



Sulfur extrusion and sulfur oxidation of 2,2'-dithiodibenzoic acid in combination with Cu(II) ion and in the absence of co-ligands: Structural, spectroscopic and thermogravimetric evidence

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ABSTRACT

The interaction of $\text{Cu}(\text{BF}_4)_2$ with 2,2'-dithiodibenzoic acid (H_2dtdb) in a $\text{CH}_3\text{OH}/\text{dmf}$ mixture leads to the formation of extended polymeric solids $\{[\text{Cu}(\text{tdb})(\text{dmf})](\text{dmf})\}_n$ (**1**) and $\{[\text{Cu}_2(\text{tdb})(\text{sdb})(\text{dmf})(\text{H}_2\text{O})]_2(\text{dmf})\}_n$ (**2**), where $\text{tdb}^{2-} = 2,2'$ -thiodibenzoate, $\text{sdb}^{2-} = 2,2'$ -sulfinatodibenzoate, $\text{dmf} = N,N'$ -dimethylformamide. In all of the cases, reactions proceed with extrusion of one S atom and in **2** with additional S oxidation. Compound **1** represents 1D coordination polymer, while **2** exhibits 2D structure. Both compounds are built from similar $[\text{Cu}_2(\mu_2\text{-RCOO})_4]$ metal clusters with the Cu(II) atom in the O_5 square-pyramidal geometry. All new solids were characterized by IR spectroscopy, thermogravimetric and single crystal X-ray diffraction analyses.

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1. Introduction

Coordination polymers (CPs) are an intensively studied field of materials science, due to the immense quantity of possible inorganic and organic building units, and their potential applications (e.g., gas storage and separation, catalysis, magnetism, nonlinear optics, sensing and heat transformation) [1,2]. Numerous organic moieties have been introduced into the CPs either by a priori ligand functionalization or by post synthetic modification [3–5]. Aromatic carboxylic acids are the most commonly used organic linkers for the self-assembly of CPs, may not only provide rich coordination modalities for the extension of metal ions into high dimensional structures but also contain potential interaction sites to generate noncovalent interactions. 2,2'-Dithiodibenzoic acid (H_2dtdb) is a multifunctional ligand containing both carboxylic and thio groups, which make this ligand flexible and at the same time rigid in coordination to metal atoms as the phenyl ring can be twisted at different degrees across the C–S and S–S single bond sites because of the steric effect. *In situ* transition metal- H_2dtdb acid reactions undergo variable transformations of S–S bond. The retrieval of Cambridge Structural Database (CSD) [6] revealed a series of transition metals that have been found to react with H_2dtdb acid gave rise to structural diversity, including mono- [7,8], binuclear [9,10], 1D [9–14],

2D [15] and 3D coordination compounds [15–17] with or without cleavage of the S–S bond and the carboxylate group acts as a monodentate or bidentate donor. Numerous works highlight that the presence of different pyridine-like co-ligands in reaction cause the formation of new products as the result of simultaneous S–S and C–S scission of dithiodibenzoic acid [7,9,18,19]. Meanwhile, no reports involve dithiodibenzoic acid, where oxidative cleavage of the S–S bond has been observed in absence of auxiliary ligand. These observations stimulated our interest to synthesized new Cu(II) coordination polymers **1** and **2** with 2,2'-dithiodibenzoic acid as a long flexible ligands in the absence of co-ligands, in which extrusion of one sulfur atom and S-oxidation of another S-atom were observed.

2. Experimental

2.1. Materials and methods

All reagents and solvents were obtained from commercial sources and were used without further purification. The IR spectra were obtained in Nujol on a FT IR Spectrum-100 Perkin Elmer spectrometer in the range of $650\text{--}4000\text{ cm}^{-1}$. The thermal analysis experiments for **1** and **2** were carried out in Derivatograph Q-1500 thermal analyzer in air flow at a heating rate of 10 °C min^{-1} in the temperature range of $20\text{--}1050\text{ °C}$. X-ray powder diffraction data was obtained using a DRON-UM1 X-ray powder diffractometer

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equipped with a Fe-K α radiation ($\lambda = 1.93604 \text{ \AA}$) source. The diffractometer was operated at 20 kV and 22 mA. The data was collected over an angle range of 3–60° at a scanning speed of 2° per minute.

2.2. Synthesis

2.2.1. Synthesis of $\{[\text{Cu}(\text{tdb})(\text{dmf})] \cdot (\text{dmf})\}_n$ (**1**)

$\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ (0.0237 g, 0.01 mmol) and H_2dtdb (0.0306 g, 0.01 mmol) were dissolved in 8 mL mixture of $\text{CH}_3\text{OH}:\text{dmf}$ (5:3) and ultrasonicated for 30 min at room temperature. The resulting transparent light yellow solution was filtered off and green crystals of prism habitus were precipitated after six months. Yield: 60% (based on Cu).

2.2.2. Synthesis of $\{[\text{Cu}_2(\text{tdb})(\text{sdb})(\text{dmf})(\text{H}_2\text{O})] \cdot 2(\text{dmf})\}_n$ (**2**)

$\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ (0.0237 g, 0.01 mmol) was dissolved in the 6 mL CH_3OH and stirred at room temperature until complete dissolution. The resulting mixture was added to the H_2dtdb (0.0612 g, 0.01 mmol) separately dissolved in the 2 mL dmf and stirred until complete dissolution for 10 min, at room temperature. The obtained solution was stirring for more 2 min. From transparent green-yellow solution green crystals of needle habitus precipitated after two months. Yield: 65% (based on Cu).

2.3. X-ray crystallography

Diffraction measurements for **1** and **2** were carried out at room temperature on a Xcalibur “Oxford Diffraction” diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK α radiation. Final unit cell dimensions were obtained and refined on an entire data set. All calculations to solve the structures and to refine the proposed models were carried out with the SHELXS97 [20] and SHELXL2014 program packages [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters with $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{C})$. The O-bounded H-atoms were found from differential Fourier maps at the intermediate stages of the refinement and their positions were restrained using DFIX instructions for O–H (0.90 Å) and H...H (1.46 Å) distances. In **2** one crystallization dmf molecules is disordered over two positions (52/48% occupation). The disordered dmf molecule has been well treated by restraining it to be the SAME as the well resolved dmf molecule and was refined isotropically. The X-ray data and the details of the refinement for **1** and **2** are summarized in Table 1. Selected geometric parameters for **1** and **2** are given in Tables 2 and 3. The figures were produced using the Mercury program [22]. Solvent accessible voids (SAVs) and Kitaigorodskii's Packing Index (PI) were calculated using PLATON [23].

3. Results and discussion

Green crystals **1** and **2** were obtained from the same reactants by stirring (**2**) and in ultrasonic bath (**1**) at room temperature (Scheme 1). Both samples were found to be air stable, soluble in CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, but insoluble in other common organic solvents. Unexpectedly, the S–S bond of the 2,2'-dithiodibenzoic acid (H_2dtdb) was cleaved *in situ* excluding one S atom forming the 2,2'-thiodibenzoate ligand (tdb^{2-}) in **1** and **2**, which additionally was S-oxidized giving rise to the 2,2'-sulfinatodibenzoate ligand (sdb^{2-}) in **2**.

In order to confirm the purity of a commercial H_2dtdb ligand, we collected X-ray powder diffraction (XRPD) data for this and

Table 1
Crystal data and structure refinement parameters for **1** and **2**.

	1	2
Empirical formula	$\text{C}_{20}\text{H}_{22}\text{CuN}_2\text{O}_6\text{S}$	$\text{C}_{37}\text{H}_{39}\text{Cu}_2\text{N}_3\text{O}_{14}\text{S}_2$
T (K)	293	293
Formula weight (g mol ⁻¹)	481.99	940.91
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a/Å	8.5736(6)	13.6617(6)
b/Å	10.8514(9)	20.8888(9)
c/Å	12.7430(10)	14.3574(6)
$\alpha/^\circ$	86.371(7)	90
$\beta/^\circ$	78.695(6)	93.651(4)
$\gamma/^\circ$	68.104(7)	90
$V/\text{\AA}^3$	1078.62(15)	4089.0(3)
Z	2	4
D_{calc} (Mg/m ³)	1.484	1.528
μ/mm^{-1}	1.148	1.212
F(000)	498	1936
Crystal size/mm ³	$0.20 \times 0.10 \times 0.06$	$0.18 \times 0.06 \times 0.04$
Reflections collected/unique	5851/3774	12970/7156
	$[R_{\text{int}} = 0.0445]$	$[R_{\text{int}} = 0.0787]$
Reflections with $[I > 2\sigma(I)]$	2350	3311
Data/restraints/parameters	3774/0/275	7156/27/529
GOF	0.995	0.928
R indices $[I > 2\sigma(I)]$, R_1 , wR_2	0.0663, 0.1106	0.0791, 0.0871
R indices (all data) R_1 , wR_2	0.1183, 0.1293	0.1852, 0.1119

Table 2
Selected bond distances (Å) and angles (°) in **1** and **2**.

1			
Cu(1)–O(1)	1.949(3)	Cu(1)–O(3) ^c	1.970(4)
Cu(1)–O(4) ^a	1.959(4)	Cu(1)–O(5)	2.133(4)
Cu(1)–O(2) ^b	1.964(3)		
O(1)–Cu(1)–O(4) ^a	89.12(16)	O(2) ^b –Cu(1)–O(3) ^c	89.49(15)
O(1)–Cu(1)–O(2) ^b	168.00(15)	O(1)–Cu(1)–O(5)	95.90(15)
O(4) ^a –Cu(1)–O(2) ^b	89.50(15)	O(4) ^a –Cu(1)–O(5)	96.83(15)
O(1)–Cu(1)–O(3) ^c	89.48(15)	O(2) ^b –Cu(1)–O(5)	96.09(15)
O(4) ^a –Cu(1)–O(3) ^c	168.46(15)	O(3) ^c –Cu(1)–O(5)	94.71(15)
2			
Cu(1)–O(1)	2.018(4)	Cu(2)–O(2)	1.950(4)
Cu(1)–O(4) ^e	2.012(4)	Cu(2)–O(3) ^e	1.955(4)
Cu(1)–O(5)	1.951(4)	Cu(2)–O(6)	2.021(4)
Cu(1)–O(9) ^d	1.947(4)	Cu(2)–O(10) ^d	1.996(5)
Cu(1)–O(11)	2.138(5)	Cu(2)–O(1W)	2.107(5)
O(9) ^d –Cu(1)–O(5)	172.9(2)	O(2)–Cu(2)–O(3) ^e	172.7(2)
O(9) ^d –Cu(1)–O(4) ^e	90.46(18)	O(2)–Cu(2)–O(10) ^d	90.56(19)
O(5)–Cu(1)–O(4) ^e	90.31(2)	O(3) ^e –Cu(2)–O(10) ^d	87.99(19)
O(9) ^d –Cu(1)–O(1)	88.50(18)	O(2)–Cu(2)–O(6)	88.63(19)
O(5)–Cu(1)–O(1)	88.64(18)	O(3) ^e –Cu(2)–O(6)	90.51(18)
O(4) ^e –Cu(1)–O(1)	162.49(19)	O(10) ^d –Cu(2)–O(6)	161.8(2)
O(9) ^d –Cu(1)–O(11)	91.48(19)	O(2)–Cu(2)–O(1W)	91.6(2)
O(5)–Cu(1)–O(11)	95.14(19)	O(3) ^e –Cu(2)–O(1W)	95.7(2)
O(4) ^e –Cu(1)–O(11)	104.9(2)	O(10) ^d –Cu(2)–O(1W)	104.7(2)
O(1)–Cu(1)–O(11)	92.61(19)	O(6)–Cu(2)–O(1W)	93.6(2)

^a $-x + 1, -y + 1, -z + 1$.

^b $-x, -y + 1, -z + 1$.

^c $x - 1, y, z$.

^d $x - 1/2, -y + 1/2, z + 1/2$.

^e $x + 1/2, -y + 1/2, z + 1/2$.

resulted experimental pattern closely resembled that simulated by the Mercury program (Fig. 1).

3.1. IR spectroscopy

In the IR spectra of the complexes, the presence of phenyl rings is indicated by the bands at 1608 cm^{-1} in **1** and 1618 cm^{-1} in **2**.

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