

Structure and Fluorescent Properties of a Chiral Cd(II) Complex: $\text{Cd}(\text{bpy})(\text{H}_2\text{O})(\text{PhCH}=\text{CHCO}_2)_2$

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Reaction of $\text{Cd}(\text{CO}_3)_2$, cinnamic acid and 2,2'-bipyridine (bpy) in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ afforded a new chiral Cd(II) complex, $\text{Cd}(\text{bpy})(\text{H}_2\text{O})(\text{PhCH}=\text{CHCO}_2)_2$ (**1**). Single crystal X-ray analysis shows that complex **1** crystallizes in the monoclinic space group $P2_1$ with the cell dimensions: $a = 10.081(2)$, $b = 9.2657(19)$, $c = 13.748(3)$ Å, $\beta = 103.02(3)^\circ$, $V = 1251.2(4)$ Å³, $Z = 2$. The seven-coordinated Cd atoms are in a severely distorted capped trigonal prism geometry. The complex molecules are assembled via strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds into chains along the [010] direction. Complex **1** exhibits weak fluorescence in the solid state at r. t.

Key words: Crystal Structure, Cadmium, Chirality, Fluorescent Properties

Introduction

The designed construction of chiral or homochiral metal-organic or coordination complexes is of great current interest because of their unique applications in asymmetric catalysis, enantioselective separations, biomimetic chemistry, and as nonlinear optical and magnetic materials [1–5]. Chiral metal-organic complexes can be generated from chiral ligands or by using achiral ligands under spontaneous resolution without any chiral sources [6–8]. Synthesis of chiral species from achiral ligands is the key issue in studying the genesis of chirality in biological systems. Carboxylate groups display a variety of binding geometries, such as monodentate terminal, chelating, bidentate bridging and monodentate bridging, in coordination chemistry of the active sites of metalloenzymes [9]. A significant number of metal-carboxylate complexes have been prepared and well characterized due to the fascinating structures of metal-carboxylate clusters and the structural details of the active site(s) that may influence the chemical mechanisms of catalysis [10–15]. Remarkably, many chiral metal-organic complexes generated from achiral carboxylate ligands not only possess intriguing aesthetic structures but also exhibit unique properties as potential functional materials [5]. 2,2-Bipyridine (bpy), 1,10-phenanthroline (phen) and

bidentate chelating ligands have been widely used as substitutes for amino acid side groups in biomimetic chemistry and as new diagnostic and therapeutic agents that can recognize and cleave DNA [16–17]. Based on the above considerations, we are devoted to exploiting the unique coordination properties of Cd(II) or Pb(II) with different carboxylic acids and chelating ligands for the development of practical extractants for toxic metal pollutants in the environment, and present here the chiral complex, $\text{Cd}(\text{bpy})(\text{H}_2\text{O})(\text{PhCH}=\text{CHCO}_2)_2$ (**1**).

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. All the excitation and emission spectra were measured with an Aminco Bowman Series 2 instrument with a xenon arc lamp as the excitation light source for the solid-state samples at r. t. The combined measurement on thermogravimetric and differential thermal analysis (TG/DTA) was carried out in the range 25–600 °C on powdered samples in a nitrogen stream using a Perkin Elmer TGS-2 analyzer with a heating rate of 10 °C min^{-1} .

Table 1. Crystal and refinement data for Cd(bpy)(H₂O)-(PhCH=CHCO₂)₂ (**1**).

Formula	C ₂₈ H ₂₄ CdN ₂ O ₅
<i>M</i> _r	580.89
Crystal size, mm ³	0.41 × 0.22 × 0.17
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> , Å	10.081(2)
<i>b</i> , Å	9.2657(19)
<i>c</i> , Å	13.748(3)
β, deg	103.02(3)
<i>V</i> , Å ³	1251.2(4)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ⁻³	1.542
μ(MoK _α), cm ⁻¹	0.914
<i>F</i> (000), e	588
<i>hkl</i> range	−13 ≤ <i>h</i> ≤ 13, −12 ≤ <i>k</i> ≤ 10, −17 ≤ <i>l</i> ≤ 17
((sin θ)/λ) _{max} , Å ⁻¹	0.0044(4)
Refl. measured	12315
Refl. unique	5090
<i>R</i> _{int}	0.024
Param. refined	334
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) ^a (all reflexions)	0.026/0.043
<i>x</i> (Flack)	−0.003(15)
GoF (<i>F</i> ²) ^a	1.073
Δρ _{fin} (max/min), e Å ⁻³	0.39/−0.33

^a $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; ^b $wR_2 = [\sigma^2(F_o^2) + (0.007P)^2 + 0.3053P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

Preparation of [Cd(bpy)(H₂O)(PhCH=CHCO₂)₂] (**1**)

Commercially available CdCO₃ (0.125 g, 1.0 mmol) was added to a solution of 2,2-bipyridine (0.167 g, 1.0 mmol) and cinnamic acid (0.144 g, 2.0 mmol) in 20 mL of C₂H₅OH/H₂O (1 : 1, v/v) with vigorous stirring under reflux conditions. The resulting white suspension was filtered and the filtrate was left to stand at 50 °C. Colorless prismatic crystals suitable for X-ray analysis were obtained two weeks later in 75 % yield (based on the initial CdCO₃ input). – C₂₈H₂₄CdN₂O₅: calcd. C 57.84, H 4.13, N 4.82; found: C 57.86, H 4.18, N 4.80. – IR: ν = 3392m, 3268w, 3103w, 1640s, 1558vs, 1496m, 1439m, 1384vs, 1247m, 1020w, 1156w, 987m, 876w, 773vs, 742s, 685m, 588m, 487w cm⁻¹.

X-Ray structural analysis

The reflection intensities of **1** were collected at 298(3) K on a Bruker SMART Apex II CCD area-detector single crystal diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) and Ψ/2θ scans. Absorption corrections were applied using the program SADABS [18]. The structure was solved with heavy-atom methods using SHELXS-97 [19,20]. The hydrogen atoms associated with carbon atoms were generated geometrically, and the hydrogen atoms of the water molecules were located in difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-

Table 2. Selected interatomic distances (Å) and angles (deg) for Cd(bpy)(H₂O)(PhCH=CHCO₂)₂ (**1**).

Cd(1)–O(1)	2.343(2)	Cd(1)–O(2)	2.4558(18)
Cd(1)–O(3)	2.2862(19)	Cd(1)–O(4)	2.618(2)
Cd(1)–O(5)	2.275(2)		
Cd(1)–N(1)	2.373(2)	Cd(1)–N(2)	2.346(2)
O(1)–C(11)	1.268(3)	O(2)–C(11)	1.232(4)
O(3)–C(20)	1.254(3)	O(4)–C(20)	1.234(3)
O(5)–Cd(1)–O(3)	106.70(8)	O(5)–Cd(1)–O(1)	101.16(8)
O(5)–Cd(1)–N(2)	91.20(8)	O(5)–Cd(1)–O(2)	86.73(10)
O(5)–Cd(1)–O(4)	77.36(8)	O(5)–Cd(1)–N(1)	158.55(7)
O(3)–Cd(1)–N(1)	92.90(8)	O(3)–Cd(1)–O(2)	137.65(8)
O(3)–Cd(1)–O(4)	51.99(7)	O(3)–Cd(1)–O(1)	83.83(7)
O(3)–Cd(1)–N(2)	125.20(8)	O(1)–Cd(1)–N(2)	143.74(7)
O(1)–Cd(1)–N(1)	89.30(8)	O(1)–Cd(1)–O(2)	53.94(7)
O(1)–Cd(1)–O(4)	131.38(7)	N(2)–Cd(1)–N(1)	69.95(7)
N(2)–Cd(1)–O(2)	93.51(7)	N(1)–Cd(1)–O(2)	84.40(9)
Hydrogen bonding parameters			
D–H...A	D–H	H...A	D...A
O(5)–H(5B)...O(1) ⁱ	0.8312	1.9428	2.6918
O(5)–H(5A)...O(3) ⁱ	0.8145	1.9204	2.6928
C(22)–H(22)...O(3)	0.93	2.5076	2.8376

Symmetry code: ⁱ 1 – *x*, 1 – 0.5*y*, –*z*.

matrix least-squares methods on *F*² using SHELXL-97 [20]. The structure analysis indicated that complex **1** crystallizes in the non-centrosymmetric monoclinic space group *P*2₁ (*Z* = 2), which was validated and supported by the successful refinement of the molecular structure. The Flack parameter refined to −0.003(15). Detailed 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 643276 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

Synthesis and IR spectra

Repeated experiments showed that the reaction temperature plays a key role in the formation of **1**. The reaction of the same materials afforded another linear trinuclear cluster complex which crystallizes in the triclinic space *P*1̄ when the reaction temperature was below 50 °C and the filtrate was left standing at r. t. The structure of this trinuclear species will be published in a forthcoming paper.

The IR spectra of **1** show the ν(OH) bands of coordinated water molecules at 3392 and 3268 cm⁻¹, and the unsaturated ν(=CH) stretching vibrations at 3103 and 3059 cm⁻¹. The absorption at 1640 cm⁻¹ can be assigned to the ν_{as}(CO₂⁻) stretching vibration of the cinnamate group, and the absorption peaks centered

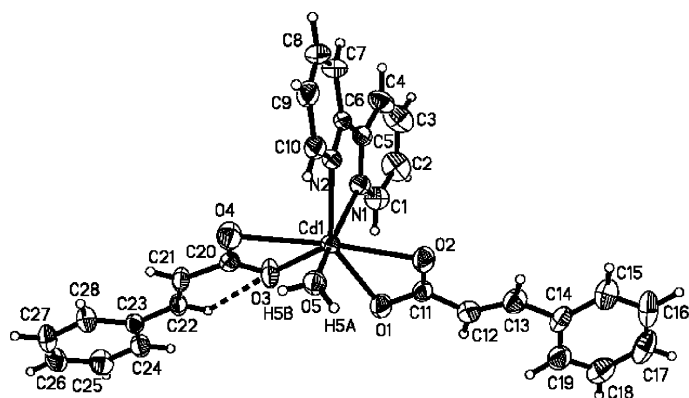


Fig. 1. ORTEP view of **1** and atomic labelling scheme adopted (the displacement ellipsoids are drawn at 40 % probability and the dashed line indicates the intramolecular hydrogen bond).

at 1384 cm^{-1} to the $\nu_s(\text{CO}_2^-)$ stretching vibration. A comparison with the characteristic carboxylate stretching vibrations of free cinnamic acid molecules shows a significant blue-shift attributed to the coordination interactions. The bpy-based absorptions (1558 , 1496 , 1439 , 773 , 742 and 685 cm^{-1}) are characteristic of the chelating form of the ligand [21, 22].

Structure description

Complex **1** consists of $[\text{Cd}(\text{bpy})(\text{H}_2\text{O})(\text{PhCH}=\text{CHCO}_2)_2]$ molecules, with two cinnamate groups and one bpy ligand chelating the Cd atom to form a Λ -shaped configuration, as shown in Fig. 1. It crystallizes in the non-centrosymmetric space group $P2_1$ with two molecules in the unit cell. By this way, molecules of **1** of like chirality assemble into one single crystal, as can be inferred from the Flack parameter refining to 0.0 (see above). One cinnamate group donates its hydrogen atom H22 to the carboxylate oxygen atom O3 to form a strong intramolecular hydrogen bond. The seven-coordinated Cd atom is in a severely distorted capped trigonal prism geometry [23] defined by two N atoms of one bpy ligand, four carboxylate O atoms and one water O atom, with one carboxylate O atom (O4) occupying the capping position. The Cd1–N1 distance ($2.373(2)\text{ \AA}$) is slightly longer than the Cd1–N2 distance ($2.346(2)\text{ \AA}$), and the Cd–N distances are similar to those in the related complexes $[\text{Cd}(\text{bpy})(\text{H}_2\text{O})(3\text{-OH-C}_6\text{H}_4\text{CH}=\text{CHCO}_2)_2]$ [24] and $[\text{Cd}(\text{bpy})(\text{H}_2\text{O})((\text{C}_5\text{H}_4\text{CO}_2)_2\text{Fe})_2]$ [25]. The Cd–O distances range from $2.275(2)$ to $2.617(2)\text{ \AA}$ with the Cd1–O4 bond being longer than the other Cd–O bonds, indicating that the coordination sphere is significantly distorted. This coordination geometry is comparable to that observed in the acrylate complex

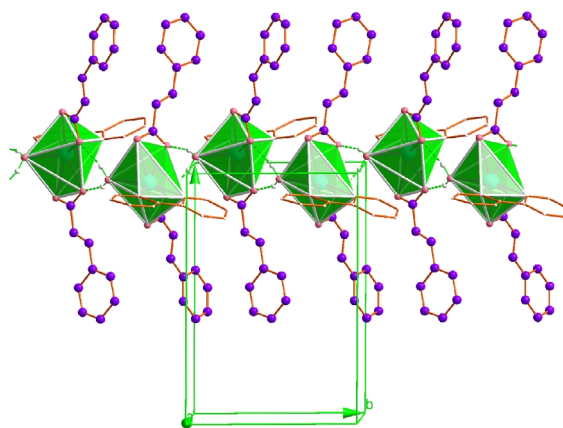


Fig. 2. The infinite chains assembled along the $[010]$ direction *via* intermolecular hydrogen bonds.

$[\text{Cd}(\text{phen})(\text{H}_2\text{O})(\text{CH}_2=\text{CHCO}_2)_2]$ [26], which crystallizes in the centrosymmetric monoclinic space group $P2_1/n$. Within the crystal structure of **1**, the complex molecules are interconnected *via* strong intermolecular $\text{O-H}\cdots\text{O}$ hydrogen bonds with the coordinating water molecules donating H atoms to the chelating carboxyl O atoms, to form infinite chains along $[010]$ directions (Fig. 2, Table 2).

Thermal behavior

Compound **1** is air-stable at r. t. The DTA curve exhibits three endothermic peaks centered at 113 , 242 , and $319\text{ }^\circ\text{C}$. The TGA curve indicates that a weight loss of 3.07% occurs in the temperature range of $88\text{--}125\text{ }^\circ\text{C}$, which agrees well with the calculated value of 3.10% for the release of one mole of H_2O per formula unit, suggesting complete dehydration. Over the range $125\text{--}600\text{ }^\circ\text{C}$, the observed weight loss of 74.53% is comparable to the calculated value of

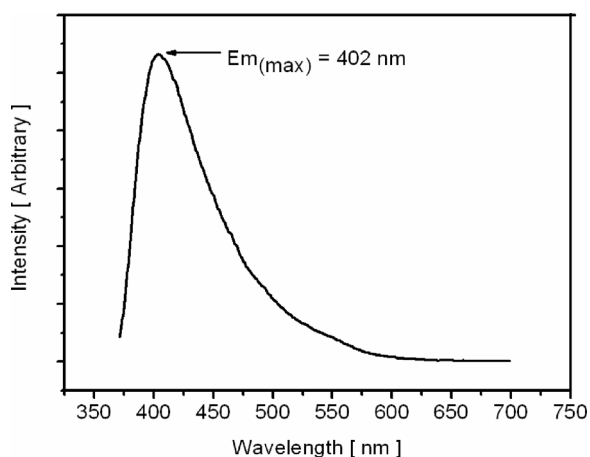


Fig. 3. Fluorescence spectrum of **1** in the solid state at r. t.

74.80% for release of one mole of bpy ligands and all other organic constituents. The powder X-ray diffraction pattern confirms the white residue

(22.40%) obtained at 600 °C to be CdO (calcd. 22.10%).

Fluorescent properties

The solid-state fluorescence spectrum of **1** at r. t. is depicted in Fig. 3. Complex **1** emits a maximum fluorescence peak at *ca.* 402 nm upon excitation at 345 nm, which can be assigned to the intra-ligand $\pi_L \rightarrow \pi_L^*$ transition of the 2,2-bpy ligand (LLCT) [27]. The free 2,2-bipyridine molecule displays a weak luminescence at *ca.* 530 nm in the solid state at r. t. The fluorescence enhancement and significant blue-shift in **1** may be due to the coordination and crystal packing interactions in the solid, which effectively increase the rigidity of the ligand and reduce the loss of energy by radiationless decay of the intraligand emission excited states [28].

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