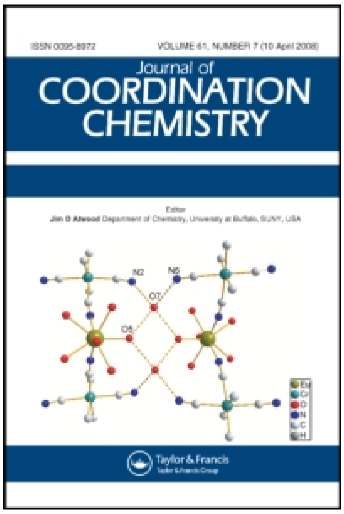

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A novel 4,4'-azopyridine-bridged binuclear zinc complex

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A NOVEL 4,4′-AZOPYRIDINE-BRIDGED BINUCLEAR ZINC COMPLEX

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A novel binuclear zinc(II) complex $[Zn_2(azpy)_3(2Cl\text{-}azpy)_2(H_2O)_6](ClO_4)_4(azpy)_4(H_2O)_{10}$ (**1**) (azpy = 4,4′-azopyridine, 2Cl-azpy = (2,6-dichloro)-4,4′-azopyridine) has been synthesized and characterized by single crystal X-ray diffraction, IR and excitation and emission spectra. The Complex **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.730(3)$, $b = 15.455(4)$, $c = 18.893(5)$ Å, $\alpha = 73.358(5)$, $\beta = 87.999(6)$, $\gamma = 71.865(6)^\circ$, $V = 2847.7(14)$ Å^3, $Z = 1$. The azpy ligand links two zinc(II) ions forming a binuclear entity. Each zinc(II) ion lies in a distorted octahedron completed by three oxygen atoms from water molecules and three nitrogen atoms from 4-pyridyl donor groups. Luminescence studies of **1** in aqueous solution show strong blue photoluminescence as the result of fluorescence from an intraligand excited state.

Keywords: Zinc(II); Crystal structure; 4,4′-Azopyridine; Photoluminescence

INTRODUCTION

Much effort has been focussed on polynuclear metal complexes in view of their promising physical and physicochemical properties and potential applications in display technology [1–3]. The chemistry of metal complexes of *N*-donor heterocycles has attracted attention due to their structural aesthetics, electrochemistry, optical properties and biological relevance [4–6]. Organic molecules containing two 4-pyridyl donor units, such as 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethene and 4,4′-azopyridine, have been extensively employed in these areas, and a number of transition metal complexes containing these ligands with diverse topological structures has been synthesized [7–18]. Organic zinc(II) complexes have attracted special attention because of their importance in optoelectronic devices [19]. In previous work, we have performed spectroscopic studies of zinc(II) complexes within one-dimensional nanoporous channels [20] and high-dimensional zinc(II) coordination polymers with chain-like [21] and sheet-like [22] molecular structure. All of these show strong blue luminescence indicating potential application in fabrication of organic light-emitting devices. Based on this,

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we have chosen the 4,4′-azopyridine (azpy) ligand as a building block for the construction of novel coordination compounds. Herein we report the synthesis, crystal structure and optical properties of a novel azpy-bridged binuclear zinc(II) complex $[Zn_2(azpy)_3(2Cl\text{-}azpy)_2(H_2O)_6](ClO_4)_4(azpy)_4(H_2O)_{10}$ (**1**) (azpy = 4,4′-azopyridine, 2Cl-azpy = (2,6-dichloro)-4,4′-azopyridine).

EXPERIMENTAL

Synthesis

The azpy ligand was synthesized according to literature methods [23,24] and 2Cl-azpy was obtained from the crude azpy product. For the synthesis of **1** a methanol solution (10 cm^3) of azpy (0.4 mmol) and 2Cl-azpy (0.1 mmol) was added to an aqueous solution (20 cm^3) of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol) with stirring. After 40 min, the reaction mixture was filtered. Orange single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of the filtrate at room temperature. Yield: 65%. *Anal.* Calcd. for **1** (%): C, 41.37; H, 3.86; N, 19.29. Found: C, 41.41; H, 3.83; N, 19.31.

Physical Measurements

Elemental analyses of C, H and N were carried out with a Perkin-Elmer model 240 instrument. The infrared spectrum of **1** was recorded using KBr discs on a Bio-Rad FTS 135 FT-IR spectrophotometer in the 4000–450 cm^{-1} range. Both excitation and emission spectra of **1** in aqueous solution were measured with an Act on Research SpectroPro-300i spectrophotometer with a xenon arc lamp as the excitation light source.

Crystal Structure Determination

An orange rod-like crystal of **1** with dimensions 0.30 × 0.25 × 0.20 mm was selected and mounted on a glass fibre. Determination of unit cell parameters and data collection were performed on a Bruker SMART 1000 CCD instrument using graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Cell parameters were determined by least-squares calculations with θ angles ranging from 2.07 to 25.03°. Intensities were collected using a multi-scan mode. Empirical absorption corrections, following the SADABS procedure were applied [25]. Some 11 688 reflections were measured in the *hkl* range −12 to 9, −18 to 18 and −22 to 22. A total of 9837 independent reflections was collected, giving 3587 observed reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-97 [26] and refined using SHELXL-97 [27]. Some 9837 reflections and 732 parameters using 28 restraints were refined by a full-matrix least-squares method based on $F^2(w = 1/[\sigma^2(F_o^2) + (0.0600P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3)$. After checking for their presence in a difference map, positions of all H atoms were geometrically idealized and allowed to ride on their parent atoms. All non-hydrogen atoms were refined anisotropically. The relevant parameters of the crystal structure are listed in Table I. Atomic coordinates and equivalent isotropic displacement parameters are given in Table II. Selected bond lengths and angles are given in Table III. Full lists of crystallographic data are available from the authors upon request.

TABLE I Crystallographic data and structure refinement for **1**

Empirical formula	$C_{90}H_{100}Cl_8N_{36}O_{32}Zn_2$
Formula weight	2612.40
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.730(3)
b (Å)	15.455(4)
c (Å)	18.893(5)
α (°)	73.358(5)
β (°)	87.999(6)
γ (°)	71.865(6)
V (Å^3)	2847.7(14)
Z	1
Density (calculated) (Mg/m^3)	1.524
Absorption coefficient (mm^{-1})	0.631
$F(000)$	1297
θ range (°)	2.07–25.03
Limiting indices	$-12 \leq h \leq 9$ $-18 \leq k \leq 18$ $-22 \leq l \leq 22$
Reflections collected	11 688
Independent reflections	9837 ($R_{int} = 0.0478$)
Completeness to $\theta = 25.03$	97.6%
Absorption correction	Semi-empirical
Max. and min. transmission	0.8843 and 0.8334
Data/restraints/parameters	9837/28/732
Goodness-of-fit on F^2	0.928
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0728$, $wR_2 = 0.1398$
Largest diff. peak and hole (e · Å^{-3})	0.633 and − 0.352

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

RESULTS AND DISCUSSION

IR Spectra

IR spectra of **1** show bands at 3040, 1604, 1417, 1225, 1112, 841, 625 and 569 cm^{-1}. N=N stretching vibrations of the azo group appear at 1417 and 1416 cm^{-1} [28]. A broad band observed at *ca* 3040 cm^{-1} corresponds to a combination of overlapping vibrations of C–H and O–H bonds.

Description of Structure

The crystal structure of **1** consists of dizinc(II) cations $[Zn_2(azpy)_3(2Cl\text{-}azpy)_2(H_2O)_6]^{4+}$, ClO_4^- counteranions, free azpy and water molecules. As depicted in Fig. 1, the azpy ligand links two zinc(II) ions forming a binuclear entity. All azpy molecules in **1** show a *trans* form. 2Cl-azpy molecules only exist as terminal ligands in this compound. The coordination geometry of the zinc(II) ion is best described as a slightly distorted octahedron completed by three nitrogen atoms of coordinated 4-pyridyl donor groups and three oxygen atoms of coordinated water molecules. N(9) of the bridging azpy ligand and O(9) of the coordinated water molecule occupy axial sites, the bondlengths Zn(1)–N(9) and Zn(1)–O(9) being 2.172(5) and 2.147(4) Å, respectively. The bond angle O(9)–Zn(1)–N(9) is 178.0(2)°, which is nearly linear. Nitrogen atoms

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Zn(1)	6075(1)	7848(1)	7080(1)	47(1)
N(1)	6613(5)	8207(4)	8030(3)	48(1)
N(2)	7049(6)	9038(5)	9915(3)	68(2)
N(3)	6621(6)	9872(5)	9855(3)	67(2)
N(4)	6688(6)	10 675(6)	11 787(4)	76(2)
N(5)	5575(5)	7517(4)	6104(3)	49(1)
N(6)	4888(7)	6313(5)	4444(3)	75(2)
N(7)	3812(7)	6292(5)	4450(3)	83(2)
N(8)	3030(7)	4917(4)	2951(3)	64(2)
N(9)	7307(5)	8615(4)	6423(3)	47(1)
N(10)	9492(6)	10 239(5)	4900(5)	92(2)
N(11)	9544(6)	1507(6)	1770(4)	79(2)
N(12)	10 129(7)	−210(5)	313(3)	84(2)
N(13)	1546(9)	5839(9)	6766(6)	153(5)
N(14)	407(6)	4759(5)	5229(3)	87(2)
N(15)	9471(15)	3884(8)	9287(7)	169(6)
N(16)	7985(8)	2573(5)	8054(4)	95(2)
N(17)	6864(9)	2679(5)	8055(4)	103(2)
N(18)	5483(10)	1444(5)	6668(4)	93(2)
C(1)	6927(6)	7601(5)	8689(4)	52(2)
C(2)	7132(6)	7855(5)	9315(4)	58(2)
C(3)	6930(6)	8805(6)	9238(4)	51(2)
C(4)	6624(6)	9424(5)	8562(4)	58(2)
C(5)	6451(6)	9124(5)	7969(3)	51(2)
C(6)	6969(7)	9779(7)	11 820(5)	84(3)
C(7)	6993(7)	9420(6)	11 225(4)	74(2)
C(8)	6718(6)	10 089(6)	10 530(4)	58(2)
C(9)	6432(7)	10 989(6)	10 503(4)	74(2)
C(10)	6433(7)	11 285(6)	11 142(4)	68(2)
C(11)	4330(7)	7618(5)	5927(3)	57(2)
C(12)	3998(8)	7263(5)	5388(4)	68(2)
C(13)	5037(9)	6800(5)	5016(3)	63(2)
C(14)	6272(8)	6742(5)	5175(4)	58(2)
C(15)	6487(7)	7096(5)	5713(3)	55(2)
C(16)	2117(8)	5417(5)	3307(4)	67(2)
C(17)	2352(8)	5876(5)	3762(4)	71(2)
C(18)	3651(10)	5795(5)	3892(4)	70(2)
C(19)	4620(7)	5319(5)	3536(4)	64(2)
C(20)	4249(8)	4894(5)	3065(4)	65(2)
C(21)	6871(7)	9192(5)	5759(4)	54(2)
C(22)	7578(9)	9691(6)	5301(4)	79(3)
C(23)	8856(10)	9544(6)	5550(5)	81(3)
C(24)	9319(8)	8957(6)	6237(5)	81(3)
C(25)	8512(7)	8517(5)	6651(4)	63(2)
C(26)	9506(8)	1900(6)	1062(5)	80(2)
C(27)	9637(8)	1425(7)	536(4)	79(2)
C(28)	9941(7)	447(7)	779(5)	69(2)
C(29)	10 056(7)	−5(6)	1516(5)	74(2)
C(30)	9833(8)	558(7)	1977(4)	86(3)
C(31)	934(11)	6434(10)	6140(8)	142(4)
C(32)	491(9)	6120(7)	5591(5)	96(3)
C(33)	758(8)	5152(7)	5744(5)	88(3)
C(34)	1443(11)	4416(10)	6390(6)	204(10)
C(35)	1767(11)	4883(8)	6823(7)	187(9)
C(36)	4742(10)	1904(8)	7096(7)	107(3)
C(37)	5157(10)	2291(6)	7550(6)	98(3)
C(38)	6447(11)	2228(6)	7562(4)	79(2)

(*Continued*)

TABLE II Continued

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
C(39)	7293(9)	1759(6)	7125(5)	88(3)
C(40)	6713(12)	1395(6)	6667(5)	92(3)
C(41)	8203(15)	3970(8)	9355(6)	145(5)
C(42)	7594(10)	3545(7)	8947(5)	110(3)
C(43)	8417(12)	3056(6)	8517(5)	89(3)
C(44)	9810(18)	2921(10)	8392(8)	216(11)
C(45)	10 133(16)	3331(12)	8807(8)	202(10)
C1(1)	3384(3)	4424(3)	8964(2)	147(1)
C1(2)	9202(3)	8331(2)	3789(2)	111(1)
C1(3)	6081(7)	11791(4)	9704(3)	95(2)
C1(4)	7156(17)	8224(8)	11 439(8)	106(5)
O(1)	3258(11)	3643(7)	8736(6)	251(5)
O(2)	2239(17)	4946(16)	9251(14)	568(17)
O(3)	4451(10)	4096(9)	9492(6)	279(5)
O(4)	4041(15)	4817(11)	8344(7)	361(8)
O(5)	8345(6)	7997(5)	4327(4)	163(3)
O(6)	10 470(7)	8075(7)	4154(4)	188(4)
O(7)	9303(10)	8006(8)	3172(5)	245(5)
O(8)	8686(8)	9317(5)	3524(4)	149(3)
O(9)	4796(4)	7129(3)	7709(2)	69(1)
O(10)	7579(4)	6548(3)	7389(2)	65(1)
O(11)	4335(4)	9028(3)	6847(2)	65(1)
O(12)	9821(6)	6235(5)	8160(4)	140(3)
O(13)	9456(10)	5725(7)	9515(5)	227(4)
O(14)	2231(5)	7392(4)	7353(3)	89(2)
O(15)	5121(13)	6036(8)	9100(4)	266(6)
O(16)	4172(5)	710(3)	5858(3)	83(2)

TABLE III Selected bondlength (Å) and angles (°) for **1**

Zn(1)–O(10)	2.087(4)
Zn(1)–O(11)	2.118(5)
Zn(1)–O(9)	2.147(4)
Zn(1)–N(1)	2.169(5)
Zn(1)–N(9)	2.172(5)
Zn(1)–N(5)	2.175(5)
O(10)–Zn(1)–O(11)	170.19(17)
O(10)–Zn(1)–O(9)	87.69(18)
O(11)–Zn(1)–O(9)	82.62(18)
O(10)–Zn(1)–N(1)	90.53(19)
O(11)–Zn(1)–N(1)	91.32(18)
O(9)–Zn(1)–N(1)	91.91(17)
O(10)–Zn(1)–N(9)	94.24(19)
O(11)–Zn(1)–N(9)	95.44(19)
O(9)–Zn(1)–N(9)	178.0(2)
N(1)–Zn(1)–N(9)	88.71(19)
O(10)–Zn(1)–N(5)	89.73(19)
O(11)–Zn(1)–N(5)	88.75(18)
O(9)–Zn(1)–N(5)	90.10(17)
N(1)–Zn(1)–N(5)	178.0(2)
N(9)–Zn(1)–N(5)	89.27(19)

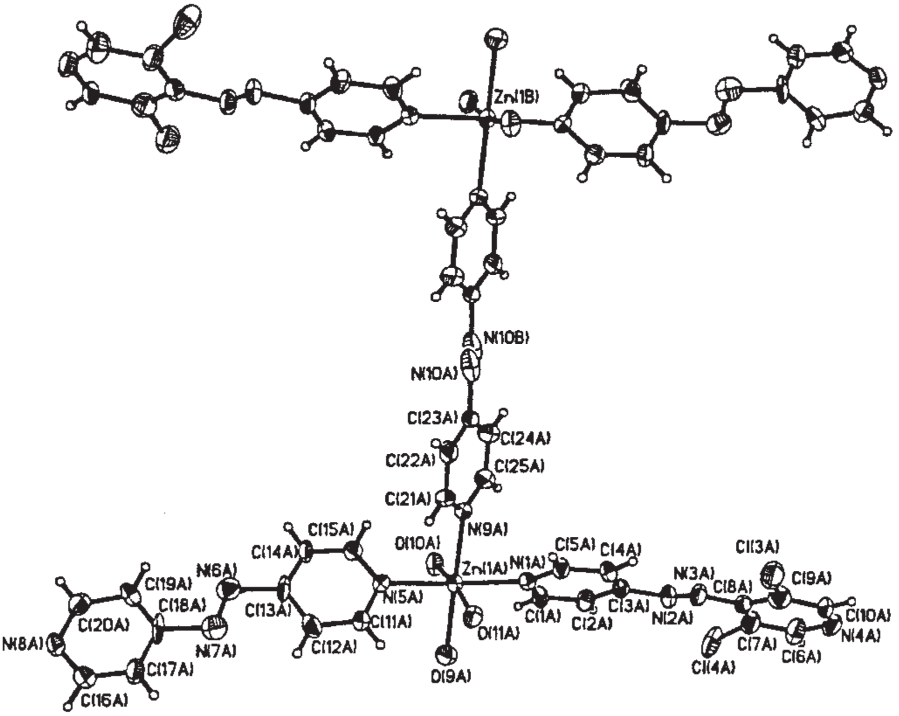

FIGURE 1 The molecular structure of **1** with the atom labelling scheme.

of coordinated azpy ligands and oxygen atoms of water molecules alternatively coordinate to zinc(II) forming the equatorial plane with Zn(1)–N(pyridyl) bondlengths (2.169(5) and 2.175(5) Å) slightly longer than Zn(1)–O(H_2O) bondlengths (2.087(4) and 2.118(5) Å). The *trans* O–Zn–N, N–Zn–N and O–Zn–O bond angles are all close to 180°, while *cis* O–Zn–N, N–Zn–N and O–Zn–O bond angles are around 90°. There are two types of azpy ligands in this dizinc(II) cation; one links two zinc(II) ions in a bridging mode and the other coordinates to only one zinc(II) ion. Therefore this complex may be useful as a synthetic precursor in designing heteropolymetallic systems.

Intermolecular hydrogen bonds are formed between oxygen atoms of coordinated water molecules and adjacent nitrogen atoms of coordinated azpy ligands [N(4)$\cdots$O(11) and N(8)$\cdots$O(10) bonddistances are 2.869 and 2.785 Å, respectively]. These hydrogen bonds lead to a condensed crystal structure.

Optical Properties

Excitation and emission spectra of **1** in aqueous solution at room temperature have been recorded. The fluorescence maximum (451 nm) is redshifted *ca* 4300 cm^{-1} from the 0–0 transition band (378 nm). Emission of **1** excited at 353 nm is neither MLCT nor LMCT in nature, and can probably be assigned to fluorescence from an intraligand emission excited state [19–22]. On the other hand, the excitation spectrum of **1** at 402 nm, is dominated by a strong absorption peak at 348 nm. The most significant luminescent behaviour of **1** is the enhancement of fluorescence intensity compared to the free azpy ligand. Enhanced luminescence efficiency is attributed to bonding of azpy to zinc(II), effectively increasing the rigidity of the ligand and reducing loss of energy via radiationless decay of the intraligand emission excited state [29]. Compound **1** may be useful for producing blue light in electroluminescent devices.

In summary, we have synthesized a novel luminescent binuclear zinc(II) complex linked by the azpy ligand. Luminescence studies of the compound show strong blue photoluminescence as a result of fluorescence from an intraligand emission excited state. The condensed structure of **1** indicates that it may be a useful and thermally stable blue fluorescent material. Efforts to further investigate the optical properties of azpy-bridged metal complexes are in progress in our laboratory.

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