

二硝酸根二 4',5'-二氮-9'-(4,5-二(硫乙基)-1,3-二硫杂环戊烯-2-叶立德)-芴合镉的合成、结构及光谱性质

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摘要: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 与配体 4',5'-二氮-9'-(4,5-二(硫乙基)-1,3-二硫杂环戊烯-2-叶立德)-芴(L)在甲醇和二氯甲烷的混合溶剂中生成配合物 $\text{Cd}(\text{NO}_3)_2(\text{L})_2$ 。晶体的空间群是 $Pbcn(\#60)$, 晶体学参数分别是 $a=1.578\,7(2)\text{ nm}$, $b=0.987\,96(11)\text{ nm}$, $c=2.719\,5(3)\text{ nm}$, $V=4.241\,6(8)\text{ nm}^3$, $Z=4$ 。2 个硝酸根离子各提供 1 个氧原子, 2 个配体 L 各提供 2 个氮原子, 形成了镉的 6 配位结构。晶体结构显示分子通过平面之间的 π - π 相互作用沿 b 轴形成柱状结构, 这些柱通过中心原子镉(II)的配位连接形成二维层状结构, 再通过 2 个硫乙基上的短距离 S...S 接触进一步形成了三维结构。对其 $^1\text{H NMR}$ 、UV-Vis 和荧光光谱进行了研究。

关键词: 氮-芴; 镉配合物; 晶体结构; 分子间相互作用

中图分类号: O614.24*2

文献标识码: A

文章编号: 1001-4861(2006)07-1170-05

Synthesis and Crystal Structure of a Cadmium Complex with 4',5'-diaza-9'-(4,5-bis(ethylthio)-1,3-dithiole-2-ylidene)-fluorene

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Abstract: Reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with 4',5'-diaza-9'-(4,5-bis(ethylthio)-1,3-dithiole-2-ylidene)-fluorene (L) in a mixture of methanol and dichloromethane forms a coordination compound $\text{Cd}(\text{NO}_3)_2(\text{L})_2$. The crystal is in orthorhombic space group $Pbcn(\#60)$ with crystallographic parameters $a=1.578\,7(2)\text{ nm}$, $b=0.987\,96(11)\text{ nm}$, $c=2.719\,5(3)\text{ nm}$, $V=4.241\,6(8)\text{ nm}^3$ and $Z=4$. The coordination sphere of Cd(II) is satisfied by coordination of two oxygen atoms from two nitrate ions and four nitrogen atoms from two ligands L. Crystal structure shows that the molecules are stacked via plane to plane π - π interactions forming columns along the b axis. These columns are linked to form two-dimensional layer structure by the coordination connection of the center atom Cd(II). There are very short S...S contact (0.329 7 nm) between two ethylthio sulfur atoms, so that a three-dimensional structure is further completed. $^1\text{H NMR}$, UV-Vis and fluorescent spectra of the title compound were studied. CCDC: 283826.

Key words: diaza-fluorene; cadmium complex; crystal structure; intermolecular interaction

Building new supramolecular architectures assembled by intermolecular interactions has been of

great interests in recent years^[1-4]. These intermolecular interactions such as S...S contacts play an important

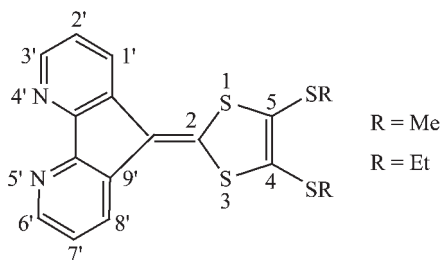
收稿日期: 2005-06-06。收修稿日期: 2006-06-01。

国家自然科学基金资助项目(No.20071024, 20371033), 江苏省有机合成重点实验室开放基金资助项目(No.JSK003)。

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part in supramolecular chemistry^[5-9]. In sulfur-rich compounds, such as tetrathiafulvalene (TTF) and its derivatives^[10-12], and 4,5-disulfanyl-1,3-dithio-2-thionate (dmit) complexes $[M(C_3S_3)_2]^n$ ^[5,6], short S...S contacts are found to be one of the most important contributors to their physical properties. Recently we became interested in ligands 4',5'-diaz-9'-(4,5-disubstituted-1,3-dithiole-2-ylidene)-fluorenes (Scheme 1). The ligands contain not only an electron donor dithiole part but also a π -electron acceptor diimine part. Some transition metal complexes of the ligands have been synthesized and characterized crystallographically^[13-17]. The crystal structures of these compounds are stabilized by inter ligand $\pi \cdots \pi$ stacking. In this manuscript, we present the synthesis and crystal structure of a Cd(II) complex with this type ligand L (R=Et). The title cadmium(II) complex displays a three dimensional framework via tail to tail S...S contact and $\pi \cdots \pi$ stacking. Therefore the compound is a new cadmium complex with unique intermolecular interactions.



Scheme 1

1 Experimental

1.1 General comments

The reagents, 4,5-diazafluorene-9-one was prepared following the method of Henderson and coworkers^[18]; 4,5-bis(ethylthio)-1,3-dithiole-2-thione was prepared according to the literatures^[19]. The ligand L was synthesized using a modified method reported by Sako^[20]. Elemental analyses of C, H and N were performed using a MOD 1106 elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FTIR spectrometer. ¹H NMR and Fluorescence spectra were measured by UNITYNOVA-400 and F-2500 spectrophotometers, respectively.

1.2 Preparation of the title crystal

The crystal of the title compound was prepared as follows. To a methanol solution (1 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.01 mmol, 3.08 mg) was slowly dropped dichloromethane solution (3 mL) of the ligand L (0.02 mmol, 7.6 mg). The mixture was stirred for 30 min at room temperature and then filtered. Then some methanol solvent was gently layered to the filtrate which was sealed in bottles and laid undisturbed about several months at room temperature. The orange single crystals suitable for X-ray diffraction were obtained. Elemental analysis calcd.(%) for $C_{36}H_{32}CdN_6O_6S_8$: C, 42.66; H, 3.18; N, 8.29. Found(%): C, 42.46; H, 3.10; N, 8.11. Important IR data: 1 538(s), 1 478(s), 1 384(m), 1 349(w), 1 295(m), 1 174(m), 866(m), 806(m), 761(m), 741(m) cm^{-1} .

1.3 Crystal structure determination

An orange crystal of $C_{36}H_{32}CdN_6O_6S_8$ with dimension of 0.10 mm \times 0.35 mm \times 0.25 mm was selected for the structural analysis. The data were collected on a Rigaku Mercury CCD area detector with graphite monochromatized Mo $K\alpha$ radiation, at a temperature of -80 ± 1 °C to a maximum 2θ value of 55.0° . Total 4 852 reflections were collected using ω scan mode, in which 352 were in the range of $I > 2\sigma(I)$. An empirical absorption correction was applied. The structure was solved by direct method using SHELXS-97^[21] and refined using SHELXL-97^[22]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2 451 observed reflections and 274 variable parameters. Due to the anions are disordered.

CCDC: 283826.

2 Results and discussion

2.1 Crystal structure

The relevant crystallographic data for the complex and details of data collection list in Table 1. The selected bond lengths and bond angles are shown in Table 2 and 3 respectively. The X-ray crystal structure of the title compound is shown in Fig.1.

The compound crystallizes in orthorhombic sys-

Table 1 Crystallographic data for the complex

Formula	C ₃₆ H ₃₂ CdN ₆ O ₆ S ₈	<i>V</i> / nm ³	4.241 6(8)
Formula weight	1 013.58	<i>Z</i>	4
Crystal size / mm	0.10 × 0.35 × 0.25	<i>D</i> _{calc} / (Mg · m ⁻³)	1.587
Crystal system	Orthorhombic	<i>F</i> (000)	2 056
Space group	<i>Pbcn</i> (#60)	2 θ _{max} / (°)	55
<i>a</i> / nm	1.578 7(2)	No. of ref. measured	352
<i>b</i> / nm	0.987 96(11)	No. of unique	4 852
<i>c</i> / nm	2.719 5(3)	No. of reflections [<i>I</i> > 3.0 σ (<i>I</i>)]	2 451
α / (°)	90	Goodness-of-fit (<i>S</i>)	1.040
β / (°)	90	<i>R</i> ₁	0.073
γ / (°)	90	<i>wR</i> ₂	0.143

Table 2 Selected bond lengths (nm)

Cd(1)-O(1)	0.228(1)	C(4)-C(5)	0.141(1)	C(13)-C(14)	0.133(1)
Cd(1)-N(1)	0.243 1(7)	C(4)-C(11)	0.146(1)	S(1)-C(12)	0.173 4(9)
Cd(1)-N(2)	0.242 4(7)	C(5)-C(10)	0.144(1)	S(1)-C(13)	0.178(1)
N(1)-C(1)	0.134(1)	C(6)-C(7)	0.138(1)	S(2)-C(12)	0.174 6(9)
N(1)-C(5)	0.133(1)	C(7)-C(8)	0.140(1)	S(2)-C(14)	0.175 3(9)
N2-C(6)	0.135(1)	C(8)-C(9)	0.140(1)	S(3)-C(13)	0.176 3(9)
N(2)-C(10)	0.133(1)	C(9)-C(10)	0.141(1)	S(3)-C(15)	0.177(2)
C(1)-C(2)	0.140(2)	C(9)-C(11)	0.147(1)	S(4)-C(14)	0.174(1)
C(2)-C(3)	0.139(1)	C(11)-C(12)	0.139(1)	S(4)-C(17)	0.179(1)
C(3)-C(4)	0.138(1)				

Table 3 Selected bond angles (°)

N(1)-Cd(1)-N(1) ⁱ	81.3(2)	C(1)-N(1)-Cd(1)	136.2(6)	C(5)-C(4)-C(11)	107.7(7)
N(1)-Cd(1)-N(2)	74.4(2)	C(1)-N(1)-C(5)	115.2(8)	C(11)-C(4)-C(3)	136.0(8)
N(1)-Cd(1)-N(2) ⁱ	80.9(2)	C(5)-N(1)-Cd(1)	108.5(5)	C(10)-C(5)-N(1)	124.2(8)
N(11)-Cd(1)-N(2)	80.9(2)	C(6)-N(2)-Cd(1)	137.1(6)	C(10)-C(5)-C(4)	109.1(7)
N(11)-Cd(1)-N(2) ⁱ	74.4(2)	C(10)-N(2)-Cd(1)	108.5(5)	C(7)-C(6)-N(2)	124.1(8)
N(2)-Cd(1)-N(2) ⁱ	147.3(2)	C(6)-N(2)-C(10)	114.3(7)	C(8)-C(7)-C(6)	120.3(8)
C(12)-S(1)-C(13)	95.7(4)	C(2)-C(1)-N(1)	123.5(9)	C(9)-C(8)-C(7)	117.5(8)
C(12)-S(2)-C(14)	96.9(4)	C(3)-C(2)-C(1)	119.1(9)	C(10)-C(9)-C(11)	108.2(7)
C(13)-S(3)-C(15)	102.8(7)	C(4)-C(3)-C(2)	119.0(9)	C(10)-C(9)-C(8)	116.6(8)
C(14)-S(4)-C(17)	102.4(5)	C(5)-C(4)-C(3)	116.2(8)	C(11)-C(9)-C(8)	135.2(8)

$$^i 1-x, y, \frac{1}{2}-z.$$

tem with four complex molecules in a unit cell. In the crystal structure, the coordination environment around the cadmium(II) center is a distorted octahedral geometry. The Cd(II) ion is coordinated by four nitrogens from two chelating ligands and the two cis oxygen atoms from two nitrate anions. The mean deviation from plane of the two ligands is the same (0.008 42 nm). The dihedral angles between least-squares planes of the two ligands is 86.443°.

The bond distances Cd(1)-N(1) (0.243 1 nm) and Cd(1)-N(2) (0.242 4 nm), are similar to those of [Cd(bipy)₂(NO₃)₂] (bipy=2,2'-bipyridyl)^[23], which is a Cd(II) nitrate compound showing a coordination environment resembling the title one. But the bond distances of the Cd(1)-O(1) (0.228(1) nm) are shorter than those of [Cd(bipy)₂(NO₃)₂], in which the distances Cd(2)-O(13) and Cd(2)-O(14) are 0.243 5(9) nm and 0.241(1) nm, respectively. Perhaps it is due to some

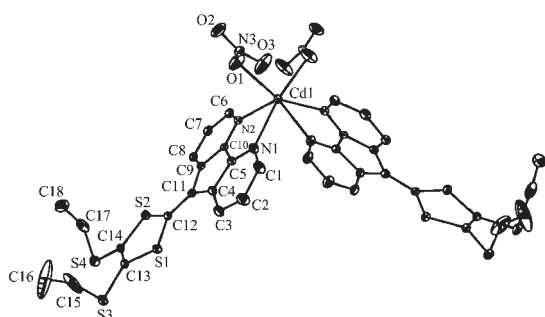


Fig.1 An ORTEP view of the title compound with the atomic labeling scheme, showing 15% probability displacement ellipsoids

weak interaction with a second oxygen of each nitrate group (Cd(2)-O(33), 0.262(1) nm; Cd(2)-O(34), 0.269(1) nm) tending to weaken the Cd-O in the latter complex^[23]. The bond angles N(1)-Cd(1)-N(2) (74.4(2)°) and C(10)-C(5)-N(1) (124.2(8)°) are also larger than those of [Cd(bipy)₂(NO₃)₂] which are 69.8(4)° and 120°.

The crystal is stabilized by inter ligand $\pi \cdots \pi$ stacking. The ligand planes from two different symmetrical molecules are alternately arranged with C \cdots C (0.339 1 nm) and C \cdots S (0.340 0 nm) interactions forming 1D ligand-columns along the b axis (Fig.2). In Fig.2, A and B represent ligands orientated in different directions and those molecules are further interacted with others in the same manner discribed above (1D ligand-columns). By the metal coordination linkage these $\pi \cdots \pi$ assembled ligand-columns form a 2D structure paralleling with {001} plane. The short S \cdots S contacts of 0.329 7 nm occur between two ethylthio sulfur atoms of the neighboring layers, which is significantly shorter than the sum of the van der Walls radii of two S atoms (0.370 nm). This indicates that there are strong interactions between two neighboring layers, which gives rise to a three-dimensional network. In general, S \cdots S contacts are in the range 0.335~0.370 nm in the crystals of sulfur-rich compounds and the contacts with distances below 0.330 nm are rarely found. An example of an unusually short contact is an organic compound with a S \cdots S distance of 0.325 1 nm^[24]. Another example having an unusually short contact is [Cu₄I₄(C₅H₄S₅)₄]^[25], in which the S \cdots S contact (0.325 7 nm) is between thioether and thiocarbonyl sulfur atoms (head to tail), while in the present case, the

contacts occur between two thioethyl sulfur atoms (tail to tail).

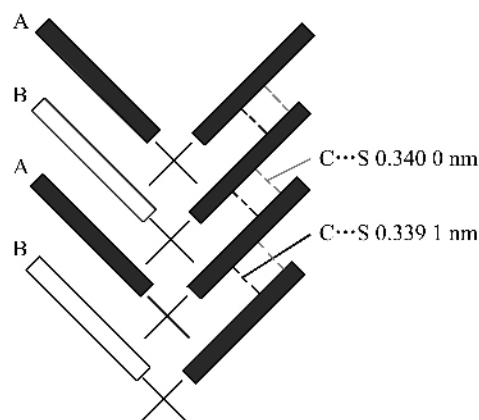


Fig.2 Schematic view of the molecular packing and intermolecular interactions

2.2 Spectral characterization

2.2.1 ¹H NMR spectra

The ¹H NMR spectrum of the title complex in CDCl₃ revealed three sets of aromatic hydrogens between 7.4~8.4 ppm. The doublet signal at 8.38 and 8.06 ppm are assigned to the H at the 3', 6' and 1', 8' ring sites of the fluorene, respectively. The quartet at 7.45 ppm is assigned to H at the 2' and 7' ring sites. By comparing with the ¹H NMR spectrum of the free ligand, 8.68 (ortho), 8.06 (para) and 7.39 (meta) ppm for the free ligand, the largest chemical shift is the signal corresponding to the protons at the 3' and 6' ortho-position of the coordinated nitrogen atoms ($\Delta\delta=0.30$ ppm). The general downfield shift can be attributed to the decrease in electron charge density at the individual carbon nuclei caused by the metal coordination. The H at 3' and 6' ring sites show up-field shift that has been found for the Pd compound with this type ligand^[17]. Miller and Prince attributed this shift to a non-bonded hydrogen-metal interaction^[26,27].

2.2.3 UV-Vis and fluorescent spectra

The UV-Vis spectral data of the ligand and the title complex in dichloromethane were measured. The overall spectral feature of the complex is similar to that of the ligand and no *d-d* absorption appear due to the *d*¹⁰ electron structure of cadmium(II). The peak at 418 nm for the free ligand arising from the ligand-centered transition is red-shifted upon the formation of

the complex (435 nm).

The fluorescent spectra (Fig.3, $\lambda_{\text{ex}}=254$ nm, in CH_2Cl_2) show that the ligand emits strong fluorescence band at $\lambda_{\text{em}}=458$ nm, and two weak peaks at about 635 and 655 nm. For the complex, the main fluorescence band shifts to 483 nm. The fluorescence data of the ligand and the title complex reveal that the energy level of the excited state S1 falls down when the ligand coordinates to the metal ion. The change is consistent with the results found from UV-Vis spectra. The other peaks with a star in the spectra are not the fluorescent bands of the ligand or the complex.

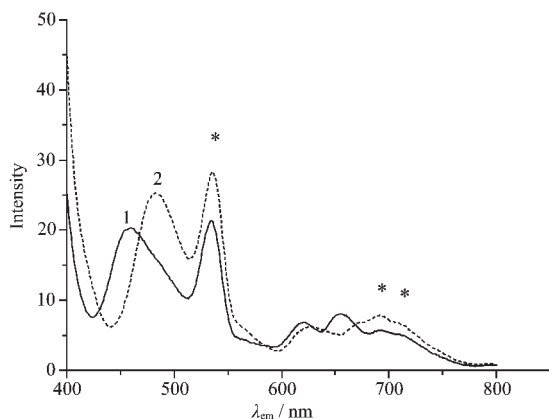


Fig.3 Fluorescence spectra ($\lambda_{\text{ex}}=254$ nm) of the free ligand (line 1) and the title complex (line 2); the peaks with a star are assigned to the solvent (CH_2Cl_2)

3 Conclusion

In this paper a new cadmium(II) complex with 4', 5' -diaz-9' -(4,5-bis (ethylthio)-1,3-dithiole-2-ylidene)-fluorene has been synthesized and characterized by elemental analyses, IR, ^1H NMR, UV-Vis, fluorescence and X-ray crystal structural analysis. The cadmium atom is in a distorted octahedral environment. The Cd(II) ion is coordinated by two chelating ligands in *cis* conformation. The notable feature of the complex is the existence of the short S...S contacts of 0.329 7 nm occurred between two neighboring layers, which gives rise to a three-dimensional network.

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