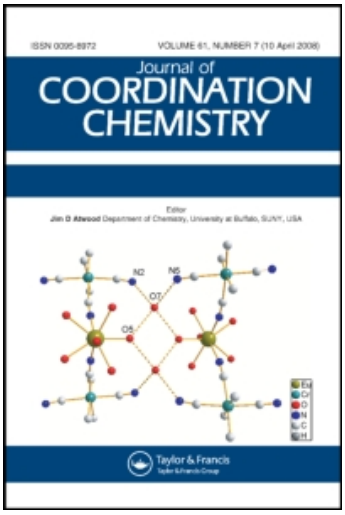

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Synthesis and crystal structure of a novel luminescent zinc complex of 2-benzoylbenzoic acid

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A novel zinc coordination compound, $Zn(BYBA)_2(2,2'\text{-bipy})$ (BYBA = 2-benzoylbenzoic acid, 2,2′-bipy = 2,2′-bipyridyl), has been obtained by a hydrothermal method and structurally characterized by X-ray diffraction. The complex is monomeric, space group $P2_1/c$, with $a = 13.226(4)$, $b = 14.278(4)$, $c = 16.843(4)$ Å, $\beta = 91.785(4)^\circ$, $V = 3179.0(15)$ Å^3, $D_c = 1.404\ \mathrm{M/m^{-3}}$, $Z = 4$, $F(000) = 1384$, goodness-of-fit = 1.008, $R_1 = 0.0422$. The photophysical properties of the complex have been studied (ultraviolet absorption, fluorescence excitation and emission spectra).

Keywords: Zinc; Monomer; 2-Benzoylbenzoic acid; 2,2′-Bipridyl; Molecular structure; Photophysics

1. Introduction

Transition metal organic coordination compounds with diverse structures and properties have attracted increasing attention not only because of their application in catalysis, their cooperative magnetic behaviour, nonlinear optical activity and electrical conductivity but also for their interesting topologies [1–7]. The design of such complexes by crystal engineering is one of the most challenging areas of current coordination chemistry. Zinc is crucial for the synthesis of nucleic acids and cellular division in biological systems and thus much study has been devoted to model complexes containing the element [8–10]. Of the various ligands used, aromatic carboxylates are perhaps the most widely used.

The hydrothermal synthesis technique is a powerful method for the preparation of new metal–organic coordination compounds [11]. In recent years, the method has been applied successfully to the syntheses of zinc complexes, and a large number of zinc complexes with one-dimensional, chain-like, two-dimensional layer-like or three-dimensional net-like open framework structures have been prepared and characterized [12–15]. Using hydrothermal synthesis methodology, we have synthesized

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

Complex	$Zn(BYBA)_2(2,2'\text{-bipy})$
Formula	$C_{38}H_{26}N_2O_6Zn$
Relative molecular weight M	671.98
Colour	Colourless
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	Mo Kα
Space group	$P2_1/c$
	Monoclinic
Unit cell dimensions	$a = 13.226(4)$ Å
	$b = 14.278(4)$ Å
	$c = 16.843(4)$ Å
	$\beta = 91.785(4)^\circ$
Volume	3179.0(15) Å^3
Z	4
Calculated density	1.404 Mg m^{-3}
Absorption coefficient	0.824 mm^{-1}
$F(000)$	1384
Crystal size	$0.15 \times 0.10 \times 0.05$ mm
θ range for data collection	1.54–26.01°
Reflections collected/unique	14 287/6234 [R(int) = 0.0286]
Completeness to $2\theta = 25.01$	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6234/0/24
Goodness-of-fit on F^2	1.008
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0422$, $wR2 = 0.0855$
Largest diff. peak and hole	0.338 and −0.327 e Å^{-3}

a novel coordination compound, $Zn(BYBA)_2(2,2'\text{-bipy})$ (BYBA = 2-benzoylbenzoic acid, 2,2′-bipy = 2,2′-bipyridyl). This complex has an interesting monomeric molecular structure rarely found for zinc carboxylate complexes formed under hydrothermal conditions.

2. Experimental

2.1. *Synthesis of $Zn(BYBA)_2(2,2'\text{-bipy})$*

$Zn(CH_3COO)_3$ (65.8 mg, 0.3 mmol), BYBA (135.7 mg, 0.6 mmol) and 2,2′-bipy (46.8 mg, 0.3 mmol) were mixed in 10 cm^3 of deionized water. After stirring for 30 min, the mixture was placed in a 25 cm^3 Teflon-lined reactor and heated at 160°C in an oven for 4 days, then cooled slowly to room temperature. Colourless columnar crystals of the complex suitable for X-ray diffraction analysis were obtained. Anal. Calcd for $Zn(BYBA)_2(2,2'\text{-bipy})$(%): C, 68.14; H, 3.72; N, 4.31. Found: C, 67.86; H, 3.87; N, 4.17. The IR spectrum exhibits an array of bands in the range 4000–400 cm^{-1}, with 1412 cm^{-1} (ν_{sCOO-}) and 1548 cm^{-1} (ν_{asCOO-}) being diagnostic.

2.2. *X-ray crystallography*

Diffraction data for a crystal of dimensions $0.15 \times 0.10 \times 0.05$ mm were collected with graphite-monochromated Mo Kα radiation on a CCD area detector four-circle diffractometer by the ω–2θ scan technique. The structure was solved by direct methods.

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^2$) for the nonhydrogen atoms.

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Zn(1)	2520(1)	3611(1)	6045(1)	52(1)
N(1)	3081(2)	4456(2)	5127(1)	62(1)
O(3)	3898(2)	−105(2)	6774(1)	77(1)
O(4)	1750(1)	4564(1)	6639(1)	61(1)
O(5)	905(1)	3248(1)	6691(1)	55(1)
O(6)	−1292(2)	2604(1)	7423(1)	70(1)
C(1)	3862(2)	2630(2)	6772(1)	54(1)
N(2)	1922(2)	2961(2)	5047(1)	58(1)
O(1)	3913(2)	3488(2)	6624(1)	80(1)
O(2)	3083(2)	2183(2)	6637(1)	75(1)
C(2)	4793(2)	2158(2)	7107(1)	44(1)
C(3)	5493(2)	2671(2)	7553(2)	55(1)
C(4)	6346(2)	2253(2)	7880(2)	67(1)
C(5)	6500(2)	1314(3)	7773(2)	71(1)
C(6)	5806(2)	788(2)	7342(2)	62(1)
C(7)	4953(2)	1205(2)	6994(1)	47(1)
C(8)	4269(2)	597(2)	6491(2)	54(1)
C(9)	4111(2)	826(2)	5632(2)	57(1)
C(10)	3368(3)	364(2)	5199(2)	80(1)
C(11)	3190(3)	575(3)	4402(2)	103(1)
C(12)	3762(4)	1236(3)	4049(2)	103(1)
C(13)	4513(3)	1679(3)	4460(2)	95(1)
C(14)	4690(2)	1473(2)	5256(2)	71(1)
C(15)	988(2)	4090(2)	6839(1)	45(1)
C(16)	171(2)	4584(2)	7269(1)	43(1)
C(17)	366(2)	5449(2)	7611(2)	57(1)
C(18)	−364(2)	5903(2)	8038(2)	69(1)
C(19)	−1281(2)	5484(2)	8131(2)	68(1)
C(20)	−1486(2)	4628(2)	7796(2)	58(1)
C(21)	−773(2)	4171(2)	7351(1)	44(1)
C(22)	−1091(2)	3255(2)	6991(2)	50(1)
C(23)	−1257(2)	3185(2)	6111(2)	56(1)
C(24)	−1641(3)	2359(2)	5798(2)	90(1)
C(25)	−1772(4)	2266(3)	4981(3)	122(2)
C(26)	−1520(3)	2966(4)	4484(2)	110(1)
C(27)	−1165(3)	3787(3)	4788(2)	87(1)
C(28)	−1037(2)	3902(2)	5600(2)	65(1)
C(29)	3644(3)	5226(3)	5203(2)	87(1)
C(30)	4039(3)	5680(3)	4557(3)	103(1)
C(31)	3849(3)	5310(4)	3825(3)	109(1)
C(32)	3272(3)	4544(3)	3730(2)	87(1)
C(33)	2870(2)	4127(2)	4393(2)	61(1)
C(34)	2183(2)	3325(2)	4345(2)	61(1)
C(35)	1766(3)	2968(3)	3641(2)	90(1)
C(36)	1082(3)	2259(3)	3668(2)	107(1)
C(37)	835(3)	1883(3)	4376(3)	102(1)
C(38)	1278(3)	2257(2)	5055(2)	79(1)

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [16, 17]. A summary of crystallographic data and refinement parameters is given in table 1.

Crystallographic data (excluding structure factors) for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-255231. Copies of the data can be obtained free

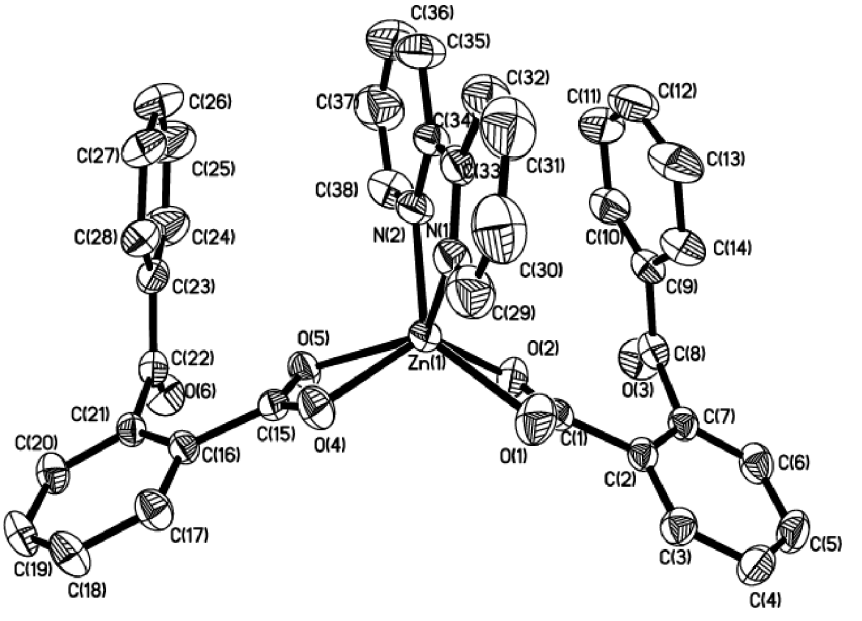

Figure 1. Molecular structure of $Zn(BYBA)_2(2,2'\text{-bipy})$ showing the atom numbering scheme.

of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

2.3. *Physical measurements*

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

3. Results and discussion

Final atomic coordinates for nonhydrogen atoms of the complex are listed in table 2. Figure 1 shows the coordination geometry and atom labeling in the complex, which consists of one Zn ion, two BYBA molecules and one chelated 2,2′-bipyridine molecule. The BYBA molecules are deprotonated and act as chelating bidentates. Zn is six-coordinate and the coordination geometry can be described as a distorted trigonal prism. Zn–O distances range from 1.9895(17) Å [Zn(1)–O(4)] to 2.4829(18) Å [Zn(1)–O(5)], average 2.229 Å. Zn–N distances involving the chelated 2,2′-bipy are 2.113(2) Å [Zn(1)–N(1)] and 2.056(2) Å [Zn(1)–N(2)]. Related bond angles are 57.73(8)° [O(1)–Zn(1)–O(2)], 57.36(7)° [O(4)–Zn(1)–O(5)] and 78.15(10)° [N(1)–Zn(1)–N(2)]. Other bond distances and angles for the complex are listed in table 3.

The ultraviolet absorption spectrum of $Zn(BYBA)_2(2,2'\text{-bipy})$ (10^{-4} mol dm^{-3} ethanol solution) shows an absorption band at 281 nm attributed to the absorption

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

Zn(1)–O(4)	1.9895(17)	Zn(1)–N(1)	2.113(2)
Zn(1)–N(2)	2.056(2)	Zn(1)–O(2)	2.379(2)
Zn(1)–O(1)	2.064(2)	Zn(1)–O(5)	2.4829(18)
O(4)–Zn(1)–N(2)	122.00(8)	O(1)–Zn(1)–O(2)	57.73(8)
O(4)–Zn(1)–O(1)	106.48(8)	N(1)–Zn(1)–O(2)	133.13(8)
N(2)–Zn(1)–O(1)	131.52(9)	O(4)–Zn(1)–O(5)	57.36(7)
O(4)–Zn(1)–N(1)	100.04(8)	N(2)–Zn(1)–O(5)	87.13(8)
N(2)–Zn(1)–N(1)	78.15(10)	O(1)–Zn(1)–O(5)	122.84(7)
O(1)–Zn(1)–N(1)	93.77(9)	N(1)–Zn(1)–O(5)	140.02(7)
O(4)–Zn(1)–O(2)	122.26(7)	O(2)–Zn(1)–O(5)	84.25(7)
N(2)–Zn(1)–O(2)	93.66(8)		

of BYBA and 2,2′-bipy. The emission spectrum shows a strong blue emission peak at 422 nm with excitation at 336 nm.

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