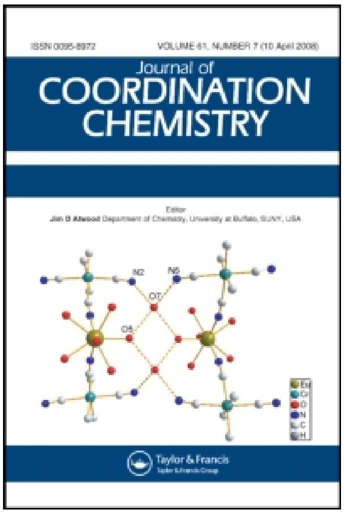

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Synthesis and crystal structure of a complex Cu(II) salt containing a taurine Schiff base and 2,2′-bipyridyl

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The complex salt $[Cu_3(TFSSB)_2(bpy)_4][Cu(TFSSB)_2]\cdot 2H_2O$ (TFSSB = the Schiff base formed by 5-formylsalicylaldehyde and taurine, bpy = 2,2′-bipyridyl) was synthesized by reaction of $Cu(CH_3COO)_2\cdot 2H_2O$, TFSSB and 2,2′-bipy in aqueous methanol (1 : 1, v/v). The complex is triclinic, space group $P\bar{1}$, with $a = 11.2433(5)$, $b = 13.6717(2)$, $c = 14.4022(11)$ Å, $\alpha = 83.588(10)$, $\beta = 87.919(12)$, $\gamma = 69.059(9)^\circ$, $V = 2054.66(18)$ Å^3, $Z = 1$. The asymmetric unit is comprised of a trinuclear coordinaton cation together with a mononuclear coordination anion and two water molecules, all of which are linked by hydrogen bonding and π–π interactions into a three-dimensional framework. The sulfonate group of the TFSSB ligand coordinates to copper(II) in the cation but not in the anion.

Keywords: Copper; Schiff base; Taurine; 5-Formylsalicylaldehyde; 2,2′-Bipyridyl; Crystal structure

1. Introduction

Transition metal complexes of Schiff bases derived from amino acids have received considerable attention due to their bio- and catalytic activities [1–3]. As for taurine (2-aminoethanesulfonic acid), a non-protein amino acid containing sulfur, which is indispensable to human beings and animals, [4–6] its Schiff base complexes have not received adequate study and the main focus on its chemistry concerns its physiology and pathology [7–8]. It seems probable that research on complexes of taurine and its Schiff bases is rather scanty due to poor coordination ability [9]. With the aim of understanding the coordination chemistry of taurine, we have recently focussed our research on coordination polymers based on the TFSSB ligand, derived by the reaction of taurine, 5-formyl-salicylaldehyde and KOH. In this article, we describe the synthesis and crystal structure of a complex salt, prepared by reaction of $Cu(CH_3COO)_2\cdot 2H_2O$ with TFSSB and 2,2′-bipyridyl (bipy) in aqueous methanol. In the salt, the cation is trinuclear and the anion mononuclear; the sulfonate group is coordinated to copper in

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the cation but not in the anion. Cations and anions are linked by hydrogen bonding and π–π interactions into a three-dimensional framework.

2. Experimental

5-Formylsalicylaldehyde, was synthesized in accordance with the procedure reported by Angyal *et al*. [10]. Other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were carried out on a Elementar Vario EL III analyzer and IR spectra (KBr pellets) were recorded on a Perkin Elmer Spectrum one FTIR spectrophotometer in the range 400–4000 cm^{-1}.

2.1. *Synthesis of TFSSB*

A solution of 2.0 mmol of taurine and 2.0 mmol of KOH in 10 cm^3 of anhydrous methanol was added to a solution of 1.0 mmol of 5-formylsalicylaldehyde in 10 cm^3 of anhydrous methanol. The mixture was stirred and refluxed at 323 K for 2 h and then cooled to room temperature to give a yellow precipitate, which was collected by filtration, recrystallized from anhydrous methanol, washed successively with anhydrous methanol and ether, and dried *in vacuo*. Yield: 360 mg (82%). Anal. Calcd for $C_{12}H_{14}K_2N_2O_7S_2$ (%): C, 32.73; H, 3.18; N, 6.36; S, 14.58. Found: C, 32.85; H, 3.12; N, 6.27; S, 14.73. IR (cm^{-1}): 1048.8s, 1152.4m, 1197.2s, 1636.2m, 3442.3w.

2.2. *Synthesis of [Cu_3(TFSSB)$_2$(byp)$_4$][Cu(TFSSB)$_2$] · 2H_2O*

TFSSB (0.44 g, 1.0 mmol) was dissolved in aqueous methanol (25 cm^3). To this solution, $Cu(CH_3COO)_2 \cdot 2H_2O$ (0.22 g, 1.0 mmol), dissolved in CH_3OH/H_2O (20 cm^3, 1 : 1, v/v) was added and the mixture refluxed for 8 h. Bipy (0.156 g, 1.0 mmol) was slowly added and the reaction continued for another 6 h. Single crystals suitable for X-ray diffraction were grown from the filtrate by slow evaporation. Yield: 140 mg (29%). Anal. Calcd for $C_{80}H_{72}Cu_4N_{12}O_{22}S_4$ (%): C, 49.59; H, 3.72; N, 8.68; S, 6.61. Found: C, 49.34; H, 3.86; N, 8.90; S, 6.47. IR (cm^{-1}): 3436.32m, 1670.25m, 1616.85s, 1600.60s, 1541.04w, 1491.79m, 1439.30s, 1402.39s, 1350.07w, 1314.58w, 1277.37w, 1207.01m, 1188.92s, 1160.69s, 1029.16s, 1014.95m, 952.35w.

2.3. *Crystallography*

Diffraction data were collected on Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. An empirical absorption correction was applied using the SADABS program [11]. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 package [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of TFSSB were generated geometrically, and no attempts were made to locate the hydrogen atoms of water. Crystallographic details for the structure determination are presented in table 1. Selected bond distance and angles are listed in table 2.

3. Results and discussion

The asymmetric unit contains four copper atoms, three of them (Cu1, Cu2, Cu1A) in the complex cation and one (Cu3) in the complex anion. In the cation, Cu2 is four coordinate through two O and two N atoms of the Schiff base ligands to form a slightly distorted square planar geometry (Cu2–O = 1.97(2) and 1.80(3) Å, Cu2–N = 2.00(3) and 2.05(3) Å). Cu1 and Cu1A lie in the same coordination environment, showing square pyramidal geometry, bonded to two bipy ligands (Cu1–N3 = 2.115(6),

Table 1. Crystal data and structure refinement parameters for the complex salt.

Empirical formula	$C_{80}H_{72}Cu_4N_{12}O_{22}S_4$
Crystal size (mm^3)	$0.25 \times 0.15 \times 0.07$
M	1935.90
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell parameters	$a = 11.2433(5)$, $b = 13.6717(2)$, $c = 14.4022(11)$ Å, $\alpha = 83.588(10)$, $\beta = 87.919(12)$, $\gamma = 69.059(9)^\circ$
V (Å^3)	2054.66(18)
Z	1
T (K)	93(2)
Density (Mg m^{-3})	1.565
$F(000)$	992
θ range (°)	3.10–25.03
h range	−11–13
k range	−16–16
l range	−17–16
Reflections collected	13094
Independent reflections	7183 [R(int) = 0.0391]
Data/restraint/parameters	7183/0/568
Goodness-of-fit on F^2	0.987
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0735$, $wR_2 = 0.2077$
R indices (all data)	$R_1 = 0.1128$, $wR_2 = 0.2830$

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Cu1–N3	2.115(6)	O3–Cu1–N5	93.6(2)
Cu1–N4	1.982(6)	O3–Cu1–N6	148.4(3)
Cu1–N5	1.974(6)	N4–Cu1–N3	78.7(3)
Cu1–N6	2.039(6)	N3–Cu1–N5	100.8(2)
Cu1–O3	2.034(5)	N5–Cu1–N6	81.6(2)
Cu2–1	2.00(3)	N6–Cu1–N4	95.0(2)
Cu2–1A	2.05(3)	N1–Cu2–O16	89.7(12)
Cu2–O16	1.97(2)	N1–Cu2–O16A	91.1(13)
Cu2–O16A	1.80(3)	N1A–Cu2–O16	85.1(10)
Cu3–2	1.96(3)	N1A–Cu2–O16A	93.3(13)
Cu3–2A	2.07(3)	N2–Cu3–O12	90.2(13)
Cu3–O12	2.01(2)	N2–Cu3–O12A	92.8(10)
Cu3–O12A	1.78(2)	N2A–Cu3–O12	83.2(8)
O3–Cu1–N3	97.8(2)	N2A–Cu3–O12A	93.4(15)
O3–Cu1–N4	90.5(2)		

Symmetry code used are (i): $-x$, $-y+1$, $-z+1$; (ii): $-x+1$, $-y+1$, $-z+1$.

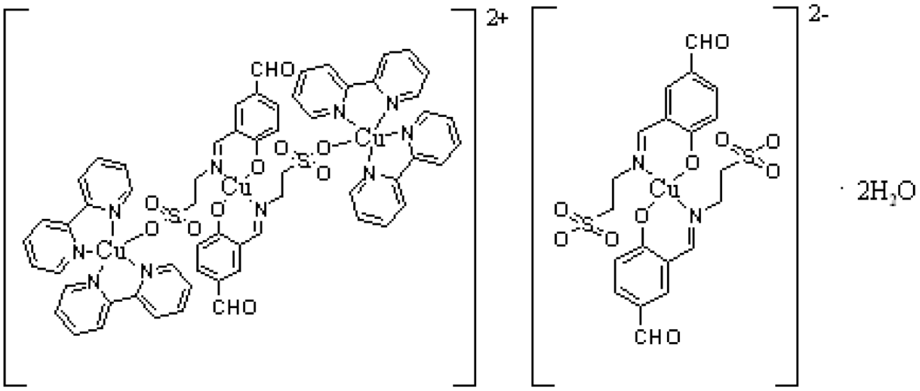

Figure 1. The constituents of the complex salt.

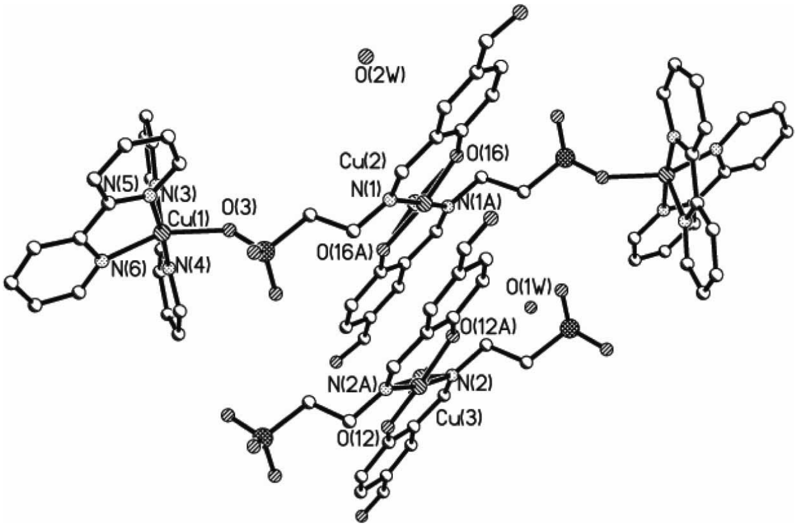

Figure 2. The molecular structure of the complex showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Cu1–N4 = 1.982(6), Cu1–N5 = 1.974(6), Cu1–N6 = 2.039(6) Å) and the O atom of the sulfonate group of the Schiff base ligand (Cu1–O3 = 2.034(5) Å). O3, N4, N5 and N6 form the base of the pyramid, with N3 at the apex. Cu1 deviates from basal plane by 0.1674 Å towards N3. In the square planar anion, two Schiff base ligands are coordinated *trans* to Cu3 via deprotonated hydroxyl O and imine N atoms (Cu3–O = 2.01(2) and 1.78(2) Å, Cu3–N = 1.96(3) and 2.07(3) Å), forming two six-membered chelate rings. The Cu2–O bond distances, 1.94(2) and 1.80(2) Å, are shorter than Cu2–N, 2.00(3) and 2.05(3) Å, while Cu2–O bond distances are shorter than Cu1–O3, 2.034(5) Å, indicating that the hydroxyl O atom forms a stronger bond than the imine N and sulfonate O atoms.The sulfonate group itself is not coordinated to Cu3, but is packed in the crystal structure to form hydrogen bonds by which the group is stabilized (figure 3). The different coordination behaviour of the sulfonate group in the cation and anion is noteworthy.

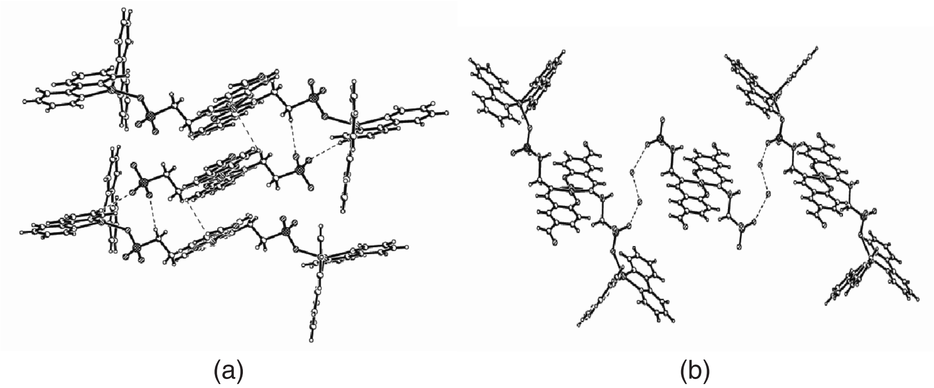
(a) (b)

Figure 3. Partial packing diagram for the complex, showing hydrogen bonds as dashed lines.

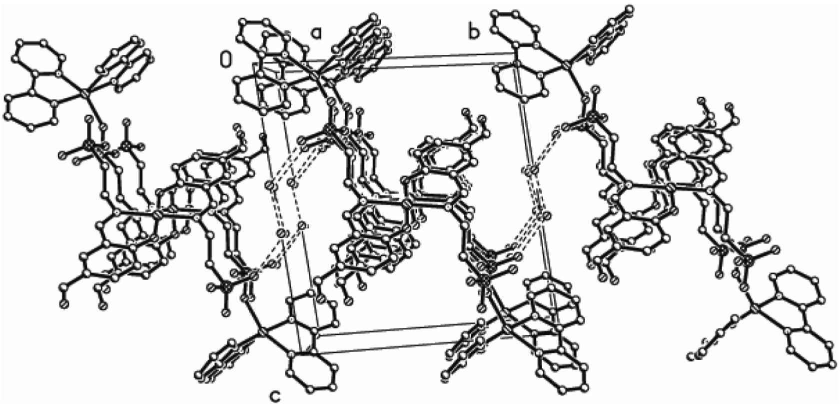

Figure 4. A perspective view of the aromatic ring interactions in the complex. Hydrogen atoms have been omitted for clarity.

The anions and cations, which are attracted by electrostatic forces, are also linked by hydrogen bonds (figure 3a). The O2W$\cdots$O1^{ii} distance of 2.734 Å, the O2W$\cdots$O1W^{ii} distance of 2.432 Å and the O5$\cdots$O1W^{ii} distance of 2.639 Å indicate significant hydrogen bonds involving water molecules and the sulfonate group at $-x+1$, $-y+1$, $-z+1$ (figure 3b). The anions and cations are arranged in alternate layers along the *a* axis, forming infinite belt-like structures. In the belts, benzene rings of the cation and anion take part in π–π interactions with an average distance of 3.241 Å. With the help of hydrogen bonds, adjacent belts are linked into supramolecular assemblies parallel to the *bc* plane (figure 4). Thus the network extends to a three-dimensional structure, stabilized by the hydrogen bond system and π–π interactions.

Supplementary material

CCDC 288538 contains supplementary crystallographic data for this article. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax; (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk.

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