Blue Fluorescence of a Binuclear Cd(II) Complex: $[Cd(ClC_2H_4CO_2)_2(phen)]_2$

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A new binuclear complex, $[Cd(ClCH_2CH_2CO_2)_2(phen)]_2$ (**1**), has been synthesized and structurally characterized by single crystal X-ray diffraction methods. The Cd atoms are linked by carboxylate oxygen atoms into a four-membered Cd_2O_2 rhombic ring with a Cd···Cd separation of 3.824 Å. Two carboxylate groups act as bidentate, and two as both bidentate bridging and bidentate chelating ligands. The hydrogen bonding and π-π stacking interactions are responsible for the supramolecular assembly and stabilization of the crystal structure. The complex has been characterized by elemental analysis, IR and UV/Vis spectra, and thermogravimetric and differential thermal analysis (TG/DTA). The complex exhibits blue fluorescence in the solid at room temperature.

Key words: Crystal Structure, Binuclear Cadmium(II) Complex, Fluorescence Properties

Introduction

F. Blau started the coordination chemistry of N-heterocyclic ligands with the synthesis of transition metal complexes of 2,2′-bipyridine [1]. Since then, large varieties of related complexes and their structural, chemical, electrochemical, photophysical and photochemical, and catalytic properties have been explored, and tremendous advancement has been observed [2 – 5]. Hydrogen bonding interactions and π-π stacking interactions and other non-covalent interactions can generate structures defined as "supramolecular synthons", which can be crucial to the topochemical reactivity of molecules in the crystalline state [6, 7]. These interactions have been extensively studied and are responsible for a wide array of phenomena in chemistry and biology, including organic transformations, molecular recognition and organization of molecular solids [8 – 10]. 1,10-Phenathroline (phen) and other bidentate chelating ligands have been widely used as substitutes for amino acid side groups in biomimetic chemistry. In this contribution, we present a new binuclear cadmium complex, $[Cd(ClCH_2CH_2CO_2)_2(phen)]_2$ (**1**).

Table 1. Crystal and refinement data for **1**.

Formula	$C_{18}H_{16}CdCl_2N_2O_4$
*M*r	507.63
Crystal size, mm^3	0.50 × 0.35 × 0.15
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	8.0306(2)
b, Å	10.9830(3)
c, Å	12.1347(3)
α, deg	109.93(1)
β, deg	99.53(1)
γ, deg	100.43(1)
V, $Å^3$	959.2(6)
Z	2
D_{calcd}, g cm^{-3}	1.75752
$\mu(MoK_\alpha)$, cm^{-1}	1.443
F(000), e	504
hkl range	±10, ±14, ±15
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	0.658
Refl. measured	8240
Refl. unique	4446
R_{int}	0.017
Param. refined	245
$R(F)\,/\,wR(F^2)$[a] (all refls.)	0.025 / 0.066
A/B values for weighting scheme[b]	0.007 / 0.3053
GoF (F^2)	1.091
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	0.44/−0.47

[a] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/2\Sigma w(F_o{}^2)^2]^{1/2}$; [b] $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Experimental Section

Measurements of physical properties

All chemicals of p. a. grade were commercially available and used without further purification. The C, H and N microanalyses were performed with a Perkin-Elmer 2400-CHNS/O elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. The combined thermo-

Table 2. Selected interatomic distances (Å) and angles (deg) for **1**[a].

Cd1–O1	2.3431(18)	Cd1–O4$^{\#1}$	2.3791(14)	Cl2–C18	1.794(3)
Cd1–N2	2.348(2)	Cd1–O2	2.3877(17)	O1–C13	1.253(3)
Cd1–O4	2.3558(16)	Cd1–O3	2.5066(16)	O2–C13	1.241(3)
Cd1–N1	2.360(2)	Cl1–C15	1.779(4)	O3–C16	1.240(2)
O4–C16	1.270(2)				
O1–Cd1–N2	167.93(7)	N2–Cd1–O4$^{\#1}$	87.14(6)	O4$^{\#1}$–Cd1–O2	83.48(6)
O1–Cd1–O4	95.31(6)	O4–Cd1–O4$^{\#1}$	72.29(6)	O1–Cd1–O3	94.89(6)
N2–Cd1–O4	94.14(6)	N1–Cd1–O4$^{\#1}$	143.33(6)	N2–Cd1–O3	84.81(6)
O1–Cd1–N1	96.97(7)	O1–Cd1–O2	55.09(6)	O4–Cd1–O3	53.16(5)
N2–Cd1–N1	70.98(6)	N2–Cd1–O2	120.65(6)	N1–Cd1–O3	84.10(5)
O4–Cd1–N1	136.34(6)	O4–Cd1–O2	136.51(6)	O4$^{\#1}$–Cd1–O3	123.87(5)
O1–Cd1–O4$^{\#1}$	102.87(6)	N1–Cd1–O2	83.10(6)	O2–Cd1–O3	145.3

[a] Symmetry code: $^{\#1}$ $1-x$, $1-y$, $1-z$.

gravimetric and differential thermal analysis (TG/DTA) was carried out in the range 29 – 773 °C on powdered samples in an air stream using a WCT-1A analyzer with a heating rate of 10 °C min^{-1}. All the excitation and emission spectra were measured with an F-4500 fluorescence spectrophotometer with a xenon arc lamp as the excitation light source for the solid samples at r. t.

*Preparation of [Cd(phen)(ClCH$_2$CH$_2$CO$_2$)$_2$]$_2$ (**1**)*

A freshly prepared precipitate of Cd(OH)$_2$ (0.146 g, 1.0 mmol), obtained from 2.0 mL (1.0 M) of NaOH added to a stirred solution of Cd(NO$_3$)$_2\cdot$4H$_2$O (0.313 g, 1.0 mmol) in 5 mL of H$_2$O, was added to a stirred aqueous solution of 1,10-phenanthroline (0.198 g, 1.0 mmol) and 2-chloropropionic acid (0.217 g, 2.0 mmol) in 20 mL of H$_2$O/ethanol (v/v 1 : 1). The mixture was stirred for another 2 h and filtered, and the resultant filtrate was allowed to stand for slow evaporation at r. t. Colorless crystals were obtained 20 d later in a yield of 80 % based on the initial Cd(OH)$_2$ input. – $C_{18}H_{16}CdCl_2N_2O_4$: calcd. C 42.58, H 3.15, N 5.52; found C 42.52, H 3.17, N 5.55. – IR: ν = 3061 (m), 2976 (m), 1574 (vs), 1516 (s), 1312 (s), 1144 (w) cm^{-1}.

X-Ray structure analysis

The reflection intensities of **1** were collected at 298(3) K using a Bruker SMART Apex II CCD area detector single-crystal diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), using $\psi/2\vartheta$ scans. Absorption correction was applied using the program SADABS [11]. The structure was solved with Direct Methods using SHELXS-97 [12] and refined by full-matrix least-squares on F^2 (SHELXL-97 [13]). All hydrogen atoms were generated geometrically. All non-hydrogen atoms were finally refined with anisotropic displacement parameters, hydrogen atoms with isotropic displacement parameters. Further information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC 671924 contains 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

IR and UV/Vis spectra

The IR spectra show the ν(=C–H) stretching vibrations at 3061 cm^{-1} and the ν(-C–H) stretching vibrations of -CH$_2$- at 2976 cm^{-1}. The strong absorptions bands located at 1574 and 1516 cm^{-1} may be assigned to phenyl group C–C stretching vibrations, the absorptions at 1312 and 1144 cm^{-1} to carboxylate group ν(C–O) stretching vibrations. The absorption at 849 cm^{-1} should be assigned to the ν(C–Cl) stretching vibration.

The UV spectrum of an aqueous solution at r. t. is depicted in Fig. 1. There are three absorption bands at 285 – 242, 240 – 211, and 209 – 200 nm, which should be assigned to the B, E2 and E1 bands of the 1,10-phenanthroline ligand, respectively. Compared with

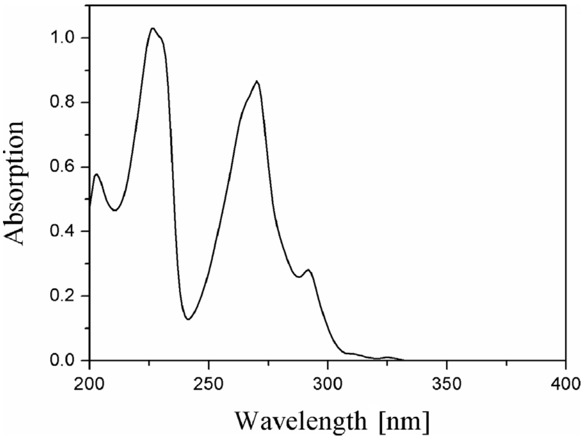

Fig. 1. UV/Vis spectrum of **1** in aqueous solution at r. t.

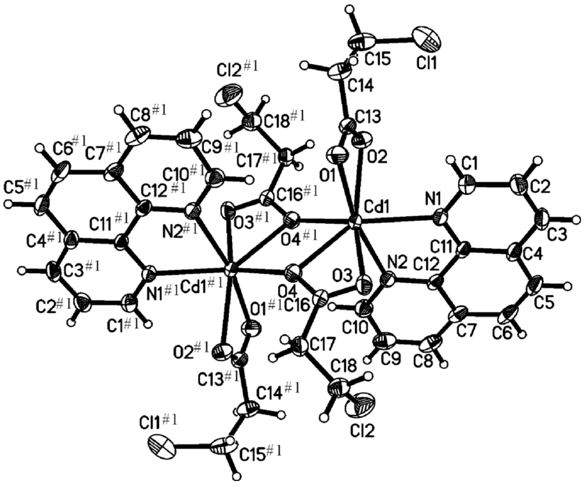

Fig. 2. ORTEP view of the molecular structure of **1** in the solid state with atom numbering (displacement ellipsoids at the 30 % probability level; symmetry code: #1 $1-x$, $1-y$, $1-z$).

those of the free 1,10-phenanthroline ligand, the absorptions are slightly red-shifted.

Structure description

Complex **1** consists of $[Cd_2(phen)_2(ClC_2H_4CO_2)_4]$ molecules. The seven-coordinated Cd atom is in a severely distorted capped trigonal prismatic geometry [14] defined by two N atoms of one phen ligand and five carboxylate O atoms, of which four come from two chelating carboxylate groups and one from the bidentate bridging carboxylate group, with the O3 atom occuping the capping position. The Cd atoms are linked by the O4 atoms of two carboxylate groups into a rhombic four-membered Cd_2O_2 ring with a Cd···Cd separation of 3.824 Å, as shown in Fig. 2. The Cd1–N2 distance (2.348(2) Å) is slightly longer than the Cd1–N1 distance (2.360 (2) Å). Both Cd–N distances are similar to those in the related complex $[Cd(H_2O)(C_3H_3O_2)_2(C_{12}H_{10}N_2)]$ [15]. The Cd–O distances range from 2.343(2) to 2.5066(16) Å, the Cd1–O3 bond length being longer than the other Cd–O distances, indicating that the coordination sphere is significantly distorted.

The complex molecules are assembled by π-π stacking of neighboring 1,10-phenanthrolines at a distance of 3.438 Å into 2D layers parallel to (111) (Fig. 3). The 2D layers are interconnected by weak C–H···O hydrogen bonds between phen and chloropionate groups to form a 3D network.

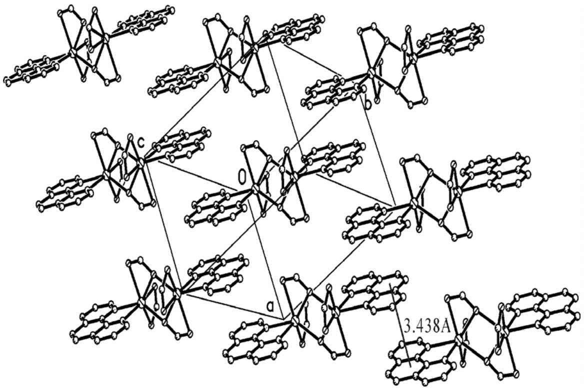

Fig. 3. The 2D structure of **1** built up through π-π stacking interactions.

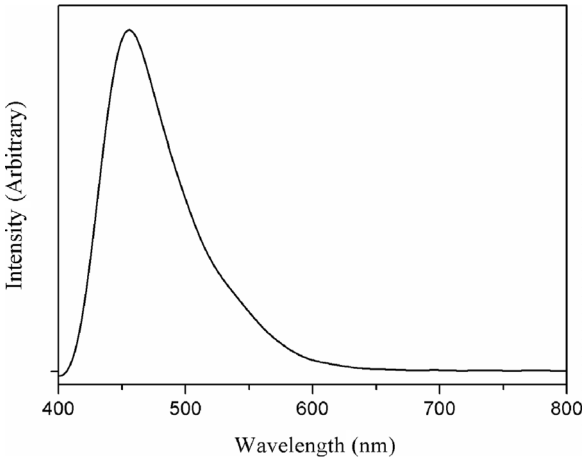

Fig. 4. Fluorescence spectrum of **1** in the solid state at r. t.

Thermal stability

Thermogravimetric analysis (TGA) reveals that **1** possesses high thermal stability. There is no weight loss from r. t. to 160 °C. The DTA curve of **1** exhibits five exothermic peaks centered at 170, 359, 433, 505 and 601 °C. The strongest exothermic reaction at 601 °C indicates that the framework collapses.

Fluorescence properties

The solid-state fluorescence spectrum of compound **1** at r. t. is depicted in Fig. 4. The blue fluorescence is stronger compared to that of the free ligand with the maximum emission at *ca.* 455 nm upon excitation at 381 nm, assigned to the ligand-ligand charge transfer $\pi_L \rightarrow \pi_L{}^*$ transition from the 1,10-phenanthroline. The free 1,10-phenanthroline molecule displays a weak luminescence at *ca.* 365 nm in the solid state at r. t.

The significant red-shift of the luminescence may be caused by the inter-planar phen-phen π-π stacking interactions, which result in a decrease of the HOMO-LUMO energy gap [16].

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