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氢键构筑的二维网状结构镍配合物[Ni(en)$_2$(dpas)$_2$]的合成、晶体结构及电化学性质

王 祥[1] 罗 芳*,[2] 高文涛[1]

([1]渤海大学超精细化学品研究所,锦州 121000)

([2]东北师范大学教育部多酸重点实验室,长春 130024)

关键词:镍(Ⅱ)配合物;氢键;晶体结构;电化学性质

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Synthesis, Crystal Structure and Electrochemical Properties of 2D Hydrogen-bonded network Complex [Ni(en)$_2$(dpas)$_2$]

WANG Xiang[1] LUO Fang*,[2] GAO Wen-Tao[1]

([1]*Research Institute of Super Fine Chemicals of Bohai University, Jinzhou, Liaoning* 121000)

([2]*Key Laboratory of Polyoxometalates Science of Ministry of Education, Northeast Normal University, Changchun* 130024)

Abstract: A new 2D Hydrogen-bonded network complex [Ni(en)$_2$(dpas)$_2$] (Nadpas=sodium diphenylamine sulphonic acid salt, en=ethanediamine) has been synthesized in aqueous solution, and characterized by elemental analysis, IR. The crystal structure was determined by single-crystal X-ray diffraction. The complex crystallizes in space group $P2_1/c$, with cell parameters a=0.605 6(5) nm, b=1.448 1(5) nm, c=1.711 9(5) nm, β=93.257(5)°, and V=1.498 9(14) nm^3, D_c=1.497 g·cm^{-3}, Z=2, F(000)=708, R=0.027 7, wR=0.072 5. The crystal structure shows that the nickel atom is coordinated with four nitrogen atoms from the two en and two oxygen atoms from two dpas to form a mononuclear complex. Furthermore, the adjacent complex units are extended into a 2D supramolecular network through hydrogen bonds. CCDC: 674868.

Key words: nickel(Ⅱ) complex; hydrogen bond; crystal structure; electrochemical property

Extended covalent organic and inorganic layered materials have been of great interest because of their potential use as host structures for various chemical processes[1]. However, because of the weak coordination strength of the sulfonate compared with that of the phosphate, the reported systems were all segregated inorganicorganic structures formed by extensive hydrogen bonding interactions. And it was concluded that divalent first row of transition metal ions show no tendency to coordinate to the sulfonate anions in the presence of water molecules. The structure of some metal complexes about single-sulfonate and double-sulfonate were already reported[2~9]. Furthermore, the electrochemical properties about the nickel atom complex or polymer are constantly studied[10,11]. So a new 2D Hydrogen-bonded network complex [Ni(en)$_2$(dpas)$_2$]

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*通讯联系人。E-mail:luof746@nenu.edu.cn

第一作者:王 祥,男,29 岁,硕士研究生,中级实验师;研究方向:有机合成及配位化学。

is synthesized, the crystal structure is determined by single-crystal X-ray diffraction, the electrochemical property of the complex is also further investigated.

1 Experimental

1.1 Reagent and apparatus

All reagents are analysis pure. Elemental analyses were performed on a Elementar vario EL-Ⅲ analyzer. The IR spectra were recorded on HYPER1700 spectrophotometer using KBr pellets. The single crystal structure was obtained on a Bruker Smart Apex CCD X-ray single-crystal diffractometer system. The electron transfer behavior of the complex was examined using cyclic voltammogram on a CHI-660 electrochemical analysis system.

1.2 Synthesis of the title complex

5 mL aqueous solution of Nickel chloride hexahydrate (0.1 mmol) and ethanediamine (0.2 mmol) was added into a 5 mL aqueous solution of Nadpas (0.1 mmol). The resulting solution was stirred ten minutes and filtrated then allowed to evaporate in air at room temperature. After a month, purple crystals of the title complex were collected in 60% yield (based on Ni). Anal. Calcd for $C_{28}H_{36}N_6NiO_6S_2$ (%): C 25.20, H, 4.23, N 4.20. Found(%): C 25.18, H 4.46, N 4.35. IR (KBr, cm^{-1}): 3 375 (s), 1 523 (s), 1 342 (s), 1 199 (s), 1 077(s), 1 027(s), 621(m).

1.3 Crystal structure determination

A purple single crystal of the title compound with dimensions of 0.36 mm ×0.18 mm ×0.17 mm was selected for structure determination. The data collection was performed on the Bruker Smart Apex 1000 CCD X-ray single-crystal diffractmeter with Mo $K\alpha$ radiation (λ =0.071 073 nm). A total of 7 407 reflections were collected in the range of $1.84° \leqslant \theta \leqslant 25°$, of which 2 637 reflections were unique with R_{int}=0.020 8 and 2 317 with $I>2\sigma(I)$ were considered as observed. The final R_1 and wR_2 were 0.027 7 and 0.072 5. The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using SHELXL-97 software[12]. All the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions and those attached to nitrogen atoms were located in the Fourier maps. A summary of the crystallographic data and structural determination for the title complex is provided in Table 1.

CCDC: 674868.

Table 1　Crystallographic data for the title complex

Empirical formula	$C_{28}H_{36}N_6NiO_6S_2$	Z	2
Formula weight	675.46	μ(Mo $K\alpha$) / mm^{-1}	0.839
Temperature / K	293(2)	F(000)	708
Crystal system	Monoclinic	Crystal size / mm	0.36×0.18×0.17
Space group	$P2_1/n$	Range of θ / (°)	1.84~25
a / nm	0.605 6(5)	Limiting indices	$-7 \leqslant h \leqslant 7$, $-17 \leqslant k \leqslant 10$, $-19 \leqslant l \leqslant 20$
b / nm	1.448 1(5)	Reflections collected / unique (R_{int})	7 407 / 2 637 (0.020 8)
c / nm	1.711 9(5)	Goodness of fit on F^2	1.048
β / (°)	93.257(5)	Final R indices [$I>2\sigma(I)$]	R_1=0.027 7, wR_2=0.072 5
V / nm^3	1.498 9(14)	R indices (all date)	R_1=0.033 3, wR_2=0.075 6
D_c / (g·cm^{-3})	1.497	Largest diff. peak and hole / (e·nm^{-3})	0.222, −0.270

2 Results and discussion

2.1 Crystal structure of the title complex

The selected bond lengths and bond angles are given in Table 2. The molecular structure of the title complex is shown in Fig.1, the 2D network structure through hydrogen bonds are located in Fig.2, respectively.

The complex crystallizes in the centrosymmetric space group $P2_1/n$. The coordination geometry is illustrated in Fig.1. The Ni(1) atom sits on crystallographic inversion center. The nickel atom is coordinated with four nitrogen atoms from the two en and two oxygen atoms from two dpas to furnish a distorted octahedron

Table 2 Selected bond lengths (nm) and bond angles (°) for the title complex

Ni(1)-N(1)	0.208 2(2)	Ni(1)-N(2)	0.209 53(19)	Ni(1)-O(3)	0.210 52(15)
Ni(1)-N(1)^{i}	0.208 2(2)	Ni(1)-N(2)i	0.209 53(19)	Ni(1)-O(3)^{i}	0.210 52(15)
N(1)-Ni(1)-O(3)	92.63(7)	N(1)-Ni(1)-N(2)	82.33(8)	N(2)-Ni(1)-O(3)	89.37(8)
N(1)-Ni(1)-O(3)^{i}	87.37(7)	N(1)-Ni(1)-N(2)^{i}	97.67(8)	N(2)-Ni(1)-O(3)^{i}	90.63(8)
N(1A-Ni (1)-N(1)	180.00(13)	O(1)-S(2)-O(2)	111.87(11)	O(1)-S(2)-O(3)	112.03(12)
N(1)A-Ni (1)-N(2)^{i}	82.33(8)	S(2)-O(3)-N (1)	138.43(9)	C(4)-N(3)-C(7)	126.05(19)

^{i} $-x+2, -y, -z$.

geometry. The nickel atom and two nitrogen atoms are on the equatorial plane, which is similar to that of the reported work[7]. The bond lengths of Ni-N(1) and Ni-N(2) are 0.208 2(2) nm and 0.209 53(19) nm. Two oxygen from the SO_3^- groups of dpas occupies the axial positions, with distance of Ni-O(3)=0.210 52(15) nm, which is shorter than that observed by Cai [0.245 73(16) nm][7]. Moreover, the mononuclear complexes are stabilized by intramolecular hydrogen bond interactions between O(2) from the SO_3^- and H(1A) from en ligands [N(1)–H1B···O(2), the N···O distance is 0.305 7(3) nm, the angle is 154(7)°].

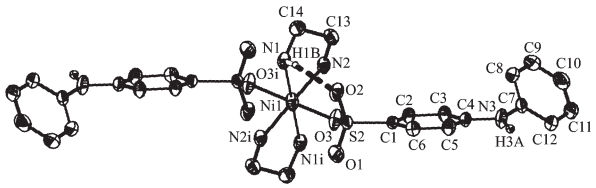
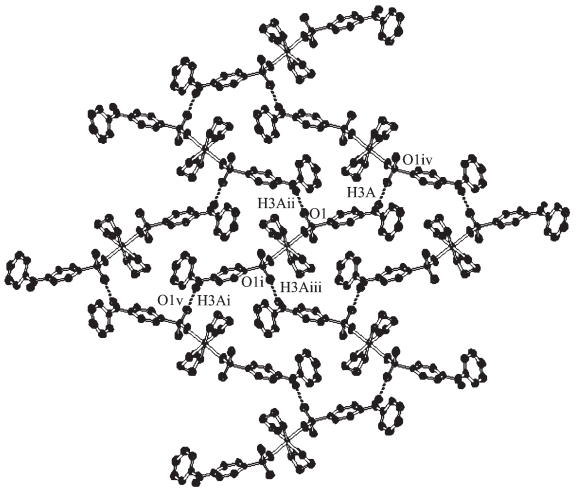


Fig.1 Molecular structure of the title complex



i: 2 $-x, -y, -z$; ii: 1.5$-x$, $-0.5+y$, $0.5-z$; iii: $0.5+x$, $0.5-y$, $-0.5+z$; iv: 1.5$-x$, $0.5+y$, $0.5-z$; v: $0.5+x$, $-0.5-y$, $-0.5+z$

Fig.2 2D Hydrogen-bonded network structure of the title complex

Interestingly, the analysis of the crystal packing of the title compound reveals that the monometallic unit is linked by four neighboring units to result in a 2D supramolecular network structure through the hydrogen bond interactions (N–H···O) between the oxygen atoms [O(1)] from SO_3^- and the hydrogen atoms[H(3A)] from -NH- groups [(N(3)–H(3A)···O(1), the N···O distance is 0.291 9(4) nm, and the angle is 164(2)°]. The 2D supramolecular network structure is showed in Fig.2.

2.2 Cyclic voltammogram

The cyclic voltammogram of the title complex was obtained in 50% (V/V) H_2SO_4 (1 mol·L^{-1}) + Na_2SO_4 (0.2 mol·L^{-1}) electrolyte solution containing 0.01 mol·L^{-1} the title complex using a conventional three-electrode system at 25 ℃. The glass-carbon working electrode was in the form of a disc and used in a stationary mode, the auxiliary electrode was a platinum plate, and the reference electrode was a saturated calomel electrode (SEC). The cyclic voltammogram were reported with 0.05 V·s^{-1} scan rate, at range from 0~0.7 V. From the voltammogram curves, it shows only one pair of oxidation-reduction peaks corresponding to the oxidation-reduction couple of Ni(Ⅲ)/Ni(Ⅱ). E_{pa}=0.446 V,

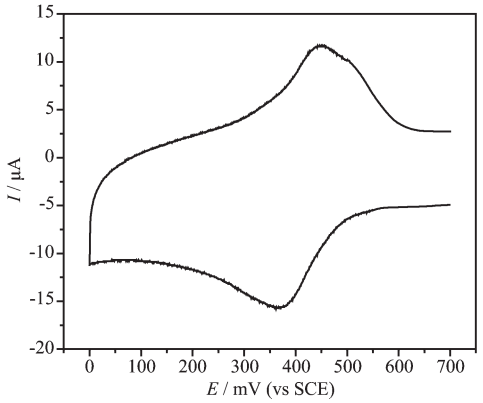


Fig.3 Cyclic voltammogram of the title complex

E_{pc}=0.370 V. The average formal potential [$E_{1/2}$=(E_{pa}+E_{pc})/2] is 0.408 V. The peak-to-peak separation between the corresponding anodic and cathodic peak is 0.076 V, exhibiting a quasi-reversible electrode process.

References:

[1] Thompson M E. *Chem. Mater*, **1994**,**6**(8):1168~1175

[2] Gunderman B J, Kabell I D, Squattrito P J, et al. *Inorg. Chim. Acta*, **1997**,**258**(2):237~246

[3] Chen C H, Cai J W, Chen X M. *J. Chem. Crystal*, **2001**,**3**(5): 271~279

[4] An D L, Gao S, Zhu Z B, et al. *Acta. Cryst. E*, **2004**,**60**(1): m111~m112

[5] Cai J W, Chen C H, Liao C Z, et al. *Dalton Trans*, **2001**,**7**: 1137~1142

[6] Cai J W, Chen C H, Feng X L, et al. *Dalton Trans*, **2001**,**16**: 2370~2375

[7] CAI Ji-Wen(蔡继文), CHEN Cai-Hong(陈彩虹), ZHOU Jin-Sen(周金森). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2003**,**19**(1):81~85

[8] SONG Yu-Mei(宋玉梅), PANG Jie(庞　洁). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2005**,**21**(9):1433~1434

[9] XIE Yong-Rong(谢永荣), YE Qiong(叶　琼). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2005**,**21**(9):1439~1440

[10]YANG Ying-Qun(杨颖群), LI Chang-Hong(李昶红), KUANG Dai-Zhi(邝代治), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2006**,**22**(2):303~306

[11]Ojani R, Raoof J B, Zavvarmahalleh S R H. *Electrochimica Acta*, **2008**,**53**(5):2402~2407

[12]Sheldrick G M. *SHELXS*-97, *Program for Crystal Structure Analysis*, University of Göttingen, Germany, **1997**.