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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF A Cd(II) COMPLEX OF RHODAMINE B

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ABSTRACT

A new solid cadmium(II) complex of Rhodamine B (RB), Cd[(RB)$(OAc)_2(H_2O)$], has been synthesized by the reaction of Rhodamine B with $Cd(OAc)_2{\cdot}2H_2O$ in the presence of $NaOC_2H_5$. The crystal structure of the complex has been determined by X-ray diffraction. The crystal belongs to the monoclinic space group $P2_1/n$ (No. 14), $a = 10.268(2)$, $b = 18.861(4)$, $c = 16.667(3)$, $\beta = 105.18(3)$, $Z = 4$, $V = 3115.2(11)$,

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$F\ (000) = 1424$, $R = 0.0409$, $wR = 0.1532$. The structure analysis reveals that the geometry around Cd is a distorted tetrahedron (Cd(II) adopts a typical sp^3 hybrid orbital).

INTRODUCTION

Rhodamine B (RB) and its derivatives are classic dyes with wide applications, such as coloring cells[1], antitumour agents[2–4], photosensitized cell killing[5,6], solar collectors[7], quantum counters[8], lasers[9], and also as dye in analytical chemistry. The applications make RB and its derivatives to be subjects of considerably fundamental interest. The crystal structure of RB has been reported[10]. Although the synthesis, characterization and fluorescence of the complexes of RB with metal ions have been discussed previously, the crystal structures of the complexes have been rarely reported. The only report was the crystal structure of a Rh(I)–RB complex[11]. In this paper, we report the synthesis and crystal structure of a new cadmium(II) complex of RB, $Cd[(RB)(OAc)_2(H_2O)]$. The results of the structure analysis reveal that the geometry around Cd is a distorted tetrahedron and Cd(II) adopts a typical sp^3 hybrid orbital.

EXPERIMENTAL

Materials

Rhodamine B was purchased from the Third Reagent Factory of Shanghai, P. R. China. Cadmium acetate dihydrate was purchased from the Reagent Factory of Shanghai, P. R. China. All other chemicals were commercially available.

Physical Measurements

The Cd content of the complex was determined by titration with EDTA. C, H and N were determined on a Vario EL elemental analyzer. Molar conductance at room temperature was measured in 10^{-3} M DMSO solution using a DDS-11A digital molar conductometer. IR spectra in the range of $4000–200\,cm^{-1}$ were recorded on a Nicolet-170SX FT-IR spectrophotometer using KBr discs. ^1H NMR spectra were recorded on a Varian FT-80A spectrometer in DMSO-d_6 with TMS as an internal reference.

Preparation of the Complex

To absolute ethanol (20 mL), was added RB (0.88 g, 0.002 mol) and heated to 30–40 °C. When RB was dissolved, a $NaOC_2H_5$ solution (20 mL of 0.1 M) was added dropwise. After 3–4 min, cadmium acetate dihydrate (0.53 g, 0.002 mol) was added quickly and the reaction mixture was refluxed with stirring for 4 h. Some undissolved material was filtered off from the hot solution. When the filtrate was cooled to room temperature, small brown crystals with green fluorescence were separated out, washed three times with ethanol and methanol (1:1), and dried in vacuum for 48 h. The yield is 0.99 g (72%). The brown crystals suitable for X-ray diffraction were formed from the mother liquor through slow evaporation after three weeks. Anal. Calc. for $C_{32}H_{38}N_2O_8Cd$ (MW 691.05): C, 55.61; H, 5.54; N, 4.05; Cd, 16.26%. Found: C, 55.31; H, 5.09; N, 4.19; Cd, 16.53%. IR (cm^{-1}): 1637 (s, $\nu_{as}(COO^-)$); 1339 (s, $\nu_s(COO^-)$); 451 (s, ν(Cd-O)). ^1H NMR (ppm, DMSO-d_6): δ 7.93 (m, 1H, H-24); 7.72 (m, 2H, H-26, H-27); 7.30 (m, 1H, H-25); 6.47 (m, 6H, H-1, H-2, H-4, H-5, H-7, H-8); 3.35 (m, 10H, $-\underline{CH_2}CH_3+H_2O$); 1.82 (s, 6H, CH_3COO-); 1.10 (m, 12H, $-CH_2\underline{CH_3}$). Λ_M (DMSO, 289K): 10.80 $S{\cdot}cm^2{\cdot}mol^{-1}$

Data Collection and Refinement of the Crystal Structure

A brown single crystal of the dimensions $0.20 \times 0.25 \times 0.30$ mm was mounted on a glass fiber. The crystal data were collected on an Enraf-Nonius CAD4 four-cycle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) using a ω-2θ scan mode with a ω scan width of $0.60+\tan\theta$, and scan rate of $8.24\,min^{-1}$. A total of 7126 independent reflections was collected, in the range $3^\circ < 2\theta < 53^\circ$ of which reflections with $I > 2.0\sigma(I)$ were used in the structure determination and refinement after ψ-scan corrections.

The structure was solved by direct methods (Sheldrick, 1990) and successive difference Fourier syntheses[12]. The hydrogen atoms in H_2O were located in difference Fourier maps, while the remaining hydrogen atoms were fixed geometrically and the distances to hydrogens were set by a program. All hydrogen atoms were included in calculations but not refined. The final least square cycle gave $R = 0.0409$ and $wR = 0.1532$ ($w = 1/\sigma^2(F_0)$). All calculations were performed on a PIII-550 computer using programs contained in the SHELX-97 package[12]. Crystal data are given in Table I. The selected bond distances and angles are listed in Table II. Figure 1 presents a perspective view of the molecular structure of the complex.

Table I. Crystal Data and Details of the Structure Determination for the Complex

Formula	$C_{32}H_{38}CdN_2O_8$
Formula weight	691.05
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a [Å]	10.268(2)
b [Å]	18.861(4)
c [Å]	16.667(3)
β [°]	105.18(3)
V [Å^3]	3115.2(11)
Z	4
Density (calculated) [g/cm^3]	1.474
μ(Mo-Kα) [mm^{-1}]	0.754
F(000)	1424
Crystal size [mm]	0.20 × 0.25 × 0.30
Temperature (K)	293
Radiation [Å]	MoKα 0.71073
θ [°]	1.7 to 27.5
Data set	$-13 < h < 12$; $0 < k < 24$; $0 < l < 21$
Total data	7126
Independent data	7126
R(int)	0.000
Observed data [I > 2.0 σ(I)]	6601
Number of reference	7216
Number of parameter	388
R, wR, S	0.0409, 0.1532, 1.09
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. resd. dens. [e/Å^3]	−0.55, 0.74

RESULTS AND DICUSSION

The elemental analyses and synthetic condition suggested that Cd(II) formed a 1 : 1 (metal : ligand) complex with RB. The complex is stable in air. It is soluble in water, EtOH and MeOH and easily soluble in DMF and DMSO. The molar conductance in DMSO ($10.80\,S{\cdot}cm^2{\cdot}mol^{-1}$) indicates that it is essentially a non-electrolyte in DMSO[13].

The reaction mechanisms of the complex are shown in Fig. 2. In ethanol solution, there exists an equilibrium between the two forms of RB: lactone and zwitterion.[7] When $NaOC_2H_5$ was added, the balance was disturbed, and then the zwitterion form of RB combined easily with $Cd(Ac)_2{\cdot}2H_2O$. After a series of electron transfers, the complex is formed.

Table II. Selected Bond Distances (Å) and Angles (°) of the Complex

Cd1-O3	1.9805(14)	N2-C6	1.3361(13)
Cd1-O5	1.9546(14)	C1-C2	1.3937(17)
Cd1-O6	2.223(3)	C1-C10	1.4104(16)
Cd1-O8W	2.000(2)	C2-C3	1.3930(16)
O1-C11	1.3238(12)	C4-C11	1.4355(16)
O1-C12	1.3849(12)	C5-C12	1.3914(16)
O2-C28	1.2466(15)	C6-C7	1.4166(14)
O3-C28	1.2411(18)	C7-C8	1.4052(14)
O4-C29	1.2280(18)	C8-C13	1.4242(14)
O5-C29	1.2471(17)	C9-C10	1.4098(14)
O6-C31	1.228(6)	C9-C13	1.4097(14)
O7-C31	1.295(7)	C10-C11	1.4022(14)
N1-C3	1.3182(6)	C12-C13	1.3810(14)
O3-Cd1-O5	107.58(6)	N1-C3-C2	124.53(12)
O3-Cd1-O6	107.18(6)	O2-C28-O3	120.80(13)
O3-Cd1-O8W	111.25(7)	O4-C29-O5	124.53(13)
O5-Cd1-O6	109.47(9)	O6-C31-O7	122.1(5)
O5-Cd1-O8W	100.01(7)	N2-C6-C7	120.72(9)
O6-Cd1-O8W	120.59(9)	C6-C7-C8	119.18(9)
C11-O1-C12	120.67(8)	C7-C8-C13	122.40(9)
Cd1-O3-C28	123.63(10)	C10-C9-C13	113.27(9)
Cd1-O5-C29	126.64(11)	C1-C10-C9	121.43(10)
Cd1-O6-C31	122.4(3)	O1-C11-C4	115.60(9)
C2-C1-C10	121.96(11)	O1-C12-C5	113.00(9)
C1-C2-C3	122.54(12)	C8-C13-C9	121.56(9)

The structure of the complex can be described as approximately orthogonal two planes and one of the planes linking up with a tetrahedron: (1) the Rhodamine chromophore (plane 1); (2) the ring carbon atoms of a benzoate group (plane 2), which binds a tetrahedron through its carboxylate group; (3) a tetrahedral coordination. The portion of the tetrahedral coordination can be described as approximately and mutually equiangular three planes: (1′) the carboxylate atoms of the benzoate group (plane 3), containing C(23), C(28), O(2), O(3), Cd and O(8); (2′) the acetate group (plane 4), containing O(4), O(5), C(29), C(30), Cd and O(8); (3′) the remaining acetate group (plane 5), containing O(6), O(7), C(31), C(32), Cd and O(8). The angles between these planes are as follows: planes 1–2, 73.38°; planes 2–3, 18.1°; planes 3–4, 69.73(4)°; planes 3–5, 70.25(8)°; planes 4–5, 40.27(8)°. The geometry around Cd may be described as a distorted tetrahedron, in which Cd(II) adopts a typical sp^3

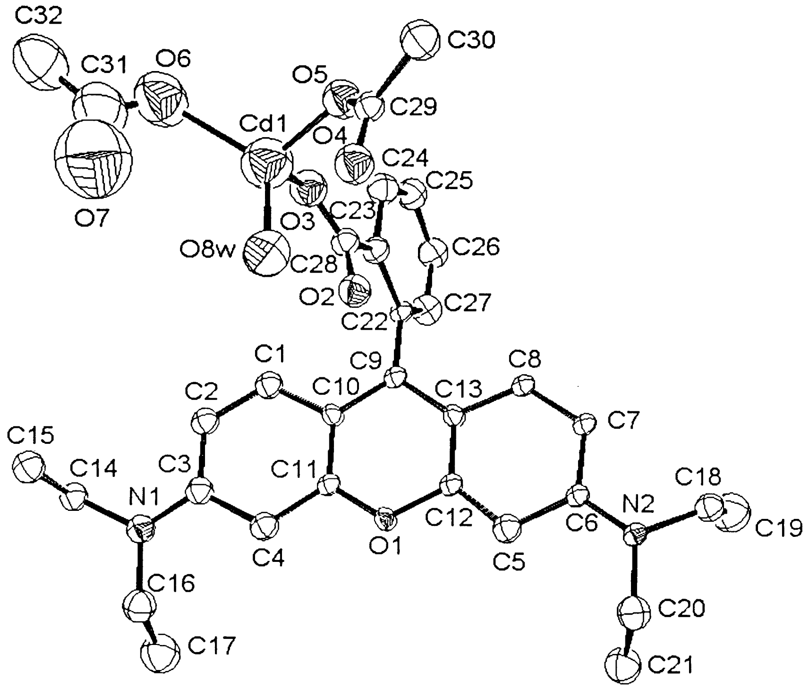

Figure 1. A perspective view of the complex showing the labeling of non-H atoms.

hybrid orbital. H-bonds can be found between coordination water, O(4) and O(7). The bond lengths and angles of hydrogen bonds are listed in Table III.

In IR spectra of the complex, a ν(Cd-O) band appears at 451 cm^{-1} (including a Cd-O bond of an acetate group)[14], while RB spectra do not exhibit such a band. The strong bands at 1637 and 1339 cm^{-1} in the complex are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes, respectively. The value of $\Delta\nu[\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)]$ is 298 cm^{-1}, indicating coordination of a RB carboxylate group with Cd(II) in a monodentate chelating fashion[15]. This is consistent with results of the X-ray diffraction. The characteristic ν(C=O) (a lactone form of RB) frequency of a RB carboxyl group (1709 cm^{-1}) disappeared in the complex, suggesting that RB exists in a zwitterion form in the complex[16]. This is also consistent with results of the X-ray diffraction.

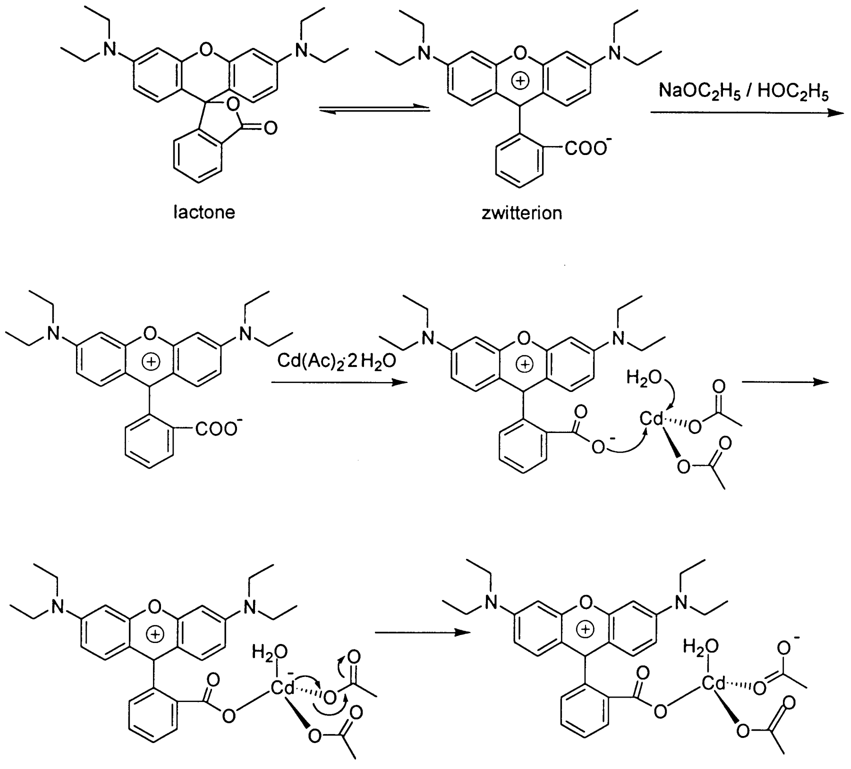

Figure 2. Reaction mechanisms of the complex.

In ^{1}H NMR spectra of the complex, a new signal assigned to CH_3COO protons appears at 1.82 ppm, while RB spectra do not exhibit such a signal, indicating that an acetate group participates in complexation. Due to the existence of H_2O in the complex, the number of protons at 3.35 ppm increases to 10 from 8.

Table III. Bond Distances (Å) and Angles (°) of Hydrogen Bonds

Bond	O=H	H-O	Distance	Angle	Symmetry
O8W H8WA O4	0.93	1.97	2.625(2)	125.4	a
O8W H8WB O7	0.85	2.54	3.390(6)	179.9	a

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