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Layered solids based on second-sphere coordination interactions: synthesis, spectroscopic characterization, crystal structure and packing of two copper(II) naphthalene-2-sulfonates

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Abstract

$[Cu(H_2O)_6](C_{10}H_7SO_3)_2$ **1** was obtained from reaction of $CuCO_3 \cdot Cu(OH)_2$ and naphthalene-2-sulphonic acid in aqueous medium in 1:4 molar ratio. It crystallizes in the monoclinic space group $P2_1/n$ with $a=7.0582(3)$ Å, $b=6.2666(3)$ Å, and $c=27.1420(10)$ Å, $\beta=92.678(4)°$, $Z=2$. The structure was determined from 1986 observed reflections and refined to $R=0.033$. When ethylenediamine was added to hexaaquacopper(II) naphthalene-2-sulfonate dissolved in water, $[Cu(en)_2(H_2O)_2](C_{10}H_7SO_3)_2$ **2** was obtained which crystallizes in the triclinic space group $P\bar{1}$ with $a=7.1491(5)$ Å, $b=7.1949(5)$ Å, and $c=14.6500(10)$ Å, $\alpha=99.025(6)°$, $\beta=98.976(6)°$, and $\gamma=104.262(6)°$, $Z=1$. The structure was determined from 2296 observed reflections and refined to $R=0.0313$. X-ray structure determination of **1** revealed an ionic structure consisting of $[Cu(H_2O)_6]^{+2}$ and two naphthalene-2-sulfonate anions while that of **2** contains $[Cu(en)_2(H_2O)_2]^{2+}$ cation and two naphthalene-2-sulfonate anions. Characteristic for the studied crystals is the alternated-layer arrangement of complex cations and naphthalene-2-sulfonate anions, linked together via hydrogen bonding, and the presence of a particularly robust $R_2^2(8)$ hydrogen-bonding motif that joins the complex cation with two oxygen atoms of the same sulfonate group. Elemental analyses, IR, UV/vis spectroscopic studies are consistent with the structures revealed by X-ray structure determination.

Keywords: Copper(II); Coordination chemistry; Naphthalene-2-sulfonates; X-ray crystallography; IR spectroscopy and UV/visible spectroscopy

1. Introduction

Copper is one of the essential elements in humans and animals. A large number of copper proteins/enzymes are known, e.g. cytochrome *c* and superoxide dismutase are involved in important biochemical functions like reduction of oxygen and destruction of harmful superoxide anion, and the disease associated with copper deficiency is anaemia and copper accumulation is Wilson's disease. Antiseptic properties of copper(II) salts (copper acetate and copper sulphate for the treatment of eye infections since earlier times) and bis copper(II) 3,5-diisopropyl salicylate as a promising radiation recovery agent for application in nuclear warfare and cancer patients [26] are also noteworthy for providing impetus to the chemistry of copper(II) complexes. A thematic issue on biomimetic inorganic chemistry [1b] has recently appeared in literature which contains extensive study of copper complexes. Besides this a large number of papers on copper complexes continue to appear in almost all the top journals of inorganic chemistry. $Cu(hfac)_2$ is widely used in the synthesis of molecular magnets [2–4]. Replacement of the native mononuclear type I copper ion in cuperedoxins with other metals has been utilized for decades to facilitate the investigation of this key family of metalloprotein [5]. Furthermore, inorganic chemistry of copper(II) is very fascinating because of a number of reasons such as (i) copper(II) exhibits a variety of coordination numbers 4–8 with associated geometries

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(ii) copper(II) complexes are liable to Jahn–Teller distortion and (iii) the anionic ligand may be non-coordinated or coordinated and (iv) it is one of the constituent metal ions in most of the superconductors. In the last decade, several reports have focused on the construction of copper(II) complexes with CD derivatives [6–9] which find applications as chiral recognition receptors. Metal-organic framework solids (layered solids) can be designed and assembled to generate cavities or channels of various sizes and shapes by appropriate choice of the building blocks. These are of current interest [10] because of their potential applications in molecular adsorption and separation processes, ion exchange, catalysis, sensor technology and optoelectronics. Generation of extended solids by exploiting both primary and secondary sphere interactions in metal sulfonate complexes has been widely studied by Shimizu and coworkers [11,12]. Due to our interest in structural chemistry of transition metals [13], and their complexes with sulfonates this paper reports the synthesis, spectroscopic characterization, crystal structure and packing in two copper(II) naphthalene-2-sulfonates. These are the first two crystal structures of divalent metal ion with naphthalene-2-sulfonate. Sulfonate anions are relatively unexplored class of ligands for the construction of coordination framework [14]. We have already reported the synthesis, characterization and crystal structures of hexaamminecobalt(III) chloride dimethanesulfonate [13] and thallium *m*-nitrobenzenesulfonate revealing a coordination network in the solid state [15].

2. Experimental

Analytical grade reagents were used throughout this work without any further purification.

2.1. Synthesis of **1**

One gram of $CuCO_3 \cdot Cu(OH)_2$ was suspended in 20 ml water. 3.7647 g of solid naphthalene-2-sulphonic acid was added to it slowly with continuous heating on a low flame. The effervescence took place and a clear blue solution resulted. The solution was then concentrated and allowed to crystallize at room temperature. The light blue crystals of $[Cu(H_2O)_6](C_{10}H_7SO_3)_2$ appeared after 3–4 h, which were collected by drawing off the mother liquor and air-dried (yield, 75%). The newly synthesized complex salt is freely soluble in water and ethanol but insoluble in chloroform. The complex salt decomposes at 90 °C. Anal. Calcd for $[Cu(H_2O)_6](C_{10}H_7SO_3)_2$: C, 40.9%; H, 4.4%. Found: C, 40.2%; H, 4.3%.

2.2. Synthesis of **2**

To 1 g of $[Cu(H_2O)_6](C_{10}H_7SO_3)_2$ dissolved in water, 0.85 ml of ethylenediamine dissolved in ethanol was added dropwise, which gave deep blue crystals of

Table 1
Details of the single-crystal X-ray diffraction experiment of **1** and **2**

Compound	**1**	**2**
Chemical formula	$[Cu(H_2O)_6](C_{10}H_7SO_3)_2$	$[Cu(en)_2(H_2O)_2](C_{10}H_7SO_3)_2$
Chemical formula weight	586.07	634.21
Cell setting	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	7.0582(3)	7.1491(5)
b (Å)	6.2666(3)	7.1949(5)
c (Å)	27.1420(10)	14.6500(10)
α (deg)		99.025(6)
β (deg)	92.678(4)	98.976(6)
γ (deg)		104.262(6)
V (Å^3)	1199.20(9)	706.21(8)
Z	2	1
D_x (Mg m^{-3})	1.623	1.491
Radiation type	Mo Kα	Mo Kα
Wavelength	0.71073	0.71073
No. of reflections for cell parameters	5217	3567
μ (mm^{-1})	1.147	0.974
Temperature (K)	293(2)	293 (2)
Crystal form	Planar	Prismatic
Crystal size (mm)	0.2×0.2×0.1	0.4×0.3×0.2
Crystal colour	Light blue	Deep blue
Diffractometer	Kuma KM4CCD κ-geometry diffractometer	Kuma KM4CCD κ-geometry diffractometer
Monochromator	Graphite	Graphite
Data collection method	ω scans	ω *scans*
No. of measured reflections	9419	7881
No. of independent reflections	2369	2771
No. of observed reflections	1986	2296
Criterion for observed reflections	$I>2\sigma(I)$	$I>2\sigma(I)$
R_{int}	0.0491	0.0418
θ_{max} (deg)	26.05	26.06
Range of h, k, l	$-6\rightarrow h\rightarrow 8$ $-7\rightarrow k\rightarrow 7$ $-32\rightarrow l\rightarrow 33$	$-8\rightarrow h\rightarrow 8$ $-8\rightarrow k\rightarrow 7$ $-18\rightarrow l\rightarrow 18$
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0330	0.0313
$wR(F^2)$	0.0784	0.0887
S	1.066	1.070
No. of reflections used in refinement	2369	2771
No. of parameters used	160	179
H-atom treatment	Riding model	Riding model
Weighting scheme	$w=1/[\sigma^2(F_o)^2+(0.0415P)^2]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o)^2+(0.0532P)^2]$ where $P=(F_o^2+2F_c^2)/3$
$\Delta\rho_{max}$ (e Å^{-3})	0.260	0.306
$\Delta\rho_{min}$ (e Å^{-3})	−0.495	−0.329
Extinction method	None	SHELXL
Extinction coefficient		0.028(3)