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

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Abstract

Three new complexes, namely $[Cu(phen)(L)(H_2O)_2]L H_2O$ **1**, $[M(phen)_2(H_2O)_2]2L GH_2O$ [M = Co(2), Ni(3)], where, HL = 4-methylbenzenesulfonic acid and phen = o-phenanthroline, have been synthesized. The crystal structures were determined by X-ray diffraction method and refined by full-matrix least-squares methods to R = 0.0535 and wR = 0.1492 using 3567 reflections with $I > 2\sigma(I)$ for **1**; R = 0.0388 and wR = 0.1223 using 3844 reflections with $I > 2\sigma(I)$ for **2**; and R = 0.0401 and wR = 0.1222 using 3425 reflections with $I > 2\sigma(I)$ for **3**. **1** Consists of cationic species $[Cu(phen)(L)(H_2 O)_2]^+$, in which Cu(II) ion is five-coordinated by two nitrogen atoms of o-phenanthroline, two water molecules and one sulfonate oxygen atom. The cations and the non-coordinating sulfonate anions are linked by hydrogen bonds to form infinite chains. Complexes **2** and **3** are isostructral compounds. Each of them consists of cationic species $[M(phen)_2(-H_2O)_2]^{2+}$, in which metal ion is six-coordinated by four nitrogen atoms from two o-phenanthroline molecules and two water oxygen atoms. The sulfonate ions do not coordinate to metal ion. The cations, non-coordinating sulfonate ions and lattice water molecules are linked by hydrogen bonds to form infinite chains. Cow set ins do not coordinate to metal ion. The cations, non-coordinating sulfonate ions and lattice water molecules are linked by hydrogen bonds to form infinite zigzag chains. CV, FT-IR, UV–Vis and TGA were also used to characterize these compounds.

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Keywords: Crystal structure; Cyclic voltammetry; FT-IR; TGA; UV-Vis

1. Introduction

It is well known that the area of metal phosphonate chemistry has been developed rapidly. A lot of new compounds have been synthesized and characterized. The interest stems from a broad range of applications, such as in the areas of sorption and ion exchange [1], sensors [2], non-linear optics [3],

and catalysis [4]. But the coordination chemistry of transition metal sulfonates is not well explored and/ or rationalized [5], owing to the preconception that they are weakly coordinating ligands. Several studies on the coordination chemistry of transition metal sulfonates and their solid-state properties have been reported. In some cases, sulfonate group can compete with water molecule and coordinate to metal ion [6]. Complexes where, sulfonate ions coordinate as monodentate [7], bidentate and tridentate [8] ligands have been reported. It is found that the coordination behavior of metal cation

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toward RSO_3^- can be tailored chemically by introducing other ligand [9]. So far several structures of metal 4-methylbenzenesulfonates have been studied [10]. To the best of our knowledge, no crystal structure and characterization of the transition metal 4-methylbenzenesulfonate complexes with *o*-phenanthroline have been reported. In this paper these complexes have been synthesized, and their coordination modes, IR, UV–Vis, TGA and electrochemistry were studied in detail.

2. Experimental

2.1. Synthesis

[*Cu*(*phen*)(*L*)(H_2O)₂]*L*· H_2O **1**. 4-Methylbenzenesulfonic acid (0.380 g, 2 mmol) was added with constant stirring to an suspension of Cu(OH)₂ (1 mmol) in 10 ml of water. Then *o*-phenanthroline (0.198 g, 1 mmol) was added to the solution with stirring. Blue crystals of complex **1** were obtained from the solution after standing at room temperature for several days (yield 73%). Calc. for C₂₆H₂₈N₂O₉-S₂Cu: C, 48.78; H, 4.41; N, 4.38. Found: C, 48.81; H, 4.26; N, 4.53%.

[*Co*(*phen*)₂(*H*₂*O*)₂]2*L*·6*H*₂*O* **2**. 4-Methylbenzenesulfonic acid (0.380 g, 2 mmol) was added with constant stirring to a suspension of CoCO₃ (0.228 g, 1 mmol) in 10 ml of water. Then *o*phenanthroline (0.198 g, 1 mmol) was added to the solution with stirring. Orange crystals of complex **2** were obtained from the solution after standing at room temperature for several days (68% yield based on Co). Calc. for C₃₈H₄₆N₄O₁₄S₂Co: C, 50.39; H, 5.12; N, 6.19. Found: C, 50.63; H, 4.98; N, 6.33%.

[*Ni*(*phen*)₂(*H*₂*O*)₂]2*L*·6*H*₂*O* **3**. 4-Methylbenzenesulfonic acid (0.380 g, 2 mmol) was added with constant stirring to a suspension of NiCO₃ (0.227 g, 1 mmol) in 10 ml of water. Then *o*-phenanthroline (0.198 g, 1 mmol) was added to the solution with stirring. The solids were filtrated and dried in air. Recrystallization of the product from a mixture of ethanol and water gave blue crystals of **3** (47% yield based on Ni). Calc. for C₃₈H₄₆N₄O₁₄S₂Ni: C, 50.40; H, 5.12; N, 6.19. Found: C, 50.67; H, 5.01; N, 6.43%.

2.2. Crystal structure determination and physical measurements

Experimental details of the X-ray analyses are provided in Table 1. Diffraction intensities for the compound 1 were collected on a Siemens P4 diffractometer using the ω scan technique. Lorentz polarization and absorption corrections were applied [11]. Diffraction intensities for the compounds 2 and 3 were collected on a Rigaku RAXIS-RAPID image plate diffractometer using ω scan technique with Mo K α radiation ($\lambda =$ 0.71069 Å). Absorption corrections were applied using multi-scan technique [12]. The structures were solved with the direct method of SHELXS-97 [13] and refined with full-matrix least-squares techniques using the SHELXL-97 program [14] within WINGX [15]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically, while the aqua hydrogen atoms were not located. Analytical expression of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated [16]. Drawings were produced with SHELXTL-PLUS [17].

The FT-IR spectrum was recorded from KBr pellets in range $4000-400 \text{ cm}^{-1}$ on a Mattson Alpha-Centauri spectrometer. UV-Vis spectrum was recorded on a 756 MC spectrophotometer. TGA was performed using a Perkin-Elmer TG-7 analyzer in nitrogen. In cyclic voltammetry (CV), 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. The reference electrode is Ag/AgCl (satd). The surface of GC electrode was polished with $0.1 \,\mu m$ α -alumina applied to a gray billiard cloth and washed with distilled water many times. CV data were collected with LK98B Electrochemical Analyzer (Changchun Institute of Applied Chemistry) coupled to a HP-55 Computer. Tetrabutylammonium perchlorate (TBAP) used as an electrolyte for electrochemical measurements was recrystallized from absolute ethanol, and dried two days in a vacuum oven before used. Doubly distilled water was used throughout. Other reagents employed are of analytical grade.

Γ.	Yang et al.	/ Journal	of Molecular	Structure 657	(2003)) 333-341
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Table 1 Crystal data for compounds **1–3**

	1	2	3
Formula	C ₂₆ H ₂₈ CuN ₂ O ₉ S ₂	$C_{38}H_{46}CoN_4O_{14}S_2$	C38H46NiN4O14S2
Formula weight	640.16	905.84	905.62
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	C2/c	C2/c
a (Å)	10.361(3)	21.314(4)	21.308(4)
b (Å)	11.690(3)	16.493(3)	16.451(3)
<i>c</i> (Å)	12.393(5)	14.285(3)	14.469(3)
α (°)	77.46(3)	90	90
β(°)	72.34(3)	122.55(3)	122.27(3)
γ (°)	75.04(3)	90	90
$V(Å^3)$	1366.0(8)	4232.8(15)	4288.6(15)
Z	2	4	4
$Dc (gcm^{-3})$	1.566	1.421	1.403
F(000)	662	1892	1896
μ (mm ⁻¹)	1.009	0.574	0.619
Reflections collected	5841	9122	9400
Unique reflections	4792	4850	4898
Observed reflections	3567	3844	3425
$(I > 2\sigma(I))$			
$R1(I > 2\sigma(I))$	0.0535	0.0388	0.0401
$wR2(I > 2\sigma(I))$	0.1492	0.1223	0.1222

3. Results and discussion

3.1. Characterization

The main IR bands of the compounds 1-3 with their group assignments are listed in Table 2. The clearly visible bands at $853-721 \text{ cm}^{-1}$ are attributed to out-of-plane C-H deformations of phen and L⁻ ligands [18]. The vibration frequencies of phen are shifted after coordination [19], the peak at 1605 cm^{-1} corresponding to ν (C=N) shifts to 1585 cm⁻¹ upon coordination, while the phen ν (C=C) frequency of 1500 cm^{-1} is shifted to about 1518 cm^{-1} [20,21]. Peaks at about 430 cm^{-1} are attributed to the M–N stretching vibration [22]. The coordination of the phen is also indicated by the heterocyclic ring breathing frequencies in the finger print region of 600- 1400 cm^{-1} in these complexes [23]. The peaks at about 1426 cm⁻¹ are attributed to the $-CH_3$ vibration of L anions. The bands at about 1038 and 1012 cm^{-1} may be assigned to the internal vibrations of CH₃C₆H₄ parts of L^- anion as described for CuL₂ [24].

Compounds 1–3 show ν_{as} (SO₃) and ν_{s} (SO₃) in the range 1184–1146 cm⁻¹ and 1125–1127 cm⁻¹ regions, respectively. The peaks of $\nu_{as}(SO_3)$ for compound 1 are clearly different from those in 2 and 3. The splitting of peaks for $\nu_{as}(SO_3)$ occurs in 1 (see Table 2). From the splitting of peaks the coordination

Table 2

The assignments of bands for 1-3 in the FT-IR spectra

Assignment	1	2	3
ν (OH) _{coor,water}	3562w	3558w	3555w
ν (OH) _{lattice water}	3443m	3443m	3441m
ν (C=N) _{phen}	1584w	1585w	1585w
$\nu (C = C)_{\text{phen}}$	1517m	1518m	1518m
ν (CH) _{phen}	853s	853s	853s
	815w	818m	818m
	777w	779w	781w
	721s	728s	728s
$\nu (CH_3)_L$	1424m	1426s	1426s
$\nu_{\rm as}({\rm SO}_3)$	1187vs	1184vs	1184vs
	1146m		
$\nu_{\rm s}({\rm SO}_3)$	1127m	1125m	1126s
CH ₃ C ₆ H ₄ (internal vibrations)	1040s	1037s	1038s
	1012s	1012s	1012s
ν (C–S)	688s	688s	688s
$\delta_{as}(SO_3)$	570s	568s	568s
$\delta_{s}(SO_{3})$	491w	490w	493w

335

of the sulfonate group in the complex **1** may be inferred as observed previously for $Co(L)_2(EtOH)_2$ [25]. The δ_{as} (SO₃) for **1–3** are observed at about 569 cm⁻¹, while the δ_s (SO₃) appear at about 491 cm⁻¹ [26].

The solution spectral studies of the complexes in the range 200-800 nm reveal that the intense absorptions (at about λ_{max} 275 nm) are due to the $\pi - \pi^*$ transition of *o*-phenanthroline. This band is blue-shifted upon coordination, showing clear evidence of C=N coordination to metal (II) center [27].

In order to characterize more fully these compounds in terms of thermal stability, we examined the complexes 1 and 2 using TGA. The two complexes were heated from 35 to 700 $^\circ\!C$ in $N_2.$ When the crystals were removed from the mother liquor, they immediately lost part of the water molecules. TGA was performed after part of their water molecules had evaporated. Weight losses corresponding to the remaining water were observed over the wide temperature range 35-105 °C for 1, and 35-120 °C for 2. After dehydration, the anhydrous compounds begin to decompose with loss of the organic portion at temperature 310 and 340 °C, respectively. Other exotherms centered at 350 and 470 °C for 1, 420 and 540 °C for 2, can be observed. However, it is difficult to determine these weight losses accurately as these processes are slightly overlapped with the weight losses due to the dissociation of the organic fractions. The final product of CuO and CoO was obtained at 560 and 580 °C, respectively.

The redox properties of 1-3 were monitored by CV in *N*, *N*-dimethylformamide (DMF) solution containing 0.1 M TBAP, and these data are summarized in Table 3. Compounds 1-3 show different electrochemical activity, which may be attributed to

Table 3 Cyclic voltammetry data for complexes **1–3**

Compound	E^{I}	E^{II}	$E^{\rm III}$	$E^{\rm IV}$	$E^{\mathbf{V}}$	$E^{\rm VI}$
1	-1772^{a}	- 1539 ^a	-202^{a}	82 ^b	248 ^a	557 ^a
2 3	- 1424 ^b - 1888 ^a	— 987 ^ь — 1183 ^ь	-100^{a} -805^{c}	343 ^c		

^a Cathodic peak potential (E_{PC}).

^b $E_{1/2} = (E_{Pa} - E_{PC})/2.$

^c Anodic peak potential (E_{Pa}).

the difference of the electrochemical activity of the metal cations [28]. As shown in Fig. 1a, the oneelectron reduction at -202 mV can be assigned tentatively to a metal-based Cu^{II}/Cu^I couple as observed in other similar copper(II) o-phenanthroline complexes [29]. On the basis of previously studied data, the couple IV at $E_{1/2} = 82 mV$ can be described as a reversible one-electron redox with the anodic to cathodic peak separation (ΔE) = 87 mV and i_a/i_c = 0.9, where, i_a and i_c are the anodic and cathodic currents, respectively [30]. Other peaks observed in this CV plot may be assumed to be a result of redox processes occurring at the ligands. In Fig. 1b two reversible peaks with $E_{1/2} = -1424$, -987 mV, $\Delta E = 90$ and 170 mV were observed. One well solved redox wave at -100 mV was detected for the cobalt(II) complex 2, which is assigned to the $Co^{II}/$ Co^I reduction, while an oxidation wave corresponding to Co^{III}/Co^{II} couple was not observed due to the unstability of the Co(III) species [28, 31]. A typical cyclic voltammetric response for the nickel(II) complex 3 is displayed in Fig. 1c. Like the copper(II) complex 1 and cobalt(II) complex 2, the ligand-based oxidation and reduction waves also occurred in complex 3. The peak I at -1888 mV, and the irreversible couple II at $E_{1/2} = -1183 \text{ mV}$ may be assigned to the ligands. The couples of Ni^{II}/Ni^I (peak III) at -805 mV and Ni^{III}/Ni^I (peak IV) at 343 mV were also observed in Fig. 1c. The similar type of electrochemical behavior was also known in the previous nickel(II) complex [30, 32].

3.2. Crystal structures

Selected bond distances and angles are given in Table 4. The structure of 1 is shown in Fig. 2. 1 consists of cationic species $[Cu(phen)(L)(H_2O)_2]^+$, in which copper (II) ion is five-coordinated by two nitrogen atoms of *o*-phenanthroline, two water molecules and one sulfonate oxygen atom. Owing to the weak coordination strength of sulfonate ion toward transition metal ion, the other sulfonate ion is non-coordinating. The Cu–N distances of 2.000 and 2.015 Å are similar to those found in other Cu(II) complex with *o*-phenanthroline [33], while the copper water oxygen distances of 1.950 and 1.984 Å are near to the values found for other Cu(II) complexes [34]. In the reported





Fig. 1. Cyclic voltammograms (a-c for 1-3, respectively) in DMF($c = 1.0 \times 10^{-3} \text{ mol } 1^{-1}$, 0.1 mol 1^{-1} TBAP) at a glass carbon electrode (scan rate = 100 mV s⁻¹).

trans-di(4-methylbenzenesulfonato)bis(1,3-diaminopropane)-copper (4) [6], the four equatorial N atoms from two chelating 1,3-diaminopropane display stronger Jahn-Teller effect than two water molecules and two N atoms from a chelating *o*-phenanthroline of **1**, hence axial Cu–O (sulfonate) distance of 2.581 Å of **4** is much longer than that of **1** (2.222 Å). The phenyl ring of the coordinating sulfonate group is parallel to *o*-phenanthroline plane with the dihedral angle of 3.0° .

337

Table 4 Selected bond distances (in Å) and angles (in °) for compounds 1-3

$\overline{[Cu(phen)(L_1)(H_2O)_2]L_1 \cdot H_2O(1)}$			
Cu–Ow1	1.984(3)	Cu–Ow2	1.950(4)
Cu-N(1)	2.000(4)	Cu-N(2)	2.015(3)
Cu-O(2)	2.222(3)	S(1)-O(2)	1.435(3)
S(1)-O(1)	1.397(4)	S(1)-O(3)	1.474(4)
Ow2-Cu-Ow1	90.07(17)	Ow2-Cu-N(1)	174.60(15)
Ow1-Cu-N(1)	91.35(15)	Ow2-Cu-N(2)	95.27(15)
Ow1-Cu-N(2)	165.81(14)	N(1)-Cu-N(2)	82.18(14)
Ow2-Cu-O(2)	93.22(17)	Ow1-Cu-O(2)	88.68(13)
N(1)-Cu-O(2)	92.02(14)	N(2)-Cu-O(2)	104.10(13)
$[Co(phen)_2(H_2O)_2]_2L_1 \cdot 6H_2O$ (2)			
Co(1)-N(1)	2.1328(18)	Co(1) - N(2)	2.1395(19)
Co(1)-Ow1	2.0746(17)		
Ow1-Co(1)-Ow1#1	88.37(10)	Ow#1-Co(1)-N(1)	93.40(7)
Ow#1-Co(1)-N(1)#1	95.55(7)	Ow1-Co(1)-N(2)#1	170.89(6)
N(1)-Co(1)-N(2)#1	93.51(7)	N(1)-Co(1)-N(2)	77.50(7)
N(2)#1-Co(1)-N(2)	88.98(10)	Ow1-Co(1)-N(1)	95.55(7)
Ow1-Co(1)-N(1)#1	93.40(7)	N(1)-Co(1)-N(1)#1	167.50(10)
Ow1#1-Co(1)-N(2)#1	92.05(8)	N(1)#1-Co(1)-N(2)#1	77.50(7)
Ow1-Co(1)-N(2)	92.05(8)	Ow1#1-Co(1)-N(2)	170.89(6)
N(1)#1-Co(1)-N(2)	93.51(7)		
$[Ni(phen)_2(H_2O)_2]2L_1 \cdot 6H_2O$ (3)			
Ni(1)-N(1)	2.088(2)	Ni(1)-N(2)	2.092(2)
Ni(1)–Ow1	2.0748(19)		
Ow1-Ni(1)-Ow1#1	87.84(11)	Ow#1-Ni(1)-N(1)	91.94(8)
Ow#1-Ni(1)-N(1)#1	95.68(8)	Ow1-Ni(1)-N(2)#1	171.40(7)
N(1)-Ni(1)-N(2)#1	92.88(8)	N(1)-Ni(1)-N(2)	79.66(8)
N(2)#1-Ni(1)-N(2)	91.06(12)	Ow1-Ni(1)-N(1)	95.68(8)
Ow1-Ni(1)-N(1)#1	91.94(8)	N(1)-Ni(1)-N(1)#1	169.4(1)
Ow1#1-Ni(1)-N(2)#1	91.17(8)	N(1)#1-Ni(1)-N(2)#1	79.66(8)
Ow1-Ni(1)-N(2)	91.17(8)	Ow1#1-Ni(1)-N(2)	171.40(7)
N(1)#1-Ni(1)-N(2)	92.88(8)		

Symmetry code for 2 and 3: #1 -x + 2, y, -z + 1.5

There are complicated hydrogen bonding interactions in the structure of **1** (Fig. 3). Each oxygen atom of the coordinating sulfonate ion is hydrogenbonded to one water molecule, while two oxygen atoms of the non-coordinating sulfonate ion are hydrogen-bonded to one water molecule respectively, and the remaining oxygen atom has no hydrogen bonding interaction. [Cu(phen)(L)(H₂O)₂]⁺ cations and the non-coordinating sulfonate ions are linked by hydrogen bonds to form infinite chains.

Complex 1 is a typical compound where, one sulfonate ion is utilized as a coordinating

counter-anion and the other as a non-coordinating counter-anion.

Complex 2 is isostructral with 3. Its structure is shown in Fig. 4. Metal ion lies on a crystallographic twofold axis. 2 consists of cationic species $[Co(phen)_2(H_2O)_2]^{2+}$, in which cobalt ion is sixcoordinated by four nitrogen atoms from two *o*phenanthroline molecules and two water oxygen atoms. Due to the weak coordination strength of sulfonate ion toward transition metal ion, the sulfonate ions are non-coordinating. Indeed, there are some examples where, the sulfonate group has



Fig. 2. View of the structure of [Cu(phen)(L)(H₂O)₂]L·H₂O with the numbering scheme.

been utilized as a non-coordinating counter-anion [35]. The cobalt water oxygen distance of 2.075 Å is similar to the values in other cobalt compound [36]. The Co–N distances of 2.133 and 2.140 Å are near to the values found in other cobalt complex with *o*-phenanthroline [37].

Two oxygen atoms of the sulfonate ion are hydrogen-bonded to one water molecule respectively, and the remaining oxygen atom forms hydrogen bonds with two water molecules. The coordinating water molecule is hydrogen-bonded to one lattice water molecule and one sulfonate oxygen atom. $[Co(phen)_2(H_2O)_2]^{2+}$ ions, sulfonate ions and lattice water molecules are linked by hydrogen bonds to form infinite zigzag chains (Fig. 5).

3.3. Conclusion

Three metal 4-methylbenzenesulfonate complexes with *o*-phenanthroline were synthesized, and they



Fig. 3. The polymeric chain linked by hydrogen bonds in $[Cu(phen)(L)(H_2O)_2]L \cdot H_2O$.

339



Fig. 4. View of the structure of [Co(phen)₂(H₂O)₂]2L·6H₂O with the numbering scheme.



Fig. 5. The polymeric zigzag chain linked by hydrogen bonds in [Co(phen)₂(H₂O)₂]2L·6H₂O.

displayed two different coordination modes. In complex 1, one sulfonate ion coordinates to copper ion, while the other plays a role of non-coordinating counter-anion. The cations and the non-coordinating sulfonate anions are linked by hydrogen bonds to form infinite chains. In complexes 2 and 3, the weak coordinating ability of the sulfonates relative to the water molecules prevents the formation of direct M-O-S bonds and two sulfonate ions only play a role of counter-anions. The cations, non-coordinating

sulfonate ions and lattice water molecules are linked by hydrogen bonds to form infinite zigzag chains. FT-IR, CV, UV–Vis and TGA results are consistent with the crystal structure.

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