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Synthesis, Structure and Non-Linear Optical Properties of a Copper(II) Ethyl Bisulfate Two-Dimensional Supramolecular Compound $[Cu(Him)_4(CH_3CH_2OSO_3H)_2]$

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A novel copper(II) ethyl bisulfate complex $[Cu(Him)_4(Eb)_2]$ **1** (Him = imidazole, Eb = ethyl bisulfate) has been prepared and characterized by means of elemental analysis, IR and ESR. The structure was determined by single crystal X-ray diffraction analysis, which suggests that compound **1** exhibits a two-dimensional supramolecular structure through hydrogen bonds. Compound **1** displays strong third-order non-linear optical (NLO) absorption and refraction with absorption coefficient α_2 1.10×10^{-11} m·w^{-1} and refractive index n_2–5.60×10^{-16}m^2·w^{-1}. The third-order non-linear optical susceptibility $\chi^{(3)}$ of compound **1** is 3.07×10^{-10} esu.

Key words: copper(II) ethyl bisulfate compound, supramolecular structure, hydrogen bond, third-order non-linear optical property

The control of molecular assembly in the solid state is an important theme of modern chemistry, because the self-assembly of molecules can form well-defined supramolecular structures under the influence of driving forces, such as hydrogen bonds [1–3], metal-ligand coordination bonds [4–5] and $\pi\cdots\pi$ stacking interactions [6]. In recent years, the research in copper self-assemble chemistry has been rapidly expanding. One aspect is the fascinating structural diversity. So far, a wide region of infinite one-, two- and three-dimensional coordination frameworks has been found, including halicates [7], diamondoid [8], honeycomb [9], square or rectangular grid [10], T-shaped [11], ladder [12], zigzag [13], brick wall [14], octahedral [15] and other uncommon frameworks [16]. Another aspect is their potential applications as functional materials in medical, catalysis, magnetism, superconductor and non-linear optical materials [17]. For example, copper(II) complexes have possible medical uses in the treatment of many diseases including cancer [18–19]. The anticancer activity may be based on the ability of the complexes to inhibit DNA synthesis. Another possible mechanism involves the scavenging of superoxide anions [18].

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As a part of our work towards rational design and preparation of functional supramolecular compounds, we carried out a study of copper(II) compound. Such complexes have extensively been studied by crystal structural analyses, but their third-order (NLO) properties have been less well noted. In this paper, we describe the synthesis, structure, spectroscopic analysis and the third-order NLO property of a new two-dimensional copper(II) ethyl bisulfate supramolecular compound [Cu(Him)$_4$(Eb)$_2$].

EXPERIMENTAL

Materials and physical measurement. The synthesis was conducted using anhydrous $CuSO_4$, Him and sulfuric acid fuming 20% from commercial sources without further purification. Infrared spectrum was recorded as a KBr pellet with Perkin-Elmer spectrophotometer in the 225–4000 cm^{-1} region. The elemental analysis (C, H, N) was determined using a Perkin-Elmer 2400 LS II elemental analyzer.

*Synthesis of compound **1***. The compound anhydrous copper(II) sulfate (0.16 g, 1 mmol) was added to a solution of Him (0.27 g, 4 mmol) in 1.2 ml of sulfuric acid fuming 20% and 70 ml of absolute alcohol. The dark blue solution was stirred for 20 min at about 40°C. Adding anhydrous isopropanol (15 ml) into the blue solution produced dark blue crystals (0.062 g, yield 38% based on Cu). Anal. Calcd. for $C_8H_{14}Cu_{0.5}N_4SO_4$: C, 32.7; H, 4.8; N, 19.1. Found: C, 32.6; H, 4.8; N, 19.1. IR (cm^{-1}): 3154 (w), 1067 (vs), 1602 (m), 1582 (m), 917 (m), 846 (s), 650 (vs), 496 (m), 459 (m).

X-ray crystal structure determination. Crystal data were collected with Mo-Kα radiation (λ = 0.71073 Å) using a Rigaku R-AXIS RAPID IP diffractometer. The sample selected for investigation had dimensions of 0.46×0.17×0.10 mm^3, *R(int)* = 0.0641. The structure was solved using direct methods with SHEXTL-97 program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydrogen atoms were placed in their calculated positions. The crystal data and selected parameters are given in Tables 1–3.

Z-scan measurement. The third-order NLO property was determined by a Z-scan technique with a Q-switched frequency-doubled Nd: YAG laser at 532 nm with 15 ns pulses. The solution of compound **1** in DMF was contained in 5 mm-thick glass cells with a concentration of 5.2× 10^{-3} M.

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

Empirical formula	$C_8H_{14}Cu_{0.50}N_4O_4S$
Formula weight	294.06
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimension	a = 8.8296(18) Å β = 106.76(3)°
	b = 9.7435(19) Å
	c = 15.137(3) Å
Volume, Z	1246.9(4) Å^3, 4
Density	1.566 g/cm^3
F(000)	610
Absorption coefficient	1.101 mm^{-1}
Crystal size	0.48×0.24×0.17 mm^3
θ range	2.41 to 27.48°
Limiting indices	–11<= h <= 10, 0 <= k <= 12, –19 <= l <= 10

Table 1 (continuation)

T (K)	293 (2)
Reflections collected/unique	2611/2611 [R(int) = 0.0641]
Data/restraints/parameters	2611/0/157
Goodness of fit indicator	0.937
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0445, wR2 = 0.1007
Largest diff. peak and hole	0.548 and –0.470 e/Å^3

Table 2. Selected geometric parameters (Å, °).

Cu–N(1)	2.006(2)
Cu–N(3)	1.987(2)
Cu–O(1)	2.645(2)
N(1)#1–Cu–N(1)	180.00(6)
N(3)–Cu–N(3)#1	180.00(16)
N(3)–Cu–N(1)#1	89.43(9)
1N(3)–Cu–N(1)	90.57(9)
N(3)#1–Cu–N(1)	89.43(9)
O(1)–Cu–O(1)#1	180.00(6)
O(1)–Cu–N(3)	89.37(7)
O(1)–Cu–N(1)	86.54(7)
O(1)–Cu–N(1) #1	93.46(7)
O(1)–Cu–N(3) #1	90.63(7)

Symmetry transformations used to generate equivalent atoms: #1 –x, –y, –z.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu	0	0	0	33(1)
S	2148(1)	3332(1)	–545(1)	31(1)
O(1)	1690(2)	2226(2)	–47(1)	43(1)
O(2)	865(2)	4156(2)	–1082(2)	49(1)
O(3)	3431(2)	4157(2)	20(1)	37(1)
N(1)	1132(2)	–78(2)	1354(1)	32(1)
N(2)	2944(3)	247(3)	2663(2)	43(1)
N(3)	–1676(2)	1174(2)	244(2)	32(1)
N(4)	–3139(2)	2974(2)	288(2)	36(1)
C(1)	722(4)	–759(3)	2031(2)	47(1)
C(2)	1840(4)	–569(3)	2850(2)	50(1)
C(3)	2475(3)	529(3)	1764(2)	42(1)
C(4)	–2963(3)	775(3)	526(2)	38(1)

Table 3 (continuation)

C(5)	–3861(3)	1884(3)	544(2)	41(1)
C(6)	–1831(3)	2522(3)	106(2)	34(1)
C(7)	4440(5)	2342(4)	–2266(2)	61(1)
C(8)	3550(4)	3326(3)	–1847(2)	48(1)
O(4)	2847(2)	2528(2)	–1252(1)	39(1)

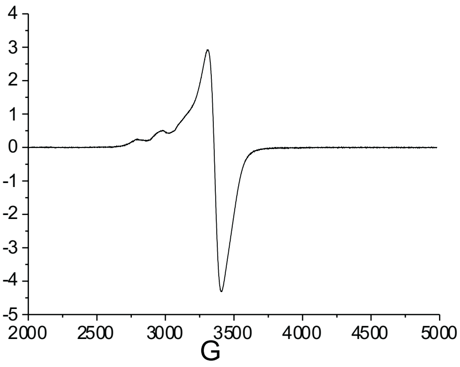

Figure 1. The ESR spectrum of [Cu(Him)$_4$(Eb)$_2$].

RESULTS AND DISCUSSION

ESR spectra. The ESR spectrum was determined using a Bruker ER 2000-SRC spectrophotometer. As shown in Figure 1, ESR spectrum of compound **1** is anisotropic having a $g_{\perp}$ parameter value of 2.06 and weak parallel components $g_{||} \approx 2.27$. The values are consistent with a model of distorted octahedral copper(II) complexes.

Synthesis. The synthesis of the title complex could be presumed as follows:

$$H_2SO_4 + CH_3CH_2OH \longrightarrow CH_3CH_2OSO_3H + H_2O \quad (1)$$

$$2CH_3CH_2OSO_3H + [Cu(Him)_4]^{2+} \longrightarrow [Cu(Him)_4(CH_3CH_2OSO_3H)_2] \quad (2)$$

*Crystal structure of **1**.* As shown in Figure 2, the copper(II) atom located on the inversion center is coordinated by four nitrogen atoms from imidazole ligands and two oxygen atoms from two ethyl bisulfate ligands. So the copper sits in a distorted octahedral environment, with the equatorial plane defined by the N(1), N(1)#1, N(3) and N(3)#1 atoms and two axial positions occupied by the O(1) and O(1)#1 atoms. The Cu–N(1) and Cu–N(3) distances in the equatorial plane are 2.006(2) Å and 1.987(2) Å, respectively, which is comparable with other analogous mononuclear imidazole derivatives of Cu(II) carboxylates [20–21]. The Cu–O distance 2.645(2) Å

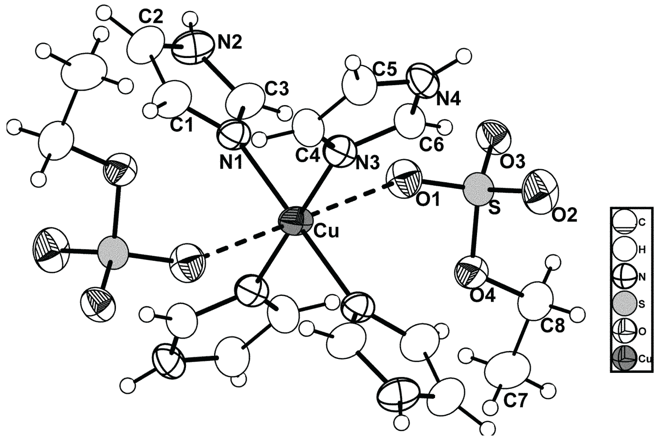

Figure 2. The molecular structure of compound **1**.

can be comparable favorably with the Cu–O distances of 2.649 Å found in the octahedral distorted $Cu(Him)_4(OAc)_2$ (OAc = acetate) [21].

The compound **1** is connected into a two-dimensional structure by two types of hydrogen bonds. O(3) as acceptor and H(4) atom bonding with N(4) from imidazole as donor form one type of hydrogen bond N(4)–H(4)· · ·O(3) [–x, –y + 1, –z] (Figure 3), which join the adjacent molecules along *b* axis to one-dimensional chain. On the other hand, the second type of hydrogen bonds N(2)–H(2)· · ·O(2) [x + 1/2, –y + 1/2, z + 1/2] (Figure 3) makes the one-dimensional chain assembled into a two-dimensional lamellar structure in *bc* plane. The parameters of all the hydrogen bonds are listed in Table 4. The distances of N(2)· · ·O(2) and N(4) · · ·O(3) (2.788(51) Å and 2.834(3) Å, respectively) are within the range of values found for medium-strong N–H· · ·O hydrogen bonds observed in metal complexes (N· · ·O = 2.69 Å – 2.98 Å) [22]. So the existing of that medium-strong hydrogen bond enhances the stability of the complex **1**.

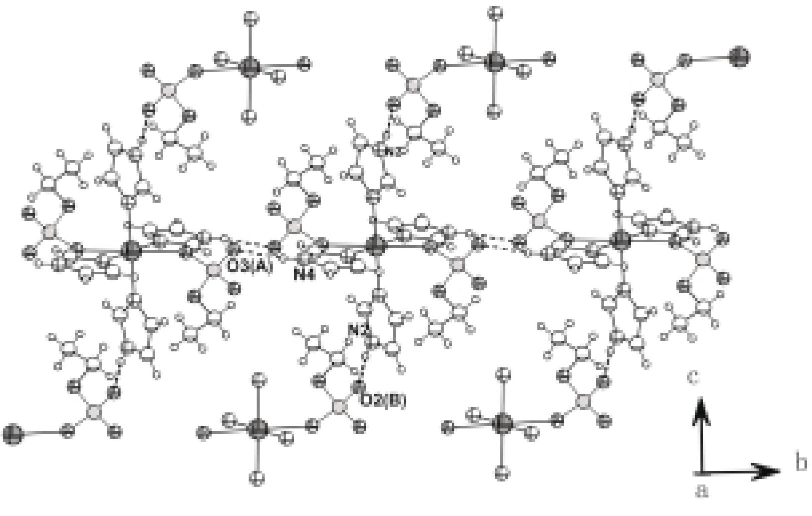

Figure 3. View of the 2-D network with hydrogen bonds shown as dashed lines.

Table 4. The distances (Å) and degrees (°) of hydrogen bonds.

D–H· · ·A	D–H	H· · ·A	D· · ·A	D–H· · ·A
N(2)–H(2)· · ·O(2)^i	0.860(15)	1.938(35)	2.788(51)	169.35(18)
N(4)–H(4)· · ·O(3)^{ii}	0.861(2)	2.023(2)	2.834(3)	156.56(14)

Symmetry operations: i [x + 1/2, –y + 1/2, z + 1/2]; ii [–x, –y + 1, –z].

NLO properties. *Electronic spectrum.* The UV-Visible absorption spectrum of the compound (9.65×10^{-5} mol·dm^{-3} in DMF) described in Fig. 4 displays two strong absorption peaks (with molar absorption coefficients in dm^3·mol·cm^{-1}) at 291 (5.70×10^4) nm and 365 (2.38×10^4) nm, the peak in 291 nm attributed to center ion←ligand charge-transfer transitions. The peak in 365 nm is a wide absorption with a long tail up to 700 nm assigned to d-d transition. Among the two absorption peaks, the first peak in the ultraviolet region indicates the presence of metal-ligands transfer transitions, and the wide peak extends to the visible region shows the presence of charge-transfer transitions.

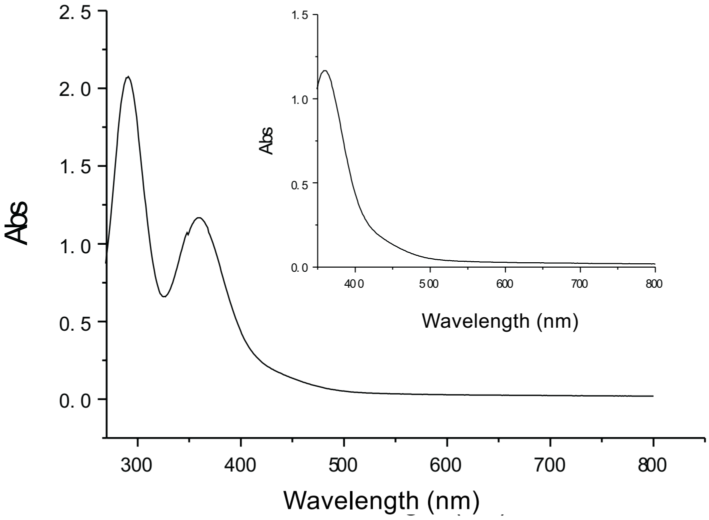

Figure 4. UV-Visible spectrum of compound **1**.

Third-order NLO property. Then we went to a further step to study its third-order NLO property using Z-scan technique in DMF solution. The results are depicted in Figure 5, where the open circles represent the experimental data and the solid curves represent the theory fits. As shown in Figure 5(a), the compound **1** shows a large non-linear optical absorption with the NLO absorption coefficient $\alpha_2 = 1.10\times10^{-11}$ m·w^{-1} in DMF solution of 5.2×10^{-3} mol·dm^{-3}. Figure 5(b) gives the NLO refractive behavior under a close-aperture configuration, which suggests that the compound has

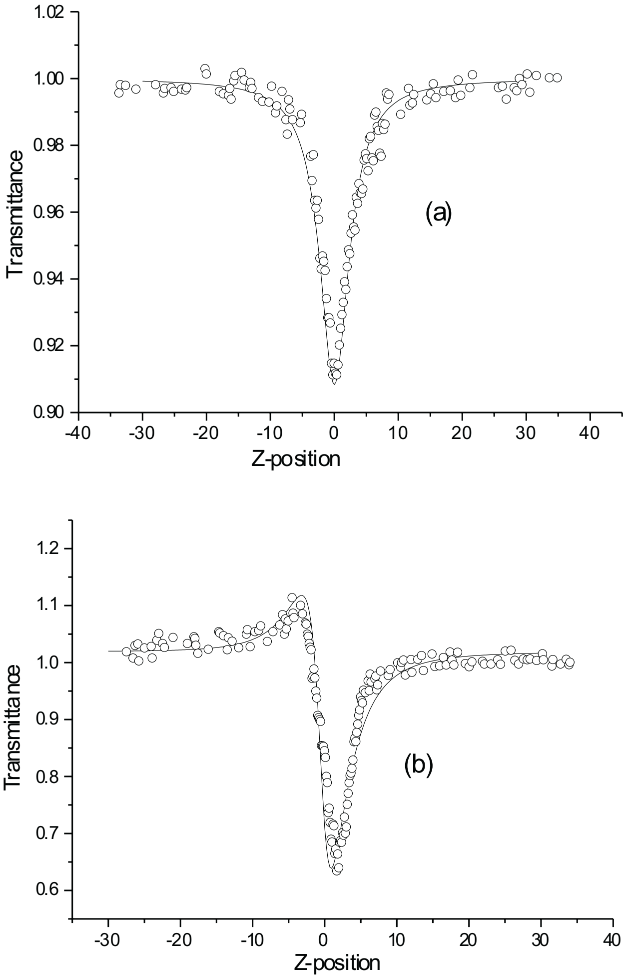

Figure 5. Z-scan data of compound **1**. (a) Collected under the open aperture configuration showing NLO absorption; (b) Collected under the closed aperture configuration showing NLO refractive behavior.

a strong self-defocusing effect with the NLO refractive index $n_2 – 5.6 \times 10^{-16}\ \mathrm{m^2 \cdot w^{-1}}$. In accordance with the observed α_2 and n_2, the modules of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by the following equation:

$$|\chi^{(3)}| = [(9 \times 10^8 n_0^2 \varepsilon_0 c \lambda \alpha_2 / 8\pi^2)^2 + (n_0 c n_2 / 80\pi^2)^2]^{1/2}$$

Where λ is the wavelength of the laser light, n_0 is the linear refractive index of the sample (n_0 can be replaced by the one of the solvent if the concentration of the sample is very small during calculation), ε_0 and c are the permittivity and speed of light *in vacuo*, respectively. For the compound **1**, the $\chi^{(3)}$ value was calculated to be 3.07×10^{-10} *esu*. The corresponding modules of the hyperpolarizabilities γ of 2.49×10^{-29} *esu* was got from $|\gamma| = |\chi^{(3)}|/NF^4$ ($F^4 = [(n^2+2)/3]^4$), n is the linear refractive index of the solvent, N is the molecular number density of the compound in the sample and F^4 is the local Lorentz field correction factor. The result suggests that this compound has very strong reverse saturable absorption (RSA) and effective self-defocusing performance in DMF solution, which is comparable to or even better than those of the best NLO materials we reported before [23]. It should be paid attention to the effects of solvent on supramolecular compound's NLO refractivity determined in solutions. The supramolecular compound will dissociate into oligomeric or monomeric species because secondary bonding interactions are destroyed in DMF solution. Therefore, the result in this paper shows the final effect of isolated compound in the DMF solution, which suggests that compound should have a better third-order NLO property in the solid state. We are trying to foster large single crystals to get third-order NLO data in the solid state structure.

Supplementary data: Supplementary data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219931. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http: // www.ccdc.cam.ac.uk)

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