

两个由异烟酰胺构筑的钴、镍配合物的合成及晶体结构

刘 博^{*1} 李秀梅² 周 实¹ 王庆伟¹ 李传碧¹
(¹ 吉林师范大学化学学院, 吉林师范大学环境友好材料制备与
应用省部共建教育部重点实验室, 四平 136000)
(² 通化师范学院化学系, 通化 134002)

摘要: 采用溶液培养法, 在室温下合成了 2 个新的过渡金属配合物 $[\text{Co}(\text{inta})_2(\text{H}_2\text{O})_4][\text{Co}(\text{H}_2\text{O})_6](\text{tdc})_2 \cdot 2\text{H}_2\text{O}$ (**1**) 和 $[\text{Ni}(\text{inta})_2(\text{H}_2\text{O})_4](\text{tdc}) \cdot 2\text{H}_2\text{O}$ (**2**) (inta=异烟酰胺, H_2tdc =2,5-噻吩二甲酸)。并对其进行了元素分析、红外光谱、紫外光谱、热重和 X-射线单晶衍射测定。这两个配合物通过氢键和 π - π 相互作用形成了三维超分子网状结构。

关键词: 晶体结构; 钴配合物; 镍配合物

中图分类号: O614.81²; O614.81³

文献标识码: A

文章编号: 1001-4861(2012)05-1019-06

Synthesis and Crystal Structure of Two Complexes of Cobalt, Nickel Assembled by Isonicotinamide

LIU Bo^{*1} LI Xiu-Mei² ZHOU Shi¹ WANG Qing-Wei¹ LI Chuan-Bi¹

(¹Department of Chemistry, Jilin Normal University, Key Laboratory of Preparation and Applications of
Environmental Friendly Materials (Jilin Normal University), Ministry of Education, Siping, Jilin 136000, China)

(²Department of Chemistry, Tonghua Teachers College, Tonghua, Jilin 134002, China)

Abstract: Two transitional metal complex $[\text{Co}(\text{inta})_2(\text{H}_2\text{O})_4][\text{Co}(\text{H}_2\text{O})_6](\text{tdc})_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{inta})_2(\text{H}_2\text{O})_4](\text{tdc}) \cdot 2\text{H}_2\text{O}$ (**2**) (inta=isonicotinamide, H_2tdc =2,5-thiophenedicarboxylic acid) have been synthesized by employing the solution a preparation method at room temperature. They were structurally characterized by elemental analysis, IR spectrum, UV spectrum, TG and single-crystal X-ray diffraction. They are further extended into a three-dimensional supramolecular network structure through hydrogen bonds and π - π interactions. CCDC: 862125, **1**; 862126, **2**.

Key words: crystal structure; cobalt complex; nickel complex

0 Introduction

The rational design and synthesis of metal-directed supramolecular frameworks have received much attention in coordination chemistry because of their interesting molecular topologies and tremendous potential applications in host-guest chemistry, catalysis, molecular selection, nonlinear optics, ion exchange and microelectronics^[1-6]. In this field, the metals often have

different valences, making a number of building blocks to fulfill special needs. Many important properties of coordination polymers depend largely on their structures and topology. Therefore, the selection of special inorganic and organic building blocks is the key to the construction of a desired framework^[7]. In this respect, the 2,5-thiophenedicarboxylic acid (H_2tdc) ligand is proved to be a good candidate due to its various bridging abilities and strong coordination

收稿日期: 2011-09-18。收修改稿日期: 2011-12-24。

吉林省教育厅科学技术研究(吉教科合字(2012)第 479 号)资助项目。

*通讯联系人。E-mail: liubo20032006@163.com

tendency with transition metals to form 2D and 3D moderately robust networks^[8-9]. On the other hand, the introduction of bi- or multi-dentate ligands containing N- or O-donors to the metal-oxalate system may lead to new structural evolution since the binding of these ligands to metal centers may adjust the dimensionality of metal-organic coordination polymers^[10-11]. Among the organic N-donors, isonicotinamide (inta) is an excellent rigid ligand for the construction of novel metal-organic coordination frameworks because of its three donor sites^[12-13]. In this paper, we report two new compounds, $[\text{Co}(\text{inta})_2(\text{H}_2\text{O})_4][\text{Co}(\text{H}_2\text{O})_6](\text{tdc})_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{inta})_2(\text{H}_2\text{O})_4](\text{tdc}) \cdot 2\text{H}_2\text{O}$ (**2**), which exhibit 3D supramolecular framework through hydrogen bonds and π - π stacking interactions and are reported scarcely.

1 Experimental

1.1 General procedures

All materials were commercially purchased and used without further purification. Infrared spectra (KBr pellets) were taken on a Perkin-Elmer 2400LS II spectrometer and elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The TG studies were performed on a Perkin-Elmer TGA7 analyzer.

1.2 Synthesis

$[\text{Co}(\text{inta})_2(\text{H}_2\text{O})_4][\text{Co}(\text{H}_2\text{O})_6](\text{tdc})_2 \cdot 2\text{H}_2\text{O}$ (**1**). An aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 10 mL) was slowly dropped into an acetonitrile solution of isonicotinamide (0.2 mmol, 10 mL) under stirring. After stirring for 30 min, an aqueous solution of sodium tdc

(0.2 mmol, 10 mL) was added into the above solution, the precipitate was filtered and the filtrate was stood for 10 d, obtaining pink block crystals suitable for X-ray structural analysis. The elemental analyses found (%): C, 31.1; H, 4.2; N, 5.9. Calcd. for $\text{C}_{24}\text{H}_{40}\text{Co}_2\text{N}_4\text{O}_{22}\text{S}_2$ (%): C, 31.4; H, 4.4; N, 6.1.

$[\text{Ni}(\text{inta})_2(\text{H}_2\text{O})_4](\text{tdc}) \cdot 2\text{H}_2\text{O}$ (**2**). An aqueous solution of $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol, 10 mL) was slowly dropped into an acetonitrile solution of isonicotinamide (0.2 mmol, 10 mL) under stirring. After stirring for 30 min, an aqueous solution of sodium tdc (0.2 mmol, 10 mL) was added into the above solution, the precipitate was filtered and the filtrate was stood for 10 d, obtaining blue block crystals suitable for X-ray structural analysis. The elemental analyses found (%): C, 39.2; H, 4.5; N, 10.0. Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_4\text{NiO}_{12}$ (%): C, 39.4; H, 4.8; N, 10.2.

1.3 Structure determination

Single crystal diffraction data of **1** and **2** were respectively collected on a Bruker SMART APEX-CCD diffractometer equipped with a graphite-monochromatic $\text{Mo K}\alpha$ ($\lambda=0.071\,073\text{ nm}$) radiation at room temperature. The structure was solved by direct methods with SHELXS-97 program^[14] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97^[15]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. The selected bond parameters are given in Table 1.

Crystal data for **1**: $\text{C}_{24}\text{H}_{40}\text{Co}_2\text{N}_4\text{O}_{22}\text{S}_2$, triclinic, space group $P\bar{1}$, $M_r=918.58$, $a=0.673\,82(5)\text{ nm}$, $b=$

Table 1 Selected bond lengths (nm) and bond angles ($^\circ$) compound for **1** and **2**

1					
Co(1)-N(1)	0.216 94(16)	Co(1)-N(1A)	0.216 94(16)	Co(1)-O(1W)	0.211 33(16)
Co(1)-O(1WA)	0.211 33(16)	Co(1)-O(2W)	0.209 01(15)	Co(1)-O(2WA)	0.209 01(15)
Co(2)-O(3W)	0.208 27(14)	Co(2)-O(3WA)	0.208 27(14)	Co(2)-O(4W)	0.205 75(15)
Co(2)-O(4WB)	0.205 75(15)	Co(2)-O(5WB)	0.214 50(13)	Co(2)-O(5WB)	0.214 50(13)
O(2W)-Co(1)-O(2WA)	180.0	O(2WA)-Co(1)-O(1W)	86.90(7)	O(2W)-Co(1)-O(1WA)	86.90(7)
O(2W)-Co(1)-O(1W)	93.10(7)	O(1W)-Co(1)-O(1WA)	180.00(8)	O(2W)-Co(1)-N(1A)	88.50(6)
O(1W)-Co(1)-N(1A)	88.45(6)	O(2W)-Co(1)-N(1)	91.50(6)	O(2WA)-Co(1)-N(1)	88.50(6)
O(1W)-Co(1)-N(1)	91.55(6)	O(1WA)-Co(1)-N(1)	88.45(6)	N(1A)-Co(1)-N(1)	180.0
O(4WB)-Co(2)-O(4W)	180.00(10)	O(4WB)-Co(2)-O(3W)	85.83(6)	O(4W)-Co(2)-O(3W)	94.17(6)

Continued Table 1

O(3W)-Co(2)-O(3WB)	180.00(9)	O(4W)-Co(2)-O(3WB)	85.83(6)	O(3W)-Co(2)-O(5WB)	86.78(6)
O(4WB)-Co(2)-O(5W)	86.78(6)	O(4W)-Co(2)-O(5W)	93.22(6)	O(3W)-Co(2)-O(5W)	90.75(5)
O(3W)-Co(2)-O(5WB)	89.25(5)	O(5W)-Co(2)-O(5WB)	180.00(7)	O(3WB)-Co(2)-O(5W)	89.25(5)
2					
Ni(1)-O(1W)	0.204 98(17)	Ni(1)-O(2W)	0.205 33(15)	Ni(1)-N(1)	0.211 91(19)
Ni(1)-O(1WA)	0.204 98(17)	Ni(1)-O(2WA)	0.205 33(15)	Ni(1)-N(1A)	0.211 91(19)
Ni(2)-O(3W)	0.205 31(15)	Ni(2)-O(4W)	0.205 83(19)	Ni(2)-N(3)	0.210 86(19)
Ni(2)-O(3WB)	0.205 31(15)	Ni(2)-O(4WB)	0.205 83(19)	Ni(2)-N(3B)	0.210 86(19)
O(1WA)-Ni(1)-O(1W)	180.0	O(1WA)-Ni(1)-O(2W)	89.41(6)	O(1W)-Ni(1)-O(2W)	90.59(6)
O(2W)-Ni(1)-O(2WA)	180.0	O(1WA)-Ni(1)-N(1)	90.81(6)	O(1W)-Ni(1)-N(1)	89.19(6)
O(2W)-Ni(1)-N(1)	92.19(6)	O(1W)-Ni(1)-N(1A)	90.81(6)	O(2WA)-Ni(1)-N(1)	87.81(6)
O(2W)-Ni(1)-N(1A)	87.81(6)	N(1)-Ni(1)-N(1A)	180.00(9)	O(3WB)-Ni(2)-O(3W)	180.0
O(3WB)-Ni(2)-O(4W)	88.97(6)	O(3W)-Ni(2)-O(4W)	91.03(6)	O(3W)-Ni(2)-O(4WB)	88.97(6)
O(4W)-Ni(2)-O(4WB)	180.0	O(3WB)-Ni(2)-N(3)	87.98(6)	O(3W)-Ni(2)-N(3)	92.02(6)
O(4W)-Ni(2)-N(3)	92.34(6)	O(3W)-Ni(2)-N(3B)	87.98(6)	O(4W)-Ni(2)-N(3B)	87.66(6)
N(3)-Ni(2)-N(3B)	180.000(1)				

Symmetry transformations used to generate the equivalent atoms: **1**: A: $-x, -y, 1-z$; B: $-x, -y, -z$; **2**: A: $-x+1, -y, -z+1$; B: $-x+1, -y, -z+2$.

0.699 53(6) nm, $c=2.014\ 64(16)$ nm, $\alpha=81.316\ 0(10)^\circ$, $\beta=81.502\ 0(10)^\circ$, $\gamma=75.904\ 0(10)^\circ$, $V=0.904\ 34(13)$ nm³, $Z=1$, $F(000)=474$, $\mu(\text{Mo } K\alpha)=1.126$ mm⁻¹, $D_c=1.687$ g·cm⁻³, 4 991 reflections measured, 3 543 unique ($R_{\text{int}}=0.012\ 8$), 3 284 observed reflections with $I>2\sigma(I)$, $R=0.029\ 8$, $wR=0.075\ 6$, $S=1.046$.

Crystal data for **2**: C₁₈H₂₆N₄NiO₁₂S, triclinic, space group $P\bar{1}$, $M_r=581.2$, $a=0.906\ 8(5)$ nm, $b=0.916\ 5(5)$ nm, $c=1.553\ 3(5)$ nm, $\alpha=80.695(5)^\circ$, $\beta=88.325(5)^\circ$, $\gamma=73.535(5)^\circ$, $V=1.221\ 5(10)$ nm³, $Z=2$, $F(000)=604$, $\mu(\text{Mo } K\alpha)=0.949$ mm⁻¹, $D_c=1.580$ g·cm⁻³, 6 765 reflections measured, 4 766 unique ($R_{\text{int}}=0.011\ 6$), 4 173 observed reflections with $I>2\sigma(I)$, $R=0.029\ 8$, $wR=0.071\ 0$, $S=1.026$.

CCDC: 862125, **1**; 862126, **2**.

2 Results and discussion

2.1 IR spectrum

The FTIR spectra of compound **1** (in KBr) show the bands as follows: 3 442, 1 680, 1 558, 1 403, 1 350, 1 128, 785, 760, 620, 542 and 468 cm⁻¹. IR spectrum of the compound shows the typical anti-symmetric (1 558 cm⁻¹) and symmetric (1 350 cm⁻¹) stretching bands of carboxylate groups. The absence of the characteristic band around 1 700 cm⁻¹ in compound **1** attributed to the

protonated carboxylic group indicates that the presence deprotonation of tdc ligand. In addition, the strong and broad band centered at 3 442 cm⁻¹ for **1** is attributable to the H-O-H stretching vibration of water molecule on the basis of the known structure.

The FTIR spectra of compound **2** (in KBr) show the bands as follows: 3 358, 1 679, 1 600, 1 555, 1 418, 1 400, 1 351, 1 312, 1 222, 1 151, 1 103, 1 064, 881, 786, 762, 662, 623, 550 and 473 cm⁻¹. IR spectrum of the compound shows the typical anti-symmetric (1 555 cm⁻¹) and symmetric (1 351 cm⁻¹) stretching bands of carboxylate groups. The absence of the characteristic band around 1 700 cm⁻¹ in compound **1** attributed to the protonated carboxylic group indicates that the present deprotonation of tdc ligand. In addition, the strong and broad band centered at 3 358 cm⁻¹ for **1** is attributable to the H-O-H stretching vibration of water molecule on the basis of the known structure.

2.2 Description of the structure

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in $P\bar{1}$ space group. The molecular structure of **1** is shown in Fig.1. There are two different coordination centers, Co(1) and Co(2), in the crystal with different coordination modes. The Co(1) ion is six-coordinated by two nitrogen atoms from

58.6% from 17 to 117 °C corresponds to the removal of water and tdc molecules (calcd. 60.5%). Upon further heating, an obvious weight loss (28.50%) occurs in the temperature range of 117~450 °C, corresponding to the release of inta ligands (calcd. 26.6%). After 450 °C no weight loss is observed, which means the complete decomposition of **1**. The residual weight should be CoO.

TG curve of **2** shows that the first weight loss of 33.1% from 15 to 151 °C corresponds to the removal of free water and tdc molecules (calcd. 35.5%). Upon further heating, an obvious weight loss (88.5%) occurs in the temperature range of 151~549 °C, corresponding to the release of coordinated water molecules and inta ligands (calcd. 89.9%). After 554 °C no weight loss is observed, which means the complete decomposition of **2**. The residual weight should be NiO.

2.4 UV spectrum

The UV spectra for the title compound **1** and inta ligand have been investigated in the solid state. Both the title compound and inta have one absorption band at about 271 nm, which should be assigned to the $n \rightarrow \pi^{*[16]}$ transition of inta. However, after inta coordinating to the Co^{2+} ion, the absorption intensity slightly increases. It is clearly that the absorption band in inta remains in the same position with that in the title compound, showing that they are not affected basically by the metal coordination.

The UV spectra for the title compound **2** and inta ligand have been investigated in the solid state. For compound **2**, there is no absorption band.

Reference:

- [1] Batten S R, Robson R. *Angew. Chem. Int. Ed.*, **1998**,**37**: 1460-1494
- [2] Hagrman P J, Hagrman D, Zubieta J. *Angew. Chem. Int. Ed.*, **1999**,**38**:2638-2684
- [3] Khlobystov A N, Blake A J, Champness N R, et al. *Coord. Chem. Rev.*, **2001**,**222**:155-192
- [4] Eddaoudi M, Moler D B, Li H, et al. *Acc. Chem. Res.*, **2001**,**34**:319-330
- [5] Carlucci L, Ciani G, Proserpio D M. *Coord. Chem. Rev.*, **2003**, **246**:247-289
- [6] Kitagawa S, Kitaura R, Noro S I. *Angew. Chem. Int. Ed.*, **2004**,**43**:2334-2375
- [7] Lu J K, Lawandy M A, Li J. *Inorg. Chem.*, **1999**,**38**:2695-2704
- [8] Huang X H, Huang C C, Wang J G, et al. *Chinese J. Struct. Chem.*, **2009**,**11**:1367-1372
- [9] MacNeill C M, Day C S, Gamboa S A. *Journal of Chemical Crystallography*, **2010**,**40**:222-230
- [10] Hagrman P J, Zubieta J. *Inorg. Chem.*, **2000**,**39**:3252-3260
- [11] Li Y G, Wang E B, Zhang H, et al. *J. Solid State Chem.*, **2002**,**163**:10-16
- [12] Baum G, Blake A J, Fenske D, et al. *Acta Crystallogr. Sect. C*, **2002**,**58**:542-544
- [13] Li X M, Wang Q W, Li D, et al. *Chinese J. Struct. Chem.*, **2007**,**11**:1339-1342
- [14] Sheldrick G M. *SHELXS 97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [15] Sheldrick G M. *SHELXS 97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [16] Mohamed G G, El-Gamel N E A. *Spectrochim. Acta, Part A*, **2004**,**60**:3141-3154