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Zn(II) and Cd(II) *N*-carbazolylacetates with strong fluorescence

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Abstract

N-carbazolylacetic acid was synthesized using a new method in a high yield and two carbazolylacetato complexes [Zn(Cabo)(phen)$_2$ClO$_4$]·0.5C$_2$H$_5$OH and [Cd(Cabo)(phen)$_2$-ClO$_4$] (Cabo = *N*-carbazolylacetate, phen = 1,10-phenanthroline) were synthesized and characterized by elemental analysis, IR, UV–Vis spectra, thermal analyses, photoluminescence measurement and X-ray diffraction studies. Both of the complexes exhibit strong blue emission in solid state as well as high thermal stability and solvent-resistant properties.

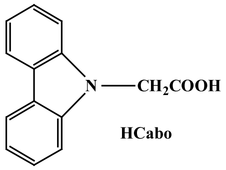
Keywords: Carbazole; *N*-carbazolylacetate; Crystal structures; Complexes; Photoluminescence

1. Introduction

A great deal of work has been devoted to inorganic–organic hybrid materials recently [1–3]. The diversity of organic components used has resulted in numerous fascinating properties. By carefully selecting the organic components, one hopes to tune the physical properties of this type of compound by tailoring their structures and realize various applications, including photoluminescence [4–7], catalysis [8] and second-order nonlinear optical properties [9,10].

Carbazole compounds are well known to exhibit good hole transporting properties and their charge transfer (CT) complexes can create free carriers in the visible region through the photocarrier generation process [11]. Acceptor-substituted carbazole derivatives were designed as novel photoconductive materials [12] and non-linear optical materials with large photorefractive effect [13,14]. Several electroluminescence (EL) materials containing carbazole group had been used in light-emitting diodes (LEDs) devices [15]. However, the devices are mostly organic compounds or polymers. Their low melting points or decomposition temperatures inhibit the applications of these materials.

We have initiated studies on *N*-carbazolylacetic acid with metal ions in an attempt to examine their modes of binding and possible properties. We report here the syntheses and crystal structures of two complexes [Zn(Cabo)(phen)$_2$ClO$_4$]·0.5C$_2$H$_5$OH (**1**) and [Cd(Cabo)(phen)$_2$ClO$_4$] (**2**) with strong blue emissions as well as high thermal stability and solvent-resistant properties.



HCabo

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2. Experimental

2.1. Materials and methods

All chemicals and solvents were dried and purified by usual methods. Elemental analyses were performed with a Perkin–Elmer 240 instrument. IR spectra were recorded with a Nicolet FT IR 170SX instrument (KBr discs) in the 4000–400 cm^{-1} region. UV–Vis spectra were recorded with an UV-265 spectrophotometer and corrected by subtracting solvent backgrounds. The photoluminescence measurements were carried out both in DMF solution and in the solid state at room temperature (r.t.) and the spectra were collected with a Perkin–Elmer LS50B spectrofluorimeter. TGA analyses were recorded with a Perkin–Elmer Pris-1 DMDA-V1 analyzer in an atmosphere of nitrogen at a heating rate of 5 °C min^{-1}. Electrospray mass spectra (ES MS) were determined with a Finnigan LCQ mass spectrograph, the concentration of the samples was about 1.0 mmol l^{-1}. The diluted solution was electrosprayed at a flow rate of 5×10^{-6} l min^{-1} with a needle voltage of 4.5 kV. The mobile phase was an aqueous solution of methanol (v/v, 1:1). The samples were run in the positive-ion mode.

2.2. Synthesis of the ligand *N*-carbazolylacetic acid

N-carbazolylacetic acid (hereafter abbreviated as HCabo) had been synthesized by several methods before [16,17], but the yield in the previous work was very low. In the present work we used a new method which gives a high yield. The synthesis procedure is described below. Carbazole (16.7 g, 0.1 mol) and sodium hydrate (12 g, 0.3 mol) dissolved in DMSO (40 ml) and heated to 85 °C yielded a dark-brown solution. After 30 min of stirring, bromacetic acid (16.68 g, 0.12 mol) was added in portions over a 30 min time span. The resulting solution was stirred overnight and then poured into 400 ml cold water. After filtration under vacuum, the pH value of the filtrate was adjusted to 3–4, during which time a white precipitate appeared. The mixture was filtered under vacuum and the product was washed exhaustively with water, and dried in air. Yield: 92%. *Anal*. Calc. for $C_{14}H_{11}O_2N$: C, 74.65; H, 4.916; N, 6.218. Found: C, 74.38; H, 4.930; N, 6.196%. IR (cm^{-1}) selected bands: 3049 (m), 2926 (m), 1716 (vs), 1703 (vs), 1486 (vs), 1459 (vs), 1406 (vs), 1326 (vs), 755 (vs), 723 (vs). UV–Vis (in DMF solution) λ (nm) (ε (M^{-1} cm^{-1})): 265 (61 400), 293 (25 300), 328 (6000), 340 (6200). EMS (*m*/*z*): 244.3.

2.3. Preparation of the complex Zn(Cabo)(phen)$_2$ClO$_4$]·0.5C$_2$H$_5$OH (**1**)

To a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.372 g, 1 mmol) in water, a solution of phen (0.38 g, 2 mmol) in ethanol was added. Sodium *N*-carbazolylacetate (0.371 g, 1.5 mmol) was then slowly added. The resultant mixture was heated to 80 °C and stirred for 30 min. The pale yellow crystalline solid was filtered and washed with ethanol and air-dried. The yield of complex **1** was 86% based on $Zn(ClO_4)_2 \cdot 6H_2O$. *Anal*. Calc: C, 60.89; H, 3.94; N, 9.34. Found for $C_{39}H_{29}ClN_5O_{6.5}Zn$: C, 60.03; H, 4.193; N, 9.271%. IR (cm^{-1}) selected bands: 1578.2 (vs), 1485 (s), 1453 (s), 1427 (s), 1387 (vs), 853(m), 753(s), 725(m); UV–Vis (in DMF solution) λ (nm) (ε (M^{-1} cm^{-1})): 266 (81 200), 292 (54 700), 325 (10 200), 340 (9800).

2.4. Preparation of the complex [Cd(Cabo)(phen)$_2$ClO$_4$] (**2**)

The pale yellow crystals of complex **2** were prepared by a procedure similar to that used for complex **1** with $Cd(ClO_4)_2 \cdot 6H_2O$ instead of $Zn(ClO_4)_2 \cdot 6H_2O$. The yield of complex **2** was 82% based on $Cd(ClO_4)_2 \cdot 6H_2O$. *Anal*. Calc: C, 57.294; H, 3.267; N, 8.795. Found for $C_{38}H_{26}ClN_5O_6Cd$: C, 57.24; H, 3.44; N, 8.64%. Crystals suitable for X-ray analysis were obtained by recrystallization in DMF. IR (cm^{-1}) selected bands: 1581 (vs), 1485 (s), 1453 (s), 1425 (s), 1385 (vs), 846 (m), 753 (s), 724 (m); UV–Vis (in DMF solution) λ (nm) (ε (M^{-1} cm^{-1})): 266 (93 200), 292 (79 700), 325 (15 100), 340 (15 100).

2.5. Crystallographic studies

Crystals of **1** and **2** suitable for X-ray analysis were obtained by recrystallization from DMF solutions. Data collections ($1.34° < \theta < 28.26°$ for **1**, $1.57° < \theta < 28.29°$ for **2**) were performed with a Siemens SMART 1K CCD area detector diffractometer with Mo Kα radiation using ω-scan mode ($\lambda = 0.71073$ Å). The structures were solved with direct methods using the program SHELXTL (Sheldrick, 1997) [18] and refined anisotropically with SHELXTL using the full-matrix least-squares procedure.

3. Results and discussion

3.1. Crystal structures of **1** and **2**

Two crystallographically independent, but very similar molecules have been found in **1**. Fig. 1 illustrates the full structure of one of them. Crystallographic data are given in Table 1 and selected bond lengths and angles are given in Table 2. In each molecule, the carboxylato group of the ligand adopts a chelating mode coordinating to the zinc ion. The full structure of one of the two molecules comprises a discrete mononuclear [Zn(phen)$_2$-(RCOO)]$^+$ cation and a perchlorate anion. As illu-

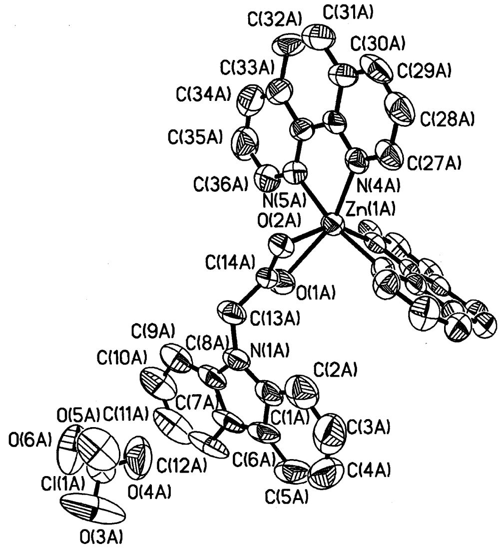

Fig. 1. Structure representation of one molecule of [Zn(Cabo)$(phen)_2ClO_4$] (**1**).

Table 1
Crystallographic data for **1** and **2**

	1	**2**
Formula	$C_{78}H_{56}N_{10}O_{13}Cl_2Zn_2$	$C_{38}H_{26}N_5O_6ClCd$
FW	1545.02	796.49
Crystal size (mm)	0.36 × 0.24 × 0.14	0.2 × 0.16 × 0.12
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	15.8184 (3)	10.9578(1)
b (Å)	22.0234 (1)	12.6511(2)
c (Å)	21.4069 (4)	13.1259(1)
α (°)	90	93.544(1)
β (°)	106.092 (1)	95.603(1)
γ (°)	90	113.339(1)
V (Å^3)	7165.42(19)	1652.66(3)
Z	4	2
ρ_{calc} (g cm^{-3})	1.432	1.601
T (K)	293	293
μ (mm^{-1})	0.817	0.799
Measured reflections	48 904	11 942
Observed reflections	17 307	7827
R_1	0.072	0.0649
wR_2	0.1833	0.1603

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

Complex **1**			
Bond lengths			
Zn1A–N3A	2.124(4)	Zn1A–O2A	2.128(4)
Zn1A–N4A	2.137(4)	Zn1A–N2A	2.155(4)
Zn1A–N5A	2.141(4)	Zn1A–O1A	2.328(4)
O1A–C14A	1.244(6)	N1A–C1A	1.393(7)
Zn1B–N3B	2.119(4)	Zn1B–N4B	2.126(5)
Zn1B–N2B	2.135(5)	Zn1B–N5B	2.141(4)
Zn1B–O1B	2.152(3)	Zn1B–O2B	2.251(4)
O1B–C14B	1.259(6)	N1B–C1B	1.420(9)
Bond angles			
N3A–Zn1A–O2A	147.53(14)	N3B–Zn1B–O2B	151.91(14)
N3A–Zn1A–N4A	110.96(14)	N3B–Zn1B–N4B	100.20(18)
O2A–Zn1A–N4A	99.61(14)	O2B–Zn1B–N4B	93.56(16)
N3A–Zn1A–N5A	97.57(17)	N3B–Zn1B–N5B	109.40(16)
N5A–Zn1A–N2A	169.55(16)	N5B–Zn1B–N2B	95.99(18)
N2A–Zn1A–O1A	95.99(14)	N2B–Zn1B–O1B	93.04(15)
Complex **2**			
Bond lengths			
Cd1–N4	2.307(4)	Cd1–O2	2.316(4)
Cd1–N2	2.320(4)	Cd1–N1	2.328(4)
Cd1–N3	2.368(4)		
Bond angles			
N4–Cd1–N2	121.81(15)	O2–Cd1–N2	92.93(15)
O2–Cd1–N1	107.89(15)	N4–Cd1–N3	71.76(15)
N2–Cd1–N3	95.86(16)	N1–Cd1–N3	159.49(15)
O2–Cd1–O1	55.63(13)	N3–Cd1–O1	100.60(15)
N4–Cd1–O2	141.15(13)		

strated in Fig. 1, the zinc atom is in a distorted octahedral ZnN_4O_2 geometry coordinated by four N atoms from two bidentate phen ligands and two O atoms from a bidentate *N*-carbazolylacetate group. The C13A, C14A, O1A, O2A, Zn1A atoms are almost in one plane (the largest deviation from the main plane is 0.0748 Å) which forms a dihedral angle of 90.2° with the carbazole moiety. There is an ethanol molecule in the crystal lattice. It should be noted that in the crystal, the carbazole rings are almost parallel to each other and interspaced with phen rings. The shortest distance between two aromatic rings is 3.42 Å indicating strong π–π interactions [19] (Fig. 3).

Crystallographic data of **2** are given in Table 1 and selected bond lengths and angles are given in Table 2. The structure of **2** comprises a discrete mononuclear $[Cd(phen)_2(RCOO)]^+$ cation and a perchlorate anion. As show in Fig. 2, each Cd(II) cation in **2** is in a distorted octahedral CdO_2N_4 geometry, being coordi-

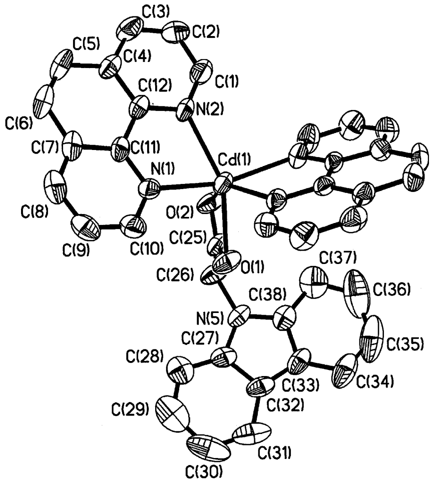

Fig. 2. Single crystal X-ray structure of the complex [Cd(Cabo)$(phen)_2ClO_4$] (**2**) (perchlorate is omitted for clarity).

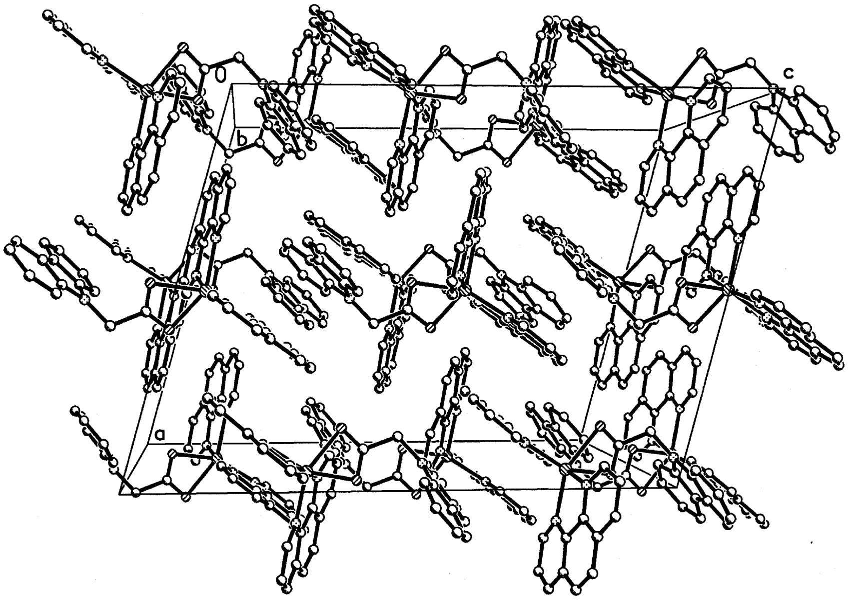

Fig. 3. Molecular packing diagram showing **1** (perchlorates are omitted for clarity).

nated by four N atoms of two phen ligands and two oxygen atoms of one chelating bidentate *N*-carbazolylacetato group. The C26, C25, O1, O2, Cd1 atoms are almost in one plane (the largest deviation from the main plane is 0.0096 Å) which forms a dihedral angle of 86.3° with the carbazole moiety. The shortest distance between two aromatic rings is 3.54 Å also indicating strong π–π interactions [19] (Fig. 4).

3.2. Thermal analyses

To study the thermal stability of compounds **1** and **2**, thermogravimetric analysis (TGA) was performed on the single crystal samples. The TGA curve of **1** indicated one striking weight loss step occurring at 231.4 °C (2.97% loss), corresponding to the removal of the ethanol molecules. The most important fact is that no weight loss was recorded between the temperatures 231.4 and 361 °C indicating the stability of the main structure. Complex **2** displays high thermal stability since there was no weight loss below the temperature 352 °C.

3.3. UV–Vis spectra

The UV–Vis spectra of **1**and **2** both show two high-energy bands at approximately 266 and 292 nm and two low-energy bands at approximately 325 and 340 nm. These bands may be assigned to the *intra*-ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the carbazole moiety [17,20] which are very similar to those of the ligand *N*-carbazolylacetic acid. No ligand to metal transition (LMCT) or metal to ligand transition (MLCT) was observed in the UV–Vis spectra.

3.4. Photoluminescence

The fluorescent emission spectrum of **1** in the solid state at room temperature is shown in Fig. 5. The emission behaviors of the complexes are similar to the free ligand in solution but differ greatly in the solid state. Strong emissions of **1**, **2** and the ligand at approximately 350 nm in DMF solution (Ex: 298 nm) were observed which can be assigned to the $\pi^* \rightarrow \pi$ transition of the carbazole moiety [21]. In the solid state, the free ligand emits at 423 nm with a shoulder at 405 nm. These bands might be assigned to the excimeric emission of the ligand [21] due to the interactions between the molecules. Both of the complexes **1** and **2** have a maximum at 493 nm and a shoulder at 517 nm with a large red shift compared with the free ligand that may be assigned to exciplex emissions [22]. The distance between the two adjacent phenanthroline rings in **1** and **2** are 3.42 and 3.54 Å, respectively, indicating strong π–π interaction [19]. The large red shifts reveal stronger interactions than that of the ligand between molecules which are resulted from the strong π–π stacking of the aromatic rings (see Figs. 3 and 4).

4. Conclusions

Two carbazolylacetato complexes with strong blue emissions in the solid state at room temperature were synthesized and characterized by X-ray diffraction analyses. Although carbazole compounds have been investigated extensively, as far as we are aware, no carbazole-containing metal complex has been reported. Owing to the blue fluorescence emission of **1** and **2**, these complexes may be used as advanced materials

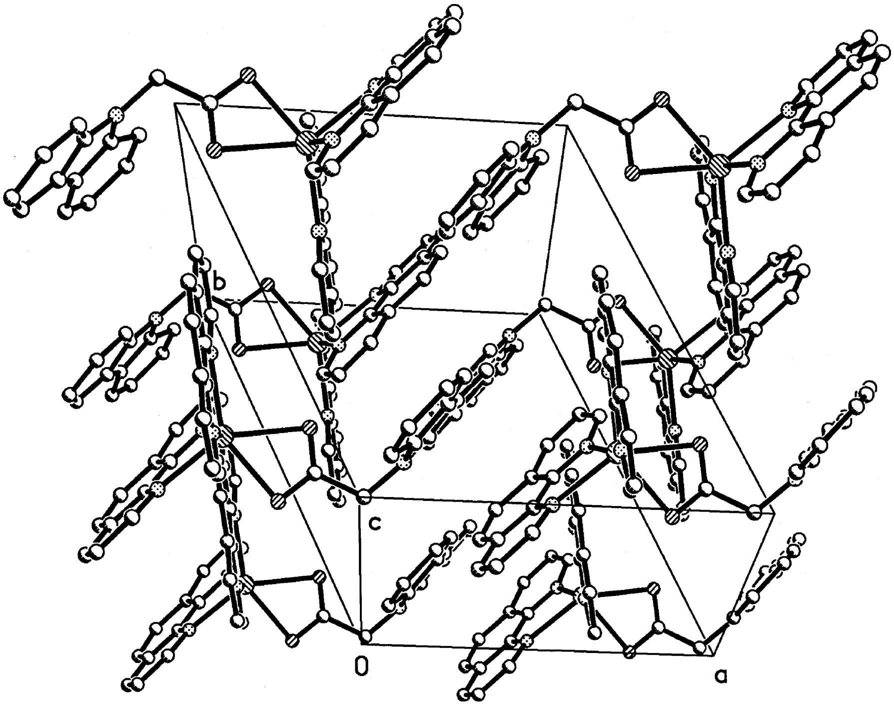

Fig. 4. Molecular packing diagram showing **2** (perchlorates are omitted for clarity).

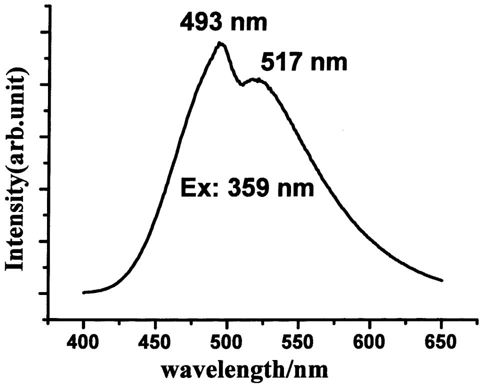

Fig. 5. The photoluminesence spectrum of **1** in the solid state at room temperature.

for blue-light emitting diode devices. These complexes may be excellent candidates since, in addition to their high thermal stability (especially **2**) they are almost insoluble in common solvents such as ethanol, chloroform, acetone, acetonitrile, benzene and water. In conclusion, the rational design of structures and introducing optical or electrical active chromophores into metal complexes provide a new synthetic route for the exploration of functional inorganic–organic hybrid materials with promising photoelectronic properties.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 181791 (**1**), 181792 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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