A New 2D Copper(II) Coordination Polymer with a Schiff Base Ligand with Weakly Coordinating Sulfonate Groups Affecting the Structure

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A new 2D copper(II) coordination polymer with the doubly deprotonated Schiff base ligand 2-(2-hydroxybenzylideneamino)ethanesulfonic acid (H_2Saes) has been synthesized, $\{[Cu(Saes)(4,4'\text{-}bpy)]_2 \cdot H_2O\}_n$ (**1**), and characterized by single-crystal X-ray diffraction, IR spectroscopy, elemental and thermogravimetric analysis. Dinuclear copper complexes serve as secondary building blocks (SBUs) to construct an unusual coordination network with an interpenetrating $CdSO_4$ topology. In the crystal, the components form a stable 3D supramolecular architecture by O–H⋯O, C–H⋯O interactions and π stacking.
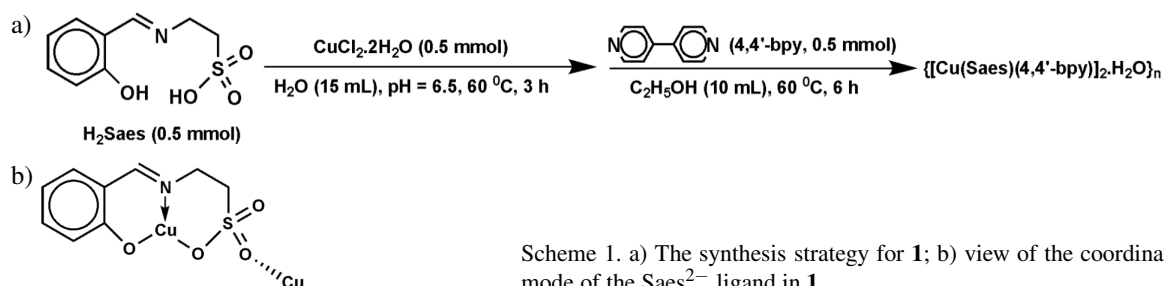
Key words: Schiff Base, Crystal Structure, Copper(II) Complex, Synthesis, Thermal Stability

Introduction

In the past decades, much effort has been devoted to designing and controlling crystallization of metal-organic frameworks (MOFs) [1] based on transition metal ions and multifunctional bridging ligands owing to their potential applications in magnetism [2], separation [3], gas storage [4], and heterogeneous catalysis [5]. Recently, many porous MOFs have been designed and constructed with polycarboxylate [6a] and phosphonate ligands [6b]; however, sulfonate ligands are rare in micro-porous MOFs [6c, d, e]. Sulfonate anions (RSO_3^-) are structurally analogous to phosphonate anions (RPO_3^{2-}), both having trioxy anionic units with an organic pendant having local C_{3v} symmetry. The obvious difference is the greater anionic charge associated with the phosphonate [6e]. However, sulfonate ligands have been much less studied owing to the preoccupation that they are weakly coordinating ligands [6c, d, e]. Significant progress has been made in understanding the supramolecular chemistry in extended solids with sulfonate groups built up by cooperative coordination and other weak intermolecular interactions [7, 8]. In particular, hydrogen bonded interactions play a key role in the guanidinium sulfonate and disulfonate compounds systematically studied by Ward and co-workers [9]. Cai [6c], Côté and Shimizu [6e] have explored the coordination chemistry of the sulfonate group and the structural properties of metal arenesulfonates. Based on this background, many transition metal sulfonate complexes with novel 0–3D porous structures were obtained showing that the sulfonate group can become directly coordinated to the metal ion [10 – 14], competing successfully with water molecules [9h].

To demonstrate the influence of the second ligand on the assembly of deprotonated sulfonate ligands of

Scheme 1. a) The synthesis strategy for **1**; b) view of the coordination mode of the $Saes^{2-}$ ligand in **1**.

the type H_2Saes (2-(2-hydroxybenzylideneamino)eth-anesulfonic acid) and metal ions as well as the framework structures of their complexes, we show the syntheses (Scheme 1) and structure of a new copper(II) compound, $\{[Cu(Saes)(4,4'-bpy)]_2 \cdot H_2O\}_n$ (**1**), which has been characterized by single-crystal X-ray diffraction. Its thermal stability has also been investigated.

Results and Discussion

Description of the structure of $\{[Cu(Saes)(4,4'-bpy)]_2 \cdot H_2O\}_n$ (**1**)

The single-crystal X-ray diffraction analysis revealed that **1** is a 2D coordination polymer, whose asymmetric unit is comprised of one Cu^{2+}, one doubly deprotonated tridentate chelating H_2Saes, two discrete half 4,4'-bipy ligands, and half of a solvate water molecule. Each Cu(II) atom is six-coordinated in the CuN_4O_2 mode exhibiting a distorted octahedral coordination sphere (Fig. 1 and Table 1). The equatorial plane is defined by the three donor atoms [O(1), O(2), N(1)] of the $Saes^{2-}$ ligand, the other atom belonging to μ_2-bridging 4,4'-bipy [N(2)] at mean distances close to 2.0 Å. The oxygen atom [O(4)] from a μ_2-bridging sulfonate of a neighboring $Saes^{2-}$ unit and the nitrogen atom [N(3)] of another μ_2-bridging 4,4'-bipy unit are situated at the axial sites with separations longer than 2.55 Å. The relatively long $Cu-O_{axial}$ and $Cu-N_{axial}$ bonds can be accounted for by the Jahn-Teller effect of the Cu(II) ion.
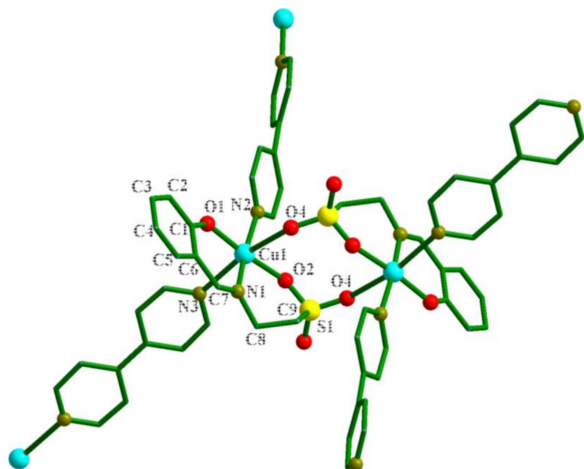

Fig. 1 (color online). The coordination environment of the Cu(II) ion in **1**. Hydrogen atoms and water molecules are omitted for clarity.

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

Formula	$[Cu(C_9H_9O_4NS)(C_{10}H_8N_2)]_2 \cdot H_2O$
M_r	911.97
Crystal size, mm³	$0.34 \times 0.21 \times 0.10$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	18.383(12)
b, Å	27.808(18)
c, Å	8.304(8)
β, deg	115.888(3)
V, Å³	3819(5)
Z	4
D_{calcd}, g cm⁻³	1.59
$\mu(MoK_\alpha)$, cm⁻¹	1.3
$F(000)$, e	1872
hkl range	$\pm 22, -31 \rightarrow 33, \pm 10$
$((\sin\theta)/\lambda)_{max}$, Å⁻¹	0.71073
Refl. measured / unique / R_{int}	10303 / 3683 / 0.0288
Param. refined	2932
$R(F)$ / $wR(F^2)^{a,b}$ (all refl.)	0.0520 / 0.0849
GoF $(F^2)^c$	1.031
$\Delta\rho_{fin}$ (max / min), e Å⁻³	0.29 / −0.31

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (Max(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

The Schiff base ligand ($Saes^{2-}$) is coordinated meridionally to Cu *via* its imine N and deprotonated phenolate and sulfonate oxygen atoms, forming two edge-sharing six-membered chelate rings (Scheme 1). The ring containing Cu1-O1-C1-C6-C7-N1 is planar (mean r. m. s. deviation of 0.0506 Å), and the ring containing the sulfonate group has an envelop conformation with C9 deviating from the Cu1-N1-C8-C9-S1-O2 plane by 0.43 Å. The O–C1–C angles are markedly unsymmetrical (119.0(2) and 124.0(2)°) as a result of the chelating coordination. Furthermore, the substituents at the N1–C7 bond form an eclipsed conformation, as noted from the C8–N1–C7–C6 torsion angle of 177.3(2)°. The C7–N1 bond length, 1.286(3) Å, is indicative of a C=N double bond, as compared to C8–N1 with 1.471(3) Å, which is in the range of C–N single bonds. Sulfonate μ_2-bridging between the subunits of [Cu(Saes)] leads to the formation of an eight-membered $(-Cu-O_{chelate}-S-O_{bridging}-)_2$ ring with crystallographic inversion symmetry. The Cu···Cu distance is 5.707(5) Å, a little longer than that reported for other comparable structures [15]. These dimeric units are secondary building blocks (SBUs) in a (4,4)-connected net, the apical site in each Cu(II) center being occupied by a nitrogen atom of a 4,4'-bipy ligand to link the neighboring dimer. The dimer is regarded as a four-connecting node to produce an overall 3D network. The structure of **1** thus shows $CdSO_4$-
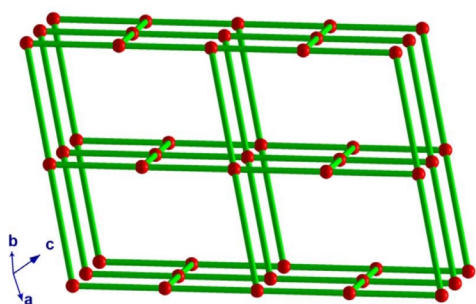
Fig 2 (color online). A view of the twofold interpenetrating three-dimensional $CdSO_4$ net of **1**.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Cu(1)–O(1)	1.9057(19)	Cu(1)–N(1)	1.981(4)
Cu(1)–O(2)	2.0003(19)	Cu(1)–N(2)	2.052(3)
Cu(1)–O(4)	2.68(2)	Cu(1)–N(3)	2.58(9)
O(1)–Cu(1)–N(1)	92.99(10)	O(1)–Cu(1)–O(2)	173.15(7)
O(1)–Cu(1)–N(2)	87.73(10)	N(1)–Cu(1)–N(2)	171.62(8)
S(1)–O(2)–Cu(1)	135.37(14)	O(4)–Cu(1)–N(3)	164.98(8)
N(1)–Cu(1)–O(2)	93.72(11)	O(2)–Cu(1)–N(2)	85.43(10)

type topology with two-fold interpenetration and with the Schäfli symbol $6^5\,8$, as show in Fig. 2 [16]. To the best of our knowledge, the well known examples of the square planar node are the $CdSO_4$ and the NbO structures. Though both structures are related, the vertex symbols for the two nets are $6.6.6.6.6_2.8$ (cds) and $6_2.6_2.6_2.6_2.8_2.8_2$ (nbo). The fundamental ring in the cds net is the hexagon, and the fundamental rings for the nbo net are the hexagon and the octagon. The nbo net is built from perpendicularly oriented square-planar units, and the cds net has only half of the neighboring rings related by 90°. This arrangement results in two similar layers arranged perpendicular to each other in the cds net.

Intermolecular hydrogen bonding and π-stacking interactions are important supramolecular forces to govern the process of recognition and self-assembly [14b]. In the crystal structure, a notable feature of **1** lies in the 3D network built through the hydrogen bonds given in Fig. 3. The neighboring 2D coordination polymers are connected by hydrogen
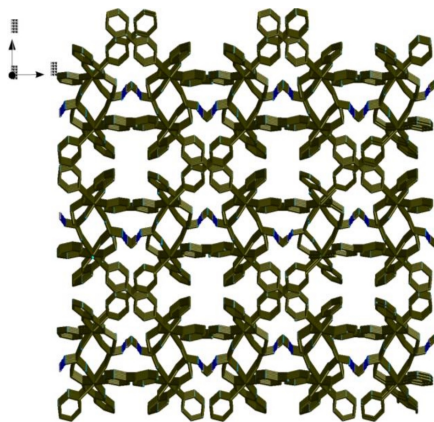
bonds O–H···O with O···O distances of 2.885(4) Å (Table 3). The neighboring layers are also connected by intermolecular C–H···O hydrogen bonds of sulfonate oxygen atoms (O3 and O4) with C···O distances of 3.223(7) to 3.447(7) Å. In addition, weak π···π stacking interactions can also be observed between the phenyl and pyridine rings of adjacent chains with the shortest interplanar perpendicular and ring centroid-to-centroid distances of 3.46(4) and 3.976(8) Å, respectively. Molecules from neighboring stacks are further interacting in the crystallographic *c* direction, thus leading to an interwoven three-dimensional network held together by O–H···O, C–H···O interactions and π···π stacking stabilizing the coordination polymer.

TG analysis

In order to explore the thermal stability of the compound TG studies have been performed in nitrogen at a heating rate of 10 °C min^{-1}. The TG curve of compound **1** shows three main steps of weight loss (Fig. 4). The result indicates that compound **1** is stable up to about 80 °C and then begins to decompose continuously. The weight loss of 2.2 % between 70 and 107 °C is attributed to the loss of one lattice wa-
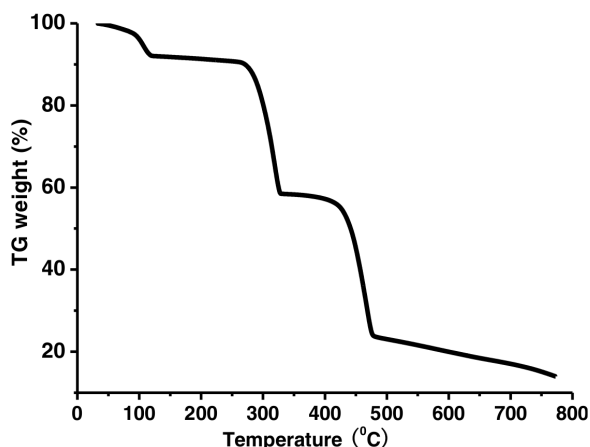

Fig. 3 (color online). View of the 3D hydrogen-bonded framework in **1**.

Fig. 4. The TGA curve of **1**.

Table 3. Hydrogen bonding geometries (Å, deg) for **1** with estimated standard deviations in parentheses[a].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
O(5)–H(1W)···O(3)[i]	0.85	2.10	2.885(6)	153
C(13)–H(13)···O(4)[ii]	0.93	2.52	3.447(7)	177

[a] Symmetry codes: [i] $1 - x$, y, $3/2 - z$; [ii] $3/2 - x$, $1/2 - y$, $2 - z$.

ter molecule for each formula unit (calcd. 2.2 %). The weight loss of about 34.4 % in the range from 107 to 310 °C is ascribed to the removal of the 4,4′-bpy ligands (calcd. 34.5 %). The decomposition process ends at about 700 °C, and the final residue was probably CuO (found 17.3 %, calcd. 17.4 %).

Conclusions

In conclusion, we have successfully synthesized a new 2D copper(II) coordination polymer with a Schiff base ligand containing a sulfonate moiety. Complex **1** presents dinuclear copper complexes as secondary building blocks forming an unusual coordination network with CdSO$_4$ topology.

Experimental Section

Materials and physical methods

All starting chemicals were commercially available and used as received without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400II elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of $4000 - 450$ cm^{-1} on a Bio-Rad FTS-7 spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10 °C min^{-1} using a Netzsch STA 449C thermogravimetric analyzer.

Synthesis of {[Cu(Saes)(4,4′-bpy)]$_2$ · H$_2$O}$_n$ (1)

H$_2$Saes (0.140 g, 0.5 mmol) was dissolved in distilled water (15 mL). Then CuCl$_2$·H$_2$O (0.0582 g, 0.5 mmol) was added. The pH value was 6.5. The mixture was stirred

at 60 °C for 3 h, then 10 mL of a methanol solution of 4,4′-bipyridine (0.5 mmol, 0.078 g) was added, and the reaction continued for 6 h. The mixture was cooled and filtered. The filtrate was allowed to slowly concentrate by evaporation at r. t. One month later, dark-blue block-shaped crystals were obtained in a yield of 5 % (based on Cu). – C$_{38}$H$_{36}$Cu$_2$N$_6$O$_9$S$_2$: calcd. C 26.83, H 3.58, N 6.26; found C 27.01, H 3.46, N 6.17. – IR (KBr, cm^{-1}): ν = 3583m, 3445s, 1627s (C=N), 1612m, 1540m, 1455m, 1414m, 1240m, 1172s, 1157m, 1057m, 1037s, 820m, 768w, 755m, 624m.

Crystal structure determination

Single crystals suitable for X-ray diffraction analysis of the complex were obtained as described above. A crystal was mounted on a Bruker SMART APEX II CCD diffractometer, and ω-2θ scans were used for the intensity data collection at r. t. The structure was solved by Direct Methods [17] and refined by full-matrix least-squares routines on F^2 using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned common isotropic displacement parameters and included in the final refinement in calculated positions using the riding model approximation. The crystallographic data are shown in Table 1, selected bond lengths and angles are listed in Table 2, parameters for the hydrogen bond geometry are provided in Table 3.

CCDC 847835 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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