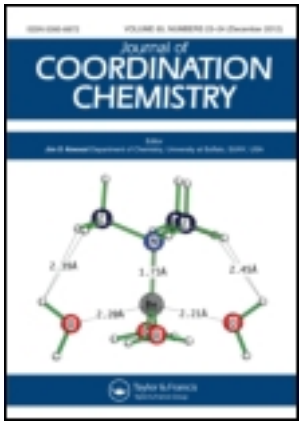

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Syntheses, crystal structures, and antimicrobial activities of nickel(II) and cadmium(II) complexes with 4-methylsulfonyl cinnamate and diamines

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Syntheses, crystal structures, and antimicrobial activities of nickel(II) and cadmium(II) complexes with 4-methylsulfonyl cinnamate and diamines

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Two metal complexes, $[Ni^{II}(mscinn)_2(pda)_2]$ (**1**) and $[Cd^{II}(mscinn)_2(dmeda)_2 \cdot 2H_2O]$ (**2**) (mscinn = 4-methylsulfonyl cinnamate, pda = propane-1,3-diamine, dmeda = N′, N′-dimethylethane-1,2-diamine), were synthesized by reacting 4-methylsulfonyl cinnamate with the diamines and metal salts. Their structures were determined by single-crystal X-ray diffraction analysis. Crystal parameters of **1**: $C_{26}H_{38}N_4NiO_8S_2$, $M = 657.43$, monoclinic, $P2_1/c$, $a = 16.6123(8)$ Å, $b = 8.5956(4)$ Å, $c = 11.2047(5)$ Å, $\beta = 107.423(1)^\circ$, $V = 1526.54(12)$ Å^3, $Z = 2$, $D_{calcd} = 1.430\ g\,cm^{-3}$, $F(000) = 692$, $\mu = 0.825\ mm^{-1}$, $R_1 = 0.0257$, $wR_2 = 0.0669$. Crystal data of **2**: $C_{28}H_{42}CdN_4O_8S_2 \cdot 2(H_2O)$, $M = 775.24$, monoclinic, $P2_1/c$, $a = 9.8278(4)$ Å, $b = 11.6611(5)$ Å, $c = 15.3972(7)$ Å, $\beta = 96.195(1)^\circ$, $V = 1754.26(13)$ Å^3, $Z = 2$, $D_{calcd} = 1.468\ g\,cm^{-3}$, $F(000) = 804$, $\mu = 0.798\ mm^{-1}$, $R_1 = 0.0299$, $wR_2 = 0.0770$. Antimicrobial activities for **1** and **2** against *Escherichia coli*, *Pseudomonas putida*, *Bacillus subtilis*, and *Bacillus cereus* had better antibacterial activity than their parent carboxylic acid against Gram-positive bacteria (*B. subtilis* and *B. cereus*). The cadmium complex of the cinnamate displayed high inhibitory activity with an MIC value of $5\ \mu g\,mL^{-1}$ against *P. putida*, while the nickel complex also exhibited good inhibitory potency with an MIC value of $5\ \mu g\,mL^{-1}$ against *B. subtilis*.

Keywords: 4-Methylsulfonyl cinnamate; Nickel; Cadmium; X-ray analysis

1. Introduction

Cinnamic acid is a natural product found in fragrances used in decorative cosmetics, fine fragrances, shampoos, toilet soaps, and other toiletries as well as in non-cosmetic products such as household cleaners and detergents [1]. In addition, cinnamic acid and its derivatives have attracted interest for their biological activities. These compounds have been reported to have anti-inflammatory and antimicrobial activities against microorganisms such as rumen bacteria or lactobacilli [2–5]. Moreover, anti-inflammatory and antibacterial activities of metal(II) complexes were higher than in the parent carboxylic acids [6–8] and the anti-bacterial effect of some drugs could be enhanced and overcome resistance when they were chelated to a metal [9, 10]. Cd(II), Ni(II), Cu(II), Co(II), Zn(II), etc., can be coordinated with a series of ligands, possessing antibacterial

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activities [11, 12]. It is important to gain knowledge about the structure and bonding relations of the complexes for the preparation of effective anti-microbial species. However, only a few metal complexes with cinnamate derivatives as ligand or co-ligand have been structurally characterized [13–16]. In this work, we prepare a 4-methylsulfonyl cinnamate by reacting 4-(methylsulfonyl)benzaldehyde with malonic acid and then synthesized metal complexes with Ni(II), Cd(II), and organic diamines. Here we report crystal structures of $[Ni^{II}(mscinn)_2(pda)_2]$ (**1**) and $[Cd^{II}(mcinn)_2(dmeda)_2]$ (**2**) (mscinn = 4-methylsulfonyl cinnamate, pda = propane-1,3-diamine, dmeda = N′,N′-dimethylethane-1,2-diamine) and their antimicrobial activities against *Escherichia coli*, *Pseudomonas putida*, *Bacillus subtilis*, and *Bacillus cereus*. The antibacterial activity of **1** and **2** was lower than the parent 4-methylsulfonyl cinnamate against Gram-negative bacteria (*E. coli* and *P. putida*), but they had better antibacterial activity than their parent carboxylic acid against Gram-positive bacteria (*B. subtilis* and *B. cereus*). Especially, the cadmium complex displayed high inhibitory activity with an MIC value of $5\,\mu g\,mL^{-1}$ against *P. putida*, while the nickel complex also exhibited good inhibitory potency with an MIC value of $5\,\mu g\,mL^{-1}$ against *B. subtilis*, indicating that these complexes are potent antimicrobial agents.

2. Experimental

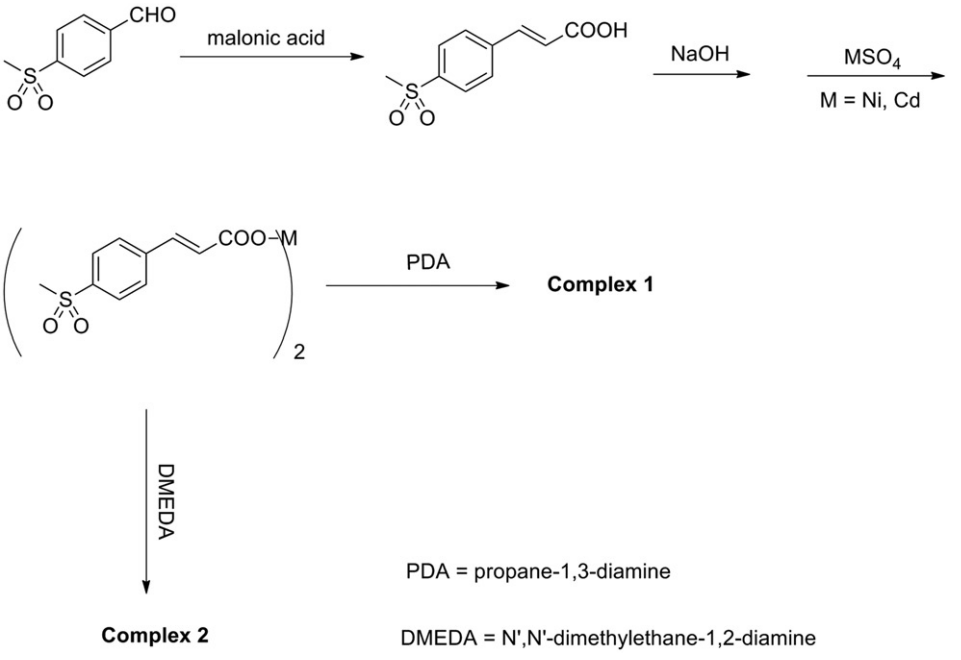
2.1. *General*

All reagents, unless otherwise stated, were purchased as AR grade and used without purification. Elemental analysis was conducted on a Perkin-Elmer 240 C elemental analyzer; IR spectra were recorded ($400–4000\,cm^{-1}$) on a FT-IR Nicolet 5700 spectrometer; ^{1}H-NMR measurement was made on an AV-300 BRUKER spectrometer; UV-Vis spectra were recorded on a UV-3600 spectrophotometer (Shimadzu); ESI mass spectra were obtained on a Mariner System 5304 mass spectrometer; melting points were recorded on a WRS-1B Digital Melting Point Apparatus.

2.2. *Synthesis*

The syntheses of **1** and **2** are outlined in scheme 1.

2.2.1. Synthesis of 4-methylsulfonyl cinnamate. The synthesis is performed according to the literature [17] with modification. Malonic acid (10.5 g, 0.1 mol) and 4-(methylsulfonyl)benzaldehyde (18.4 g, 0.1 mol) in ethanol (50 mL) were added in a 500-mL-round-bottomed flask, fitted with a reflux condenser and a thermometer. Pyridine (5 mL) was then added and the mixture was heated under reflux (90–95°C) for 12 h. The reaction mixture was cooled to 0°C and light-yellow crystals precipitated were separated by filtration and washed four times with 20 mL portions of cold water. The product was dried at 60–70°C. The yield was 18 g (80%) of 4-methylsulfonyl cinnamate, m.p. = 286.8–288.0°C, without further purification for the next synthesis of metal complexes.



Scheme 1. Synthesis of **1** and **2**.

2.2.2. Synthesis of 1. 4-Methylsulfonyl cinnamate (0.01 mol, 2.26 g) and sodium hydroxide (0.4 g) were dissolved in water (30 mL) and then a nickel sulfate solution (0.25 mol L^{-1}, 20 mL) was added dropwise with stirring. The precipitate was collected by filtration and washed thrice with 5 mL portions of cold water. The nickel 4-methylsulfonyl cinnamate was dried at 60–70°C to yield 1.6 g (62.7%) of compound **1**.

The nickel 4-methylsulfonyl cinnamate (0.0511 g, 0.1 mmol) was added to a methanol solution (15 mL) of 1,3-propylene diamine (0.1 mmol, 0.0072 g). The mixture was stirred at room temperature for 1 h to give a clear blue solution. After keeping the solution in air for 7 days, blue block-shaped crystals were formed at the bottom of the vessel on slow evaporation of the solvent. The yield was 42.2%. Anal. Calcd for $C_{26}H_{38}N_4NiO_8S_2$ (%): C, 47.02; H, 5.77; N, 8.44. Found (%): C, 47.38; H, 5.74; N, 7.52. IR (cm^{-1}): 3288.6 ν(NH, stretching), 2926.2 ν(Ar–CH), 1640.7 ν(NH, deformation), 1595.1 $\nu_{as}(COO^-)$, 1556.3 ν(Ar–C=C), 1437.0 ν(Ar–C=C), 1409.9 $\nu_s(COO^-)$, 1320.7 $\nu_{as}(SO_2)$, 1155.2 $\nu_s(SO_2)$, 1021.7 ν(C–N), 541.8 ν(O–M), 440.3 ν(N–M). MS (ESI): 658.4 ($[M+H]^+$). UV-Vis (DMSO, λ_{max} (nm)): 221, 277.

2.2.3. Synthesis of 2. Complex **2** was synthesized analogously to that of **1** by using cadmium 4-methylsulfonyl cinnamate instead of nickel 4-methylsulfonyl cinnamate and employing N′,N′-dimethylethane-1,2-diamine instead of 1,3-propylene diamine. Colorless block-shape crystals were obtained at the bottom of the vessel on slow evaporation of the solvent. The yield is 48.1%. Anal. Calcd for $C_{28}H_{42}CdN_4O_8S_2 \cdot 2(H_2O)$ (%): C, 46.06; H, 6.63; N, 7.67. Found (%): C, 46.25; H, 6.58; N, 7.43.

Table 1. Crystallographic data and details of diffraction experiments for **1** and **2**.

	1	**2**
Empirical formula	$C_{26}H_{38}N_4NiO_8S_2$	$C_{28}H_{42}CdN_4O_8S_2{\cdot}2(H_2O)$
Color	Blue	Colorless
Formula weight	657.43	775.24
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	16.6123(8)	9.8278(4)
b	8.5956(4)	11.6611(5)
c	11.2047(5)	15.3972(7)
α	90	90
β	107.423(1)	96.195(1)
γ	90	90
Volume (Å^3), *Z*	1526.54(12), 2	1754.26(13), 2
F(000)	692	804
Calculated density (g cm^{-3})	1.4827(1)	1.4677(1)
Absorption coefficient (mm^{-1})	0.825	0.798
Temperature (K)	296(2)	296(2)
Reflections collected	2588	3233
Independent reflection	2433	2959
Refined parameters	188	208
θ range for data collection (°)	2.7–25.0	2.7–25.0
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0257$, $wR_2 = 0.0657$	$R_1 = 0.0299$, $wR_2 = 0.0740$
R indices (all data)	$R_1 = 0.0271$, $wR_2 = 0.0669$	$R_1 = 0.0328$, $wR_2 = 0.0770$
Goodness-of-fit on F^2	1.03	1.07
Largest difference peak and hole (e Å^{-3})	0.33 and −0.21	0.82 and −0.40

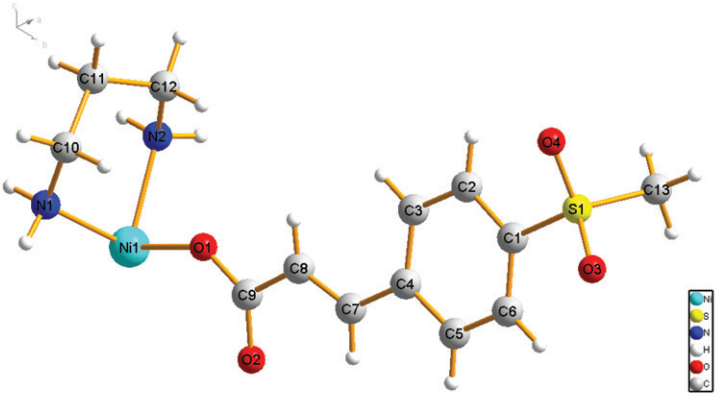
^{1}H-NMR (DMSO-d_6, δ (ppm)): 7.842–7.914 (m, 4H, Ar–H), 7.456 (d, 1H, CH=), 6.716 (d, 1H, CH=), 3.269 (s, 3H, –SO_2–CH_3), 2.421–2.730 (m, 4H, –CH_2–), 2.275 (s, 6H, −CH_3); IR (KBr, ν (cm^{-1})): 3420.9 ν(OH, water) 3264.9 ν(NH, stretching), 2925.6 ν(Ar–CH), 1644.1 ν(NH, deformation), 1545.6 ν_{as}(COO^-), 1411.4 ν(Ar–C=C), 1393.7 ν_s(COO^-), 1305.7 ν_{as}(SO_2), 1183.4 ν(C–N), 1149.5 ν_s(SO_2), 535.7 ν(O–M), 430.2 ν(N–M). MS (ESI): 758.3 ($[M + H]^+$). UV-Vis (DMSO, λ_{max} (nm)): 223, 278.

2.3. *Structure determination*

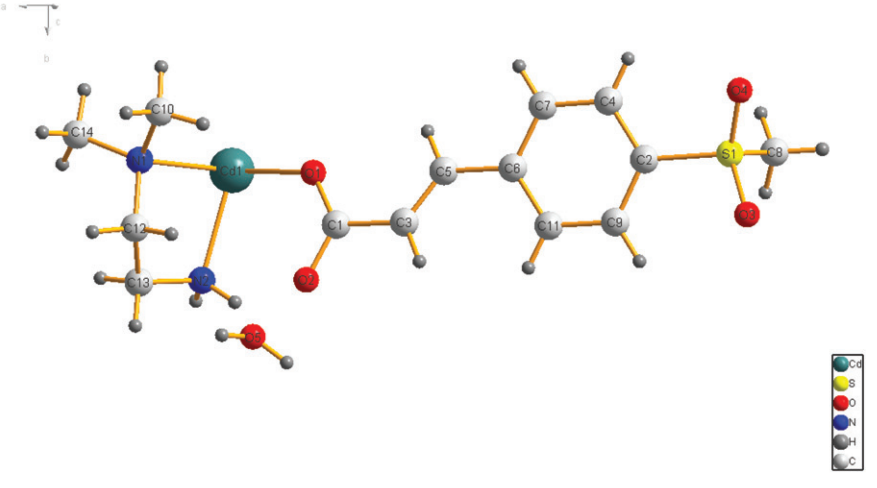
The data were collected on a Bruker D8 VENTURE PHOTON diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the Genenic omega scan technique. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares with Bruker's SHELXL-97 program [18]. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. Experimental details for X-ray data collection of **1** and **2** are presented in table 1. For further details on the crystal structure investigations of **1** and **2**, see the section "Supplementary material."

2.4. *Antimicrobial activity*

The antibacterial activities of the compounds were tested against *E. coli*, *P. putida*, *B. subtilis*, and *B. cereus* using the Mueller–Hinton medium (MH medium: casein



Complex **1**



Complex **2**

Figure 1. The structure of **1** and **2**.

hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 2.0 g, distilled water 1000 mL). The MICs of the test compounds were determined by a colorimetric method using the dye 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl trtrazolium bromide (MTT) [19]. A stock solution of the synthesized compound (50 μg mL^{-1}) in DMSO was prepared and graded quantities of the test compounds were incorporated in a specified quantity of sterilized MH medium. A specified quantity of the medium containing the test compound was poured into microtitration plates. Suspension of the microorganism was prepared to contain approximately 10^5 cfu mL^{-1} and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37°C for *E. coli* and *B. subtilis*, at 30°C for *P. putida*, and *B. cereus* for 24 h. After the MICs were visually determined on each microtitration plate, 50 mL of Phosphate Buffered Saline (PBS 0.01 $molL^{-1}$, pH 7.4, 2.9 g of $Na_2HPO_4 \cdot 12H_2O$, 0.2 g of KH_2PO_4, 8.0 g of NaCl, 0.2 g of KCl, 1000 mL of distilled water) containing 2 $mgmL^{-1}$ of MTT was added to each well. Incubation was continued at room temperature for 4–5 h.

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

Ni(1)–O(1)	2.0969(12)	C(1)–C(2)	1.381(2)
Ni(1)–N(1)	2.1124(15)	C(1)–C(6)	1.375(3)
Ni(1)–N(2)	2.1040(14)	C(2)–C(3)	1.377(3)
S(1)–O(3)	1.4247(17)	C(3)–C(4)	1.390(2)
S(1)–O(4)	1.4245(15)	C(4)–C(5)	1.388(2)
S(1)–C(1)	1.7680(18)	C(4)–C(7)	1.464(2)
S(1)–C(13)	1.744(3)	C(5)–C(6)	1.381(3)
O(1)–C(9)	1.256(2)	C(7)–C(8)	1.318(2)
O(2)–C(9)	1.245(2)	C(8)–C(9)	1.492(2)
N(1)–C(10)	1.477(3)	C(10)–C(11)	1.511(3)
N(2)–C(12)	1.475(2)	C(11)–C(12)	1.508(2)
O(1)–Ni(1)–N(1)	90.64(6)	Ni(1)–O(1)–C(9)	132.37(12)
O(1)–Ni(1)–N(2)	88.88(5)	Ni(1)–N(1)–C(10)	117.65(11)
N(1)–Ni(1)–N(2)	86.06(6)	Ni(1)–N(2)–C(12)	118.24(11)
O(3)–S(1)–O(4)	118.33(10)	S(1)–C(1)–C(2)	119.36(13)
O(3) –S(1)–C(1)	108.34(9)	S(1)–C(1)–C(6)	120.35(13)
O(3) –S(1)–C(13)	108.52(12)	C(2)–C(3)–C(4)	121.42(17)
O(4)–S(1)–C(1)	108.18(8)	C(3)–C(4)–C(5)	117.85(16)
O(4)–S(1)–C(13)	107.96(12)	C(3)–C(4)–C(7)	121.83(15)
C(1) –S(1)–C(13)	104.67(11)	O(1)–C(9)–O(2)	125.50(16)
C(2)–C(1)–C(6)	120.29(17)	N(1)–C(10)–C(11)	111.49(17)

The content of each well was removed, and 100 mL of isopropanol containing 5% of 1 mol L^{-1} HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 550 nm. The observed MICs are presented in table 5.

3. Results and discussion

3.1. *Single crystal X-ray diffraction analysis*

Complexes **1** and **2** display similar structures, although different metal ions and diamine ligands were employed during the synthetic procedure.

3.1.1. Structure of 1. Single-crystal X-ray diffraction analyses revealed that **1** consisted of half molecule of $C_{26}H_{38}N_4NiO_8S_2$ in the asymmetric unit. The molecular structure of **1** is shown in figure 1. The complex crystallizes in monoclinic space group $P2_1/c$ with two formula units in the unit cell. Selected bond lengths and angles are given in table 2. The coordination sphere of nickel is composed of two oxygen atoms from two 4-methylsulfonyl cinnamate ligands and four nitrogen atoms from two 1,3-propylene diamines. The 4-methylsulfonyl cinnamate is monodentate with the Ni–O bond length (2.0969(12) Å), slightly longer than 2.06 Å (normal distance of Ni–O) [20]. Due to small steric hindrance between the uncoordinated carboxylate oxygen and the 1,3-propylene diamine ligand, the O1–Ni1–N1 and O1–Ni1–N2 angles (90.64(6)° and 88.88(5)°, respectively) are close to the ideal 90° values.

Complex **1** is linked to infinite 1-D chains running along the crystallographic *b*-axis (figure 2a). The chains are connected by intermolecular N1–H1B···O2 and

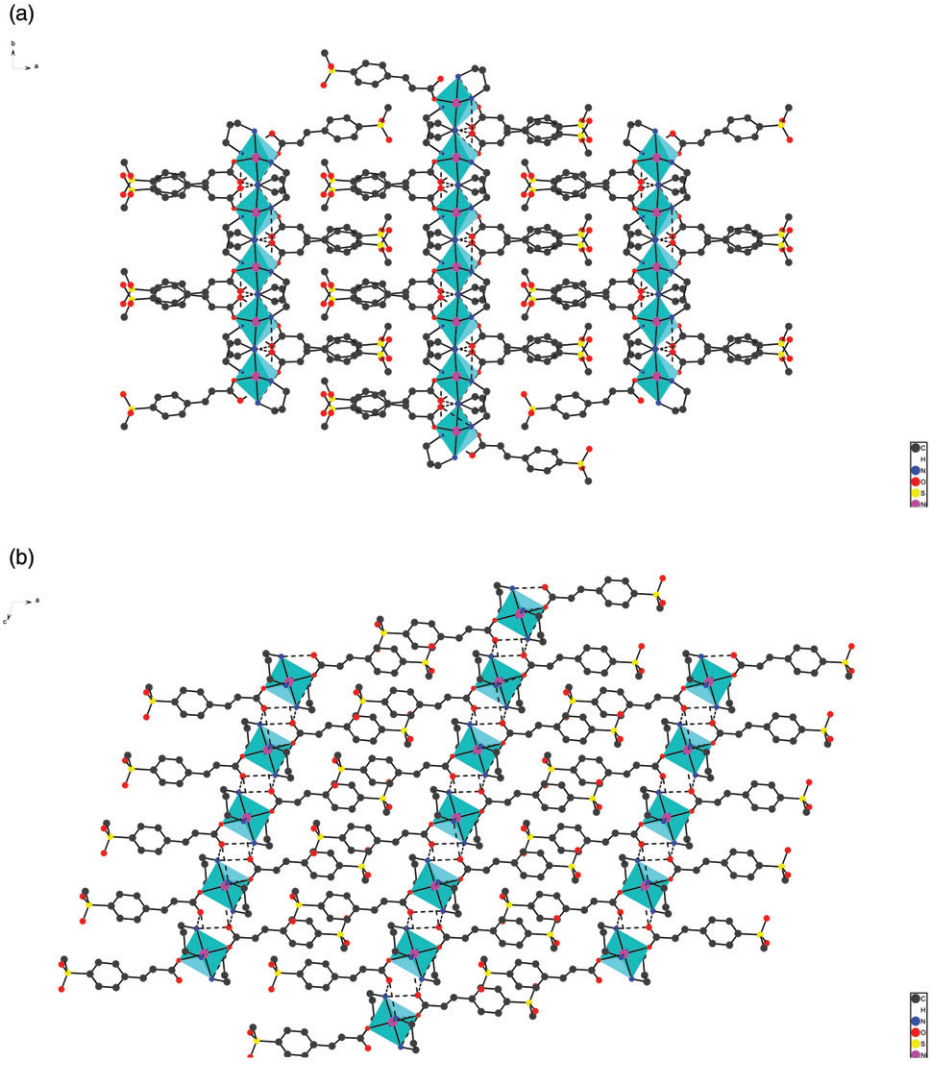


Figure 2. (a) View of the 1-D chains of **1** running along the *b*-axis; (b) hydrogen bonds connecting adjacent chains to a 2-D network in the *c*-axis (hydrogen atoms are omitted for clarity).

N2–H2A···O2 hydrogen bonds in the *c* direction to form a 2-D network (figure 2b). In addition, intramolecular N1–H1A···O2 and N2–H2B···O2 hydrogen bonds contribute to the stability of the crystal structure of **1** (table 3).

3.1.2. Structure of 2. The structure of **2** is shown in figure 1. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with one-half of $C_{28}H_{42}CdN_4O_8S_2{\cdot}2H_2O$ and a water molecule in the asymmetric unit. Selected bond lengths and angles are given in table 4. Each Cd(II) is octahedrally coordinated by two carboxylate oxygen atoms and four nitrogen atoms from two N,N′-dimethylethane-1,2-diamine ligands. In the diamine,

Table 3. Hydrogen-bonding geometry (Å and °) for **1** and **2**.

Bond	Distance (D–A, Å)	Angle (°)	Symmetry code
Complex **1**			
N(1)–H(1 A)···O(2)	3.238(2)	134	$-x, 1-y, 2-z$
N(1)–H(1B)···O(2)	3.041(2)	170	$-x, -1/2+y, 3/2-z$
N(2)–H(2 A)···O(2)	3.051(2)	159	$x, 3/2-y, 1/2+z$
N(2)–H(2B)···O(2)	3.0105(19)	143	$-x, 1-y, 2-z$
Complex **2**			
N(2)–H(2 A)···O(5)	3.178(4)	148	$x, 3/2-y, -1/2+z$
N(2)–H(2B)···O(2)	2.970(3)	137	
O(5)–H(5B)···O(1)	2.847(3)	120	$1-x, 1/2+y, 1/2-z$
C(8)–H(8 C)···O(3)	3.316(4)	165	$-1-x, 1-y, 1-z$
C(8)–H(8 A)···O(2)	3.415(4)	145	$-x, -1/2+y, 1/2-z$
C(13)–H(13 A)···O(3)	3.183(4)	121	$1+x, 3/2-y, -1/2+z$
C(14)–H(14B)···O(4)	3.438(5)	156	$1+x, 1/2-y, -1/2+z$

Table 4. Selected bond lengths (Å) and angles (°) for **2**.

Cd(1)–O(1)	2.418(2)	Cd(1)–N(2)	2.272(2)
Cd(1)–N(1)	2.421(2)	S(1)–O(3)	1.437(2)
S(1)–O(4)	1.429(2)	C(1)–C(3)	1.496(4)
S(1)–C(2)	1.766(3)	C(2)–C(4)	1.383(5)
S(1)–C(8)	1.748(3)	C(2)–C(9)	1.378(5)
O(1)–C(1)	1.261(4)	C(3)–C(5)	1.276(5)
O(2)–C(1)	1.240(4)	C(4)–C(7)	1.385(4)
N(1)–C(10)	1.479(5)	C(5)–C(6)	1.484(4)
N(1)–C(12)	1.443(4)	C(6)–C(7)	1.380(5)
N(1)–C(14)	1.464(4)	C(6)–C(11)	1.385(5)
N(2)–C(13)	1.467(5)	C(9)–C(11)	1.399(4)
O(1)–Cd(1)–N(1)	90.66(7)	Cd(1)–N(1)–C(10)	109.16(18)
O(1)–Cd(1)–N(2)	92.76(7)	Cd(1)–N(1)–C(12)	102.53(19)
N(1)–Cd(1)–N(2)	77.77(8)	Cd(1)–N(1)–C(14)	114.0(2)
O(3)–S(1)–O(4)	118.05(14)	C(10)–N(1)–C(12)	110.2(3)
O(3)–S(1)–C(2)	108.33(14)	C(10)–N(1)–C(14)	106.5(3)
O(3)–S(1)–C(8)	108.86(15)	C(12)–N(1)–C(14)	114.5(3)
O(4)–S(1)–C(2)	108.55(14)	Cd(1)–N(2)–C(13)	108.94(18)
O(4)–S(1)–C(8)	108.53(15)	O(1)–C(1)–O(2)	125.2(3)
C(2)–S(1)–C(8)	103.57(14)	O(1)–C(1)–C(3)	119.6(3)
Cd(1)–O(1)–C(1)	126.41(18)	S(1)–C(2)–C(4)	120.0(3)

N1 is different from N2, as the former is a tertiary amine. The steric hindrance for N1 connected with two methyl groups results in the distortion of the octahedron around the cadmium. The most remarkable deviation from ideal was observed for N1–Cd–N2 angles (77.77(8)°). For the same reason, Cd–N1 bond length (2.421(2) Å) is longer than 2.272(2) Å of the Cd–N2 bond, which is normal for the Cd–N bond [16]. The structure of **2** is stabilized by a complicated hydrogen bonding network (figure 3). These hydrogen bonds include not only classic N2–H2A···O5 and O5–H5B···O1 hydrogen bonds (symmetry code: $x, 3/2-y, -1/2+z$ and $1-x, 1/2+y, 1/2-z$, respectively), but also weak C–H···O hydrogen bonds (table 3). In addition, there are S1–O3···π interactions at 3.786(2) Å of S1–O3 → Cg(3) in **2**. These hydrogen bonding, S1–O3···π interactions, and van der Waals interactions lead to a 3-D network structure.

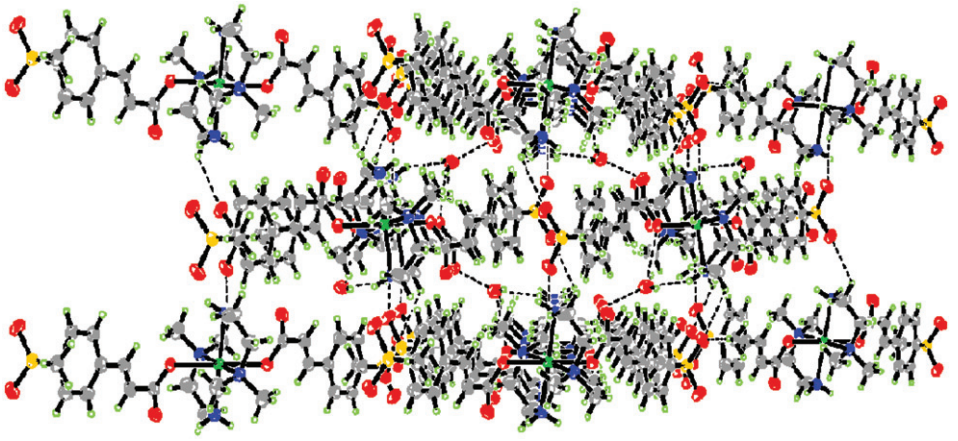


Figure 3. The molecular structure of **2** drawn with 30% probability displacement ellipsoids for nonhydrogen atoms (dashed lines indicate hydrogen bonds).

Table 5. MIC of **1** and **2** against the growth of four bacteria.

	Minimum inhibitory concentration (MIC, $\mu g\,mL^{-1}$)			
	Gram-negative		Gram-positive	
Compounds	*E. coli*	*P. putida*	*B. subtilis*	*B. cereus*
4-Methylsulfonyl cinnamate	2.5	5	20	10
Propane-1,3-diamine	50	30	30	50
N,N′-Dimethylethane-1,2-diamine	50	>50	40	>50
Cadmium acetate	>50	50	50	>50
Nickel acetate	50	>50	>50	50
Complex **1**	10	10	5	10
Complex **2**	50	5	10	5
Streptomycin	10	10	15	15

3.2. *IR spectra*

Determination of carboxylate binding with the metal ions is made on the basis of the value of separation between the asymmetric and symmetric carboxylate stretches, $\Delta = \nu_{as(COO^-)} - \nu_{s(COO^-)}$. In **1** and **2**, two bands attributing to the asymmetric carboxylate stretches (1595.1 and 1545.6 cm^{-1}) and two bands attributing to the symmetric carboxylate stretches (1409.9 and 1393.7 cm^{-1}) were observed. The Δ values are 185.2 and 151.9 cm^{-1}, respectively. The two Δ values (185 and 151.9 cm^{-1}) are higher than the value for sodium cinnamate (143 cm^{-1}) [12], suggesting a monodentate coordination of 4-methylsulfonyl cinnamate in **1** and **2**.

3.3. *Antimicrobial activity*

For *in vitro* antimicrobial activity, **1** and **2** were tested against four bacteria. MIC values are summarized in table 5. Comparative study of the ligand and their complexes

(MIC values) showed that the antibacterial activity of the two metal complexes was not higher than that for 4-methylsulfonyl cinnamate against Gram-negative bacteria (*E. coli* and *P. putida*). However, they had better antibacterial activity than their parent carboxylic acid against Gram-positive bacteria (*B. subtilis* and *B. cereus*). Cadmium coordination of cinnamate displayed high inhibitory activity with an MIC value of $5\,\mu g\,mL^{-1}$ against *P. putida*, while the nickel complex exhibited good inhibitory potency with an MIC value of $5\,\mu g\,mL^{-1}$ against *B. subtilis*.

Regarding the lower activity of the complexes than the parent *p*-methylsulfonyl cinnamate against *E. coli* and *P. putida* and the higher activity than their parent carboxylic acid against *B. subtilis* and *B. cereus*, we do not have a reasonable explanation. Usually, bioactivities of metal complexes are higher than the ligands themselves, which may explain the higher activity against *B. subtilis* and *B. cereus*. Sometimes when metal ions combine with a potent organic compound, the metal ions may act as slow releases, which may explain the lower activity of the complexes than the parent *p*-methylsulfonyl cinnamate against *E. coli* and *P. putida*.

4. Conclusion

Two metal complexes have been synthesized and characterized with an octahedral geometry around metals and both crystallize in the monoclinic space group $P2_1/c$. The antibacterial activity indicated that the metal complexes were less effective than 4-methylsulfonyl cinnamate against *E. coli* and *P. putida*, but better than their parent carboxylic acid against *B. subtilis* and *B. cereus*.

Supplementary material

CCDC 882 154 and CCDC 882 155 contain the supplementary crystallographic data for $C_{26}H_{38}N_4NiO_8S_2$ and $C_{28}H_{42}CdN_4O_8S_2{\cdot}2H_2O$, respectively. These can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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