

## 四(1-乙基咪唑)二异硫氰酸镉的晶体结构和电化学性能

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### Crystal and Electrochemical Property of Tetrakis(1-vinyl-1H-imidazole-*k*N<sup>3</sup>)diisothiocyanatocadmium(II)

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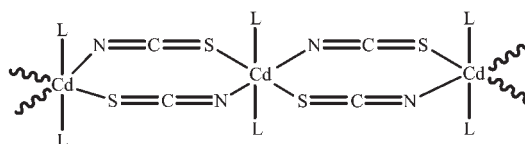
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**Abstract:** A complex  $[\text{Cd}(\text{NCS})_2(\text{Vim})_4]$  (where Vim=1-vinylimidazole) was synthesized and its crystal structure was determined by X-ray diffraction technique. The compound crystallizes in the Monoclinic space group  $P2_1/c$  with the parameters:  $a=0.858\ 50(17)$  nm,  $b=0.909\ 90(18)$  nm,  $c=1.782\ 3(4)$  nm,  $\beta=100.14(3)^\circ$ ,  $V=1.370\ 5(5)$  nm<sup>3</sup>,  $Z=2$ . In the structure, each Cd atom is coordinated by four 1-vinylimidazole ligands and a pair of monodentate isothiocyanic groups, affording a compressed octahedral  $\text{CdN}_6$  core. The  $\text{NCS}^-$  anions are trans and four N atoms from the 1-vinylimidazole ligands define the equatorial plane. From the cyclic voltammogram measurement in  $\text{H}_2\text{O}$ , we know that the electrode reaction was a quasi-reversible process. CCDC: 630897.

**Key words:** cadmium(II) complex; thiocyanato complex; cyclic voltammetry; crystal structure

The structures of a few polymeric Lewis-base adducts of cadmium(II) thiocyanate,  $[\text{Cd}(\text{SCN})_2(\text{L})_2]_n$  (where L is 2-, 3-, or 4-methylpyridine, imidazole, *N*-methylimidazole, benzylamine, dibenzylamine, tri-*m*-tolylphosphine or 1H-1,2,4-triazole), have been reported<sup>[1-5]</sup>. In all these compounds, each pair of adjacent metal atoms are bridged by a pair of  $\text{SCN}^-$  groups through both ends, resulting in a chain-like structure comprising  $(-\text{N}-\text{C}-\text{S}-\text{Cd})_2$  eight-membered rings (Scheme 1). In this paper, however, we report a Lewis-base adducts of cadmium(II) thiocyanate with the structure of  $[\text{Cd}(\text{SCN})_2(\text{Vim})_4]$  (**1**), in which no  $(-\text{N}-\text{C}-\text{S}-\text{Cd})_2$  eight-membered

rings were found.



Scheme 1 Classic  $[\text{Cd}(\text{SCN})_2(\text{L})_2]_n$  structure

## 1 Experimental

### 1.1 Physical measurements

Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Electronic spectra were taken on a UV-Vis-NIR spectrophotometer. The cyclic

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voltammetry was performed by CHI 832 electrochemical analyzer with three-electrode system consisted of a glass carbon electrode ( $\Phi=3$  mm) as the working electrode, a Ag/AgCl electrode as the reference electrode, and a platinum wire as the auxiliary electrode. All the electrochemical measurements were carried out in a 10 mL electrolytic cell using  $0.01 \text{ mol} \cdot \text{L}^{-1}$  KCl solution as supporting electrolyte.

## 1.2 Synthesis

The title compound was prepared by the reaction of 1-vinylimidazole (1.88 g, 20 mmol) with  $\text{CdCl}_2 \cdot 0.5\text{H}_2\text{O}$  (1.14 g, 5 mmol) and potassium thiocyanate (0.98 g, 10 mmol) by means of hydrothermal synthesis in a stainless-steel reactor with a Teflon liner at 383 K for 24 h. Single crystals suitable for X-ray measurements were obtained by recrystallization from methanol at room temperature. The C, H and N content was determined by elemental analysis (Anal. Calcd. (%) for  $\text{C}_{22}\text{H}_{24}\text{CdN}_{10}\text{S}_2$ : C, 43.67; H, 3.99; N, 23.15. Found(%): C, 43.57; H, 4.07; N, 23.43).

## 1.3 Crystal structure determination

The crystal with approximate dimensions of  $0.40 \text{ mm} \times 0.30 \text{ mm} \times 0.30 \text{ mm}$  was selected for the structure analysis. The diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\,073 \text{ nm}$ ) at the temperature of 293(2) K, using an  $\omega$ - $2\theta$  scan mode

( $2.32^\circ < \theta < 25.98^\circ$ ). The total collected reflections were 2 874, in which 2 689 were independent ones. The diffraction intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using NRCVAX<sup>[6]</sup> program.

The structure was solved by direct methods using SHELXS-97<sup>[7]</sup> program. All the non-hydrogen atoms were refined on  $F^2$  anisotropically by full-matrix least squares method using SHELXL-97<sup>[7]</sup> program. All hydrogen atoms were placed in calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic  $U$  of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave  $R_1=0.040\,4$ ,  $wR_2=0.100\,8$  for 2 010 observed reflections with  $I > 2\sigma(I)$ ; the weighting scheme,  $w=1/[\sigma^2(F_o^2) + (0.072\,5)^2]$ , where  $P=(F_o^2 + 2F_c^2)/3$ , the maximum shift  $(\Delta/\sigma)_{\text{max}}=0.000$  and  $S=1.015$ . The maximum and minimum peaks on the final difference Fourier map corresponded to  $634 \text{ e} \cdot \text{nm}^{-3}$  and  $-935 \text{ e} \cdot \text{nm}^{-3}$ , respectively. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography<sup>[8]</sup>. Crystal and refinement data for the title complex are listed in Table 1.

CCDC: 630897.

Table 1 Crystal data and structure refinement parameters for the title compound

Empirical formula	$\text{C}_{22}\text{H}_{24}\text{CdN}_{10}\text{S}_2$	$\mu / \text{mm}^{-1}$	0.979
Formula weight	605.03	$F(000)$	612
Temperature / K	293(2)	Crystal size / mm	$0.40 \times 0.30 \times 0.30$
Crystal system	Monoclinic	$\theta$ range for data collection / ( $^\circ$ )	2.32 to 25.98
Space group	$P2_1/c$	Limiting indices	$0 \leq h \leq 10, 0 \leq k \leq 11, -21 \leq l \leq 21$
$a / \text{nm}$	0.858 50(17)	Reflections collected / independent reflections	2 874 / 2 689 ( $R_{\text{int}}=0.019\,8$ )
$b / \text{nm}$	0.909 90(18)	Refinement method	Full-matrix least-squares on $F^2$
$c / \text{nm}$	1.782 3(4)	Data/restraints/parameters	2 689 / 1 / 161
$\beta / (^\circ)$	100.14(3)	Goodness-of-fit on $F^2$	1.015
$V / \text{nm}^3$	1.370 5(5)	Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.040\,4$ , $wR_2=0.100\,8$
$Z$	2	$R$ indices (all data)	$R_1=0.061\,2$ , $wR_2=0.114\,9$
$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.466	Largest diff. peak and hole/ ( $\text{e} \cdot \text{nm}^{-3}$ )	634 and -935

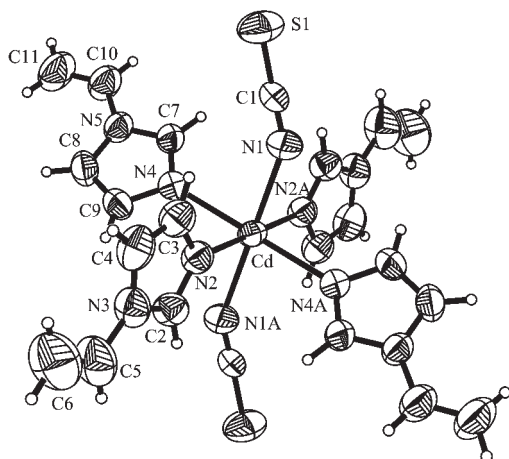
## 2 Result and discussion

### 2.1 Crystal structure description

Fig.1 shows the structure of the title compound,

showing 50% probability displacement ellipsoids and the atom-numbering scheme, and Fig.2 shows a perspective view of the crystal packing in the unit cell.

Selected bond lengths and bond angles are presented in Table 2.



Symmetry code: A:  $-x+1, -y, -z$

Fig.1 Structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme

The molecular structure of **1** is shown in Fig.1. The Cd atom displays a compressed octahedral coordination geometry, with six N atoms from two thio-cyanate anions and four 1-vinylimidazole ligands. The equatorial plane of the complex is formed by four Cd-N(Vim) bonds, and the axial positions are occupied by two N-bonded NCS groups. The bond lengths of Cd-N2, N4 are 0.234 7(3) and 0.233 4(3) nm, respectively, which are comparable to the Cd-N(MeIM) [MeIM is 1-methylimidazole] distances reported previously, e.g. 0.232 0(3) nm in  $[\text{Cd}(\text{MeIM})_4[\text{Ag}(\text{CN})_2]_n[\text{Ag}(\text{CN})_2]_n$ <sup>[9]</sup>, but longer than those in the classic  $[\text{Cd}(\text{SCN})_2(\text{L})_2]_n$  complexes, e.g. 0.228 6(3) nm in  $[\text{Cd}(\text{N-MeIM})_2(\text{SCN})_2]_n$ <sup>[5]</sup>, 0.227 4(2) nm in  $[\text{Cd}(\text{IM})_2(\text{SCN})_2]_n$  [IM is imidazole]<sup>[4]</sup>.

The Cd-N(NCS) bond lengths of 0.234 0(4) nm are also longer than those in the classic  $[\text{Cd}(\text{SCN})_2(\text{L})_2]_n$  complexes, e.g. 0.234 4(3) nm in  $[\text{Cd}(\text{N-MeIM})_2(\text{SCN})_2]_n$ <sup>[5]</sup>, 0.232 2(2) nm in  $[\text{Cd}(\text{IM})_2(\text{SCN})_2]_n$ <sup>[4]</sup>.

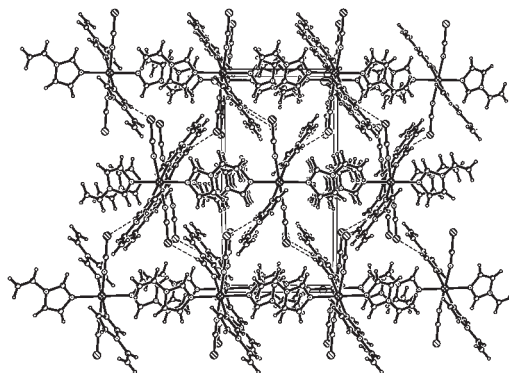


Fig.2 View of the crystal packing down the *a* axis, C-H...S intermolecular interactions were showed in dashed lines

The values of the bond angles around cadmium are close to those expected for a regular octahedral geometry (Table 1), The trans angles are all 180° for symmetry requirements and the cis ones are all close 90° with ranges from 86.94(12)° to 93.06(12)°. The four imidazole rings are planar as expected. The thio-cyanate ligands are almost linear [177.7(4)°], whereas a significant bending is displayed at the Cd-N-C-S linkage [147.8(4)°].

There exist some potentially weak C-H...S intermolecular interactions<sup>[10]</sup> in the structure. The S1 atom with C7 atoms form weak C-H...S intermolecular interactions, and the donor and acceptor distances are 0.374 1(5) nm [Symmetry code:  $-x+1, y-1/2, -z+1/2$ ].

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

Cd-N(4)	0.233 4(3)	N(1)-C(1)	0.113 0(5)	C(5)-C(6)	0.124 5(7)
Cd-N(1)	0.234 0(4)	N(3)-C(5)	0.144 5(9)	C(10)-C(11)	0.128 4(7)
Cd-N(2)	0.234 7(3)	N(5)-C(10)	0.141 9(5)		
S(1)-C(1)	0.161 5(4)	C(3)-C(4)	0.134 8(7)		
N(4)#1-Cd-N(1)	93.06(13)	N(1)-Cd-N(2)	92.66(14)	C(6)-C(5)-N(3)	123.6(8)
N(4)-Cd-N(1)	86.94(13)	N(1)#1-Cd-N(2)	87.34(14)	C(11)-C(10)-N(5)	124.5(5)
N(4)#1-Cd-N(2)	93.10(12)	C(1)-N(1)-Cd	147.8(4)		
N(4)-Cd-N(2)	86.90(12)	N(1)-C(1)-S(1)	177.7(4)		

Symmetry code: #1:  $-x+1, -y, -z$ .

## 2.2 Absorption spectroscopic studies

The solution electronic spectrum of the title compound in  $\text{C}_2\text{H}_5\text{OH}$  exhibits an intense band at 210 nm, which is assigned to the  $n \rightarrow \pi^*$  transition of the Vim ligands. There are not other transition peaks in electronic spectrum being assigned to LMCT and  $d \rightarrow d$  transition.

## 2.3 Electrochemical studies

The cyclic voltammetry behaviors of the titled complex from  $-0.5 \sim -1.1$  V were studied and the results were shown in Fig.3. The diagram displayed the one electron oxidation and reduction of metal center. The peak separation  $\Delta E$  between anodic and cathode peaks was 0.156 V with  $E_{\text{pa}} = -0.783$  V and  $E_{\text{pc}} = -0.939$

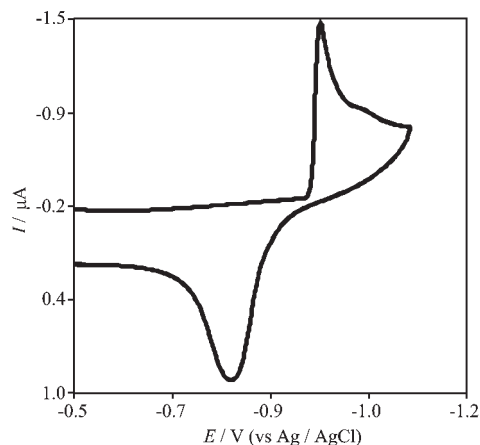


Fig.3 Cyclic voltammogram of  $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  title compound in  $0.01 \text{ mol} \cdot \text{L}^{-1}$  KCl

V, therefore the electrode reaction was a quasi-reversible process at scan rate  $10 \text{ mV} \cdot \text{s}^{-1}$  corresponding to the redox couple of  $\text{Cd(II)/Cd(I)}$ .

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