0^\circ$  and  $f$  is 7 cal/mol degree<sup>2</sup>. Since  $U = RT/2f$  we expect an rms torsional angle of  $6.5^\circ$ , which is four times smaller than the rms-value calculated for the free oxamate(-1) ion. The rms torsional angle for an isolated zinc(II) complex is about twice the value of  $L_{11}^{1/2}$  observed in the solid state.

#### 4. Summary, conclusions and perspectives

The present study, along with recent results from our groups and literature reports [35], shows that: (i) the monoanions of alkyl-substituted oxamic acids behave as O<sub>amide</sub>, O<sub>carboxylate</sub>-bidentate chelating ligands; and (ii) vibrational spectroscopy can safely be used to predict this coordination mode. We believe that the RHNCOO<sup>-</sup> ions are also capable of acting as bridging ligands and much work still remains to be done in exploring their structural chemistry. More recent work has unearthed novel lanthanide(III) and yttrium(III) complexes in which RHNCOO<sup>-</sup> behave as bridging ligands. Work is also in progress for the preparation and characterization of *N*-alkyloxamato(-2) complexes. The dianions RNCOCOO<sup>2-</sup> are proven to be reactive and excellent springboards into new cluster and polymer chemistry; our studies, already well advanced, will be reported soon.

The comparison between the coordinating abilities of EtHNCOCOO<sup>-</sup> (present work) and the simple oxamate anion, H<sub>2</sub>NCOCOO<sup>-</sup> [6], towards copper(II) reveals the same coordination mode for both ligands, a similar stereochemistry (square planar) in the

complexes and comparable metal–ligand bond strengths (as deduced from far-IR spectroscopy). Obviously, the replacement of the primary amide function by the secondary amide group has little structural effect.

A final point of interest is the fact that even though the syntheses of RHNCOO<sup>-</sup> (R = Me, Et) and [Cu(EtHNCOCOO)<sub>2</sub>] took place in an aqueous environment, these compounds are anhydrous. On the contrary, H<sub>2</sub>NCOCOOK·H<sub>2</sub>O [13] and [Cu(H<sub>2</sub>NCOCOO)<sub>2</sub>]·H<sub>2</sub>O [6] incorporate a solvent molecule into their lattices as revealed by X-ray single-crystal crystallography and analytical/vibrational data, respectively. An obvious reason for the anhydrous nature of the compounds described in this work is the hydrophobic character of the alkyl groups. Aakeröy and coworkers [13] have explained the presence of water in H<sub>2</sub>NCOCOOK·H<sub>2</sub>O in terms of the hydrogen-bond donor/acceptor ratio. A crystal structure of anhydrous potassium oxamate would have a surplus of hydrogen-bond acceptors (three acceptor atoms, two donor atoms). One way in which potassium oxamate could achieve a more desirable ratio would be to include a water molecule, since potassium oxamate monohydrate is well balanced with four acceptor atoms and four donor atoms. This, in combination with the fact that the small K<sup>+</sup> ion is capable of interacting with (coordinating) H<sub>2</sub>O molecules, is the likely explanation for the appearance of one solvent molecule in H<sub>2</sub>NCOCOOK·H<sub>2</sub>O. The hydrophobic nature of the ethyl group makes this explanation not valid here, even though the crystal structure of anhydrous MeHCOO<sup>-</sup> has a clear surplus of hydrogen-bond acceptors.

#### 5. Supplementary material

Atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors for both X-ray structures included in this work are available from S.P.P. upon request.

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