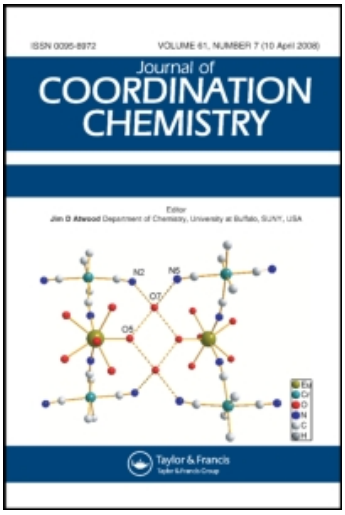

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Syntheses, crystal structures and antibacterial activities of $[Cu_2(C_{11}H_{11}NO_5S)_2(H_2O)_4]\cdot 5H_2O$ and $[Ni_2(C_{11}H_{11}NO_5S)_2(H_2O)_4]\cdot 2H_2O$

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The binuclear complexes $[Cu_2L_2(H_2O)_4]\cdot 5H_2O$ (**1**) and $[Ni_2L_2(H_2O)_4]\cdot 2H_2O$ (**2**) (where $L = C_{11}H_{11}NO_5S$, H_2L = 2-[(3-formyl-5-methyl-2-hydroxy-benzylidene)-amino]ethanesulfonic acid) have been synthesized and characterized by IR, elemental analysis and X-ray diffraction. The crystals belong to the monoclinic system, space group $P2_1/c$. Complex **1**: $a = 16.8902(12)$, $b = 11.2829(6)$, $c = 17.4249(11)$ Å; $\beta = 106.709(4)^\circ$; $S = 1.131$; $V = 3180.5(3)$ Å^3; $Z = 4$; $D_{Calcd} = 1.729$ g cm^{-3}; $F(000) = 1712$; $\mu = 1.554$ mm^{-1}; $R_1 = 0.0519$, $wR_2 = 0.1349$; complex **2**: $a = 11.399(2)$, $b = 19.985(3)$, $c = 7.3694(10)$ Å; $\beta = 108.664(7)^\circ$; $S = 1.157$; $V = 1590.6(4)$ Å^3; $Z = 2$; $D_{Calcd} = 1.604$ g cm^{-3}; $F(000) = 800$; $\mu = 1.388$ mm^{-1}; $R_1 = 0.1859$, $wR_2 = 0.4346$. The geometry around each metal(II) center can be described as slightly distorted octahedral. Water-sulfonic clusters and $(H_2O)_4$ water clusters can be observed for **1** from the crystal packing diagram, while cavity and offset face-to-face π–π stacking can be observed for **2**. The complexes have been tested for the antibacterial activities which show antibacterial activities of **1** for β-hemolytic streptococcus, *Staphylococcus aureus* and *Escherichia coli*, and the antibacterial activity of **2** only for β-hemolytic streptococcus.

Keywords: Binuclear complex; Crystal structure; Water-sulfonic clusters; Antibacterial activities

1. Introduction

Dinuclear metal complexes of multidentate heteroatomic ligands have attracted considerable interest because of their intriguing structural motifs, promising electrochemical and magnetic properties, and potential applications in catalysis

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and medicine [1–9]. Because phenolate can bridge two metals, we synthesized 2,6-diformyl-4-methyl-phenol, *N,N′-bis*(3-formyl-5-methyl-salicylidene)ethanesulfonic acid dipotassium salt, and two new binuclear complexes $[Cu_2L_2(H_2O)_4]\cdot 5H_2O$ and $[Ni_2L_2(H_2O)_4]\cdot 2H_2O$.

Taurine (2-aminoethanesulfonic acid), is a special amino acid of considerable importance [10–11]. Studies of taurine and its Schiff-base complexes have been reported [12–18], but studies on their biological activities have been inadequate [9].

Although copper and nickel are important biological metals, copper and nickel salts not bonded to protein are toxic in vivo; even small amounts of unbound copper can cause adverse side effects such as nausea and vomiting. The human body has a variety of copper transport proteins such as serum albumin and transcuprein which scavenge copper in the blood stream. Many copper chelating ligands have insufficient stability to these proteins *in vivo* for medical use (ex. acyclic polyaminocarboxylates). Transchelation of copper from polycyclic amines to superoxide dismutase has also been shown *in vivo*.

In the literature [9], antibacterial activities, antitumoural activities, and acute and toxic activities of a dinuclear copper complex of a taurine Schiff base have been reported. In order to investigate their potential applications in medicine, the crystal structures of the title complexes were determined and their antibacterial activities were examined.

2. Experimental

2.1. *Physical measurements*

All solvents and chemicals were commercial reagents and used without purification. Using *p*-cresol, 2,6-*bis*(hydroxymethyl)-4-methylphenols were synthesized [19], and 2,6-diformyl-4-methylphenols were synthesized [20]. The elemental analyses for C, H, N and S were performed on a PE2400II elemental analyzer.

2.2. *Syntheses of the complexes*

2.2.1. Syntheses of *N,N′-bis*(3-formyl-5-methyl-salicylidene)ethanesulfonic acid dipotassium salt $[K_2(C_{13}H_{16}N_2O_7S_2\cdot CH_3OH]$. A solution of taurine (1.26 g, 10 mmol) and KOH (0.85 g, 15 mmol) in 50 mL methanol was added to 30 mL methanol solution of 2,6-diformyl-4-methylphenol (0.82 g, 5 mmol). The reaction mixture was stirred at 323 K for 2 h and then cooled for filtration. The product was washed by using methanol and ether. The yellow solid (2.5 g) dried by vacuum was collected for further use. According to the IR, the elemental analysis data and the literature [13], the yellow solid is *N,N′-bis*(3-formyl-5-methyl-salicylidene) ethanesulfonic acid dipotassium salt $[K_2(C_{13}H_{16}N_2O_7S_2)\cdot CH_3OH]$. Found (%): C, 33.53; H, 3.99; N, 5.71; S, 12.66. Anal. Calcd (%) for $C_{14}H_{20}N_2O_8S_2K_2$: C, 34.56; H, 4.11; N, 5.75; S, 13.18. IR(cm^{-1}): for SO_3^-: 1195.53(vs), 1054.66(vs); for C=N: 1645.95(vs); for O–H: 3436.67(vs) (vs: very strong).

In the course of syntheses of **1** and **2**, one taurine Schiff-base group of *N,N′-bis* (3-formyl-5-methyl-salicylidene)ethanesulfonic acid dipotassium salt had one "–CH=N–" decompose to –CHO, and the ligand (L) is 2-[(3-formyl-5-methyl-2-hydroxy-benzylidene)-amino]ethanesulfonic acid anion not *N,N′-bis*(3-formyl-5-methyl-salicylidene)ethanesulfonic acid anion, dissimilar to that observed for $[Co(C_{13}H_{16}N_2O_7S_2)(H_2O)_3]_2 \cdot H_2O$ [13]. In the crystal structure of $[Co(C_{13}H_{16}N_2\ O_7S_2)(H_2O)_3]_2 \cdot H_2O$, the ligand ($C_{13}H_{16}N_2O_7S_2$) was *N,N′-bis*(3-formyl-5-methyl-salicylidene)ethanesulfonic acid anion, and the two taurine Schiff-base groups were retained, but only one coordinated with cobalt(II) to form a mononuclear cobalt(II) complex. The title complexes in this contribution were the binuclear. Second, the O atoms from sulfonic groups coordinate with Co(II) for $[Co(C_{13}H_{16}N_2O_7S_2)(H_2O)_3]_2 \cdot H_2O$ but not with Cu(II) or Ni(II) for the title complexes.

2.2.2. Synthesis of 1. A solution of $CuSO_4$ (0.08 g, 0.5 mmol) in methanol-water (1 : 1, 10 mL) was added to solution of *N,N′-bis*(3-formyl-5-methyl-salicylidene)ethanesulfonic acid dipotassium salt (0.2433 g, 0.5 mmol) in methanol-water (4 : 1, 25 mL) under stirring. The mixture was stirred at 323 K for 12 h. Subsequently, the reagents were filtered. The resulting solution was left at room temperature; green crystals were obtained after 8 d and identified as $[Cu_2(C_{11}H_{11}NO_5S)_2(H_2O)_4] \cdot 5H_2O$, mp: 279.6–279.7°C. Found (%): C, 31.13; H, 4.75; N, 3.32; S, 7.46. Anal. Calcd (%) for $C_{22}H_{40}Cu_2N_2O_{19}S_2$: C, 31.92; H, 4.88; N, 3.38; S, 7.75. IR (cm^{-1}): for SO_3^-: 1185.70(s), 1034.82(s); for C=O: 1648.84(s); for C=N: 1627.81(s); for benzene group and conjugation benzene group with C=O: 1601.53(s), 1544.42(s), 1446.48(s); for water O–H: 3460.57(vs) (vs: very strong; s: strong).

2.2.3. Synthesis of 2. A solution of $NiCl \cdot 6H_2O$ (0.1290 g, 0.5 mmol) in ethanol-water (or acetonitrile-water) (1 : 1, 10 mL) was added to another solution of *N,N′-bis* (3-formyl-5-methyl-salicylidene)ethanesulfonic acid dipotassium salt (0.2433 g, 0.5 mmol) in ethanol-water (or acetonitrile-water) (4 : 1, 25 mL) under stirring at 323 K for 7 h. Following filtration, the resulting solution was left at room temperature giving green crystals after some days, identified as $[Ni_2(C_{11}H_{11}NO_5S)_2(H_2O)_4] \cdot 2H_2O$. Found (%): C, 34.42; H, 4.46; N, 3.65; S, 8.09. Anal. Calcd (%) for $C_{22}H_{34}Ni_2N_2O_{16}S_2$: C, 34.58; H, 4.48; N, 3.67; S, 8.39. IR (cm^{-1}): for SO_3^-: 1174.58(s), 1040.67(s); for C=O: 1638.97(s); for C=N: 1626.64(s); for benzene group and conjugation benzene group with C=O: 1551.60(s), 1451.74(m); for water O–H: 3451.58(vs) (m: medium).

2.3. *Structural determination and refinement*

Data were collected on a Bruker P_4 diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K using an ω-scan mode, and reduced with Bruker SHELXTL. The structure was solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined by full-matrix least-squares techniques on F^2 using SHELX-97 (Sheldrick, 1997) for all reflections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. Crystallographic details for the structure determination are presented

in table 1. Selected bond distances and angles are listed in tables 2 and 3. Hydrogen bond lengths and angles are listed in tables 4 and 5. The molecular structure of **1** is illustrated in figure 1, the packing diagram illustrated in figure 2, and water-sulfonic clusters and water clusters in figure 3. The molecular structure of **2** is illustrated in figure 4, the packing diagram and the π–π stacking diagram in figures 5–8.

2.4. *Materials for antibacterial studies*

Taurine, $CuSO_4$ (A.R.), $NiCl_2 \cdot 6H_2O$(A.R.), the dipotassium salt of taurine Shiff base ($K_2(C_{13}H_{16}O_7N_2S_2 \cdot CH_3OH$), **1** ($[Cu_2(C_{11}H_{11}NO_5S)_2(H_2O)_4]\cdot 5H_2O$), **2** ($[Ni_2(C_{11}H_{11}NO_5S)_2(H_2O)_4] \cdot 2H_2O$) and dimethylsulfoxide (A.R.).

Penicillin (20050202; a piece of circularity article (diameter, 6 mm) contains 10 ug penicillin), streptomycin (20050303; a piece of circularity article (diameter, 6 mm) contains 10 μg streptomycin), β-hemolytic streptococcus (32210), *S. aureus* (26001), *E. coli* (44104), *P. aeruginosa* (10211) (0050202, 20050303, 32210, 26001, 44104 and 10211 are pharmic batch marks).

Common agar-agar flat, serum of the rabbit (10%) agar-agar flat.

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

Parameters	**1**	**2**
Empirical formula	$C_{22}H_{40}Cu_2N_2O_{19}S_2$	$C_{22}H_{34}N_2Ni_2O_{16}S_2$
Formula weight	827.80	764.08
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)		
a	16.8902(12)	11.399(2)
b	11.2829(6)	19.985(3)
c	17.4249(11)	7.3694(10)
α	90	90
β	106.709(4)	108.664(7)
γ	90	90
V (Å^3)	3180.5(3)	1590.6(4)
Z, D_{Calcd} (Mg m^{-3})	4, 1.729	2, 1.604
Absorption coefficient (mm^{-1})	1.554	1.388
F(000)	1712	800
Crystal size (mm^3)	0.2000 × 0.3500 × 0.4500	0.1000 × 0.2500 × 0.2500
θ range for data collection	3.0 – 25.1°	2.1 – 25.0°
Limiting indices	$-20 \le h \le 19$ $-13 \le k \le 12$ $-20 \le l \le 20$	$-11 \le h \le 13$ $-23 \le k \le 23$ $-8 \le l \le 7$
Reflections collected	19691	9889
Independent reflections	5590 ([R(int) = 0.023]	2810([R(int) = 0.0200]
Observed data	5239 [$I > 2\sigma(I)$]	2771 [$I > 2\sigma(I)$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Nref/Npar/Nres	5653/424/0	2810/208/0
Final R, wR, S [$I > 2\sigma(I)$]	$R_1 = 0.0519$, $wR_2 = 0.1349$, $S = 1.131$	$R_1 = 0.1859$, $wR_2 = 0.4346$, $S = 1.157$
Final R, wR, S (all data)	$R_1 = 0.0507$, $wR_2 = 0.1373$, $S = 1.131$	$R_1 = 0.1867$, $wR_2 = 0.4348$, $S = 1.157$

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

Cu(1)–O(1)	2.038(3)	Cu(2)–O(4)	2.030(3)	S(1)–O(8)	1.457(4)
Cu(1)–O(2)	2.031(3)	Cu(2)–O(3)	2.027(3)	S(1)–O(9)	1.457(3)
Cu(1)–O(3)	2.017(2)	Cu(2)–O(2)	2.014(2)	S(1)–O(10)	1.440(3)
Cu(1)–N(1)	2.019(3)	Cu(2)–N(2)	2.025(3)	S(2)–O(5)	1.403(6)
Cu(1)–O(3W)	2.087(3)	Cu(2)–O(4W)	2.098(3)	S(2)–O(6)	1.444(8)
Cu(1)–O(2W)	2.111(3)	Cu(2)–O(1W)	2.094(3)	S(2)–O(7)	1.421(6)
O(3)–Cu(1)–N(1)	91.92(12)	O(3)–Cu(1)–O(2W)	91.26(12)	O(2)–Cu(2)–O(4)	169.14(11)
O(3)–Cu(1)–O(2)	79.76(10)	N(1)–Cu(1)–O(2W)	89.37(13)	O(2)–Cu(2)–O(1W)	95.01(14)
O(2)–Cu(1)–O(1)	88.73 (11)	O(2)–Cu(1)–O(2W)	90.15(11)	N(2)–Cu(2)–O(1W)	85.45(14)
N(1)–Cu(1)–O(1)	99.60(13)	O(1)–Cu(1)–O(2W)	89.15(13)	O(3)–Cu(2)–O(1W)	92.86(12)
N(1)–Cu(1)–O(2)	171.65(12)	O(3W)–Cu(1)–O(2W)	174.50(13)	O(4)–Cu(2)–O(1W)	86.33(15)
O(3)–Cu(1)–O(1)	168.48(11)	O(2)–Cu(2)–N(2)	91.56(12)	O(2)–Cu(2)–O(4W)	90.46(12)
O(3)–Cu(1)–O(3W)	94.05(12)	O(2)–Cu(2)–O(3)	79.92(10)	N(2)–Cu(2)–O(4W)	91.19(12)
N(1)–Cu(1)–O(3W)	89.03(12)	O(3)–Cu(2)–O(4)	89.25(11)	O(3)–Cu(2)–O(4W)	91.26(10)
O(2)–Cu(1)–O(3W)	92.19(11)	N(2)–Cu(2)–O(4)	99.29(13)	O(4)–Cu(2)–O(4W)	88.90(13)
O(1)–Cu(1)–O(3W)	85.93(13)	N(2)–Cu(2)–O(3)	171.16(12)	O(1W)–Cu(2)–O(4W)	173.65(13)
Cu(1)–O(2)–Cu(2)	100.15(10)	Cu(1)–O(3)–Cu(2)	100.16(10)	O(8)–S(1)–O(9)	112.4(2)

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Ni(1)–O(2)	2.035(15)	Ni(1)–N(1)	2.028(19)	S(1)–O(3)	1.43(2)
Ni(1)–O(2A)#*a*	2.012(14)	Ni(1)–O(1W)	1.91(2)	S(1)–O(4)	1.47(2)
Ni(1)–O(1A)#*a*	2.040(18)	Ni(1)–O(2W)	2.128(14)	S(1)–O(5)	1.41(2)
N(1)–Ni(1)–O(2)	92.1(7)	O(2)–Ni(1)–O(1A)#*a*	168.2(7)	O(2A)#*a*–Ni(1)–O(2W)	83.6(8)
N(1)–Ni(1)–O(1A)#*a*	98.7(7)	O(1W)–Ni(1)–O(2A)#*a*	86.8(8)	N(1)–Ni(1)–O(2W)	93.8(7)
O(2A) #*a*–Ni(1)–O(1A)#*a*	89.4(6)	O(1W)–Ni(1)–O(2)	83.2(9)	O(2)–Ni(1)–O(2W)	90.8(8)
O(2)–Ni(1)–O(2A) #*a*	80.0(6)	O(1W)–Ni(1)–N(1)	95.2(8)	O(1A)#*a*–Ni(1)–O(2W)	93.1(8)
O(2A) #*a*–Ni(1)–N(1)	171.6(7)	O(1W)–Ni(1)–O(1A)#*a*	91.1(8)	O(1W)–Ni(1)–O(2W)	169.4(8)
Ni(1)–O(2)–Ni(1A)#*a*	100.0(5)	O(3)–S(1)–O(5)	113.0(14)	O(3)–S(1)–O(4)	106.9(12)

Translation of symmetry code to equivalent position $a = [3557] = -x, -y, 2-z$.

Table 4. Hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry (Å)
O(1W)–H(1WB)–O(9W)#*c*	0.8503	1.9856	2.793(8)	158.30	2656
O(1W)–H(1#)–O(5W)	0.8493	1.8856	2.727(5)	170.38	
O(2W)–H(2WB)–O(5W)	0.8499	2.1007	2.860(5)	148.43	
O(2W)–H(2WA)–O(6W)#*d*	0.8502	1.8631	2.696(9)	165.99	3676
O(3W)–H(3WB)–O(9)#*h*	0.8500	1.9606	2.792(5)	165.82	2545
O(3W)–H(2#)–O(8)#*i*	0.8502	1.9537	2.785(4)	165.46	4575
O(4W)–H(4WB)–O(8)#*i*	0.8499	2.0622	2.910(5)	174.79	4575
O(4W)–H(4WA)–O(9)#*h*	0.8494	1.9559	2.771(4)	160.53	2545
O(5W)–H(3#)–O(5)#*d*	0.8510	1.9471	2.778(7)	164.97	3676
O(5W)–H(5WB)–O(7)#*p*	0.8499	1.9817	2.813(7)	165.78	4564
O(7W)–H(4#)–O(8W)#*t*	0.8530	2.5889	3.10(5)	119.74	3666
O(7W)–H(7WB)–O(9W)#*u*	0.8474	2.5381	3.30(3)	150.81	2646
O(8W)–H(8WB)–O(7W)#*t*	0.8620	2.2542	3.10(5)	167.68	3666
O(9W)–H(5#)–O(7W)#*c*	0.8510	2.4748	3.30(3)	164.86	2656
O(9W)–H(6#)–O(7)	0.8495	2.4320	3.090(8)	134.76	
C(19)–H(19A)–O(10)#*l*	0.9299	2.4586	3.362(5)	164.03	3575
C(21)–H(21B)–O(1)	0.9698	2.5345	3.257(4)	131.26	
C(22)–H(22B)–O(4W)#*p*	0.9598	2.4881	3.401(6)	158.93	4564

Translation of symmetry code to equivalent position: $c = [2656.00] = 1-x, 1/2+y, 3/2-z$; $d = [3676.00] = 1-x, 2-y, 1-z$; $h = [2545.00] = -x, -1/2+y, 1/2-z$; $i = [4575.00] = x, 5/2-y, 1/2+z$; $l = [3575.00] = -x, 2-y, -z$; $p = [4564.00] = x, 3/2-y, -1/2+z$; $t = [3666.00] = 1-x, 1-y, 1-z$; $u = [2646.00] = 1-x, -1/2+y, 3/2-z$.

Table 5. Hydrogen bond lengths (Å) and angles (°) for **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry (Å)
O(2W)–H(2WA)–O(2W)#*f*	0.8506	2.3993	3.13(2)	143.76	3556
O(2W)–H(2WA)–O(1W)#*a*	0.8506	2.2697	2.76(3)	116.40	3557
O(1W)–H(1WB)–O(3W)#*b*	0.8502	2.2781	3.02(3)	145.72	1546
O(3W)–H(3WB)–O(1W)#*t*	0.8498	2.2503	3.02(3)	150.46	1564
O(4W)–H(4WB)–O(5)#*k*	0.8531	2.3417	2.96(4)	129.18	4555
O(4W)–H(4WA)–O(5)	0.8469	2.3426	2.87(4)	121.01	
C(3)–H(3A)–O(4W)#*p*	0.9304	2.5819	3.47(3)	159.53	1455
C(5)–H(5A)–O(3W)#*l*	0.9650	2.4811	3.41(4)	162.42	2546
C(11)–H(11A)–O(1)#*a*	0.9710	2.4776	3.21(3)	131.94	3557

Translation of symmetry code to equivalent position: $a=[3557]=-x,\ -y,\ 2-z$; $b=[1546]=x,\ -1+y,\ 1+z$; $f=[3556]=x,\ -1+y,\ 1+z$; $k=[4555]=-x,\ -y,\ 1-z$; $l=[2546]=-x,\ -1/2+y,\ 3/2-z$; $p=[1455]=-1+x,\ y,\ z$; $t=[1564]=x,\ 1+y,\ -1+z$

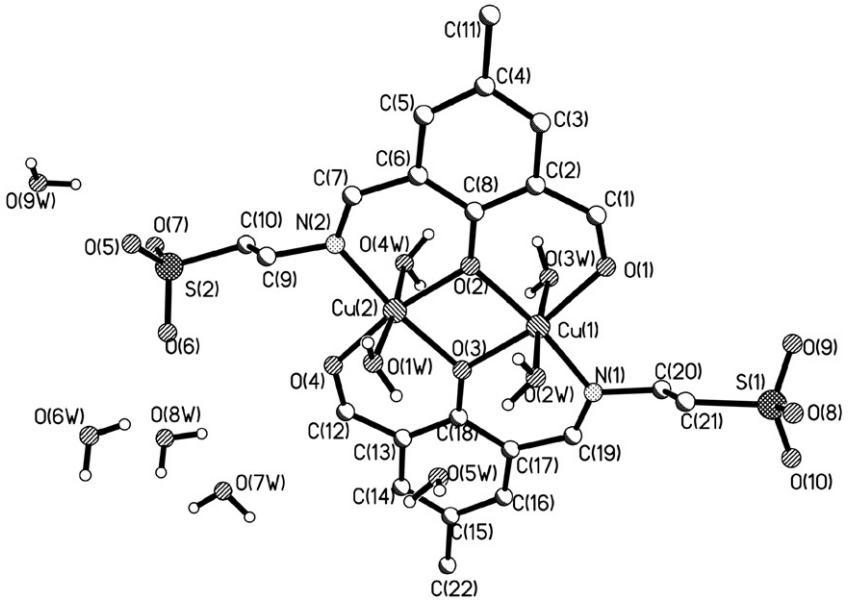

Figure 1. Crystal structure of **1**. Displacement ellipsoids are drawn at 50% probability level. Some H atoms are omitted for clarity.

2.5. *Experiment method for antibacterial studies*

Solutions of taurine ($0.125\,g\cdot mL^{-1}$), the dipotassium salt of taurine Shiff base ($0.08\,g\cdot mL^{-1}$) in water, $CuSO_4$ and $NiCl_2$ in water and the title complexes in dimethylsulfoxide with c_1 ($0.08\,g\cdot mL^{-1}$), c_2 ($0.04\,g\cdot mL^{-1}$), c_3 ($0.02\,g\cdot mL^{-1}$), c_4 ($0.01\,g\cdot mL^{-1}$), c_5 ($0.005\,g\cdot mL^{-1}$) and c_6 ($0.0025\,g\cdot mL^{-1}$), respectively, were prepared for the antibacterial properties using the Kirby-Bauer method of agar diffusion test [22]. After these solutions were taken into ampoules and disinfected by pressure steam at 380 K for 0.5 h, they were put into the aseptic room to be tested for antibacterial activities when they were cool: First, using the aseptic cotton *S. aureus*, *E. coli* and *P. aeruginosa* were placed onto the common agar-agar flat and β-hemolytic

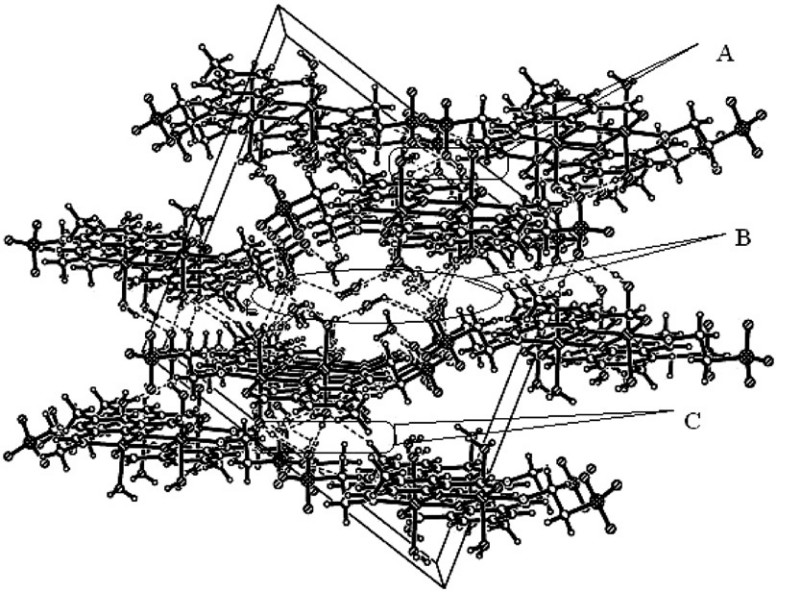

Figure 2. Crystal packing diagram of **1** in a cell along the *a* axis. Some hydrogen atoms are omitted for clarity.

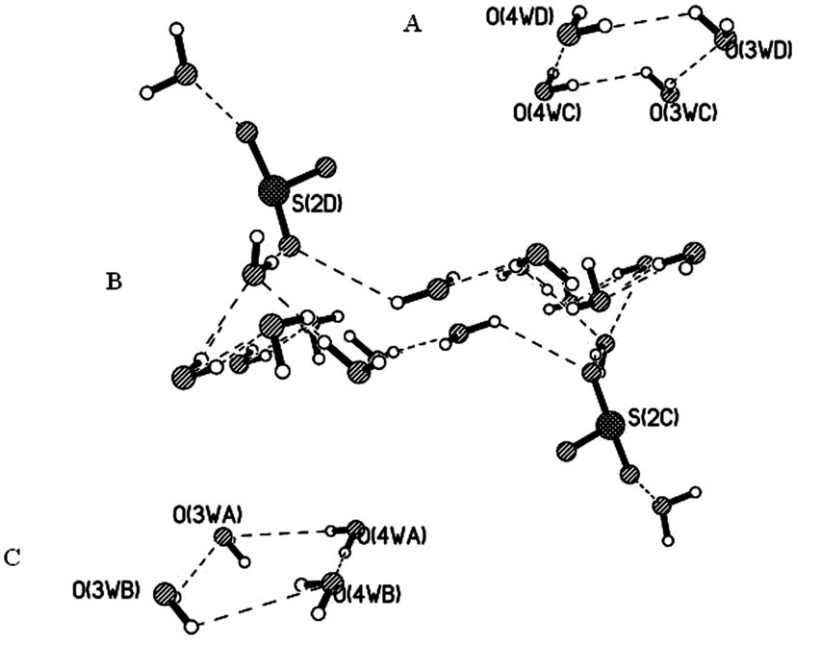

Figure 3. Water-sulfonic clusters and water clusters of **1**. Displacement ellipsoids are drawn at 50% probability level.

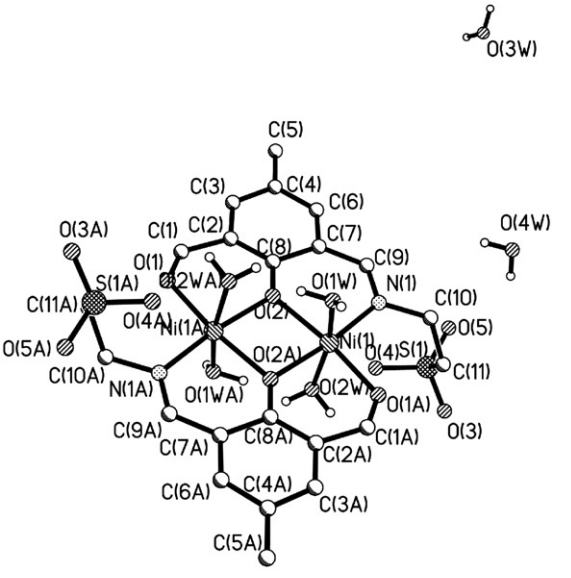

Figure 4. Crystal structure of **2**. Displacement ellipsoids are drawn at 50% probability level. Some H atoms are omitted for clarity.

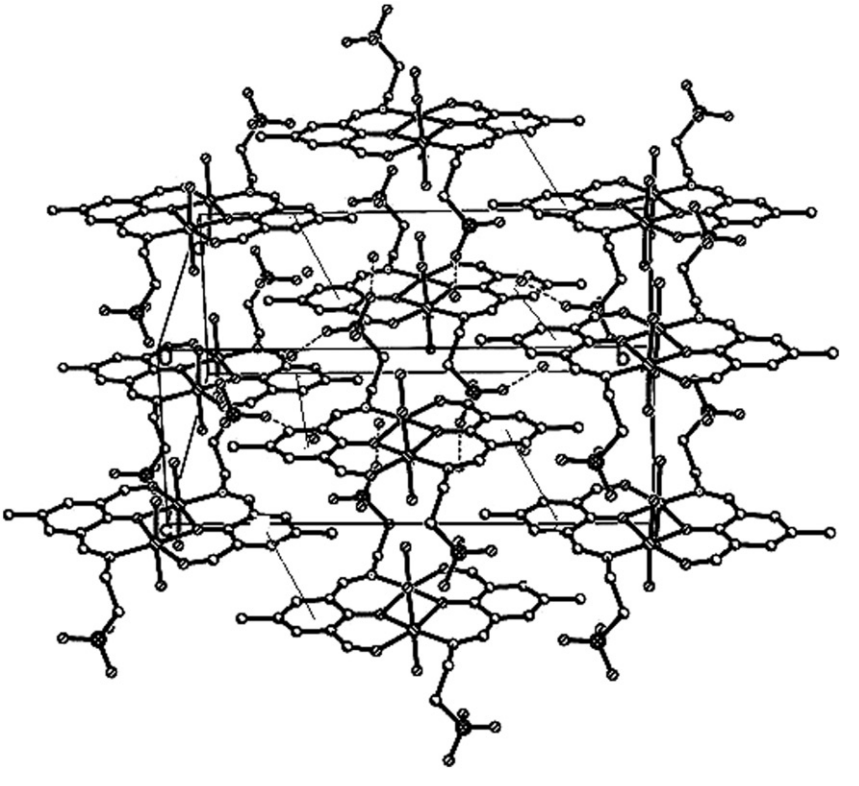

Figure 5. Crystal packing diagram along the *a* axis of **2** (hydrogen atoms and free water molecules are omitted for clarity). Displacement ellipsoids are drawn at 50% probability level.

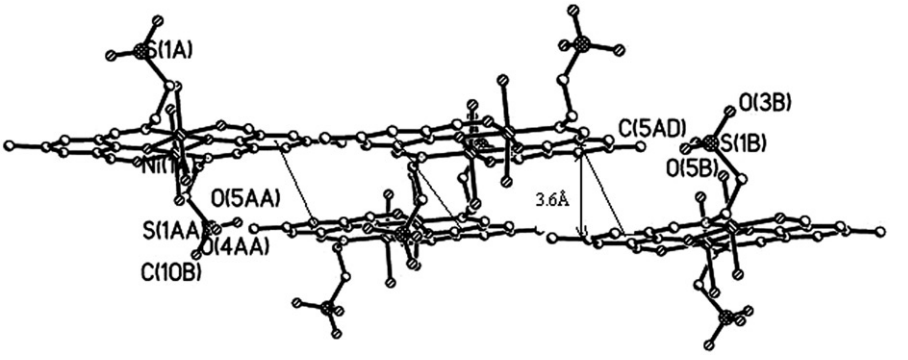

Figure 6. The π–π stacking of intermolecules ellipsoids of 50% displacement (hydrogen atoms are omitted for clarity).

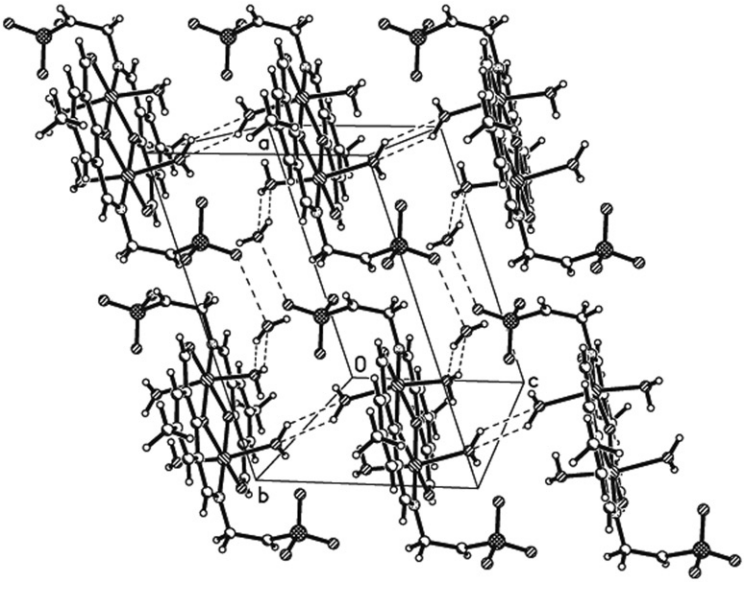

Figure 7. Crystal packing diagram along the *b* axis of **2**. Displacement ellipsoids are drawn at 50% probability level.

streptococcus onto the agar-agar flat with serum of rabbit (10%). Second, aseptic circularity filter article (diameter, 6 mm) with those solutions were put on these flats and taken to constant temperature at 310 K for 24 h; Then, the diameters of antibacterial rings were measured (table 6).

3. Results and discussion

3.1. *Structure of* $[Cu_2(C_{11}H_{11}NO_5S)_2(H_2O)_4]\cdot 5H_2O$

X-ray crystallography reveals that **1** is a binuclear complex with five crystal waters. The crystal structure does not correspond to a planar species with a Cu_2O_2 plane which

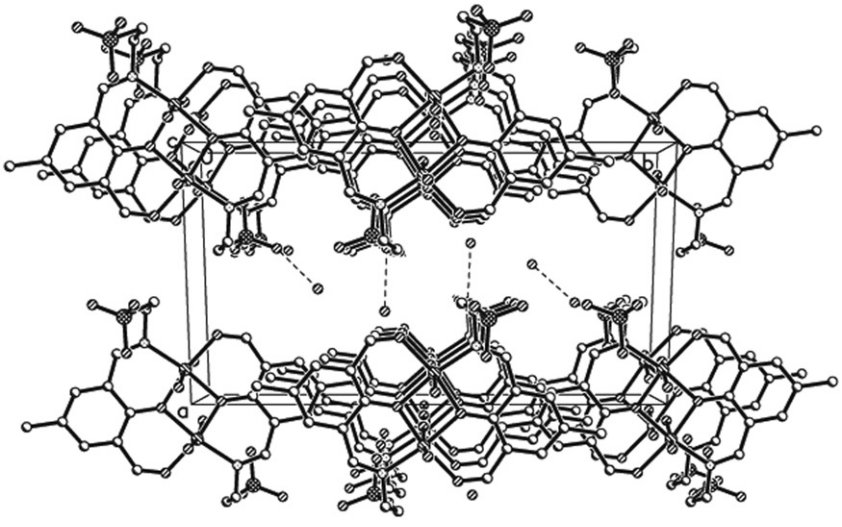

Figure 8. Crystal packing diagram along the *c* axis of **2**. Displacement ellipsoids are drawn at 50% probability level (hydrogen atoms are omitted for clarity).

Table 6. The average dimension of antibacterial rings (mm).

1

bacteria	**I**	**II**	c_1	c_2	c_3	c_4	c_5	c_6	III	IV	V
1	–	–	28	25	20	18	15	–	30	16	–
2	–	12	26	21	17	15	12	–	42	21	–
3	–	19	24	20	18	15	12	–	12	20	–
4	–	–	10	9	–	–	–	–	12	13	–

2

bacteria	**I**	**II**	c_1	c_2	c_3	c_4	c_5	c_6	III	IV	V
1	–	–	31	30	24	20	15	13	30	16	–
2	–	12	–	–	–	–	–	–	42	21	–
3	–	19	–	–	–	–	–	–	12	20	–
4	–	–	–	–	–	–	–	–	12	13	–

	$CuSO_4$						$NiCl_2$					
bacteria	c_1	c_2	c_3	c_4	c_5	c_6	c_1	c_2	c_3	c_4	c_5	c_6
1	25	22	18	14	11	7	28	25	16	11	7	–
2	28	23	16	7	–	–	28	18	13	8	–	–
3	26	21	13	11	7	–	25	21	16	8	7	–
4	18	14	11	9	7	–	26	21	20	14	7	–

1: β-hemolytic streptococcus; 2: *S. aureus*; 3: *E. coli*; 4: *P. aeruginosa*; I: taurine; II: dipotassium salt of taurine Shiff base; III: penicillin; IV: streptomycin; V: dimethylsulfoxide

presents an inversion center, and is not similar to the one from the literature [2, 5] (figure 1).

The geometry around each copper(II) can be described as a slightly distorted and elongated octahedron. The Cu(1) is coordinated by a nitrogen [N(1)] and an oxygen atom [O(3)] from one ligand anion, two oxygen atoms [O(1), O(2)] from the same ligand,

and two oxygen atoms [O(2W), O(3W)] from two water molecules to form an elongated octahedron with oxygens [O(2W), O(3W)] at apical positions subtending an O(2W)–Cu(1)–O(3W) angle of 174.50(13)° [O(1W)–Cu(2)–O(4W) angle of 173.65(13)° is for Cu(2) cation]. The sum of bond angles O(3)–Cu(1)–N(1) (91.92°), O(3)–Cu(1)–O(2) (79.76°), O(2)–Cu(1)–O(1) (88.73°) and N(1)–Cu(1)–O(1) (99.60°) is 360.0°, which means that O(1), O(2), O(3) and N(1) are coplanar. The equatorial ligands of Cu(1) atom are planar with the mean deviation of the atoms from this plane being 0.0000 Å and the dihedral angles being 0.7° and 0.3° between the Cu(1)–N(1)–O(3) and Cu(1)–O(3)–O(2) planes and the Cu(1)–N(1)–O(3) and Cu(1)–N(1)–O(1) planes, respectively. The interatomic distances of Cu(1)–O(1), Cu(1)–O(2), Cu(1)–O(3), Cu(1)–N(1), Cu(1)–O(3W) and Cu(1)–O(2W) are 2.038(3), 2.031(3), 2.017(2), 2.019(3), 2.087(3) and 2.111(3) Å, respectively. The Cu(1)–O[O(1), O(2), O(3)] and Cu(1)–N(1) distances are shorter than those of Cu(1)–O[O(2W), O(3W)] because O(2W) and O(3W) are at the apical positions with Jahn–Teller distortion. The equatorial ligand distances with copper are longer than those of other complexes with the range of 1.922 ~ 2.002 Å observed [2, 5], and the distances of the axial ligands with copper are shorter with the range of 2.287 ~ 2.712 Å, which means that the Jahn-Teller distortion of **1** is weaker than those of previous complexes.

Reported complexes present different geoometrical parameters: a copper-copper separation of 3.087 Å and a phenoxo bridge of 102.86° for $[Cu_2L(acetate)_2(H_2O)_2]$ [2], a copper-copper separation of 2.968 Å and a phenoxo bridge of 99.40° for $[Cu(H_2sb)(CCl_3CO_2)_2]_2$, and a copper-copper separation of 3.001 Å and a phenoxo bridge of 99.9° for $[Cu(H_2sb)(ClO_4)(C_2H_5OH)_2]_2$ [5], as compared to 3.101 Å (Cu···Cu) and 100.15° (Cu–O–Cu) for **1**. Magnetic properties are usually ascribed to the Cu–O–Cu angle. Unfortunately, magnetic data could not be collected.

Water-sulfonic clusters [figure 3(b)] and two discrete water clusters $(H_2O)_4$ [figures 3(a) and 3(c)] exist between adjacent sheets (figure 2). The water-sulfonic cluster, different from the report [21], is formed by two sulfonic groups and eighteen water molecules involving crystal water and coordinated water *via* hydrogen bonds (O–H···O). Two discrete water clusters $(H_2O)_4$ are formed by coordinated water hydrogen bonds (O–H···O). From the packing diagram, coterminous molecules are linked by hydrogen bonds O(W)–H(W)···O(W) and O(W)–H(W)···O (from sulfonic groups) to generate a three-dimensional network structure.

3.2. *Structure of* $[Ni_2(C_{11}H_{11}NO_5S)_2(H_2O)_4]\cdot 2H_2O$

X-ray crystallography reveals that **2** is also binuclear with two crystal waters with a symmetrical structure; the symmetrical center is the crossover point of the lines O(2)O(2A) and Ni(1)Ni(1A). The crystal structure shows a planar Ni_2O_2 with an inversion center (figure 4), dissimilar to **1**. The geometry around each nickel(II) center can be described as slightly distorted octahedral. The basal plane is similar to **1**, with Ni(1)–O(1A), Ni(1)–O(2A), Ni(1)–O(2) and Ni(1)–N(1) interatomic distances being 2.040(18), 2.012(14), 2.035(15), 2.028(19) Å, respectively. The Ni–O (phenolate oxygen) (2.012, 2.035 Å) distances are slightly different from those of Cu–O (phenolate oxygen) (2.017, 2.031) for **1**. The axial ligands are two water molecules [Ni(1)–O(1W), 1.91(2) Å; Ni(1)–O(2W), 2.128(14) Å], subtending a O(1W)–Ni(1)–O(2W) angle of 169.4(8)°. The two nickel atoms are separated by 3.099 Å with Ni–O–Ni bridge angles of 100.0(5)°, slightly different from

$Ni_2L(ClO_4)_2$ with an inversion center and five-coordinated environment with nickel atoms separated by 3.092 Å with the two Ni–O–Ni bridge angles of 100.7(2)° [6].

From the packing diagrams, the two-dimensional network structure is stabilized by offset face-to-face π–π stacking (figure 5) at 3.6 Å (figure 6) along the *bc* plane and by hydrogen bonds O(W)–H(W)···O(W) and O(W)–H(W)···O (from sulfonic groups) along the *ac* plane (figure 7). Molecules are linked by hydrogen bonds and π–π stacking to generate a three-dimensional network structure. A long cavity occupied by crystal hydrogen-bonded water molecules is formed along the ab plane (figure 8).

4. Antibacterial properties

Taurine and dimethylsulfoxide do not show antibacterial activity for β-hemolytic streptococcus, *S. aureus*, *E. coli* and *P. aeruginosa*; the dipotassium salt of taurine Shiff base shows antibacterial activities for *S. aureus* and *E. coli*. Complex **1** shows antibacterial activities for β-hemolytic streptococcus, *S. aureus*, *E. coli* and *P. aeruginosa* with concentration increasing, whereas **2** shows antibacterial activity only for β-hemolytic streptococcus with concentration increasing. Although solutions of $CuSO_4$ and $NiCl_2$ show antibacterial activities with concentration increasing, and are almost as effective antibiotics as **1** and **2**, they are toxic.

The antibacterial activities of **1** and **2** for β-hemolytic streptococcus are stronger than those of the dipotassium salt of taurine Shiff base, the corresponding copper and nickel salts and streptomycin, and near to that of penicillin when they are in $0.08\,g{\cdot}mL^{-1}$. Complex **1** shows antibacterial activities for β-hemolytic streptococcus, *S. aureus* and *E. coli* stronger than for *P. aeruginosa*. The minimal inhibitory concentration of **1** is about $0.005\,g{\cdot}mL^{-1}$, and is similar to that observed [9]. However, the antibacterial activity of **2** is selective only for β-hemolytic streptococcus, not for *S. aureus*, *E. coli* and *P. aeruginosa*. The antibacterial activity for β-hemolytic steptococcus is stronger than $NiCl_2$ with corresponding concentration.

The nickel complex **2** has limited activity, whereas the copper complex **1** has a broad range of activity, offering potential applications in medicine.

Supplementary material

CCDC 663933 contains supplementary crystallographic data for **1** ($[Cu_2(C_{11}H_{11}NO_5S_2)_2(H_2O)_4]\cdot 5H_2O$) and CCDC 663932 contains supplementary crystallographic data for **2** ($[Ni_2(C_{11}H_{11}NO_5S_2)_2(H_2O)_4]\cdot 2H_2O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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