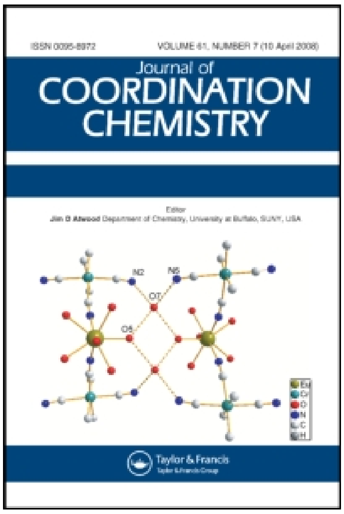

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A novel dicyanamide-bridged zinc(II) complex incorporating the 4,4'-azopyridine ligand

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A novel dicyanamide-bridged zinc(II) complex incorporating the 4,4′-azopyridine ligand

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A novel complex $\{[Zn(azpy)_2(dca)(H_2O)_2]\cdot ClO_4\cdot azpy\cdot 2H_2O\}_n$ (**1**) has been synthesized and structurally and spectroscopically characterized, where azpy is the 4,4′-azopyridine and dca the dicyanamide. The crystal structure analysis of **1** shows that in **1** the dca ligands act as $\mu_{1,5}$-bridges linking the zinc(II) ions into 1D covalent bonding chains. The zinc(II) ion lies in a distorted octahedral environment completed by two nitrogen atoms from two terminal azpy groups, two nitrogen atoms from two dca bridges, and two water molecules. The most striking feature of **1** is that the 1D covalent bonding chains are linked through O–H···N hydrogen bonds and π–π stacking interactions into a 3D supramolecular structure.

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

1. Introduction

The field of molecular materials has known rapid development in recent years, and molecular-based compounds exhibiting physical properties such as magnetic, optical, catalytic, electrochemistry, etc., have been described [1–7]. One of the requirements to observe these macroscopic properties is to create interactions between the molecular units or the active sites within the crystal lattice. Suitably tailored ligands for constructing assembled structures can provide opportunities [8]. 4,4′-Azopyridine (azpy) and dicyanamide (dca) ligands are known as bridges to link metal ions together and have been used in design and construction of complexes with interesting topological structures and properties by covalent bonding and/or weak intermolecular interactions [9–19]. On the other hand, blue luminescent metal complexes and coordination polymers, especially zinc(II) complexes have been of particular interest because

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they are one of the key color components required for full-color electroluminescent displays [20, 21]. With these considerations in mind and in continuation of our early work [7, 17–19, 22, 23], here, we report the synthesis, structure and spectroscopic properties of a novel complex $\{[Zn(azpy)_2(dca)(H_2O)_2]ClO_4 \cdot azpy \cdot 2H_2O\}_n$ (**1**).

2. Experimental

2.1. *Materials and synthesis*

All chemicals were reagent grade and used without further purification. Azpy (4,4′-azopyridine) was prepared according to the literature method [24]. For the synthesis of **1**, a methanol solution (10 mL) of azpy (0.4 mmol) was added to a mixed aqueous solution (10 mL) of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol) and sodium dicyanamide (0.2 mmol) under continuous stirring. After 30 min, the reaction mixture was filtered. Orange single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the filtrate at room temperature. Yield: 56%. M.p.: 238°C. FT-IR (KBr, cm^{-1}): 3350br, 2290w, 2235w, 2170vs, 1603m, 1583m, 1564m, 1484w, 1412s, 1370w, 1220w, 1143m, 1108s, 1089s, 1026w, 836s, 669w. Anal. Calcd for $C_{32}H_{32}ClN_{15}O_8Zn$ (%): C, 44.92; H, 3.77; N, 24.56. Found: C, 44.88; H, 3.74; N, 24.55.

2.2. *Physical measurements*

Elemental analyses were carried out with a Perkin-Elmer analyzer model 240. Melting points (m.p.) were measured with a Gallenkamp MBF-595 apparatus. IR spectra were recorded as KBr wafers on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} region. UV-Vis spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer in the range of 220–700 nm. Photoluminescence spectra were measured on an Acton Research SpectroPro-300i spectrophotometer with a xenon arc lamp as the excitation light source.

2.3. *X-ray crystallography*

An orange crystal of **1** with the dimensions $0.25 \times 0.20 \times 0.20$ mm was selected and mounted on a glass fiber. Determinations of unit cell parameters and data collection were performed on a Bruker SMART 1000 CCD diffractometer at 293 K using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by least-squares calculations with $2.45 \leq \theta \leq 26.44°$. Semiempirical absorption corrections were applied using the SADABS program [25]. Some 20518 reflections were measured in the index ranges $-12 \leq h \leq 13$, $-7 \leq k \leq 16$, $-33 \leq l \leq 33$. A total of 7568 [$R_{int} = 0.1376$] independent reflections were collected. The structures were solved by direct methods using the program SHELXS-97 [26]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97 [27]. Some 7568 reflections and 490 parameters using 11 restraints were refined by a full-matrix least-squares method based on F^2 ($w = 1/[\sigma^2(F_o^2) + (0.0800P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms attached to carbon were inserted at calculated positions and constrained with isotropic thermal parameters. The hydrogen atoms of water in the structure were not located.

Table 1. Crystal data and structure refinement summary for **1**.

Empirical formula	$C_{32}H_{32}ClN_{15}O_8Zn$
Formula weight	855.54
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	
a (Å)	10.791(3)
b (Å)	13.175(4)
c (Å)	27.063(9)
β (°)	96.167(7)
V (Å^3)	3825(2)
Z	4
ρ_{calc} (g cm^{-3})	1.486
Absorption coefficient (mm^{-1})	0.782
$F(000)$	1760
Crystal size (mm^3)	$0.25 \times 0.20 \times 0.20$
θ range (°)	2.45–26.44
Index ranges	−12/13, −7/16, −33/33
Reflection collected	20518
Independent reflections	7568 [$R_{int} = 0.1376$]
Absorption correction	SADABS
Max./min. transmission	0.8593/0.8285
Parameters	539
Goodness-of-fit on F^2	0.937
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0786$ $wR_2 = 0.1536$

The final agreement factor values are $R_1 = 0.0786$, $wR_2 = 0.1536$ [$I > 2\sigma(I)$]. Crystal data and structure refinement parameters are listed in table 1. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in table 2. Selected bond lengths and angles are given in table 3.

3. Results and discussion

3.1. *Description of structure*

Compound **1** crystallizes in the monoclinic space group $P2(1)/n$ with the cell constants $a = 10.791(3)$ Å, $b = 13.175(4)$ Å, $c = 27.063(9)$ Å, $\beta = 96.167(7)°$ and $Z = 4$. The molecular unit and atom-labeling scheme of **1** is given in figure 1. Each unit consists of the Zn(II) cation $[Zn(azpy)_2(dca)(H_2O)_2]^+$, the counter anion ClO_4^-, two half uncoordinated azpy molecules, and two free water molecules. Each Zn(II) ion is six-coordinated by two nitrogen atoms (Zn(1)–N(5) = 2.140(5) Å, Zn(1)–N(1) = 2.156(5) Å) from two terminal azpy ligands, two nitrogen atoms (Zn(1)–N(9) = 2.069(6) Å, Zn(1)–N(11) = 2.076(6) Å) from two dca bridges, and two water molecules (Zn(1)–O(1) = 2.135(4) Å, Zn(1)–O(2) = 2.137(4) Å). The Zn–N and Zn–O distances are within the range observed for octahedral complexes (2.05–2.25 Å) [28]. It is noticeable that the Zn–N bond involving the dca nitrogen is ca 0.07 ∼ 0.08 Å shorter than that involving the azpy nitrogen. The local coordination environment of the Zn(II) ion can be described as a distorted octahedral geometry with O(1), O(2), N(9), and N(11) forming the equatorial plane and N(1) and N(5) occupying the axial sites. The equatorial atoms deviate slightly from the plane (O(1), 0.0208 Å; O(2), −0.0207 Å; N(9), 0.0195 Å; N(11), −0.0197 Å), and the Zn(II) atom is displaced from

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$). 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)	10139(1)	658(1)	2384(1)	43(1)
O(1)	9232(4)	2096(3)	2323(2)	46(1)
O(2)	8348(4)	−5(4)	2421(2)	44(1)
N(1)	9829(4)	523(4)	1584(2)	39(1)
N(2)	8550(5)	205(5)	73(2)	50(2)
N(3)	8326(6)	1012(5)	−154(2)	52(2)
N(4)	6826(6)	840(6)	−1642(2)	59(2)
N(5)	10281(5)	778(4)	3179(2)	35(1)
N(6)	10442(6)	1188(5)	4722(2)	53(2)
N(7)	11412(6)	1050(5)	4967(2)	55(2)
N(8)	11426(8)	1572(6)	6494(2)	68(2)
N(9)	10896(5)	−784(5)	2486(2)	40(1)
N(10)	11590(5)	−2389(5)	2864(2)	50(2)
N(11)	11801(5)	1438(4)	2350(2)	45(2)
N(12)	7428(7)	2506(6)	5668(4)	80(3)
N(13)	5143(18)	279(8)	5010(10)	183(6)
N(14)	3367(6)	98(6)	8406(3)	66(2)
N(15)	4885(6)	378(4)	9886(2)	55(2)
C(1)	9749(6)	1345(5)	1296(3)	42(2)
C(2)	9363(6)	1295(6)	790(3)	46(2)
C(3)	9045(6)	368(6)	588(3)	40(2)
C(4)	9182(6)	−480(6)	873(3)	45(2)
C(5)	9570(6)	−384(5)	1367(3)	43(2)
C(6)	7829(6)	898(6)	−654(3)	47(2)
C(7)	7719(8)	1747(6)	−942(3)	63(2)
C(8)	7276(8)	1682(7)	−1426(3)	61(2)
C(9)	6911(7)	5(7)	−1361(3)	58(2)
C(10)	7406(7)	6(6)	−869(3)	49(2)
C(11)	9276(6)	1021(5)	3408(3)	46(2)
C(12)	9353(6)	1152(6)	3921(3)	48(2)
C(13)	10462(7)	1006(5)	4205(3)	45(2)
C(14)	11509(6)	783(5)	3968(3)	44(2)
C(15)	11355(6)	670(5)	3453(2)	40(2)
C(16)	11366(7)	1236(6)	5484(3)	46(2)
C(17)	10307(8)	1497(6)	5691(3)	63(2)
C(18)	10382(8)	1685(7)	6189(3)	67(2)
C(19)	12443(8)	1268(8)	6288(3)	75(3)
C(20)	12442(8)	1089(7)	5794(3)	64(2)
C(21)	11272(6)	−1554(6)	2643(2)	35(2)
C(22)	12534(6)	2028(5)	2277(2)	33(2)
C(23)	6863(10)	1846(10)	5935(3)	79(3)
C(24)	6110(8)	1091(7)	5735(4)	67(2)
C(25)	5897(8)	1008(6)	5241(4)	69(3)
C(26)	6481(11)	1699(10)	4948(4)	91(3)
C(27)	7193(9)	2438(9)	5197(5)	95(3)
C(28)	3550(8)	−701(7)	8691(3)	68(2)
C(29)	4049(7)	−692(6)	9175(3)	63(2)
C(30)	4386(6)	246(6)	9378(3)	52(2)
C(31)	4166(7)	1079(7)	9091(3)	61(2)
C(32)	3665(8)	1000(7)	8621(4)	71(3)
Cl(1)	385(2)	3659(2)	8429(1)	57(1)
O(3)	826(11)	4230(9)	8027(4)	211
O(4)	1416(8)	3205(9)	8702(4)	185
O(5)	−579(9)	3764(9)	8728(4)	193
O(6)	−144(10)	2830(8)	8120(4)	203
O(7)	9442(6)	6123(4)	7615(2)	82(2)
O(8)	3104(5)	7259(5)	7545(2)	73(2)

Table 3. Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–N(9)	2.069(6)	Zn(1)–N(11)	2.076(6)
Zn(1)–O(1)	2.135(4)	Zn(1)–O(2)	2.137(4)
Zn(1)–N(5)	2.140(5)	Zn(1)–N(1)	2.156(5)
N(11)–C(22)	1.141(8)	N(9)–C(21)	1.157(8)
N(9)–Zn(1)–N(11)	97.6(2)	N(9)–Zn(1)–O(2)	87.96(18)
N(9)–Zn(1)–O(1)	174.59(19)	O(1)–Zn(1)–O(2)	87.76(16)
N(11)–Zn(1)–O(2)	174.37(19)	N(11)–Zn(1)–N(5)	92.0(2)
N(9)–Zn(1)–N(5)	87.7(2)	O(2)–Zn(1)–N(5)	87.11(17)
O(1)–Zn(1)–N(5)	88.80(18)	N(11)–Zn(1)–N(1)	92.12(19)
N(9)–Zn(1)–N(1)	93.9(2)	O(2)–Zn(1)–N(1)	88.55(17)
O(1)–Zn(1)–N(1)	89.28(18)	C(21)–N(10)–C(22)#1	122.4(6)
N(5)–Zn(1)–N(1)	175.32(19)	N(9)–C(21)–N(10)	172.2(7)
N(11)–Zn(1)–O(1)	86.65(19)	N(11)–C(22)–N(10)#2	171.1(7)

Symmetry transformations used to generate equivalent atoms: #1 $-x+5/2$, $y-1/2$, $-z+1/2$; #2 $-x+5/2$, $y+1/2$, $-z+1/2$.

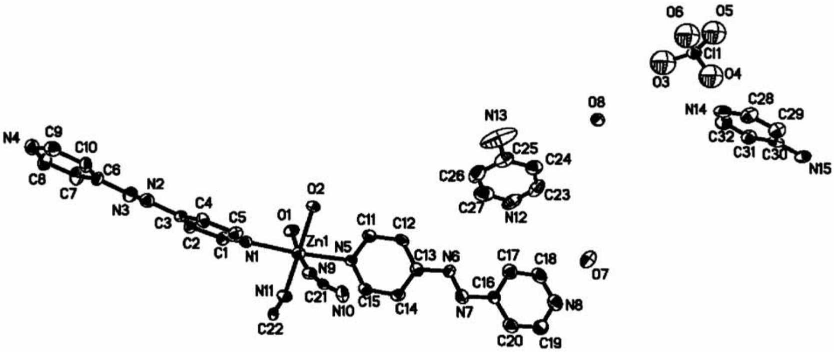

Figure 1. ORTEP view of the dissymmetric molecular unit and atom-labeling scheme of **1**. Thermal ellipsoids are drawn at the 30% probability level.

the least-squares plane by 0.0202 Å. The *trans* N–Zn–N and O–Zn–N bond angles are close to 180°, and the *cis* N–Zn–N, O–Zn–N, and O–Zn–O bond angles are around 90° (see table 3), which also confirmed the environment around Zn(II) ions. The terminal azpy ligand involving N(5) is perpendicular to the equatorial plane (Zn(1), O(1), O(2), N(9), N(11)) with a dihedral angle of 90.5°, while the terminal azpy ligand involving N(1) is sloped to the equatorial plane with a dihedral angle of 106.8°. The coordinated azpy ligands are not completely planar with an average dihedral angle of the two pyridine rings of 5.5°, while the uncoordinated azpy ligands are planar. The azpy ligands are *trans*. The dca ligand has nearly ideal C_{2v} symmetry with C≡N bond distances averaging 1.149 Å, typical for this ligand (see table 3) [14]. Each dca ligand is μ-bonded to two Zn(II) ions with the end-to-end coordination forming a 1D zigzag chain (see figure 2a). The zigzag chain presents an H-shaped structure viewed along the *b* axis (see figure 2b).

The most striking feature of **1** is that the $\mu_{1,5}$-dca bridged 1D covalent bonding chains are linked together through O–H···N hydrogen bonds and π–π stacking interactions into a 3D supramolecular structure. The two coordinated azpy ligands, one coordinated water and one uncoordinated azpy ligand are involved in formation of the supramolecular structure of **1**. As depicted in figure 3, adjacent 1D covalent

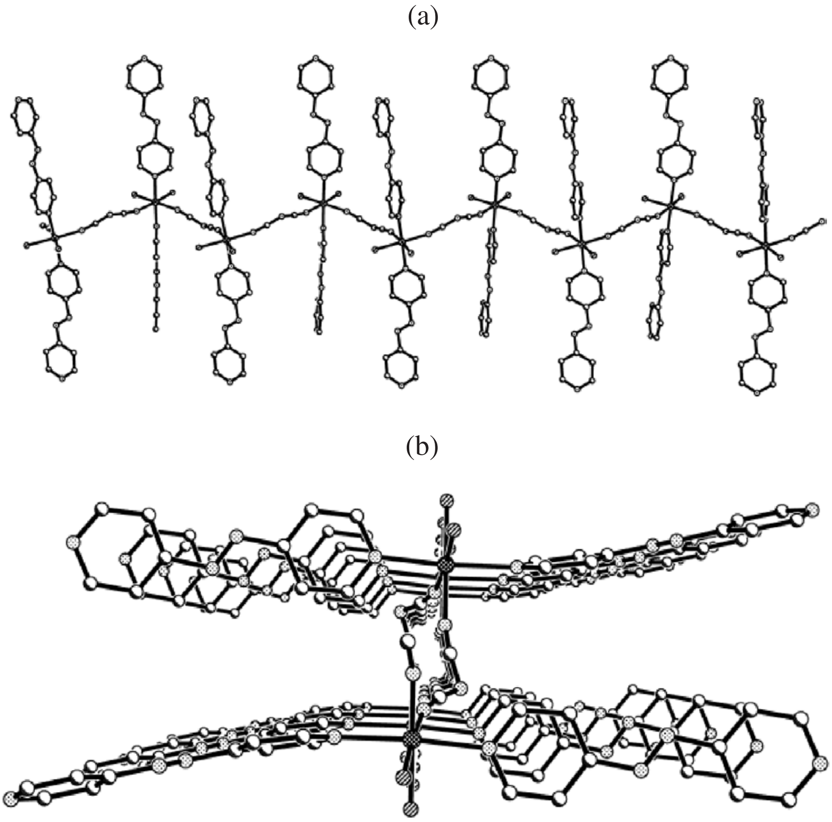

Figure 2. The 1D covalent bonding chain of **1**: (a) view along [100] direction; (b) view along [010] direction.

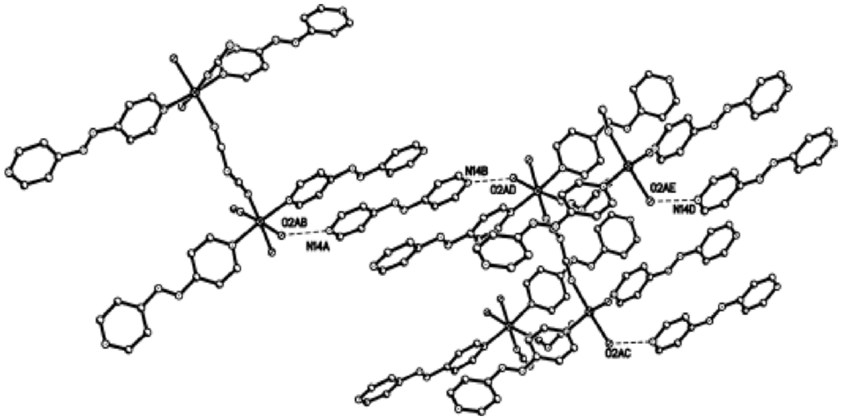

Figure 3. Schematic representation for the formation of the 2D layer by hydrogen bonds and π–π interactions via the uncoordinated azpy ligands.

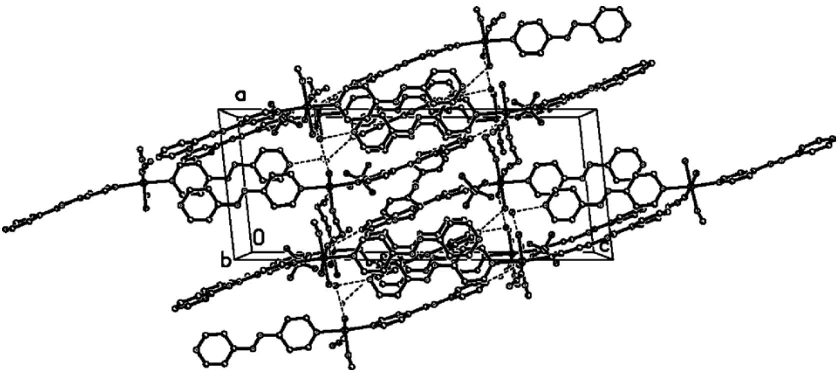

Figure 4. The 3D supramolecular structure of **1** viewed along *b* axis.

bonding chains are connected through hydrogen bonds and π–π stacking interactions via the uncoordinated azpy ligands involving N(14) as a weak interaction to form a 2D supramolecular layer. The typical hydrogen bond is O(2)$\cdots$N(14) with a distance of 2.748 Å. The pyridine rings of the terminal azpy ligand involving N(1) and the pyridine rings of the uncoordinated azpy ligand involving N(14) are close to parallel with a dihedral angle of 5.7° and short contacts in the range 3.421–3.672 Å. Adjacent 2D layers are parallel with each other and construct a 3D supramolecular framework through intermolecular π–π interactions between pyridine rings of the terminal azpy ligands involving N(5) as shown in figure 4. The azpy ligands involving N(5) belong to the different parallel molecules, displaced with respect to each other; short contacts range from 3.428 to 3.522 Å. Hydrogen bonds and π–π interactions enhance stability of the compound. The free water molecules, ClO_4^- anions and uncoordinated azpy ligands involving N(12) reside in holes of the 3D supramolecular framework.

In **1** the well-known bridging ligand azpy acts as a terminal ligand and the free molecule co-crystallized in the structure rather than bridging **1** presents an interesting crystal architecture rather than the expected 2D or 3D porous structure constructed by both dca and azpy bridging zinc(II) ions. The syntheses aimed at porous structures by reducing the amount of azpy at room temperature in methanol-aqueous solvent always led to **1**, even with molar ration of the azpy, $Zn(ClO_4)_2 \cdot 6H_2O$ and sodium dicyanamide is 1 : 2 : 2. The easy formation of **1** can be attributed to the compact supramolecular structure of **1** constructed by hydrogen bonds and π–π stacking interactions. Although the distal pyridyl N of azpy ligands is not coordinated to another zinc(II) ion, it favors formation of the supramolecular interactions in **1**.

3.2. *Spectroscopic properties*

The IR spectrum of **1** clearly shows the existence of the dicyanamide, azpy, and ClO_4^- moieties. The split bands at 2290, 2235, 2170 cm^{-1} can be assigned to the C≡N stretch of the dca group [13]. The strong band at 1412 cm^{-1} can be assigned to the N=N stretch of azpy [29]. The broad strong bands around 1100 cm^{-1} are attributed to the absorption of ClO_4^-.

The electronic spectrum of **1** in aqueous solution shows a broad intense band between 230 and 350 nm with the center at ca 280 nm corresponding to the $\pi \rightarrow \pi^*$

transition of azpy, and a very weak broad band between 390 and 560 nm with the center at ca 440 nm corresponding to the $n \rightarrow \pi^*$ transition of the azpy ligand.

Photoluminescence measurements for **1** in the solid state were performed at room temperature. Compound **1** displays no fluorescence in the solid state. Comparing the strong luminescent binuclear Zn(II) complex with azpy as ligand reported previously [19], the luminescent properties of **1** may be attributed to the dca group containing two –C≡N groups, which generally decrease fluorescence intensity or quench fluorescence emission [30].

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications No. CCDC-208126. 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).

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