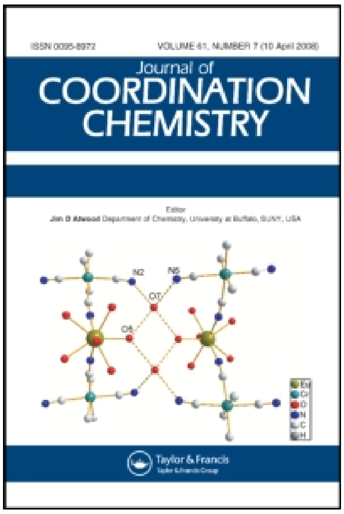

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Syntheses, crystal structures and characterization of divalent transition metal sulfonate complexes with *O*-phenanthroline

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SYNTHESES, CRYSTAL STRUCTURES AND CHARACTERIZATION OF DIVALENT TRANSITION METAL SULFONATE COMPLEXES WITH *O*-PHENANTHROLINE

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Two new complexes, $[Zn(phen)_2(H_2O)_2]2L \cdot H_2O$ (**1**) and $[Cu(phen)(L)(H_2O)_2]L \cdot 3H_2O$ (**2**), where HL = 4-aminobenzenesulfonic acid and phen = *o*-phenanthroline, have been synthesized and their crystal structures determined by X-ray diffraction. In the complexes the Cu(II) and Zn(II) atoms revealed two different coordination environments. Complex **1** consists of a cation $[Zn(phen)_2(H_2O)_2]^{2+}$, in which Zn(II) is six-coordinated by four nitrogen atoms from two *o*-phenanthroline molecules and by two water molecules. Complex **2** has two crystallographically unique Cu(II) ions, where Cu(II) ion is five-coordinate with two nitrogen atoms of *o*-phenanthroline, two water molecules and one sulfonate oxygen atom. The electrochemical behavior and FT-IR of the two compounds have also been studied in detail.

Keywords: 4-Aminobenzenesulfonic acid; FT-IR; Cyclic voltammetry; Crystal structure

INTRODUCTION

Metal phosphonate chemistry has developed rapidly, with new compounds synthesized and characterized, due to their broad applications [1–4]. The coordination chemistry of transition metal sulfonates has not been well explored and/or rationalized, owing to the preconception that sulfonates are weakly coordinating ligands [5]. Several groups have studied the interesting coordination chemistry of transition metal sulfonates and their solid-state properties. In some cases, sulfonate can compete with water and coordinate to metal ions [6]. The coordination behavior of the metal ion toward RSO_3^- can be tailored chemically by introducing other ligands [7]. As far as we know, crystal structures and electrochemistry for transition metal 4-aminobenzenesulfonate complexes with *o*-phenanthroline have not been reported. In this paper two complexes have been synthesized and their coordination modes, electrochemistry and FT-IR studied in detail.

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EXPERIMENTAL

Preparation of $[Zn(phen)_2(H_2O)_2]2L \cdot H_2O$ (1)

4-Aminobenzenesulfonic acid (0.346 g, 2 mmol) was added with constant stirring to a suspension of ZnO (0.081 g, 1 mmol) in water (10 mL). Then *o*-phenanthroline (0.198 g, 1 mmol) was then added to the solution with stirring. The resultant solids, which were collected by filtration and dried in air, were dissolved in a mixture of water and ethanol (1:1). Colorless crystals of **1** were then obtained from the solution after standing at room temperature for several weeks (77% yield based on Zn). Anal. Calc. for $C_{36}H_{34}N_6O_9S_2Zn$ (%): C, 52.42; H, 4.13; N, 10.20. Found: C, 52.61; H, 4.07; N, 10.33. IR (KBr, cm^{-1}): 3347(m), 3226(w), 3063(w), 1625(m), 1599(s), 1519(m), 1503(m), 1428(vs), 1297(w), 1181(s), 1121(vs), 1031(s), 1005(m), 849(m), 726(s), 696(s), 573(s).

Preparation of $[Cu(phen)(L)(H_2O)_2]L \cdot 3H_2O$ (2)

4-Aminobenzenesulfonic acid (0.346 g, 2 mmol) was added with constant stirring to a suspension of $Cu(OH)_2$ (1 mmol) in water (10 mL). *o*-Phenanthroline (0.198 g, 1 mmol) was then added to the solution with stirring. Blue crystals of complex **2** were obtained from the solution after standing at room temperature for several days (yield 71%). Anal. Calcd. for $C_{24}H_{28}N_4O_{11}S_2Cu$ (%): C, 42.47; H, 4.42; N, 8.26%. Found: C, 42.51; H, 4.26; N, 8.33%. IR (KBr, cm^{-1}): 3453(m), 1628(m), 1601(m), 1500(w), 1430(m), 1181(vs), 1124(s), 1034(m), 1008(w), 842(m), 698(s), 574(s).

Physical Measurements

All materials were commercially available and used as received. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. Electrochemical measurements were performed using a three-electrode cell at room temperature. A glass carbon (GC) working (3 mm in diameter) and a Pt wire counter electrode were employed, with Ag/AgCl (satd) as the reference electrode. The surface of the GC electrode was polished with 0.1 μm α-alumina applied to a gray billiard cloth and washed with distilled water many times. Cyclic voltammetry (CV) data were collected with an LK98B Electrochemical Analyzer (Changchun Institute of Applied Chemistry, Chinese Academy of Science) coupled to a HP-55 computer. The concentrations of **1** and **2** for CV were 10^{-3} M. Tetrabutylammonium perchlorate (TBAP) used as an electrolyte for electrochemical measurements was recrystallized from absolute ethanol, and was dried for two days in a vacuum oven before use. Doubly distilled water was used throughout. Other reagents employed are of analytical grade.

Crystal Structure Determination

Crystals of **1** and **2** obtained directly from solution were suitable for X-ray diffraction analysis. Diffraction intensities for the two compounds were collected on a Rigaku RAXIS-RAPID image plate diffractometer using the ω scan technique with MoKα

radiation ($\lambda = 0.71069$ Å) in the range $1.71^\circ < \theta < 27.48^\circ$ ($R_{\text{int}} = 0.0180$) for **1** and $1.56^\circ < \theta < 27.45^\circ$ ($R_{\text{int}} = 0.0296$) for **2**. Absorption corrections were applied using the multi-scan technique [8]. The structure was solved with the direct method of SHELXS-97 [9] and refined with full-matrix least-squares techniques using the SHELXL-97 program [10] within WINGX [11] (final $R = 0.0430$, $wR = 0.1235$ for **1** and $R = 0.0447$, $wR = 0.1202$ for **2**). Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically, while the aqua hydrogen atoms were not located. An analytical expression of neutral-atom scattering factors was employed, and anomalous dispersion corrections incorporated [12].

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{36}H_{34}N_6O_9S_2Zn$ (**1**), $M = 824.18$, triclinic, space group $P\bar{1}$, $a = 12.594(3)$, $b = 12.710(3)$, $c = 13.405(3)$ Å; $\alpha = 77.10(3)^\circ$, $\beta = 62.63(3)^\circ$, $\gamma = 70.16(3)^\circ$, $V = 1786.5(6)$ Å^3, $z = 2$, $D_c = 1.532\ \text{g cm}^{-3}$, $F(000) = 852$, $\mu(\text{MoK}\alpha) = 0.870\ \text{mm}^{-1}$; $C_{24}H_{28}CuN_4O_{11}S_2$ (**2**), $M = 678.18$, orthorhombic, space group $Pbca$, $a = 20.580(4)$, $b = 21.346(4)$, $c = 26.164(5)$ Å; $\alpha = \beta = \gamma = 90^\circ$, $V = 11494(4)$ Å^3, $z = 16$, $D_c = 1.568\ \text{g cm}^{-3}$, $F(000) = 5616$, $\mu(\text{MoK}\alpha) = 0.971\ \text{mm}^{-1}$.

Selected bond distances and angles for **1** and **2** are listed in Table I. Complex **1** (Fig. 1) consists of cationic species $[\text{Zn(phen)}_2(\text{H}_2\text{O})_2]^{2+}$, in which Zn(II) is six-coordinated

TABLE I Selected bond distances (Å) and angles (°) for compounds **1** and **2**

*[Zn(phen)$_2$(H$_2$O)$_2$] 2L · H$_2$O (**1**)*			
Zn(1)–N(1)	2.160(2)	Zn(1)–N(3)	2.166(3)
Zn(1)–N(2)	2.169(2)	Zn(1)–N(4)	2.143(2)
Zn(1)–Ow1	2.108(2)	Zn(1)–Ow2	2.168(2)
Ow1–Zn(1)–N(4)	94.30(10)	N(4)–Zn(1)–N(1)	171.39(9)
N(4)–Zn(1)–N(3)	77.96(11)	Ow1–Zn(1)–Ow2	86.36(8)
N(1)–Zn(1)–Ow2	93.51(9)	Ow1–Zn(1)–N(2)	92.84(9)
N(1)–Zn(1)–N(2)	76.99(9)	Ow2–Zn(1)–N(2)	170.47(8)
Ow1–Zn(1)–N(1)	89.77(9)	Ow1–Zn(1)–N(3)	163.79(8)
N(1)–Zn(1)–N(3)	99.89(10)	N(4)–Zn(1)–Ow2	94.32(9)
N(3)–Zn(1)–Ow2	80.13(9)	N(4)–Zn(1)–N(2)	95.21(9)
N(3)–Zn(1)–N(2)	101.96(9)		
*[Cu(phen)(L)(H$_2$O)$_2$] L · 3H$_2$O (**2**)*			
Cu(1)–Ow1	1.973(3)	Cu(1)–N(2)	1.999(3)
Cu(1)–Ow2	2.007(3)	Cu(1)–N(1)	2.013(3)
Cu(1)–O(11)	2.284(3)	Cu(2)–Ow4	1.975(3)
Cu(2)–N(3)	1.990(4)	Cu(2)–Ow3	2.017(3)
Cu(2)–N(4)	2.032(3)	Cu(2)–O(21)	2.313(3)
Ow1–Cu(1)–N(2)	174.03(14)	N(2)–Cu(1)–Ow2	92.82(13)
N(2)–Cu(1)–N(1)	81.77(14)	Ow1–Cu(1)–O(11)	83.58(12)
Ow2–Cu(1)–O(11)	79.58(11)	Ow4–Cu(2)–N(3)	173.37(14)
N(3)–Cu(2)–Ow3	93.33(13)	N(3)–Cu(2)–N(4)	81.47(14)
Ow4–Cu(2)–O(21)	86.40(12)	Ow3–Cu(2)–O(21)	78.54(11)
Ow1–Cu(1)–Ow2	93.04(12)	Ow1–Cu(1)–N(1)	92.50(13)
Ow2–Cu(1)–N(1)	172.28(12)	N(2)–Cu(1)–O(11)	96.40(12)
N(1)–Cu(1)–O(11)	106.40(12)	Ow4–Cu(2)–Ow3	92.97(13)
Ow4–Cu(2)–N(4)	92.47(14)	Ow3–Cu(2)–N(4)	172.08(13)
N(3)–Cu(2)–O(21)	92.84(13)	N(4)–Cu(2)–O(21)	107.56(12)

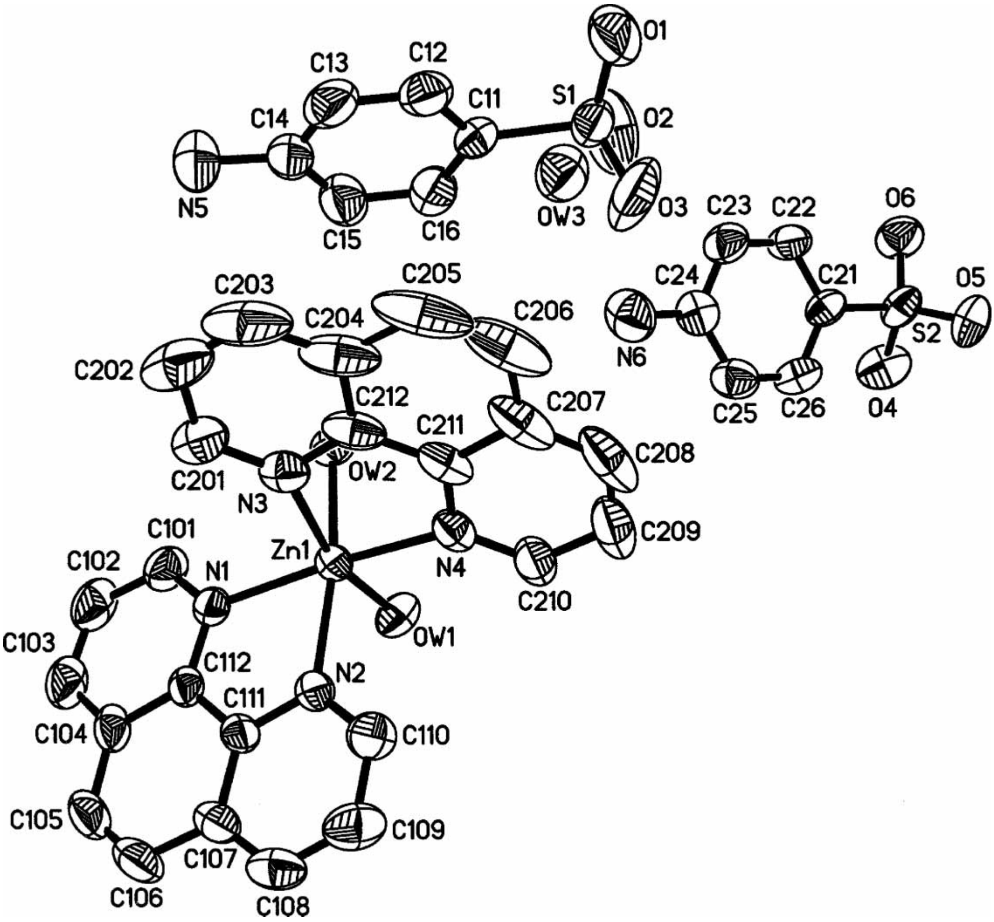

FIGURE 1 Structure of $[Zn(phen)_2(H_2O)_2]2L \cdot H_2O$ (**1**) with numbering scheme (lattice water molecules and hydrogen atoms omitted for clarity).

by four nitrogen atoms from two *o*-phenanthroline molecules and two water oxygen atoms. The sulfonate ions are non-coordinating, as in some reported compounds [13]. The Zn–O (water) distances are somewhat shorter than in other zinc compounds [14]. The Zn–N distances are very similar to the reported values [15].

Complex **2** (Fig. 2) has two crystallographically unique Cu(II) ions and consists of cationic species $[Cu(phen)(L)(H_2O)_2]^+$, in which copper(II) is five-coordinated by two nitrogen atoms from *o*-phenanthroline, two water molecules and one sulfonate oxygen atom. There is one non-coordinated sulfonate anion per formula unit. The Cu–O (sulfonate) distance (2.299 Å) is near that of the related complex $[CuCl(L')(phen)(H_2O)]$, where $L' = p$-toluenesulfonate anion [16], but is much shorter than that of $[Cu(pn)_2L'_2]$, where pn = 1,3-diaminopropane [6]. The Cu–N distances are similar to those in other Cu(II) complexes with *o*-phenanthroline [16,17], and the copper–water oxygen distances are close to the values found for other Cu(II) complexes [16,18]. There is a long contact between Cu(II) and the N atom of the sulfonate anion with distances of 2.646 Å (Cu1–N6i, symmetry code i: x, $0.5 - y$, $-0.5 + z$) and 2.567 Å (Cu2–N5).

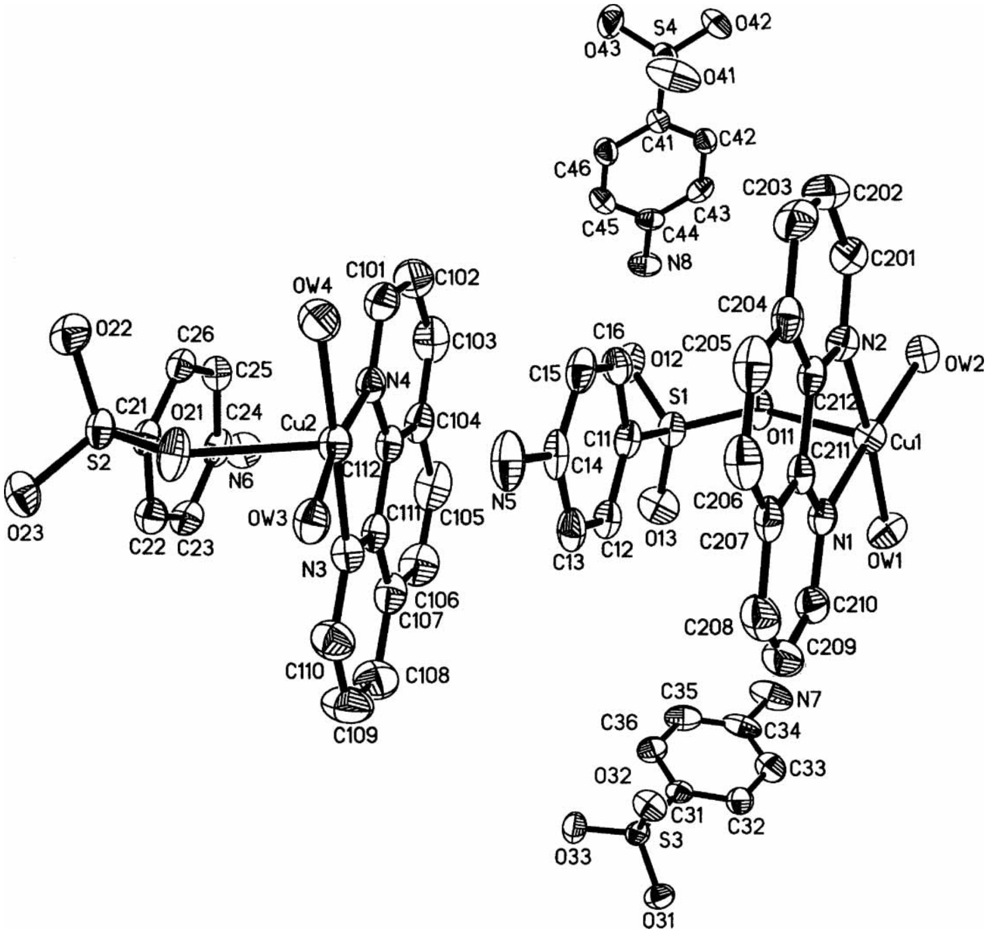

FIGURE 2 Structure of [Cu(phen)(L)$(H_2O)_2$]L · $3H_2O$ (**2**) with numbering scheme (lattice water molecules and hydrogen atoms omitted for clarity).

Infrared Spectrum

In the IR spectra, **1** and **2** show absorption bands at 3340–3453 cm^{-1}, corresponding to the presence of water. The C–H stretching modes for the phenyl rings are relatively weak and are observed at about 3050 cm^{-1}. Peaks at about 1625 and 1590 cm^{-1} are attributed to $\nu_{C=N}$ stretches [19]. The well-resolved frequencies of aromatic rings span the regions 600–930 and 1240–1630 cm^{-1}. Bands characteristic of the fundamental and the split ν_3(S–O) stretching modes are observed in the range 1000 to 1240 cm^{-1} [20]. These features were completely confirmed by the single-crystal X-ray diffraction study.

Cyclic Voltammetry

The redox properties of **1** and **2** were monitored by cyclic voltammetry (CV) in *N*,*N*-dimethylformamide (DMF) solution containing 0.1 M TBAP. Compounds **1** and **2**

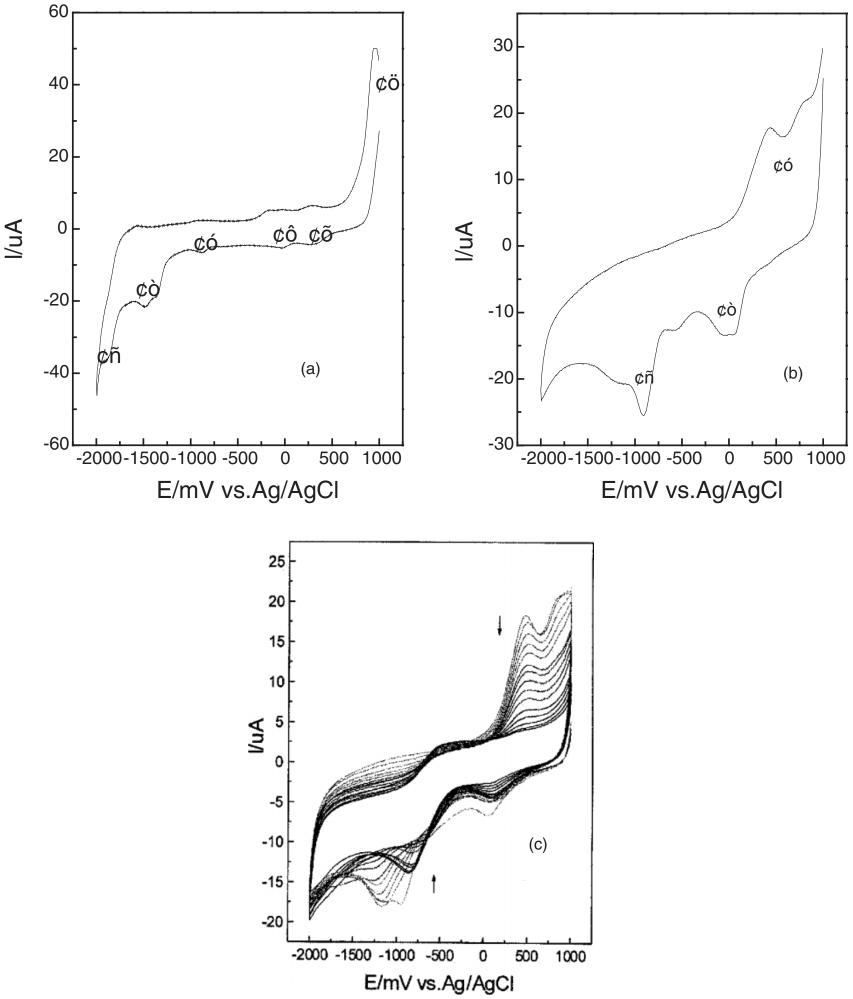

FIGURE 3 Cyclic voltammograms of **1** (a) and **2** (b) in DMF ($c = 1.0 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$, $0.1\,\mathrm{mol\,l^{-1}}$ TBAP) at a glass carbon electrode (scan rate $= 100\,\mathrm{mV\,s^{-1}}$). (c) Cyclic voltammograms of the electropolymerization films of **2** under the above conditions.

show different electrochemical activity, which may be attributed to the difference of the electrochemical activity of metal cations and the coordination mode of the central metal cations [21]. In the CV of complex **1** [Fig. 3(a)], the cathodic peak at 946 mV is ascribed to the oxidation process of the amino group of the L^- anion, and others may be tentatively attributed to the phenanthroline ligand [22]. In the CV of **2** [Fig. 3(b)], the one-electron reduction at −57 mV can be assigned to a metal-based Cu^{II}/Cu^{I} couple, as observed in similar copper(II) *o*-phenanthroline complexes [23]. Other peaks (peak I at −907 mV and peak III at 438 mV) in this CV plot may be assumed to be due to redox processes occurring at the ligands. Figure 3(c) shows that the peak currents decrease gradually with the scan cycles. This electrochemical phenomenon is due to electropolymerization of the attached aniline groups [24], which forms a light-green, non-conducting film.

Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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