Synthesis and Crystal Structure of a New 1D Oxamidato-bridged Heterobimetallic Polymer

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A new 1D ladder-like chain coordination polymer, namely, $\{[Cu(aeoe)Zn(H_2O)_3 \cdot 1.5H_2O]_2\}_n$ (H_4aeoe = 2-(2-(2-aminoethylamino)-2-oxoacetamido)terephthalic acid) has been synthesized and characterized by IR, thermogravimetric and single-crystal X-ray diffraction analyses (triclinic, space group $P\bar{1}$, with a = 9.443(7), b = 9.519(7), c = 11.124(9) Å, α = 65.094(10)°, β = 77.559(10)°, γ = 81.752(10)°, Z = 1).

Key words: Copper, Zinc, Oxamidato Bridging, Coordination Polymer, Crystal Structure

Introduction

The construction of new coordination polymers attracts fast growing interest in the fields of supramolecular chemistry and crystal engineering, not only for the interesting molecular topologies and crystal packing motifs [1, 2], but also for the potential applications of new functional materials [3, 4]. One of the best strategies to design and synthesize heterobinuclear complexes is the "complex as ligand" approach. Anionic precursors are particularly suitable for designing heterobinuclear complexes [5 – 11]. Oxamidate derivatives are known to be versatile organic ligands which can chelate as well as bridge various compounds to construct discrete and extended structures, depending on the "second" metal ion [12]. The *cis*-oxamidates usually give discrete polynuclear species, whereas the *trans* isomers can afford extended structures. It is well known that carboxylate ligands play an important role in coordination chemistry and can adopt various binding modes such as terminal monodentate, chelating one metal center, bridging two metal centers in a *syn-syn*, *syn-anti* and *anti-anti* configuration, and bridging two metal centers in a tridentate form [13]. From this point of view, we synthesized a new dissymmetrical oxamidato ligand containing both of the two bridging groups (Scheme 1). Through the "complex as ligand" approach, we have already synthesized several heterometallic coordination polymers [14]. In this paper, we present a new 1D ladder-like chain coordination polymer $\{[Cu(aeoe)Zn(H_2O)_3 \cdot 1.5H_2O]_2\}_n$ (**1**).

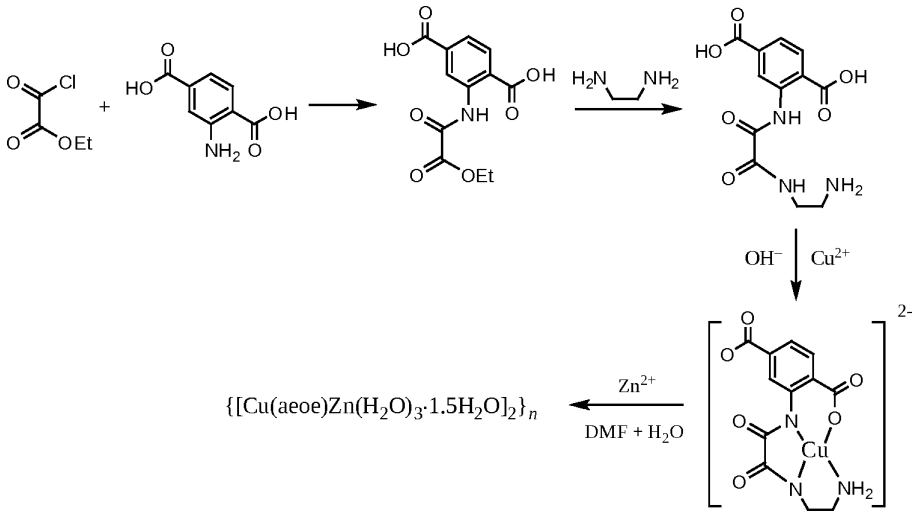
Results and Discussion

IR spectra

The ligand H_4aeoe exhibits one $\nu_{C=O}$ band of the oxamidato group at *ca.* 1632 cm^{-1} [15], one $\nu_{as(COO)}$ (ν_{COOH}) band at *ca.* 1667 cm^{-1} [16], and two ν_{N-H} bands of the oxamidato groups at *ca.* 3016 and 3114 cm^{-1}. These bands are all missing in the copper precursor complex because of the loss of protons of the COOH and N-H (oxamidato) groups. One new sharp strong band observed in complex **1** (1652 cm^{-1}) is the result of an overlap of $\nu_{as(coo)}$ of the carboxylate group and $\nu_{C=O}$ of the oxamidato group. In addition, the -NH_2 vibration at *ca.* 3307 cm^{-1} for H_4aeoe is still present for complex **1** with a small shift (to 3322 cm^{-1}). Such a red shift indicates that the -NH_2 group is coordinated to the copper ion.

Thermal properties

Thermogravimetric analysis (TGA) has shown that compound **1** loses 14.9 % of its total weight in the 30 – 220 °C temperature range, corresponding to the loss of one solvate and three coordinated water molecules (expected: 14.4 %). Compound **1** decomposes at about 350 °C, and thus is more stable than the copper precursor complex.



Scheme 1. Synthetic route to complex **1**.

UV spectra

The electronic absorption spectra of the complex was recorded in aqueous solution. The *d-d* transitions of the complex show broad bands centered at 582 nm, being suggestive of an approximate square-planar geometry at the Cu(II) ion.

Description of the structure

Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$. Its structure is similar to those recently reported by us [14]. It consists of a binuclear neutral molecule, three coordinated and one and a half solvate water molecules (Fig. 1). The dinuclear molecules are linked through coordination between carboxylic oxygen atoms (O6 and O6#1) and Zn atoms to give a tetranuclear neutral loop in the *ac* plane. These

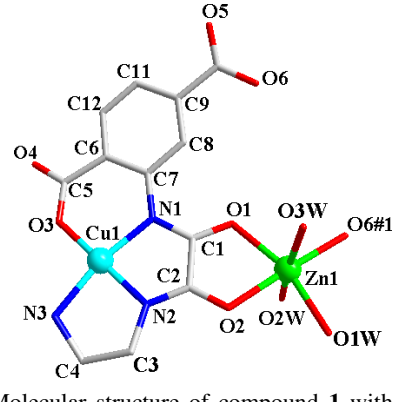


Fig. 1. Molecular structure of compound **1** with hydrogen atoms omitted for clarity. Symmetry code: #1 $2-x$, $1-y$, $1-z$.

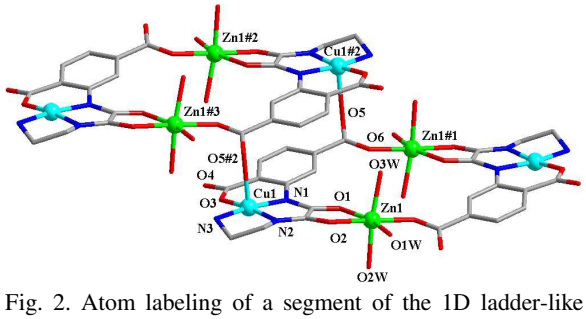


Fig. 2. Atom labeling of a segment of the 1D ladder-like chain of compound **1**. Symmetry transformations used to generate equivalent atoms: #1 $2-x$, $1-y$, $1-z$; #2 $1-x$, $1-y$, $1-z$; #3 $-1+x$, y, z.

tetranuclear neutral loops are further associated by coordinative bonds between carboxylic oxygen atoms (O5 and O5#2) and Cu ions (Cu1#2 and Cu1) to form a new 1D ladder-like chain structure along the *b* axis (Fig. 2).

The Cu(II) ions are in a distorted square pyramidal CuN_3O_2 surrounding. The Cu atom occupies an inner site of the triply deprotonated ligand with a CuN_3O environment in the equatorial plane, but is displaced 0.075 Å from this plane towards the apical position, which is comparable with the values found in another complex reported by us [14]. The apical position is occupied by one carboxylic oxygen atom from another tetranuclear unit with a bond length of 2.524 Å. This value is slightly larger than those in the complex with the same chain [14]. The Zn(II) ion has a distorted octahedral environment with four coplanar bonds of nearly equivalent length (Zn1–O6#1, 2.063(3); Zn1–O1W, 2.133(3); Zn1–O1,

2.145(3); Zn1–O2, 2.090(3) Å) and two apical bonds (Zn1–O2W, 2.069(3); Zn1–O3W, 2.087(3) Å). The Cu–Zn distances are 5.3938(7) Å. The equatorial plane of Cu1 (N1, N2, N3 and O3) and the equatorial plane of Zn1 (O6#1, O1W, O2 and O1) make angles of 176.92° and 175.90° with the bridge plane (O1, O2, N1, N2) and 172.96° with each other.

Experimental Section

Materials

The ligand H_4aeoe and the copper precursor (Na_2[Cu(aeoe)] · $3H_2O$) were prepared by the literature method [14]. Other chemicals were of reagent grade and obtained commercially without further purification.

Physical measurements

Elemental analysis for C, H and N were carried out on a Perkin-Elmer elemental analyzer, model 2400II. The infrared spectrum was recoded on an Avater-360 spectrometer using KBr pellets in the region 400 – 4000 cm^{-1}. Thermogravimetric analysis was performed with an EXSTAR6000 TG/DTA6300 SII-type analyzer in a nitrogen atmosphere, and the complex was heated to 900 °C at a heating rate of 10 °C min^{-1}.

Preparation of $\{[Cu(aeoe)Zn(H_2O)_3 \cdot 1.5H_2O]_2\}_n$ ***(1)***

0.1 mmol (0.0455 g) Na_2[Cu(aeoe)] · $3H_2O$ was dissolved in 17 mL of water, and 17 mL of a DMF solution containing 0.1 mmol (0.022 g) of $Zn(CH_3COO)_2 \cdot 4H_2O$ was added under constant stirring. The resulting violet solution was filtered, and finally well-shaped violet single crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the solution (yield 46 %). – Analysis for $C_{12}H_{18}CuZnN_3O_{10.5}$: calcd. C 28.75, H 3.62, N 8.38; found C 28.68, H 3.56, N 8.42. – IR (KBr): $\nu_{C=O}$ 1652 cm^{-1}.

X-Ray analysis

The single crystal used for data collection of compound **1** was selected and mounted on a Bruker Smart APEX diffractometer with a CCD detector using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Lorentz and polarization corrections were applied for the intensity data, and absorption corrections were performed using the program SADABS [17]. The structure was solved using SHELXTL and refined with full-matrix least-squares methods [18]. The positions of hydrogen atoms were calculated at idealzed positions and included in the final cycles of refinement in a riding model along with the attached carbons. Crystal data and data collection and refinement parameters are given in Table 1.

Table 1. Crystal data and numbers pertinent to data collection and refinement for **1**.

Formula	$C_{12}H_{18}CuZnN_3O_{10.5}$
M_r	501.2
Crystal size, mm^3	$0.30 \times 0.15 \times 0.12$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	9.443(7)
b, Å	9.519(7)
c, Å	11.124(9)
α, deg	65.094(10)
β, deg	77.599(10)
γ, deg	81.752(10)
V, $Å^3$	884.13(12)
Z	1
F(000), e	508
$D_{calcd.}$, g cm^{-3}	1.88
μ(MoK_α), mm^{-1}	2.6
θ range data collection, deg	2.05 – 25.00
hkl range	$-11 \le h \le 11$, $-9 \le k \le 11$, $-13 \le l \le 12$
Refl. measured / unique / R_{int}	4606 / 3064 / 0.0731
Param. refined / restraints	253 / 6
$R1/wR2$ (all data)	0.044 / 0.1375
GoF (F^2)	1.047
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	1.986 / −0.846

Table 2. Selected bond lengths (Å) and angles (deg) for compound **1**[a].

Distances			
Cu1–O3	1.906(3)	Cu1–N1	1.982(3)
Cu1–N2	1.897(4)	Cu1–N3	2.048(4)
Cu1–$O5^{\#2}$	2.523(4)		
Zn1–$O6^{\#1}$	2.060(3)	Zn1–O1W	2.133(3)
Zn1–O2	2.090(3)	Zn1–O3W	2.087(3)
Zn1–O1	2.145(3)	Zn1–O2W	2.069(3)
Angles			
O3–Cu1–N2	171.70(14)	O3–Cu1–N1	94.15(13)
N2–Cu1–N1	84.58(14)	O3–Cu1–N3	97.75(13)
N1–Cu1–N3	167.77(15)	N2–Cu1–N3	83.23(15)
$O6^{\#1}$–Zn1–O1W	94.52(11)	$O6^{\#1}$–Zn1–O2	177.39(12)
O1W–Zn1–O2	83.15(12)	$O6^{\#1}$–Zn1–O3W	83.71(13)
O1W–Zn1–O3W	96.09(14)	O2–Zn1–O3W	97.69(13)
$O6^{\#1}$–Zn1–O1	103.97(11)	O1W–Zn1–O1	161.32(12)
O2–Zn1–O1	78.30(11)	O3W–Zn1–O1	88.61(14)
$O6^{\#1}$–Zn1–O2W	87.69(12)	O1W–Zn1–O2W	87.03(13)
O2–Zn1–O2W	91.00(12)	O3W–Zn1–O2W	171.05(13)
O1–Zn1–O2W	91.07(12)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $2-x, 1-y, 1-z$; #2 $1-x, 1-y, 1-z$.

CCDC 752501 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.com.ac.uk/data_request/cif.

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