

## 芳香二磺酸的配位化学研究

化合物  $[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$  (1) 和  
 $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$  (2) 的合成与结构

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合成了两个二价的过渡金属磺酸化合物, 并通过 X-射线衍射单晶结构分析进行结构表征。化合物  $[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$  (1) 以  $P2(1)/c$  空间群结晶, 晶胞参数为  $a = 8.583(5)$ ,  $b = 10.533(6)$ ,  $c = 12.946(7)$  Å,  $\beta = 92.433(9)^\circ$ 。  $[\text{Ni}(\text{cyclam})]^{2+}$  与两个磺酸基团形成弱配位, 从而构筑了一维的配聚物。  $[\text{Ni}(\text{cyclam})]^{2+}$  与磺酸基团之间的作用还通过  $\text{O}_2\text{S}-\text{O}\cdots\text{H}-\text{N}$  型氢键进一步被加强。化合物  $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$  (2) 以  $P\bar{1}$  空间群结晶, 晶胞参数为  $a = 8.738(5)$ ,  $b = 9.324(5)$ ,  $c = 10.118(5)$  Å,  $\alpha = 81.382(8)$ ,  $\beta = 64.868(8)$ ,  $\gamma = 62.999(8)^\circ$ 。在该化合物中, 磺酸基团没有与  $\text{Co}^{2+}$  形成配位键, 而是以平衡离子的形式存在并与配离子形成氢键, 构筑了有序的三维结构。

关键词: 镍(II) 钴(II) 配位化学 1,5-萘二磺酸根离子 氢键  
分类号: O614.81

Coordination Chemistry of Arenedisulfonate  
Syntheses and Crystal Structures of  $[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$  (1)  
and  $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$  (2)

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Two novel divalent transition metal disulfonates were synthesized and characterized by X-ray single crystal diffraction.  $[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$  (1) crystallized in space group  $P2(1)/c$  with unit cell parameters  $a = 8.583(5)$ ,  $b = 10.533(6)$ ,  $c = 12.946(7)$  Å, and  $\beta = 92.433(9)^\circ$ . The  $\text{Ni}^{2+}$  center is coordinated by the cyclam ligand and two sulfonate groups. The interactions between  $[\text{Ni}(\text{cyclam})]^{2+}$  and the sulfonates are further enhanced by multiple hydrogen bonds of type  $\text{O}_2\text{S}-\text{O}\cdots\text{H}-\text{N}$ .  $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$  (2) crystallized in space group  $P\bar{1}$  with unit cell parameters  $a = 8.738(5)$ ,  $b = 9.324(5)$ ,  $c = 10.118(5)$  Å,  $\alpha = 81.382(8)$ ,  $\beta = 64.868(8)$ , and  $\gamma = 62.999(8)^\circ$ . The sulfonate groups do not have any direct contact with the  $\text{Co}^{2+}$  center, instead, they form second sphere coordination with  $\text{Ni}^{2+}$  via hydrogen bonds and extend the structure into a 3-D network. CCDC: 194341, 194342.

Keywords: nickel (II) cobalt (II) coordination chemistry 1,5-naphthalenedisulfonate anion  
hydrogen bond

收稿日期: 2002-09-26。收修改稿日期: 2002-10-29。

国家自然科学基金资助项目(No. 20271053)。

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## 0 Introduction

We have been investigating the coordination behavior of sulfonate anions with metal cations, especially the coordination behavior of arenedisulfonate anions toward divalent transition metal cations including  $\text{Cu}^{2+}$ <sup>[1]</sup>,  $\text{Ni}^{2+}$ <sup>[2]</sup> and  $\text{Cd}^{2+}$ <sup>[3]</sup>. Our primary results, together with others<sup>[4]</sup>, have revealed that the sulfonate group, as a weak Lewis base, shows weak coordination strength with divalent transition metal cations, in comparison with phosphonate, its structural analog. Most of the transition metal sulfonates obtained from aqueous solution are aqua-metal sulfonate salts. Nevertheless, after introducing other organic ligands as auxiliaries to the metal centers, sulfonate anions can compete with water molecules and coordinate with transition metals<sup>[2]</sup>. This observation indicates that the coordination strength of metal cation with sulfonate anion is tunable. Moreover, the sulfonate group shows more variant and flexible coordination modes than phosphonate, which warrants further investigation from both the coordination and structural points of view.

Herein, as part of the on-going research interest,

we report the solid state structures of two novel metal sulfonates with 1, 4, 8, 11-tetraazacyclotetradecane (cyclam) ligand, namely  $[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$  (**1**) and  $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$  (**2**) (1, 5nds = 1, 5-naphthalenedisulfonate anion).

## 1 Experimental

All materials were commercially available and used as received.

Compounds **1** and **2** were obtained according to the procedures described previously to produce the  $\text{Cu}^{2+}$  analogue<sup>[2]</sup>.

## 2 Crystallographic Studies

Experimental details of the X-ray analyses are provided in Table 1. All diffraction data were collected on a Bruker Smart 1000 CCD diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. Absorption corrections were applied by SADABS<sup>[5]</sup>. The structures were solved by direct methods and refined using full-matrix least-squares/difference Fourier techniques using

Table 1 Crystal Data and Structure Refinement for Compounds 1-2

compound	1	2
formula	$\text{C}_{20}\text{H}_{30}\text{N}_4\text{NiO}_6\text{S}_2$	$\text{C}_{20}\text{H}_{38}\text{CoN}_4\text{O}_{10}\text{S}_2$
formula weight	551.26	617.59
crystal class	monoclinic	triclinic
space group	$P2(1)/c$	$P\bar{1}$
$a/\text{\AA}$	8.583(5)	8.738(5)
$b/\text{\AA}$	10.533(6)	9.324(5)
$c/\text{\AA}$	12.946(7)	10.118(5)
$\alpha/^\circ$	90	81.382(8)
$\beta/^\circ$	92.433(9)	64.868(8)
$\gamma/^\circ$	90	62.999(8)
$V/\text{\AA}^3$	1169.4(11)	664.0(6)
Z	2	1
density (calc.)/( $\text{g} \cdot \text{cm}^{-3}$ )	1.566	1.544
absorption coefficient/ $\text{mm}^{-1}$	1.055	0.863
$F(000)$	579	325
$\theta$ range for data collection/ $^\circ$	2.37 to 26.37	2.23 to 27.18
reflections collected/unique	6583 / 2312	4374 / 2794
observed reflections ( $I > 2\sigma(I)$ )	1995	2448
transmission factors	0.7784 ~ 0.6657	0.8814 ~ 0.7295
data/restraints/parameters	2312 / 0 / 155	2794 / 0 / 171
goodness of fit	0.995	1.218
$R(F)$ ; $R_w(F)$ ( $I > 2\sigma(I)$ )	0.0266, 0.0697	0.0439, 0.1037

SHELXTL<sup>[6]</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. After that, all hydrogen atoms of the ligands were placed at idealized positions and refined as riding atoms with the relative isotropic parameters of the heavy atoms to which they are attached. Hydrogen atoms of some water molecules were located from the difference Fourier map at the finale state of refinement. Selected bond lengths and angles were provided in Table 2.

In Complex 1, the occupancy of the crystalline water molecule was refined and converged to 0.17, which was then fixed at the final stage of refinement.

### 3 Results and Discussion

$[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$  (1): It crystallized in the same unit cell and space group as that of the  $\text{Cu}^{2+}$  analogue<sup>[2]</sup>. The coordination geometry is illustrated in Fig. 1a. Both the Ni cation and 1, 5nds anion are located on the crystallographic inversion centers, while the crystalline water molecules are only partially occupied. The  $\text{Ni}^{2+}$  center adopted a distorted octahedral geometry, in which the four N-atoms from the cyclam ligand trap  $\text{Ni}^{2+}$  and two  $\text{SO}_3^-$  groups from

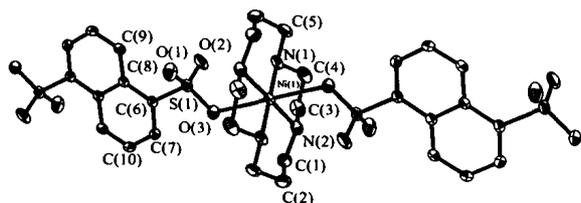


Fig. 1a Coordination structure of the  $\text{Ni}^{2+}$  center in compound 1, with 30% probability displacement ellipsoids. Only the unique portion is labeled. All H-atoms are omitted for clarity.

two 1, 5nds anions occupied the axial positions, with distance of  $\text{Ni}-\text{O} = 2.4573(16)$  Å. It is interesting to note that the  $\text{Ni}-\text{N}$  distances are 1.9630(17) and 2.1057(19) Å, significantly longer than that observed in  $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ <sup>[7]</sup>. The approaching of the bulky  $\text{SO}_3^-$  groups might cause such expansion. The interactions between  $[\text{Ni}(\text{cyclam})]^{2+}$  and 1, 5nds anions are further enhanced by hydrogen bonds formed between the  $\text{SO}_3^-$  O-atoms and the amino H-atoms of the cyclam ligand ( $\text{N1}\cdots\text{O2} = 3.052(2)$  Å,  $\text{N1}-\text{H}\cdots\text{O2} = 160.2^\circ$ ;  $\text{N2}\cdots\text{O1} = 2.996(3)$  Å,  $\text{N2}-\text{H}\cdots\text{O1} = 163.0^\circ$ ). Consequently, a 1-dimensional chain is constructed via weak coordination and hydrogen bonds, as showed in Fig. 1b. Previously, we have reported the syntheses and crystal structures of four nickel(II) 1,5-naphthalenedisulfonate complexes, namely  $[\text{Ni}(\text{H}_2\text{O})_6](1, 5\text{nds})$ , *trans*- $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot \text{H}_2\text{O}$ , and  $[\text{Ni}(\text{dien})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$  (where en = ethylenediamine, tren = tris(2-aminoethyl) amine, dien = diethylenetriamine)<sup>[1]</sup>. These compounds and the title compound 1 were obtained using the same procedure. However, weak coordination interaction is only observed in 1 where the auxiliary ligand is the macrocyclic cyclam. This observation further supports our previous observation that the coordination strength of transition metal cation with sulfonate can be tailored by the nature of

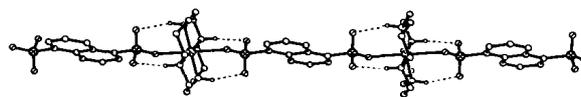


Fig. 1b 1-dimensional chain constructed both by weak coordination and hydrogen bonds in compound 1. C-H hydrogen atoms are omitted for clarity.

Table 2 Selected Bond Lengths(Å) and Angles(°)

$[\text{Ni}(\text{cyclam})(1, 5\text{nds})] \cdot 1/3\text{H}_2\text{O}$ (1)							
Ni(1)-N(1)	1.9630(17)	Ni(1)-N(2)	2.1057(19)	Ni(1)-O(3)	2.4573(16)	S(1)-O(2)	1.4017(17)
S(1)-O(3)	1.4842(16)	S(1)-O(1)	1.4856(17)	S(1)-C(6)	1.7416(18)		
N(1)-Ni(1)-N(2)	85.43(8)	N(1)-Ni(1)-O(3)	89.03(7)	N(2)-Ni(1)-O(3)	88.90(7)	S(1)-O(3)-Ni(1)	118.24(9)
$[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1, 5\text{nds}) \cdot 2\text{H}_2\text{O}$ (2)							
Co(1)-O(1W)	1.921(2)	Co(1)-N(2)	1.964(3)	Co(1)-N(1)	1.975(3)	S(1)-O(3)	1.437(2)
S(1)-O(1)	1.456(2)	S(1)-O(2)	1.458(3)	S(1)-C(3)	1.791(3)		
O(1w)-Co(1)-N(2)	89.48(11)	O(1w)-Co(1)-N(1)	88.43(11)	N(2)-Co(1)-N(1)	93.88(12)		

the amino ligand<sup>[2,3]</sup>.

[Co(cyclam)(H<sub>2</sub>O)<sub>2</sub>](1, 5nds) · 2H<sub>2</sub>O (2): The coordination geometry of the complex cation is showed in Fig. 2a. In this compound, the SO<sub>3</sub><sup>-</sup> group is not involved in any direct interaction with Co<sup>2+</sup>. The Co<sup>2+</sup> caenter is coordinated octahedrally by four N-atoms of the cyclam ligand and two water molecules, while the 1, 5nds exists as counter anion. Both the complex cation and the anion are located on the crystallographic inversion centers. The Co-N distances are 1.964(3) and 1.975(3) Å, in agreement with that of the reported [Co(cyclam)(H<sub>2</sub>O)R](ClO<sub>4</sub>)<sub>2</sub>(R = Et<sup>[8]</sup> or COCH<sub>3</sub><sup>[9]</sup>). However, the bond length between the Co<sup>2+</sup> and water molecule, Co-O<sub>w</sub> = 1.921(2) Å, is significantly shorter than that observed in the above analogues, which are around 2.2 Å. As far as we are aware, structure of the complex cation [Co(cyclam)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> has never been reported before.

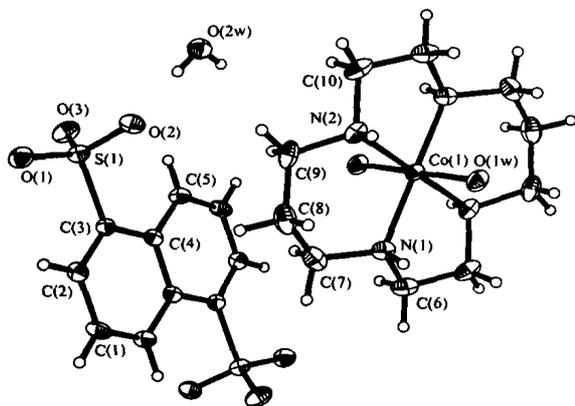


Fig. 2a Compound 2, with 30% probability displacement ellipsoids  
Only the unique portion is labeled

As shown in Fig. 2b, the 1, 5nds anions form second sphere coordination with Ni<sup>2+</sup> via hydrogen bonds and result in well-ordered cation-anion arrangement. All of the SO<sub>3</sub><sup>-</sup> O-atoms and the amino H-atoms are involved in hydrogen bonds with each other, resulting extended 3-dimensional structures (N1...O3#1 = 2.913(4) Å, N1-H...O3#1 = 135.1 Å; N2...O2#2 = 3.079(4) Å, N2-H...O2#2 = 149.7 Å; N2...O1#2 = 3.361(4) Å, N2-H...O1#2 = 142.9 Å, symmetry codes #1:  $x+1, y-1, z$ ; #2:  $-x+2, -y+1,$

$-z+1$ ). The crystalline water molecules fill in the gaps formed by the two SO<sub>3</sub><sup>-</sup> groups and two complex cations, anchored by forming hydrogen bonds with the SO<sub>3</sub><sup>-</sup> O-atoms (O2w...O2 = 2.788(4) Å, O2w-H...O2 = 174.4°), as showed in Fig. 2c.

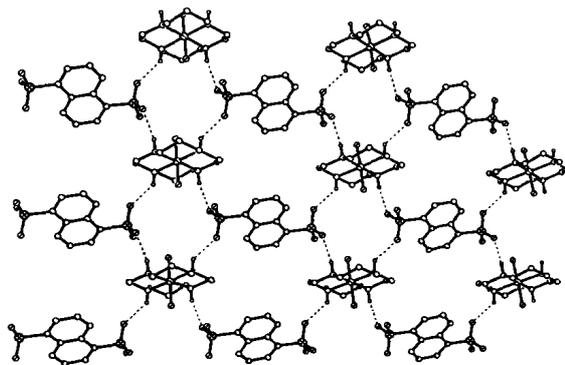


Fig. 2b 2-D net formed by hydrogen bonds in compound 2  
The C-H hydrogen atoms and crystalline water molecules are omitted for clarity

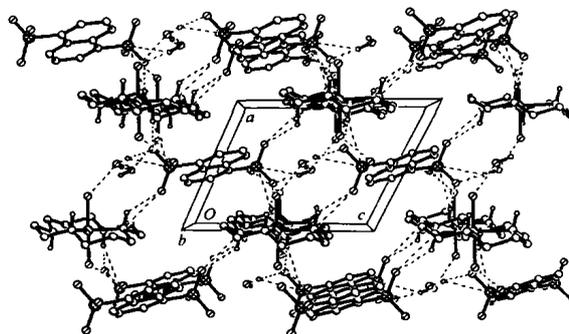


Fig. 2c Packing arrangement of compound 2 along the *b* axis  
Note the channels constructed along the *b* axis are filled by water molecules

In summary, the structures of compounds 1 and 2, together with the results published previously<sup>[11]</sup>, reveal that the coordination strength of Ni<sup>2+</sup> with the 1, 5nds anion can be enhanced by the introduction of the macrocyclic cyclam ligand. Also, the 1, 5nds anion shows the weakest coordination strength with Co<sup>2+</sup>, in comparison with other investigated divalent transition metals such as Ni<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup><sup>[1-3]</sup>.

#### 4 Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallo-

graphic Data Centre, CCDC Nos. 194341 and 194342 for compounds **1** and **2**, respectively. Copies of this information can be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

### References

- [1] Chen C. -H., Cai J., Feng X. -L., Chen X. -M. *J. Chem. Cryst.*, **2001**, **3**(5), 271.
- [2] Cai J., Chen C. -H., Liao C. -Z., Yao J. -H., Hu X. -P., Chen X. -M. *J. Chem. Soc. Dalton. Trans.*, **2001**, 1137.
- [3] (a) Cai J., Chen C. -H., Feng X. -L., Chen X. -M. *J. Chem. Soc. Dalton. Trans.*, **2001**, 2370;
- (b) Chen C. -H., Cai J., Liao C. -Z., Feng X. -L., Chen X. -M., Ng S. W. *Inorg. Chem.*, **2002**, **19**, 4967.
- [4] (a) Kosnic E. J., McClymont E. L., Hodder R. A., Squattrito P. J. *Inorg. Chim. Acta*, **1992**, **201**, 143;
- (b) Shubnell A. J., Kosnic E. J., Squattrito P. J. *Inorg. Chim. Acta*, **1994**, **216**, 101;
- (c) Gunderman B. J., Kabell I. D., Squattrito P. J., Dubey S. N. *Inorg. Chim. Acta*, **1997**, **258**, 237.
- [5] Blessing R. *Acta Cryst.*, **1995**, **A51**, 33.
- [6] Sheldrick G. M. *SHELX-97, Program for X-ray Crystal Structure Solution and Refinement*, Gottingen University, Germany, **1997**.
- [7] Prasad L., Nyburg S. C., McAuley A. *Acta Crystallogr., Sect. C*, **1987**, **C43**, 1038.
- [8] Bakac A., Espenson J. H. *Inorg. Chem.*, **1987**, **26**, 4353.
- [9] Bakac A., Espenson J. H., Young V. G. Jr *Inorg. Chem.*, **1992**, **31**, 4959.