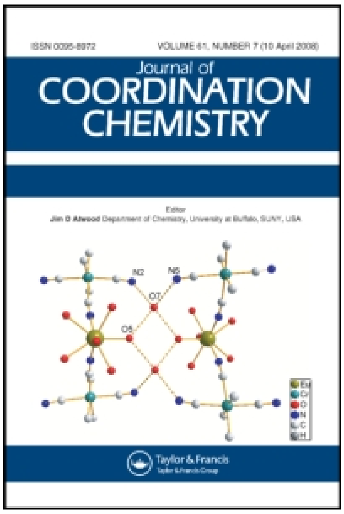

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Shou-Wu Wang[ab]; Yu-Mei Zhang[a]; Bao-Long Li[ac]; Yong Zhang[a]
[a] College of Chemistry and Chemical Engineering, Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, Suzhou 215006, P.R. China [b] Donggang College, Huaihai Institute of Technology, Lianyungang 222069, P.R. China [c] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China

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Synthesis, structure and luminescent properties of a new two-dimensional (4,4) network cadmium coordination polymer with dicyanamide and benzimidazole ligands

SHOU-WU WANG†‡, YU-MEI ZHANG†, BAO-LONG LI*†§
and YONG ZHANG†

†College of Chemistry and Chemical Engineering, Key Laboratory of Organic Synthesis
of Jiangsu Province, Suzhou University, Suzhou 215006, P.R. China
‡Donggang College, Huaihai Institute of Technology, Lianyungang 222069, P.R. China
§State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093,
P.R. China

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The new cadmium coordination polymer $[Cd(bim)_2(dca)_2]_n$ (**1**), (bim = benzimidazole, dca = dicyanamide) was synthesized and characterized by IR, thermogravimetric analysis and luminescent properties. The coordination geometry of cadmium atom is distorted octahedral, coordinated equatorially by four nitrogen atoms from four dicyanamide ligands, and axially by two nitrogen atoms from two benzoimidazoles. Each dca ligand links two cadmium(II) atoms and **1** forms a two-dimensional (4,4) network.

Keywords: Cadmium complex; Crystal structure; Coordination polymer; Two-dimensional network; Luminescence; Dicyanamide

1. Introduction

Design and synthesis of coordination polymers have been an area of rapid growth, because of their intriguing structural topologies and interesting applications in magnetic, optical and electronic properties [1–6]. The dicyanamide ligand, $[N(CN)_2]^-$, is a remarkably versatile building block for the construction of coordnation polymers, since it can act in a mono-, bi-, or tridentate ligand. A large number of dicyanamide coordination polymers were synthesized due to their fascinating structural and magnetic properties [7–18]. However, structurally characterized cadmium(II) dicyanamide complexes are relatively few [14–18]. On the other hand, polynuclear d^{10} metal complexes have attracted extensive interest in recent years because of appealing structures and photoluminescent properties [19–23]. In this work, a new cadmium coordination polymer $[Cd(bim)_2(dca)_2]_n$ (**1**), (bim = benzimidazole, dca = dicyanamide) was

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*Corresponding author. Email: blli1965@pub.sz.jsinfo.net

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synthesized and characterized by IR, thermogravimetric analysis and luminescent properties and the structure determined.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were of analytical grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. TG and DSC analyses were done on a Thermal Analyst 2100 TA Instrument and SDT 2960 Simultaneous TGA-DTA Instrument in flowing dinitrogen at a heating rate of $10^{\circ}\mathrm{C\,min}^{-1}$. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a Perkin-Elmer LS50B spectrofluorimeter.

2.2. *Synthesis of [Cd(bim)$_2$(dca$_2$)$_n$] (1)*

A methanolic solution (15 mL) of benzimidazole (bim) (0.117 g, 1.0 mmol) was added slowly to an aqueous solution (15 mL) of $\mathrm{Cd(NO_3)_2 \cdot 4H_2O}$ (0.156 g, 0.5 mmol) with stirring. To this colorless transparent solution, an aqueous solution (10 mL) of sodium dicyanamide (0.089 g, 1.0 mmol) was added dropwise with constant stirring. The resulting solution was filtered and the filtrate was allowed to stand in air at room temperature. After several days, well-shaped colorless single crystals of **1** were obtained. Yield: 76%. Found: C, 45.04; H, 2.06; N, 29.21. Calcd for $\mathrm{C_{18}H_{10}CdN_{10}}$ (**1**): C, 45.16; H, 2.11; N, 29.26%. Main IR absorption bands (KBr, cm^{-1}): 3296w, 3129w, 2280m, 2230m, 2164vs, 1626w, 1495w, 1458w, 1416m, 1335m, 1254m, 1006w, 934w, 887w, 745m, 671w, 610w, 529w and 428w cm^{-1}.

2.3. *Crystal structure determination*

A single crystal of **1** with approximate dimensions $0.50 \times 0.15 \times 0.07\,\mathrm{mm}^3$ was selected for lattice parameter determination and collection of intensity data using a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Intensities were collected by the ω scan technique. Data intensity was corrected with multi-scan mode and empirical absorption [24]. The structures were solved by direct methods and refined with full-matrix least-squares technique (SHELXTL-97) [25]. The positions of hydrogen atoms were assumed. The final cycle of refinement including 134 variable parameters converged to $R = 0.0279$, $wR = 0.0640$ ($w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.9816P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 1868 observed reflections ($I > 2\sigma(I)$), $S = 1.069$, $(\Delta/\sigma)_{\max} = 0.000$, $(\Delta\rho)_{\max} = 0.795$ and $(\Delta\rho)_{\min} = -0.371\,\mathrm{e\,Å}^{-3}$. The parameters of the crystal data collection and refinement of complex **1** are given in table 1. Selected bond lengths and bond angles are shown in table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC reference number is 283259.

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{18}H_{10}CdN_{10}$
Formula weight	478.76
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.3497(14)
b (Å)	10.0099(15)
c (Å)	10.1720(17)
β (°)	107.242(4)
V (Å^3)	909.2(2)
Z	2
$F(000)$	472
ρ (g cm^{-3})	1.749
μ (mm^{-1})	1.229
Crystal size (mm^3)	0.50 × 0.15 × 0.07
θ range for data collection (°)	3.30 to 27.47
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-13 \le l \le 13$
Refinement method	Full-matrix least-squares on F^2
Independent reflections	2080 [$R(\text{int}) = 0.0233$]
Parameter	134
Max. and min. transmission	0.919 and 0.578
Goodness of fit S	1.069
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0279, 0.0640
R_1 and wR_2 indices (all data)	0.0331, 0.0664
Largest diff. Peak and hole (e Å^{-3})	0.795 and −0.371

Table 2. Selected bond lengths (Å) and angles (°) for **1**; symmetry codes: A $-x+1$, $-y+1$, $-z+1$; B $-x+1/2$, $y-1/2$, $-z+1/2$; C $x+1/2$, $-y+3/2$, $z+1/2$.

Cd(1)–N(1)	2.309(2)	Cd(1)–N(4)	2.344(2)
Cd(1)–N(5B)	2.365(2)	N(3)–C(8)	1.314(3)
N(4)–C(8)	1.153(3)	N(5)–C(9)	1.153(3)
N(1)–Cd(1)–N(1A)	180.0	N(1)–Cd(1)–N(4)	87.45(8)
N(4A)–Cd(1)–N(4)	180.0	N(1)–Cd(1)–N(5B)	88.32(8)
N(4)–Cd(1)–N(5B)	90.33(8)	N(5B)–Cd(1)–N(5C)	180.0
C(8)–N(3)–C(9)	118.9(2)	N(3)–C(8)–N(4)	173.5(3)
N(3)–C(9)–N(5)	174.1(3)		

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the local coordination of the cadmium(II) in **1**. Each cadmium(II) is situated at the center of symmetry in a distorted octahedral coordination geometry, coordinated equatorially by four nitrogen atoms from four symmetry-related dca ligands, and axially by two nitrogen atoms from two benzimidazoles.

This cordination environment is similar to those observed in $[Cd(dca)_2(dadpm)]_n$ (dadpm = 4,4′-diaminodiphenylmethane) [16] and $[Cd(dca)_2(bpp)]_n$ (bpp = 1,3-bis (4-pyridyl)propane) [17, 18]. The N–Cd–N bond angles are in the range 87.45(8) to 92.55(8)°, close to 90°. The Cd–N(dca) bond lengths [Cd(1)–N(4) 2.344(2) Å, Cd(1)–N(5B) 2.365(2) Å] and Cd–N(bim) bond lengths [Cd(1)–N(1) 2.309(2) Å] in **1** are similar to corresponding values reported in $[Cd(dca)_2(dadpm)]_n$ [Cd–N(dca) 2.31(1), 2.33(1) Å; Cd–N(dadpm) 2.39(1) Å] [16] and $[Cd(dca)_2(bpp)]_n$ [Cd–N(dca) 2.325(3), 2.331(3) Å; Cd–N(bpp) 2.317(3) Å] [17, 18].

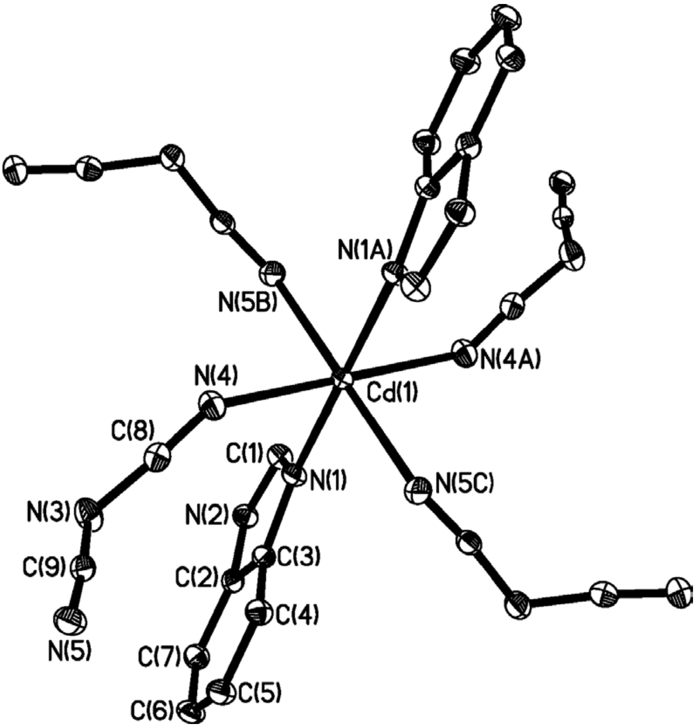

Figure 1. Local coordination of Cd(II) in the complex **1** with 30% thermal ellipsoids.

The nitrile C–N bond lengths of dca are 1.153(3) Å for N(4)–C(8) and 1.153(3) Å for N(5)–C(6). The bond angle related to amide nitrogen C(8)–N(3)–C(9) is 118.9(2)°, corresponding to the amide nitrogen atom with an sp^2 hybrid orbital; those related to nitrile N(3)–C(8)–N(4) and N(3)–C(9)–N(5) are 173.5(3) and 174.1(3)°, respectively, corresponding to N(4), C(8), C(9) and N(5) with sp hybrid orbitals.

The dicyanamide (dca) adopts end-to-end coordination. Each dca links two cadmium(II) atoms into a two-dimensional network, resulting in an "hourglass-shaped" 24-membered $Cd_4(dca)_4$ metallacycle (figure 2). Such a $Cd_4(dca)_4$ arrangement is unusual. To the best of our knowledge, the only example is $[Cd(dadpm)(dca)_2]_n$ [16]. The Cd···Cd distance separated by dca is 7.760 Å, similar to the corresponding distances 7.67 Å in $[Cd(dca)_2(pyridine)_2]_n$ [15] and 7.597 Å in $[Cd(dadpm)(dca)_2]_n$ [16].

The two-dimensional sheets are stacked parallel. The adjacent benzimidazole rings are absolutely parallel with a perpendicular distance 3.497 Å and the centeriod-to-centeriod distance of 3.838 Å for benzimidazole rings, exhibiting obvious π–π stacking interactions [14, 15, 26, 27]. The three-dimensional network forms via π–π stacking interactions of the benzimidazole rings of the adjacent two-dimensional sheets (figure 3). The shortest Cd···Cd distance is 9.320 Å between adjacent sheets.

3.2. *IR, thermogravimetric analysis and luminescence properties*

The absorption bands of **1** at 2280, 2230 and 2164 cm^{-1} are assigned to the C≡N symmetric stretch (ν_{sym}), the asymmetric stretch (ν_{asym}) and the combination band

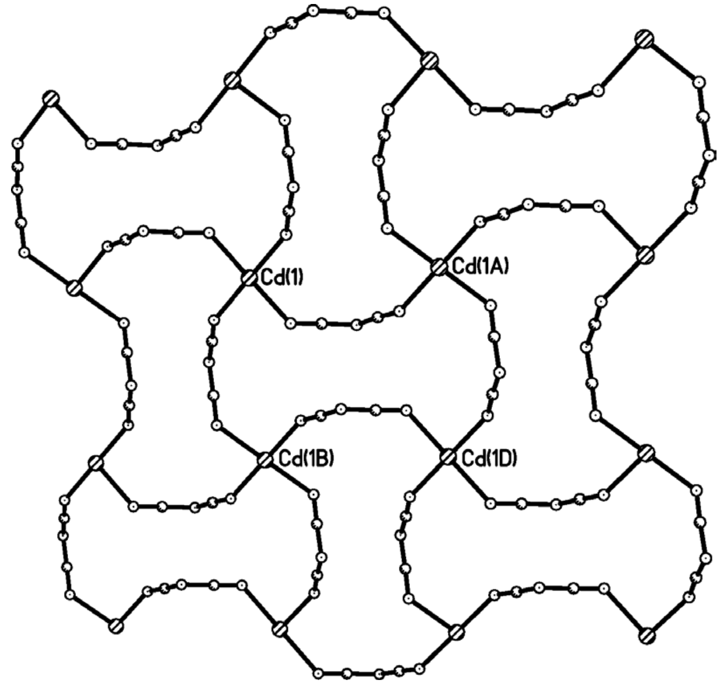

Figure 2. Two-dimensional network of **1**, omitting the benzimidazole ligands for clarity.

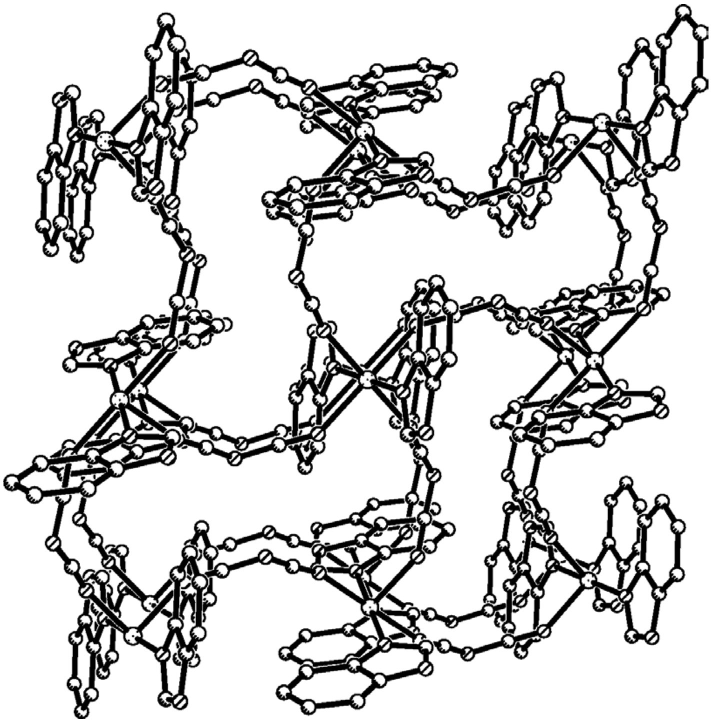

Figure 3. The stacking of two adjacent sheets in **1**.

for ν_{sym} and ν_{asym} of dca. The large shift towards high frequencies, compared with free dca in $NaN(CN)_2$ (2232 and 2179 cm^{-1}), confirmed that dca bridged the metal centers [8–18].

The thermal behavior of **1** was measured with TG-DSC under nitrogen and shows that **1** is stable up to 208°C (figure 4). The mass lost about 2.5% (corresponding to molecule weight 12.0) from 210 to 276°C and shows a large heat peak at 254°C. Then 17.9% mass (corresponding to molecule weight 85.7) was continuously lost from 276°C to 500°C with the residue (79.6%). The residue can not be assigned to a definite compound.

Measurement of the solid state luminescence spectrum of **1** reveals a strong blue emission maximum at approximately 419 nm, upon excitation at 364 nm (figure 5).

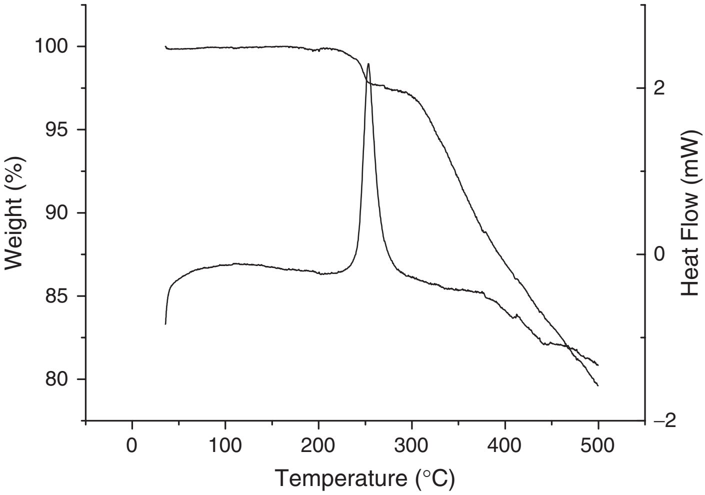

Figure 4. TG-DSC curves of **1**.

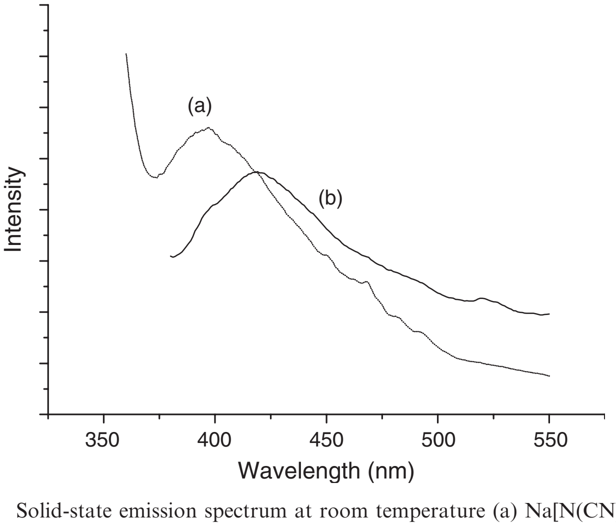

Figure 5. Solid-state emission spectrum at room temperature (a) $Na[N(CN)_2]$ (b) **1**.

Free benzimidazole in the solid state at room temperature does not emit luminescence when excited in the range of 280 to 420 nm. $Na[N(CN)_2]$ displays an emission band centered at about 397 nm when excited at 340 nm (figure 4). The 22 nm red-shift of the luminescence of **1** compared to that of the $Na[N(CN)_2]$ may be attributed to the light-to-metal charge transfer (LMCT) [19–23].

Acknowledgements

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