One-dimensional Coordination Polymers of Cadmium Thiolates with 4,4′-Trimethylenebipyridine Ligands

Chao Xu[a], Fang-Hui Wu[a], Taike Duan[a], and Qian-Feng Zhang[a,b]

[a] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology,
Ma'anshan, Anhui 243002, P. R. China
[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210009, P. R. China

Reprint requests to Dr. Qian-Feng Zhang. Fax: +86-555-2312041. E-mail: zhangqf@ahut.edu.cn

Z. Naturforsch. **2009**, *64b,* 805 – 808; received February 11, 2009

Hydrothermal reactions of $Cd(SAr)_2$ with 4,4′-trimethylenebipyridine (tmdp) at 145 °C yielded new complexes, $[Cd(SAr)_2(tmdp)_2]_n$ (Ar = Ph, **1**, C_6H_4Me-4, **2**), which are one-dimensional wave-like coordination polymers with distorted tetrahedral CdN_2S_2 coordination environments. The thermal stability of the two complexes was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

Key words: Cadmium(II), 4,4′-Trimethylenebipyridine, Thiolate, Coordination Polymer,
Crystal Structure

Introduction

Thiolate ligands are extensively employed in transition metal chemistry, and the versatility of sulfur as a ligand in organotransition metal chemistry has been widely established [1]. Although thiolate ligands are well known for their bridging behavior, they were found to be poor bridging ligands for d^{10} (closed *d* shell) metals such as Zn(II), Cd(II), Hg(II), Cu(I), and Ag(I) atoms in the presence of bridging bidentate bipyridyl ligands, *e. g.* 4,4′-bipyridine (bipy), 1,2-bis-(4-pyridyl)ethane and *trans*-1,2-bis(4-pyridyl)ethene [2 – 6]. For example, thiocarboxylate complexes of Zn(II) and Cd(II) with bipy have one-dimensional zig-zag polymeric structures in which the metal atoms possess tetrahedral coordination geometry with terminal thiolate ligands [7]. Dinuclear six-coordinate Cd(II) complexes with bridging chalcogenolate and chelating 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) ligands were found to exhibit interesting photophysical and electrochemical properties [8]. Pyrazines, bridging bidentate bipyridyl ligands, and nitrile-substituted pyridines are the most commonly used difunctional donor ligands in coordination polymers forming numerous one-, two- and three-dimensional organic/inorganic composite materials [9 – 11].

As a part of general studies of transition metal complexes bearing sulfur and nitrogen donors, we are interested in the reactions of $Cd(SAr)_2$ [12] with long bridging bipyridyl ligands, expecting to investigate polymeric cadmium complexes featuring a tetrahedral CdS_2N_2 coordination geometry. Although thiolate and selenolate complexes of Cd(II) are known, and most of them possess a tetrahedral CdS_4 core, four-coordinate Cd(II) complexes with a CdS_2N_2 core have remained relatively less explored [13]. Few complexes such as $[Cd(S\text{-}2,4,6\text{-}{}^i Pr_3\text{-}C_6H_2)_2(1\text{-Me-imid})_2]$ (Himid = imidazole), $[Cd(S\text{-}2,4,6\text{-}{}^i Pr_3C_6H_2)_2(bipy)_2]$ and $[Cd(S\text{-}2,4,6\text{-}{}^i Pr_3C_6H_2)_2(phen)]_2$ with CdS_2N_2 coordination character were synthesized as models in transcription factor proteins [14, 15]. In this report, the X-ray crystal structures of two such complexes, $[Cd(SAr)_2(tmdp)_2]_n$ (Ar = Ph, **1**, C_6H_4Me-4, **2**; tmdp = 4,4′-trimethylene-bipyridine), obtained from reactions of $Cd(SAr)_2$ with tmdp under hydrothermal conditions, are described which are one-dimensional wave-like coordination polymers with a distorted tetrahedral CdN_2S_2 coordination environment.

Experimental Section

Materials and measurements

Complexes $Cd(SAr)_2$ (Ar = Ph, C_6H_4Me-4) were prepared according to the literature method [12]. The ligand, 4,4′-trimethylenebipyridine (tmdp), was purchased from Alfa Chemical Company and was used as supplied. All other reagents and solvents were used without further purification.

0932–0776 / 09 / 0700–0805 $ 06.00

NMR spectra were recorded on a Bruker ALX 300 spectrometer, and the ^{1}H chemical shifts (δ in ppm) are reported with reference to $SiMe_4$. Infrared spectra were recorded on a Nicolet 170sx FT-IR spectrophotometer with use of pressed KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer, thermogravimetric analysis by using a Delta TGA instrument.

*Preparation of $[Cd(SPh)_2(tmdp)_2]_n$ (**1**)*

A mixture of $Cd(SPh)_2$ (66.2 mg, 0.2 mmol), tmdp (60.0 mg, 0.3 mmol), and distilled water (10 mL) was sealed in a 25-mL Teflon-lined reactor. The reactor was heated in an oven to 145 °C for 72 h and then cooled to r. t. at a rate of 5 °C h^{-1}. Colorless needle crystals were obtained and air dried. Yield: 92 mg, 74 %. – IR (KBr, cm^{-1}): ν = 2940 (m), 2185 (m), 2162 (m), 1602 (s), 1554 (m), 1498 (m), 1451 (m), 1212 (s), 1058 (vs), 1034 (s), 851 (s), 826 (s), 788 (s), 600 (s), 504 (s). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.08 (m, 4H, -CH_2-), 2.77 (t, 8H, pyCH_2-), 6.53 – 6.79 (m, 20H, Ph), 7.53 (q, 8H, py), 8.56 (q, 8H, py). – Anal. for $C_{25}H_{24}N_2S_2Cd$: calcd. C 56.8, H 4.57, N 5.30; found C 56.4, H 4.51, N 5.25.

*Preparation of $[Cd(SC_6H_4Me\text{-}4)_2(tmdp)_2]_n$ (**2**)*

This complex was prepared similarly as described for **1** using $Cd(SC_6H_4Me\text{-}4)_2$ (71.7 mg, 0.2 mmol) instead of $Cd(SPh)_2$. Colorless flake crystals were obtained and air dried. Yield: 101 mg, 78 %. – IR (KBr, cm^{-1}): ν = 2943 (m), 2187 (m), 2160 (m), 1601 (s), 1552 (m), 1501 (m), 1453 (m), 1214 (s), 1055 (vs), 1037 (s), 854 (s), 828 (s), 782 (s), 598 (s), 501 (s). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.05 (m, 4H, -CH_2-), 2.13 (s, 12H, CH_3), 2.79 (t, 8H, pyCH_2), 6.51 – 6.76 (m, 16H, Ph), 7.57 (q, 8H, py), 8.61 (q, 8H, py). – Anal. for $C_{27}H_{28}N_2S_2Cd$: calcd. C 58.2, H 5.07, N 5.03; found C 58.1, H 5.03, N 5.00.

X-Ray crystallographic study

Single crystals of **1** and **2** were mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation using an ω scan mode. The collected frames were processed with the software SAINT [16]. The data were corrected for absorption using the program SADABS [17]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [18]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96 and C_{sp^2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

Table 1. Crystal data, data collection parameters and details of the structure refinement.

Complex	**1**	**2**
Empirical formula	$C_{25}H_{24}N_2S_2Cd$	$C_{27}H_{28}N_2S_2Cd$
Formula weight	528.98	557.03
Color, habit	colorless, bar	colorless, flake
Crystal size, mm^3	0.42×0.18×0.16	0.52×0.38×0.12
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a, Å	12.0023(2)	11.9475(3)
b, Å	15.2047(2)	16.8215(4)
c, Å	13.0702(2)	12.8709(3)
β, deg	90.900(1)	90.980(1)
Volume, Å^3	2384.90(6)	2586.35(11)
Z	4	4
Density (calcd.), g cm^{-3}	1.47	1.43
Absorption coeff., mm^{-1}	1.1	1.0
Temperature, K	293(2)	293(2)
F(000), e	1072	1136
Radiation; wavelength, Å	— MoK_α; 0.71073 —	
Reflections collected	11198	12219
Independent reflections	2718	2987
R_{int}	0.0198	0.0214
Reflections with $[I \geq 2\sigma(I)]$	2465	2676
Parameters refined	137	147
Final $R1/wR2$ (all data)[a]	0.0265/0.0602	0.0296/0.0693
Weighting scheme *a/b*	0.0332/0.9203	0.0402/0.7190
Goodness of fit (GoF)[b]	1.05	1.05
Final diff. peaks (max/min), e Å^{-3}	+0.61/−0.21	+0.51/−0.18

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = [\Sigma w|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + aP^2 + bP]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$;
[b] GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

CCDC 719658/719659 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Hydrothermal reaction of $Cd(SAr)_2$ with tmdp in a 1 : 1.5 molar ratio at 145 °C produced new complexes $[Cd(SAr)_2(tmdp)_2]_n$ (Ar = Ph, **1**, C_6H_4Me-4, **2**). The complexes are stable in air and insoluble in water and most common organic solvents except DMSO and DMF. It is noteworthy that the hydrothermal method is crucial to the preparation of the present complexes because of the effect of temperature and pressure on crystallization. With the solution method at r. t. and under ambient conditions, a large amount of a precipitate formed upon mixing of $Cd(SAr)_2$ with tmdp in DMF. Few colorless crystals identified as the known adamantanoid cage clusters [12] could be isolated instead by direct crystallization from the DMF filtrate. The IR absorption bands with variable intensity in the

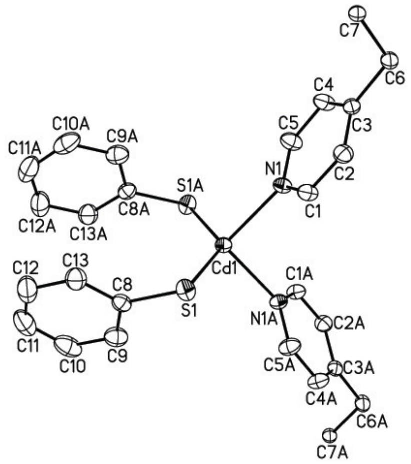

Fig. 1. ORTEP drawing of a structural unit of [Cd $(SPh)_2(tmdp)_2]_n$ (**1**) and crystallographic numbering scheme adopted (displacement ellipsoids drawn at the 40 % probability level; H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Cd(1)–S(1) 2.4441(5), Cd(1)–N(1) 2.3203(15); N(1A)–Cd(1)–N(1) 99.77(8), N(1A)–Cd(1)–S(1) 105.59(4), N(1)–Cd(1)–S(1) 103.99(4), S(1A)–Cd(1)–S(1) 133.33(3). (Symm. operation A: $-x+1$, y, $-z+1/2$).

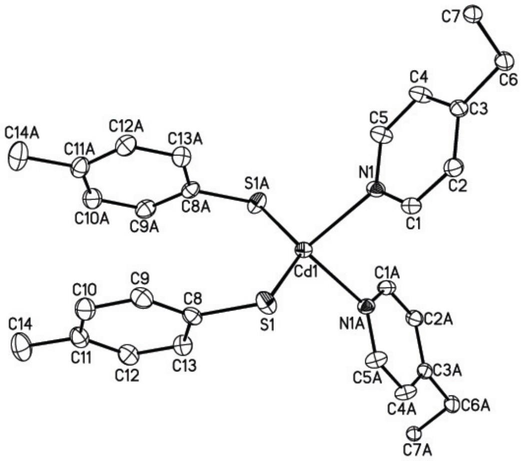

Fig. 2. ORTEP drawing of a structural unit of $[Cd(SC_6H_4Me\text{-}4)_2(tmdp)_2]_n$ (**2**) and crystallographic numbering scheme adopted (displacement ellipsoids drawn at the 40 % probability level; H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Cd(1)–S(1) 2.4384(5), Cd(1)–N(1) 2.3206(15); N(1A)–Cd(1)–N(1) 93.56(8), N(1A)–Cd(1)–S(1) 108.62(5), N(1)–Cd(1)–S(1) 103.89(5), S(1A)–Cd(1)–S(1) 131.79(3). (Symm. operation A: $-x+1$, y, $-z+1/2$).

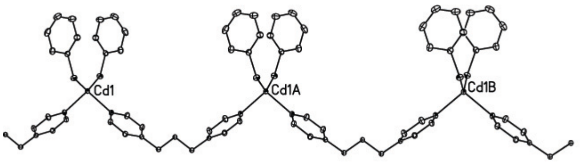

Fig. 3. The one-dimensional wave-like structure of $[Cd(SPh)_2(tmdp)_2]_n$ (**1**) in the crystal.

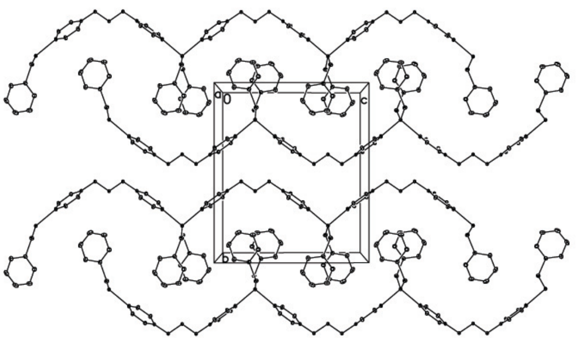

Fig. 4. Perspective view of the unit cell contents of $[Cd(SPh)_2(tmdp)_2]_n$ (**1**) as seen along the crystallographic *b* axis.

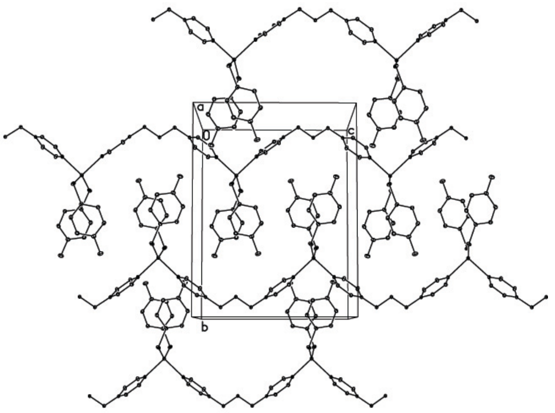

Fig. 5. Perspective view of the unit cell contents of $[Cd(SC_6H_4Me\text{-}4)_2(tmdp)_2]_n$ (**2**) as seen along the *b* axis.

range of 1400 – 1610 cm^{-1} for **1** and **2** correspond to vibrations of the pyridyl rings of the tmdp ligands. The strong peaks in the range of 500 – 900 cm^{-1} for ν(C–S) indicate the presence of thiolates in complexes **1** and **2**. The ^1H NMR spectra of the $[D_6]DMSO$ solution of complexes **1** and **2** display two distinct resonance signals assigned to the different protons of the pyridyl group of the tmdp ligands, probably due to rapid site exchange of the pyridine units in DMSO solution. Both complexes also display two other signals at *ca.* 2.10 and 2.80 ppm assigned to the protons of the $–CH_2–CH_2–CH_2–$ unit of the ligand tmdp.

X-Ray structure analyses revealed that complexes **1** and **2** form one-dimensional wave-like coordination polymers and crystallize in the monoclinic space group $C2/c$. The crystal structures with atomic numbering are depicted in Figs. 1 and 2, respectively. The cadmium center adopts a distorted tetrahedral geometry with S(1)–Cd(1)–S(1a) and N(1)–Cd(1)–N(1a) (a: $-x+1$, y, $-z+{}^1/_2$) angles of 133.33(3) and 99.77(8)° for **1**, and 131.79(3) and 93.56(8)° for **2**. The average Cd–S bond lengths are 2.4441(5) and 2.4384(5) Å for **1** and **2**, respectively, which are comparable to that in [Cd(S-2,4,6-^{i}Pr$_3$-C$_6$H$_2$)$_2$(1-Me-imid)$_2$] (Himid = imidazole) (av. 2.463(2) Å) [14], but shorter than those of the bridging thiolate ligands in [(phen)$_2$Cd(μ-SC$_6$H$_4$Me-4)$_2$]$_2$(PF$_6$)$_2$ (av. 2.666(1) Å) [8] and [Cd$_4$(μ-SPh)$_8$] (av. 2.538(3) Å) [12]. The average Cd–N bond lengths are 2.3203(15) and 2.3206(15) Å for **1** and **2**, respectively, which agree well with those in [Cd(S-2,4,6-^{i}Pr$_3$-C$_6$H$_2$)$_2$(1-Me-imid)$_2$] (av. 2.281(7) Å) [14] and [CdI$_2$(tmdp)$_2$]$_n$ (av. 2.285(7) Å) [10].

The tmdp ligands as well as the thiolate groups in complexes **1** and **2** generate angular nodes at the metal moieties. The nitrogen atoms of tmdp are linked to two different cadmium atoms, and the thiolates are coordinated to cadmium *via* their sulfur atoms but are not bridging two cadmium atoms, forming one-dimensional wave-like coordination polymers, as shown in Fig. 3 for complex **1**. The two pyridine rings of tmdp are inclined to one another at an angle of 73.8° for **1** and 77.2° for **2**. It is therefore reasoned that the conformation of tmdp plays an important role in the formation of the wavy backbone structure. Perspective views of the polymer packing for complexes **1** and **2** are shown in Figs. 4 and 5, respectively. The coordination polymer chains are aligned parallel in the *ac* plane along [101] direction. It is interesting to note that a pair of wavy lines arranges in the *ac* plane alternatively with opposite orientation, suggestive of supramolecular behavior in both complexes.

In order to examine the thermal stability of the two complexes, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out for the two complexes between 30 and 700 ℃ in a static atmosphere of air. Complexes **1** and **2** are stable up to 223 ℃ at which temperature they start decomposing. The release of the tmdp molecule takes place at 223 – 414 ℃ with one exothermic effect at 388 ℃. The solid residue formed at around 600 ℃ is suggested to be cadmium sulfide (CdS) which at higher temperature is evaporated. In summary, the thermogravimetric analysis shows that both frameworks have a remarkable thermal stability and only decompose above a temperature of *ca.* 223 ℃. Both coordination polymers are potential single-source precursors for nano-crystalline cadmium sulfide materials [7]. Further study of this aspect will be carried out in this laboratory.

Acknowledgement

This work was supported by the National Basic Research Program of China (973 Program, 2008CB617605) and the Program for New Century Excellent Talents in University of China (NCET-06-0556).

[1] V. W. W. Yam, K. K. W. Lo, W. K. M. Fung, C. R. Wang, *Coord. Chem. Rev.* **1998**, *171*, 17, and refs. therein.
[2] I. G. Dance, *Polyhedron* **1986**, *5*, 1037.
[3] P. J. Blower, J. R. Dilworth, *Coord. Chem. Rev.* **1987**, *76*, 121.
[4] J. Chai, C. S. Lai, J. Yan, E. R. T. Tiekink, *Appl. Organomet. Chem.* **2003**, *17*, 249.
[5] G. Mahmoudi, A. Morsali, L. G. Zhu, *Polyhedron* **2007**, *26*, 2885.
[6] J. T. Sampanthar, J. J. Vittal, *J. Chem. Soc., Dalton Trans.* **1999**, 1993.
[7] J. J. Vittal, J. T. Sampanthar, Z. Lu, *Inorg. Chim. Acta* **2003**, *343*, 224.
[8] V. W. W. Yam, Y. L. Pui, K. K. Cheung, *New J. Chem.* **1999**, *23*, 1163.
[9] Y. B. Dong, M. D. Smith, R. C. Layland, H. C. zur Loye, *Inorg. Chem.* **1999**, *38*, 5027.
[10] Y. Niu, H. Hou, Y. Zhu, *J. Cluster Sci.* **2003**, *14*, 483.
[11] S. Hu, A. J. Zhou, Y. H. Zhang, S. Ding, M. L. Tong, *Crystal Growth & Design* **2006**, *6*, 2543.
[12] I. G. Dance, R. G. Garbutt, D. C. Craig, M. L. Scudder, *Inorg. Chem.* **1987**, *6*, 4057.
[13] G. S. H. Lee, D. C. Craig, M. L. Scudder, I. G. Dance, *J. Am. Chem. Soc.* **1990**, *112*, 6435.
[14] D. T. Corwin, Jr., E. S. Gruff, S. A. Koch, *J. Chem. Soc., Chem. Commun.* **1987**, 996.
[15] R. A. Santos, E. S. Gruff, S. A. Koch, G. S. Harbison, *J. Am. Chem. Soc.* **1990**, *112*, 9257.
[16] SMART and SAINT+ for Windows NT (version 6.02a), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1998**.
[17] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1996**.
[18] G. M. Sheldrick, SHELXTL Software Reference Manual (version 5.1), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1997**; see also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.