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Synthesis and crystal structure of a novel luminescent cadmium complex

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A novel cadmium complex $\text{Cd}(\text{IPA})_2(\text{phen})_2$ (IPA = isophthanic acid, phen = 1,10-phenanthroline) was synthesized by hydrothermal methods and characterized structurally by X-ray diffraction. The complex possesses a monomeric molecular structure. $\text{Cd}(\text{IPA})_2(\text{phen})_2$ is orthorhombic, space group $Aba2$, with $a = 14.670(7)$, $b = 22.876(8)$, $c = 9.473(6)$ Å, $V = 3179(3)$ Å³, $D_c = 1.573$ Mg m⁻³, $Z = 4$, $F(000) = 1520$, $GOF = 1.027$, $R1 = 0.0299$, $wR2 = 0.0617$. Photophysical properties (fluorescence excitation and emission spectra) are reported.

Keywords: Cadmium complex; Monomeric molecular structure; Luminescence

1. Introduction

Transition metal complexes are attracting increasing attention not only because of their applications in areas of catalysis, cooperative magnetic behaviour, non-linear optical activity and electrical conductivity, but also because of their interesting topologies [1–7]. The design of complexes with novel architectures and desired functionalities using principles of crystal engineering is one of the most challenging subjects in current coordination chemistry. Polybenzene carboxylic acids are good candidates for this task and have important advantages over other organic ligands. They have two or more carboxyl groups that can be completely or partially deprotonated, leading to various coordination modes, they can act both as hydrogen bond acceptors and donors, and they may connect metal ions in different directions due to their rigidity. Furthermore, they seem to form crystalline complexes easily and complexes always show high dimensionality [8–13].

The hydrothermal synthesis technique has proved to be a powerful method for preparation of new coordination compounds [14]. Recently, the method has been applied successfully in the syntheses of cadmium complexes, and a large number of them, with one-dimensional chain-like, two-dimensional layer-like or three-dimensional

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net-like open framework structures, have been prepared and characterized [15–18]. Use of hydrothermal methods has led to a novel coordination compound, $\text{Cd}(\text{IPA})_2(\text{phen})_2$. It possesses an interesting monomeric molecular structure, which is rarely found for cadmium polycarboxylate complexes.

2. Experimental

2.1. $\text{Cd}(\text{IPA})_2(\text{phen})_2$

$\text{Cd}(\text{CH}_3\text{COO})_3$ (0.3 mmol), IPA H (0.6 mmol) and phen (0.3 mmol) were mixed in 10 cm^3 of deionized water. After stirring for half an hour, the mixture was placed in a 25 cm^3 Teflon-lined reactor, heated at 433 K in an oven for 4 days, then cooled slowly to room temperature. Colourless crystals suitable for X-ray diffraction analysis were obtained (752.99). Anal. Calc. for $\text{C}_{36}\text{H}_{24}\text{CdN}_4\text{O}_8$ (%): C, 57.37; H, 3.18; N, 7.44%. Found: C, 57.26; H, 3.27; N, 7.49 IR: 1417 cm^{-1} ($\nu_{\text{sCOO-}}$), 1552 cm^{-1} ($\nu_{\text{asCOO-}}$).

2.2. X-ray crystallography

Diffraction data for a crystal of dimensions $0.25 \times 0.10 \times 0.10\text{ mm}$ were collected using graphite-monochromated Mo $\text{K}\alpha$ radiation on a CCD area detector four-circle diffractometer with the ω – 2θ scan technique. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [19, 20]. A summary of crystallographic data and refinement parameters is given in table 1.

Table 1. Crystal data and structure refinement details for the complex.

Complex	$\text{Cd}(\text{IPA})_2(\text{phen})_2$
Formula	$\text{C}_{36}\text{H}_{24}\text{CdN}_4\text{O}_8$
M	752.99
Colour	Colourless
Temperature	293(2) K
Space group	$\text{Ab}a2$
Unit cell dimensions	$a = 14.670(7)\text{ \AA}$ $b = 22.876(8)\text{ \AA}$ $c = 9.473(6)\text{ \AA}$
V	$3179(3)\text{ \AA}^3$
Z	4
Calculated density	1.573 mg m^{-3}
Absorption coefficient	0.748 mm^{-1}
$F(000)$	1520
θ range for data collection	1.78 to 26.00°
Reflections/collected/unique	7124/2889 [$R(\text{int}) = 0.0405$]
Completeness to $2\theta = 25.01$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2889/1/222
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0299$, $wR2 = 0.0617$
Largest diff. peak and hole	0.607 and -0.332 e \AA^{-3}

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-273887. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk).

2.3. Physical measurements

Elemental analyses (C, H, N) were determined on an Elementar Carlo EL instrument. Infrared spectroscopy (KBr pellets) was performed on a Nexus 912 AO446 FT-IR spectrophotometer in the 4000–400 cm^{-1} range. Electronic spectra were obtained with an Agilent 8453 spectrophotometer. Excitation and emission spectra for a solid sample of the complex were measured with a Perkin–Elmer LS-55 spectrophotometer.

3. Results and discussion

3.1. Description of the structure

Final atomic coordinates for non-hydrogen atoms of $\text{Cd}(\text{IPA})_2(\text{phen})_2$ are listed in table 2. Figure 1 shows the coordination geometry and atom labelling in the structure, which consists of one Cd ion, two monodentate IPA ions and two chelated phen molecules. The cadmium ion has C_2 symmetry and lies on a crystallographic

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the non-hydrogen atoms.

Atom	x/a	y/b	z/c	$U(\text{eq})$
Cd(1)	0	5000	8348(1)	41(1)
N(1)	1597(2)	4916(1)	8811(3)	53(1)
N(2)	480(2)	5646(1)	10165(4)	47(1)
O(1)	265(2)	4282(1)	6809(4)	59(1)
O(2)	−1030(2)	3789(1)	7112(3)	62(1)
O(3)	2864(2)	3231(2)	4953(6)	122(2)
O(4)	2681(2)	2549(2)	3543(9)	131(2)
C(1)	2129(3)	4534(2)	8126(6)	70(1)
C(2)	3055(3)	4508(2)	8308(7)	77(1)
C(3)	3451(3)	4886(2)	9214(6)	79(2)
C(4)	2925(3)	5275(2)	9918(5)	68(1)
C(5)	1992(2)	5286(2)	9704(4)	46(1)
C(6)	1381(2)	5688(2)	10473(4)	48(1)
C(7)	1694(3)	6076(2)	11476(5)	66(1)
C(8)	1080(3)	6422(2)	12182(5)	78(1)
C(9)	177(3)	6379(2)	11870(6)	74(1)
C(10)	−96(3)	5990(2)	10850(6)	60(1)
C(11)	−258(3)	3842(2)	6654(4)	48(1)
C(12)	159(2)	3343(2)	5818(4)	45(1)
C(13)	−390(3)	2892(2)	5327(4)	52(1)
C(14)	−13(3)	2448(2)	4518(5)	63(1)
C(15)	892(3)	2437(2)	4193(5)	64(1)
C(16)	1423(3)	2887(2)	4693(5)	56(1)
C(17)	1074(3)	3339(2)	5487(4)	54(1)
C(18)	2386(3)	2887(2)	4366(6)	67(1)

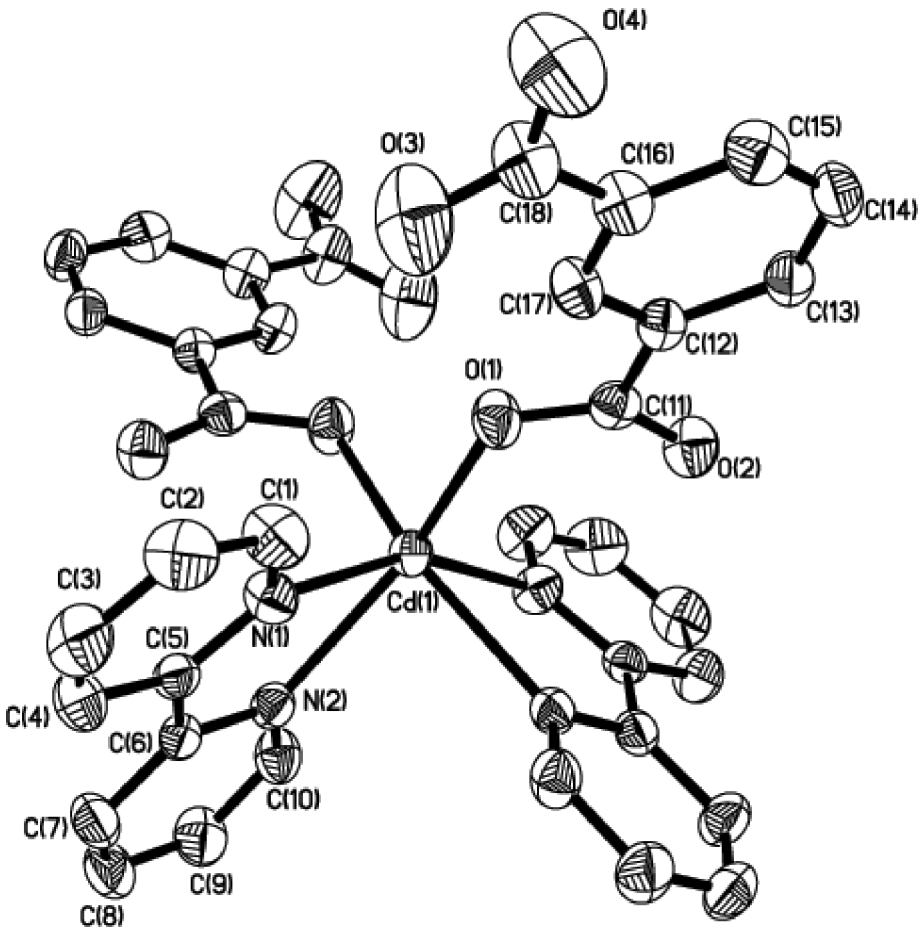


Figure 1. Molecular structure of Cd(IPA)₂(phen)₂ showing the atom labelling scheme.

Table 3. Selected bond distances (Å) and bond angles (°) for the title complex.

Cd(1)–O(1)	2.231(3)	Cd(1)–N(1)	2.392(3)
Cd(1)–N(2)	2.376(4)		
O(1)–Cd(1)–O(1)#1	98.39(19)	N(2)–Cd(1)–N(1)#1	96.20(11)
O(1)–Cd(1)–N(2)	151.65(10)	O(1)–Cd(1)–N(1)	83.69(11)
O(1)#1–Cd(1)–N(2)	93.84(12)	O(1)#1–Cd(1)–N(1)	110.45(11)
O(1)–Cd(1)–N(2)#1	93.84(12)	N(2)–Cd(1)–N(1)	68.06(11)
N(2)–Cd(1)–N(2)#1	87.13(17)	N(2)#1–Cd(1)–N(1)	96.20(11)
O(1)–Cd(1)–N(1)#1	110.45(11)	N(1)#1–Cd(1)–N(1)	158.88(16)

Symmetry transformation used to generate equivalent atoms #1 is $-x, -y+1, z$.

twofold axis. The coordination geometry can be described as a distorted antiprism. Two oxygen atoms from IPA groups have a Cd–O1 distance of 2.231(3) Å; the two distances are 2.392(3) and 2.376(4) Å for Cd–N1 and Cd–N2, respectively. The O(1)–Cd(1)–O(1#) bond angle is 98.39(19)° and (N(1)–Cd(1)–N(2) is 68.06(11)°. Selected bond distances and angles for the complex are listed in table 3.

3.2. Luminescence properties

The complex exhibits blue photoluminescence upon irradiation by UV light in the solid state at room temperature. The excitation band (447 nm) has one main peak at 237 nm. Emission is broad band and ranges from 300 to 500 nm with the maximum emission at 405 nm. The emission spectrum of free IPAH molecule has a maximum at 380 nm and no emission in the visible region. The lower energy band could be assigned to ligand-to-metal charge transfer, and the luminescence of the complex is attributed to the coordinated IPA ligand. In addition, the free phen molecule can exhibit weak luminescence in the solid state at room temperature, and can contribute to intraligand charge transfer [21].

Acknowledgements

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