

SYNTHESIS AND CRYSTAL STRUCTURE OF THE ADDUCT: COPPER(II) FORMATE - FORMIC ACID (1:2) - A NEW POLYMORPHIC FORM (β -form)**Nina Lah, Primož Šegedin and Ivan Leban****Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, P.O. Box 537, SI-1001 Ljubljana, Slovenia*

† This paper is dedicated to the memory of our colleague Dr. Karel Lutar.

*Received 10-12-2001***Abstract**

A new polymorphic adduct of copper(II) formate with formic acid, catena-*bis*(μ_2 -formato-*O,O'*)-*bis*(formic acid-*O*)-copper(II) (β -form) has been prepared and structurally characterised by single crystal X-ray diffraction. Compound crystallizes in the orthorhombic space group *Pbca* with the following cell dimensions: $a = 7.8773(17)$, $b = 8.4775(2)$ and $c = 12.1423(3)$ Å. The results show polymeric structure of the $[\text{Cu}(\text{HCOO})_2(\text{HCOOH})_2]_n$ composition with copper atoms being connected by formate anions in *anti-anti* mode into layers, parallel to *ab* plane with Cu-O distances 1.9453(10) and 1.9750(9) Å. Formic acid molecules are coordinated to copper ions at longer distances of 2.4346(12) Å as monodentate terminal ligands and are involved in a hydrogen bond connection of the neighbouring layers.

Introduction

Carboxylate anions are very versatile ligands in the light of the wide variety of coordination modes they exhibit in many metal coordination compounds. Among copper(II) carboxylates the nuclearity varies from monomeric to dimeric, oligomeric as well as polymeric compounds. Polymeric complexes can be formed by means of bridging carboxylate ions or by means of other ligands with the bridging ability. Carboxylate group can link two copper(II) ions as a bridging bidentate or as monoatomic bridging ligand. In the case of bridging bidentate coordination three distinctive arrangements are possible: *sys-syn*, *syn-anti* and *anti-anti* binding modes. Formate ion is the smallest among carboxylic ligands and has been often used in the synthesis of copper compounds. As the consequence of this fact there is a great number of published structures, which include the formate ion as the only ligand coordinated to copper or the compounds contain additional, either N- or O-donor ligands (after survey through Cambridge Structural Database).¹

This investigation is a part of our continuous endeavour to find new synthetic methods for preparation of copper carboxylates using several additional ligands.^{2,3,4} Here, we report the synthesis and the crystal structure of the orthorhombic form of the polymeric adduct of copper(II) formate – formic acid (1:2). A previous structure determination was reported for the similar monoclinic structure (α -form) of catena-*bis*(μ_2 -formato-*O,O'*)-*bis*(formic acid-*O*)-copper(II).⁵ The CSD *refcode* for this compound from reference 1 is DOKPOI from CSD release 5.2.1, April 2001.

Experimental

Synthesis and X-ray Crystallographic Work

A small amount of copper(II) formate tetrahydrate was dissolved in the hot formic acid (98%) to achieve a saturation at approximately 80° C. The saturated solution was filtered off and slowly cooled to room temperature and then left in the refrigerator for one week. The obtained crystals were very unstable when taken from the mother liquor and were transferred immediately into the cold nitrogen stream of the diffractometer at

Table 1. Crystal Data and Data Collection Summary

Empirical formula	[C ₄ H ₆ O ₈ Cu] _n
Formula weight	245.63
Crystal shape, colour	prismatic, sky-blue
Crystal dimensions / mm	0.22, 0.20, 0.20
Radiation MoK α / Å	0.71073
<i>T</i> / K	150
Crystal system	orthorhombic
Space group	Pbca
<i>a</i> / Å	7.8773(2)
<i>b</i> / Å	8.4775(2)
<i>c</i> / Å	12.1423(3)
<i>V</i> / Å ³	810.86(3)
<i>Z</i>	4
Density (g.ml ⁻¹)	2.012
μ / mm ⁻¹	2.708
Reflections collected	5791 (θ_{\max} =27.5°)
Independent reflections	916
Reflections with $I > 2\sigma(I)$	787
R_{int}	0.025
R_1, wR_2 (observed reflections)	0.022, 0.059
R_1, wR_2 (all reflections)	0.028, 0.069

150 K. The data were collected on a KappaCCD Nonius diffractometer which is equipped with the low-temperature Oxford Cryosystem device 700 using Collect⁶ and processed with DENZO and SCALEPACK programmes⁷. The structure was solved by direct methods implemented in SHELXS-97 and refined by full-matrix least squares using SHELXL-97.⁸ All hydrogen atoms were found in the difference electron-density map and were included in the refinement with isotropic displacement parameters. The figures were prepared with the aid of ORTEP-III and PLATON programmes.^{9,10} Additional crystallographic data for the structure reported in this paper are available on request at the Cambridge Crystallographic Data Centre with quotation number 175622.¹¹

Results and discussion

The formal composition found in the structural work can be represented as $[\text{Cu}(\text{HCOO})_2(\text{HCOOH})_2]_n$. ORTEP-III view of one building unit is presented in Figure 1. Copper atoms are located on an a special position (0,0,0) in a square planar coordination environment, formed by four oxygen atoms from four formate ions. Only two of the oxygen atoms are crystallographically unique and are located at the distances of 1.9453(10) and 1.9750(9) Å (for geometrical details see Table 2). The most typical pseudo-octahedral 4+2 coordination is completed by formic acid molecule, coordinated to the copper ion through oxygen atom at a distance of 2.4345(12) Å as a terminal ligand.

The divalent copper ions are connected through the formate bridges in a typical *anti-anti* mode presented on Figure 1. Thus, the sheets of CuO_4 units are formed, parallel to *ab* plane. View of one such sheet is depicted in Figure 2. Formic acid molecules protrude from these planes on both sides as shown on Figure 3. There is no covalent interaction between the sheets. However, the planes of copper(II) formate units are linked by hydrogen bonds of the type O-H...O between formic acid molecules (O4 acting as a donor) and formate oxygen atoms of a neighbouring sheet (O1 and O2 are the corresponding acceptors). The bond lengths and angles within formic acid molecules and formate moieties are normal and in agreement with the values for the related compounds.

Comparison of the two polymorphic forms

It should be noted, that polymeric layered structure has been commonly observed also in other copper(II) formates.¹ In all of these structures *anti-anti* carboxylate binding mode is predominant. The structure of monoclinic form of the title compound has already

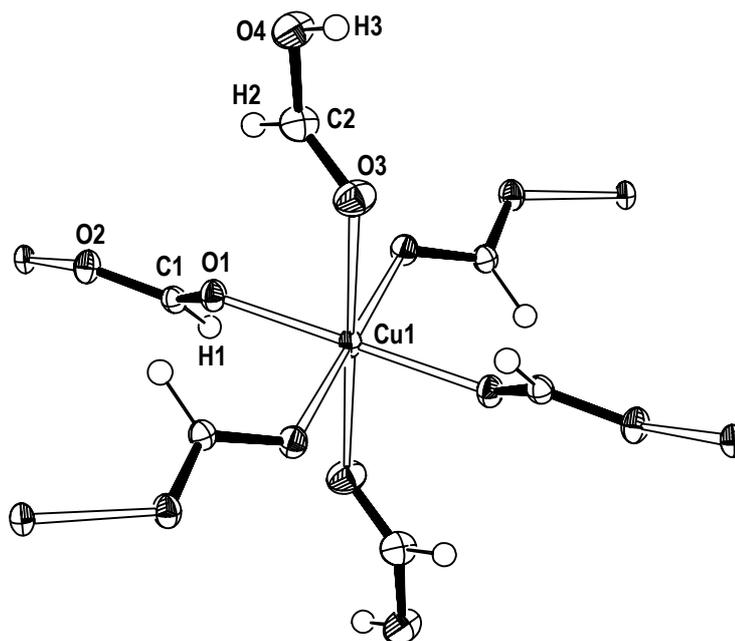


Figure 1. Ortep-III view of the coordination of formic acid molecules and formate ions around Cu^{2+} ion in β -form. Only the atoms of the asymmetric unit are labelled. Displacement ellipsoids are drawn at 50% probability level.

Table 2. Selected geometrical parameters (\AA , $^\circ$)

Cu-O1	1.9453(10)	C1-O1	1.2521(18)	
Cu-O2 ⁱ	1.9750(10)	C1-O2	1.2651(19)	
Cu-O3	2.4345(12)	C2-O3	1.205(2)	
		C2-O4	1.310(3)	
Hydrogen bonds:				
D-H...A	d(D-H)	d(H...A)	d(D...A)	<DHA
O4-H3...O2 ⁱⁱ	0.78(3)	1.93(3)	2.6777(17)	159(3)
O4-H3...O1 ⁱⁱ	0.78(3)	2.58(3)	3.1826(19)	135(3)
i) $x-0.5, -y+0.5, -z+1$; ii) $-x+1, y-0.5, -z+1.5$				
Interplanar angles		Monoclinic form ⁵	Orthorhombic form (this study)	
C1,O1,O2	C2,O3,O4	73.3(9)	78.6(1)	
C1,O1,O2,Cu1	C2,O3,O4,Cu1	59.4(8)	49.3(1)	

been published.⁵ However, there are no information available on H atoms positions for the α -form. The linkage of copper ions via formate ions in the monoclinic form within the sheet is very close to the arrangement in the orthorhombic β -form. There are only subtle differences in the packing modes for the monoclinic and the orthorhombic structures. There are no significant differences between Cu-O distances in the sheet. The coordination distances Cu-O range from 1.954(6) to 1.988(6) Å in the monoclinic form,

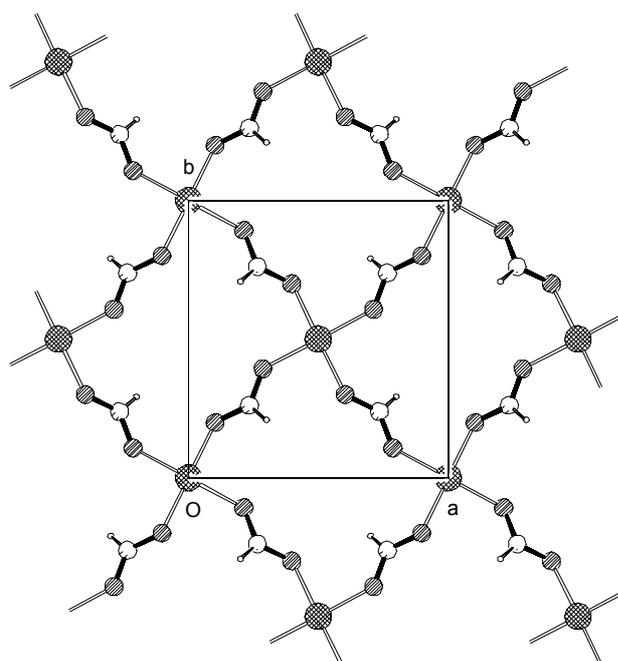


Figure 2. View of a sheet of copper ions linked by formate anions in an anti-anti mode. Formic acid molecules, that are located above and below each of such planes coordinated to copper ion, are omitted for clarity.

whereas these values are between 1.945(1) and 1.975(1) Å in the orthorhombic form. There is a considerable elongation of the Cu-O distance to the apically coordinated formic acid in the orthorhombic form. The value Cu-O of 2.435(1) Å is found for the orthorhombic form compared to the 2.360(14) Å in the monoclinic form. The elongation could be explained by a stronger hydrogen bond O4-H3...O2 2.678(2) Å in the orthorhombic form (Table 2) compared to 2.956(17) Å, found in the previous determination of the monoclinic form. The difference in packing (Figure 3) can also be

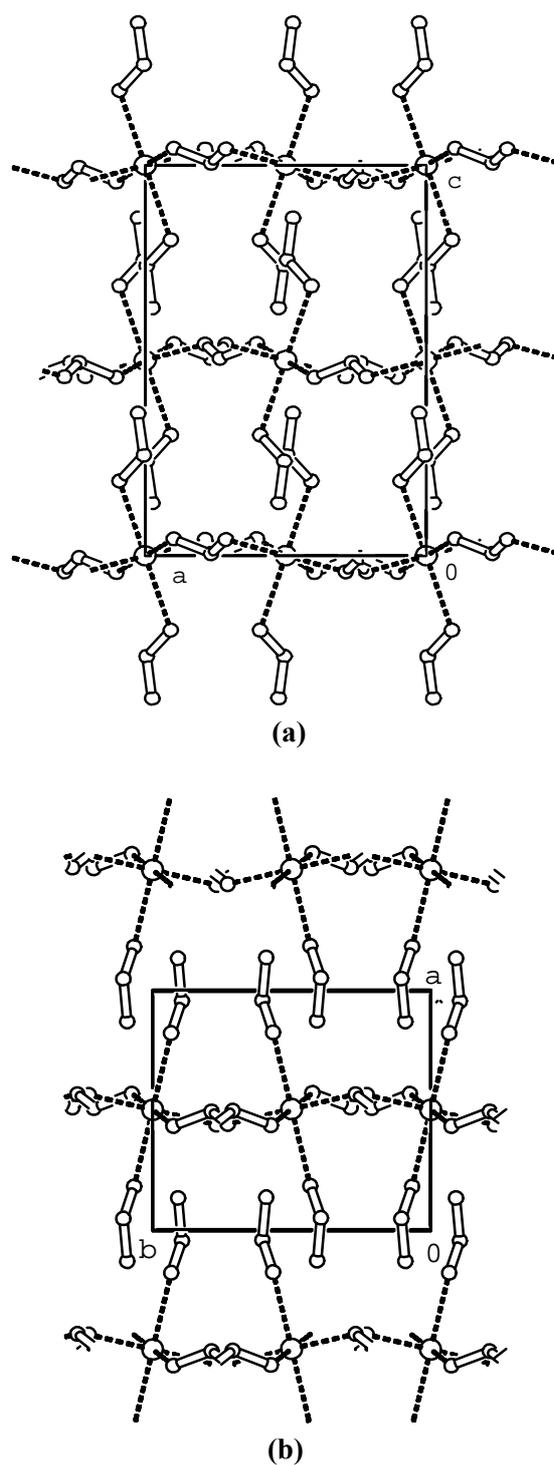


Figure 3. Packing diagrams for orthorhombic (this study) (a) and monoclinic form⁵ (b) viewed along the CuO₄ sheets. The sheets of copper ions, connected through the formate ions, are arranged in parallel planes. Molecules of formic acids, apically coordinated to copper ions, protrude from the planes on both sides of the CuO₄ sheets. Hydrogens are omitted for clarity.

attributed to the different orientation of the formic acid with respect to the sheet containing copper atoms (Table 2). The corresponding torsion angles Cu1-O1-C1-O2 and Cu1-O3-C2-O4 are: $-179.98(9)$ and $-175.86(16)^\circ$ for this study, and $-174(1)$ and $-159(1)^\circ$ for the monoclinic form, respectively. The protrusion of formic acid ligands of one sheet into the other is therefore much more pronounced in the orthorhombic than in monoclinic form and as the consequence, the orthorhombic structure is more densely packed ($D_x=2.012 \text{ g cm}^{-3}$) compared to the monoclinic form ($D_x=1.823 \text{ g cm}^{-3}$). The effective distance between the sheets of copper formates are consequently: 6.071 \AA for the orthorhombic and 7.778 \AA for the monoclinic structure, respectively.

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Povzetek

Pripravili smo novo polimorfno obliko adukta bakrovega(II) formiata z mravljinčno kislino in jo strukturno okarakterizirali z metodo rentgenske difrakcije na monokristalu pri 150 K. Spojina kristalizira v ortorombski prostorski skupini $Pbca$ z naslednjimi parametri osnovne celice: $a=7.8773(17)$, $b=8.4775(2)$ and $c=12.1423(3)$ Å. Spojina ima polimerno zgradbo. Bakrovi ioni so preko mostovnih formiatnih anionov povezani v plasti (*anti-anti* način vezave) vzporedne z ravnino ab . Molekule mravljinčne kisline so koordinirane na bakrov ion kot enovezni ligand in so vključene v tvorbo vodikovih vezi, ki bakrove formiatne plasti povezujejo med seboj v kristalno strukturo.