

Blue luminescent complexes based on 5-aminodiacetic isophthalic ligand

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Received 17 November 2005; received in revised form 25 December 2005; accepted 27 December 2005

Available online 28 February 2006

Abstract

The reactions of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 5-aminodiacetic isophthalic acid (H_4adip) with 1,10'-phenanthroline (phen) ligand gave rise to two blue luminescent coordination mononuclear complexes: $[\text{Cd}(\text{phen})(\text{H}_3\text{adip})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ (**1**) and $\text{Zn}(\text{phen})(\text{H}_3\text{adip})_2$ (**2**), respectively. **1** crystallizes in the triclinic space group $P\bar{1}$, with $a=6.2889(2)$, $b=16.1556(5)$, $c=18.4277(7)$ Å, $\alpha=97.722(12)$, $\beta=94.338(9)$, $\gamma=95.039(7)^\circ$, $V=1840.86(11)$ Å³, $Z=2$. Complex **2** crystallizes in monoclinic, space group $C2/c$ with $a=22.639(8)$, $b=9.813(3)$, $c=15.708(6)$ Å, $\beta=110.928(4)^\circ$, $V=3259(2)$ Å³, $Z=4$. Carboxylic groups in both structures are involved in strong hydrogen bonding interactions. At room temperature, complex **1** exhibits an intense emission at 474 nm upon 380 nm excitation, while complex **2** exhibits an intense emission at 485 nm upon 365 nm excitation, which are contributed from ligand-to-metal charge-transfer (LMCT).

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Keywords: Mononuclear; Supramolecule; Carboxylate; Hydrogen bond; Luminescence

1. Introduction

In recent years, chemists have devoted a great deal of effort to metal-organic coordination polymers [1–5]. In particular, aromatic multi-carboxylate ligands have been shown to be good building blocks in the design of metal-organic materials with desired topologies owing to their rich coordination modes [6–9]. However, most adopted ligands possess rigid carboxylate arms, e.g. 1,3,5-benzenetricarboxylate [10], 1,2,4,5-benzenetetracarboxylate [11], 1,4,5,8-naphthalenetetracarboxylate [12], etc. Relative fewer compounds are reported derive from flexible carboxylate arms [13,14]. But as known that the crystal structure formation is sensitive to the flexibility of carboxylate arms, and such flexibility may increase the probability of making tube-like or cage-like structure. Taking account of these, we feel it significant to take on the exploration on carboxylate ligand with flexible carboxylate arms. So, we designed and synthesized a new bridging chelating multi-carboxylate ligand 5-aminodiacetic isophthalic acid (H_4adip). H_4adip not only has two rigid carboxyl groups, but also has two flexible acetic groups with suitable lengths. Moreover, the nitrogen atom of aminodiacetic group is also possible to participate in the coordination sphere. In addition,

like other multi-carboxylate ligands, it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the number of deprotonated carboxyl groups, which contribute to the stability of supramolecular network. Recently, we began to assemble H_4adip and transition metal ions into polymeric complexes under hydrothermal conditions. We hope the rich information stored in H_4adip will induce novel polymeric structures. Through carefully controlling the reaction conditions, we have found that H_4adip is a versatile building block for the construction of metal-organic complexes through complete or partial deprotonation of its carboxyl groups. A series of interesting structures from 1D to 3D architectures have been successfully obtained in our experiments [15]. Herein, we reported two transition metal complexes derived from H_4adip and phen under strong acidic conditions: $[\text{Cd}(\text{phen})(\text{H}_3\text{adip})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ (**1**) and $\text{Zn}(\text{phen})(\text{H}_3\text{adip})_2$ (**2**). Such discrete molecules are further linked together by hydrogen bonds or $\pi \cdots \pi$ interactions to generate interesting supramolecular architectures, and both show intense blue luminescence in solid state at room temperature.

2. Experimental section

2.1. General

The H_4adip were prepared as described in our work elsewhere [15], and the other starting materials were purchased commercially and used without further purification. Elemental

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analyses were determined on an Elemental Vario ELIII elemental analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT IR spectrometer in the range of 200–4000 cm^{-1} . Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FL920.

2.2. Synthesis of $[\text{Cd}(\text{phen})(\text{H}_3\text{L})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ (**1**)

A mixture of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.134 g, 0.5 mmol), H_4adip (0.148 g, 0.5 mmol) and 1,10-phen (0.099 g, 1.0 mmol) dissolved in distilled water (6 ml)/ CH_3COOH (6 ml) was sealed in a 25 ml Teflon-lined autoclave and heated under autogenous pressure at 90 °C for 3 days. The resulting colorless prismatic crystals of **1** were filtered, and air-dried at room temperature. Yielded (0.157 g), produced in 67.6% (based on H_4adip). IR (KBr pellet, cm^{-1}): 3425(br), 2972(w), 2911(w), 2844(w), 1696(s), 1602(s), 1468(s), 1423(s), 1383(m), 1325(s), 1383(m), 1293(m), 995(m). Anal. Calcd for $\text{C}_{36}\text{H}_{33}\text{CdN}_4\text{O}_{18.5}$: C 46.49, H 3.58, N 6.02%. Found: C 46.42, H 3.71, N 5.98%.

2.3. Synthesis of $\text{Zn}(\text{phen})(\text{H}_3\text{L})_2$ (**2**)

Complex **2** was synthesized by the same procedure as above but adding $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ instead of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. Pale-yellow prism crystals are obtained by filtration. Yielded (0.075 g), produced in 36.2% (based on H_4adip). IR (KBr pellet, cm^{-1}): 3436.9(br), 3075.6(w), 2921.54(w), 2865.02(w), 2361.7(w), 1718.63(vs), 1597.8(m), 1555.49(m), 1467.63(m), 1421.97(m), 1383.83(m), 1267.9(w), 1216.5(m), 1192.47(m), 990.58(m), 846.79(w). Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_{16}\text{Zn}$: C 51.60, H 3.37, N 6.69%. Found: C 51.52, H 3.42, N 6.64%.

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

	1	2
Empirical formula	$\text{C}_{36}\text{H}_{33}\text{CdN}_4\text{O}_{18.5}$	$\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_{16}\text{Zn}$
Temp. (K)	173(2)	173(2)
Cryst. color	Colorless	Colorless
Cryst. size (mm^3)	$0.20 \times 0.10 \times 0.08$	$0.20 \times 0.10 \times 0.05$
Mr	930.06	837.99
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$C2/c$
a (Å)	6.2889(2)	22.639(8)
b (Å)	16.1556(5)	9.813(3)
c (Å)	18.4277(7)	15.708(6)
α (°)	97.722(12)	90
β (°)	94.338(9)	110.928(4)
γ (°)	95.039(7)	90
V (Å ³)	1840.86(11)	3259(2)
Z	2	4
Density (mg/m^3)	1.678	1.708
Abs. coeff. (mm^{-1})	0.684	0.846
$F(000)$	946	1712
Refln collections	14204	12279
Indep. Reflins	8293 [$R(\text{int})=0.0259$]	3719 [$R(\text{int})=0.0315$]
Params	547	314
S on F^2	1.142	1.076
$R1, wR2$ [$I > 2\sigma(I)$]	0.0534, 0.1176	0.0393, 0.0928
$R1, wR2$ (all data)	0.0609, 0.1216	0.0459, 0.0973

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

	Bond length (Å)		Bond angle (°)
Complex 1			
Cd(1)–O(18)	2.274(3)	N(2)–Cd(1)–N(1)	70.67(11)
Cd(1)–O(8)	2.306(3)	O(8)–Cd(1)–O(14)	152.75(11)
Cd(1)–N(2)	2.336(3)	O(18)–Cd(1)–O(17)	89.80(13)
Cd(1)–O(14)	2.340(3)	O(8)–Cd(1)–N(1)	87.36(11)
Cd(1)–N(1)	2.403(3)	O(18)–Cd(1)–N(2)	162.06(11)
Cd(1)–O(17)	2.412(3)	O(18)–Cd(1)–N(1)	113.45(12)
O(13)–C(36)	1.247(5)	O(14)–Cd(1)–N(1)	118.94(10)
O(14)–C(36)	1.278(5)	N(1)–Cd(1)–O(17)	152.48(12)
O(7)–C(13)	1.272(6)		
O(8)–C(13)	1.235(5)		
Complex 2			
Zn(1)–N(2A)#1	2.0641(17)	N(2A)#1–Zn(1)–N(2)	81.92(9)
Zn(1)–N(2)	2.0641(17)	O(1)–Zn(1)–O(2)	59.97(6)
Zn(1)–O(1A)#1	2.1252(16)	O(1A)#1–Zn(1)–O(1)	153.73(8)
Zn(1)–O(1)	2.1252(16)	N(2A)#1–Zn(1)–O(2A)#1	153.19(6)
Zn(1)–O(2A)#1	2.2347(15)	N(2)–Zn(1)–O(1A)#1	105.37(6)
Zn(1)–O(2)	2.2347(15)	O(1)–Zn(1)–O(2A)#1	101.43(6)
Zn(1)–C(8A)#1	2.517(2)	N(2)–Zn(1)–O(2A)#1	96.43(6)
O(1)–C(8)	1.257(2)		
O(2)–C(8)	1.262(3)		

Symmetry code: #1 $-x, y, -z + 1/2$.

2.3.1. X-ray structure analyses

X-ray intensity data of both complexes were collected on a Mercury CCD diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 173 K. Empirical absorption corrections were applied to the data using the SADABS program [16]. The structures were solved by the direct method and refined by the full-matrix least squares on F^2 using the SHELXTL-97 program [17]. All of the non-hydrogen atoms were refined anisotropically. The H atoms bonded to C atoms were positioned geometrically and refined using a riding model [$C-H$ 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]. The H atoms bonded to O atoms were located from difference maps and refined isotropically. Crystallographic data and structure refinements for **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. CCDC numbers are 290056 for compound **1** and 290057 for compound **2**, respectively.

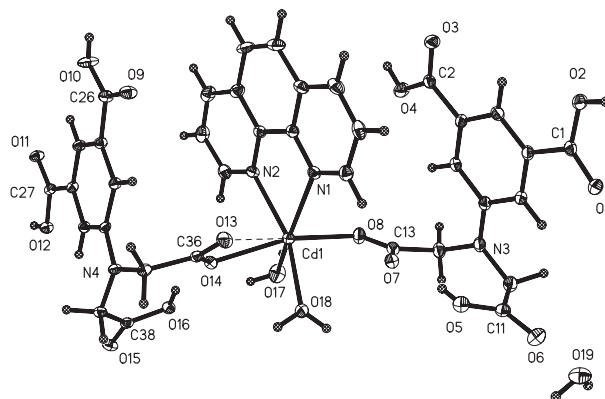


Fig. 1. ORTEP drawing of **1**, drawn with displacement ellipsoids at the 30% probability.

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