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HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF $[Zn(pytpy)_2][NO_3]_2 \cdot 2H_2O$

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The title compound, $[Zn(pytpy)_2][NO_3]_2 \cdot 2H_2O$ (pytpy = 4′-(4-pyridyl)-2,2′: 6′,2″-terpyridine), has been synthesized by the reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with pytpy, and its crystal structure was determined by single-crystal X-ray diffraction. The crystal belongs to tetragonal space group $P4_3$ with $a = 0.90873(8)$, $b = 0.90873(8)$, $c = 4.4741(6)$ nm, $V = 3.6946(7)$ nm^3, $Z = 4$, $D_c = 1.521$ g/cm^{-3}, $\mu = 0.736$ mm^{-1}, $F(000) = 1744$, $R = 0.0871$, $wR = 0.1302$ for 5553 observed reflections with $I > 2\sigma(I)$. X-ray analysis has revealed that the Zn^{II} ion is surrounded by six N atoms from two pytpy ligands leading to a distorted octahedral geometry. In the crystal structure there are numerous strong intermolecular and intramolecular H-bonds and π—π interactions.

Keywords: pytpy, zinc complex, crystal structure, hydrothermal synthesis.

Introduction. The properties and crystal structures of 2,2′:6′,2″-terpyridine metal complexes have been well documented to date due to their applications in coordination chemistry, drug chemistry, material chemistry and so on [1—6]. It was found that (2,2′:6′,2″-terpyridine) platinum(II) complexes possess pronounced cytostatic activities against trypanosomes and leishmania, and they are irreversible inhibitors of trypanosoma cruzi trypanothione reductase but not of human glutathione reductase [7]. Due to presence of two linearly disposed pendant pyridine donors in pseudo-octahedral complexes $[M(pytpy)_2]^{n+}$ they are considered as expanded 4,4′-bipyridine ligands [8]. The chemistry of $[M(pytpy)_2]^{n+}$ complexes includes the effects of protonation and N-alkylation, as well as the formation of metallomacrocyclic and polymeric complexes [9—12].

Although the central $\{M(pytpy)_2\}^{n+}$ domain is constrained to the structural motif common to all of the complexes, free rotation about the C_{tpy}—C_{py} bond allows the pendant pyridine rings to adopt different conformations with respect to the central $\{M(pytpy)_2\}^{n+}$ unit [13].

As a part of our ongoing structural studies, in this paper we report the single crystal structure of $[Zn(pytpy)_2][NO_3]_2 \cdot 2H_2O$ and the effect of water molecules on the solid-state structure of the complex (**I**).

Experimental. Equipments and measurements. IR spectra were recorded on a Perkin-Elmer 983 infrared spectrophotometer using KBr discs in 4000—400 cm^{-1} region. Element analyses for C, H and N were carried out with a Perkin-Elmer 2400 analyzer. Crystal structure was determined on a Siemens SMART-CCD diffractometer.

Synthesis of the title complex. 4′-(4‴-Pyridyl)-2,2′:6′,2″-terpyridine was synthesized according to the literature method [2].

The title compound (**I**) was prepared as follows: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol), 4′-(4‴-Pyridyl)-2,2′:6′,2″-terpyridine (0.2 mmol), H_2O (3.0 ml) was placed in a Parr Teflonlined

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stainless steel vessel (10 ml), and then the vessel was sealed and heated at 120 °C for 3 d. After the mixture was slowly cooled to room temperature, several pale yellow crystals of (**I**) were obtained. Anal. Calcd. for $C_{40}H_{32}N_{10}O_8Zn$ (%): C 56.78, H 3.81, N 16.56. Found: C 56.01, H 3.96, N 15.99. IR (cm^{-1}): 3307 (w), 1596 (s), 1560 (s), 1474 (s), 1422 (s), 1248 (m), 1122 (s), 1080 (vs), 849 (w), and 791 (m).

Structure determination and refinement. A pale yellow single crystal of the title compound with the dimensions 0.13 mm×0.12 mm×0.11 mm was mounted on a Siemens SMART-CCD diffractometer (graphite-monochromated MoK_α radiation, $\lambda = 0.071073$ nm, room temperature). A total of 20089 reflections were collected in the range of $2.24 \le 2\theta \le 26.00°$, and 6965 were independent ($R_{int} = 0.0622$), of which 5553 observed reflections with $I \ge 2\sigma(I)$ were used in the succeeding structure determination and refinement. The raw data were corrected and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full-matrix least-squares calculations on F^2 were applied to the final refinement. It converged at $R_1 = 0.0871$ and $wR_2 = 0.1302$ ($w = 1/[s^2(F_o^2) + (0.0410P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The residual peaks on the final difference Fourier map are 678.0 and –432.0 e/nm^3, respectively. The goodness-of-fit indicator (S) is 1.164 and $(\Delta/\sigma)_{max}$ 0.011.

CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 691653, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/ci

Results and discussion. The molecular structure of **I** is shown in Fig. 1. The compound consists of a cationic ion $[Zn(pytpy)_2]^{2+}$, two nitrate anions and two uncoordinated water molecules. The crystal of (**I**) crystallizes in the tetragonal space group $P4_3$. The central zinc ion displays a distorted octahedral configuration, composed of six N atoms of two pytpy ligands. This multidentate binding leads to four five-membered rings (Cg1: N(1)/Zn(1)—N(3); Cg2: N(3)/Zn(1)—N(4); Cg3: N(5)/Zn(1)—N(7); Cg4: N(7)/Zn(1)—N(8)). N(3), N(5), N(7) and N(8) comprise the equatorial plane, which is essentially planar, with the torsional angle (N(3)—N(5)—N(7)—N(8)) of 5.37°. The distance from the central Zn ion to the equatorial plane is 0.006 nm. N(1) and N(4) occupy the two axial sites of the octahedron, and they are displaced from the ideal positions (N(1)—Zn(1)—N(4) = 151.63°).

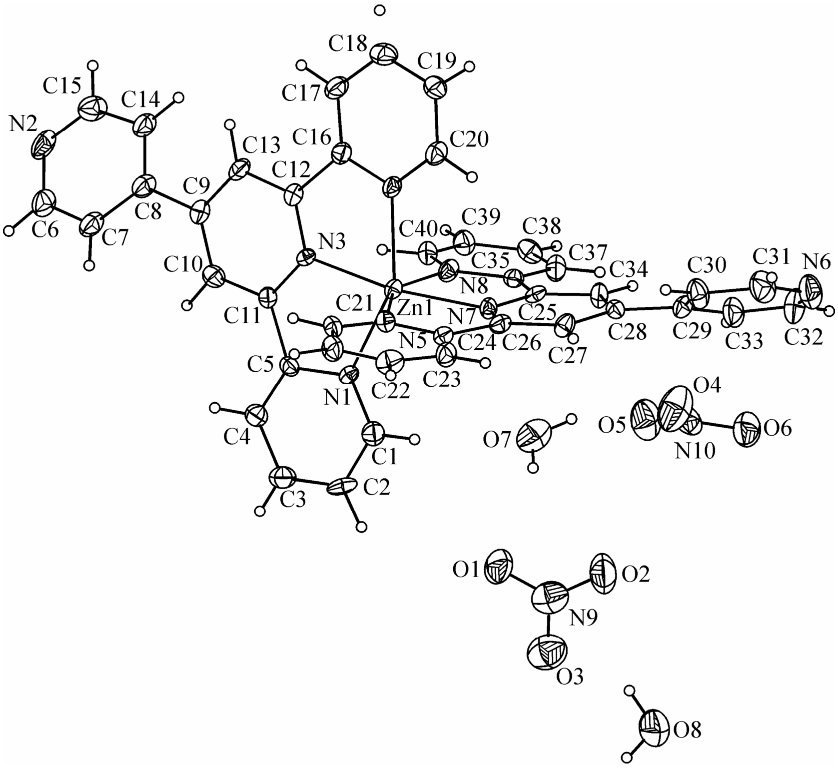

Fig. 1. Molecular structure of **I**

Table 1

Selected Bond Lengths (*d*, nm) *and Bond Angles* (ω, deg.)

Bond	*d*	Angles	ω	Angles	ω
Zn(1)—N(3)	0.2058(6)	N(3)—Zn(1)—N(7)	169.50(19)	N(7)—Zn(1)—N(4)	97.6(2)
Zn(1)—N(7)	0.2065(5)	N(3)—Zn(1)—N(1)	76.2(2)	N(1)—Zn(1)—N(4)	151.6(2)
Zn(1)—N(1)	0.2146(5)	N(7)—Zn(1)—N(1)	110.6(2)	N(5)—Zn(1)—N(4)	94.2(2)
Zn(1)—N(5)	0.2177(6)	N(3)—Zn(1)—N(5)	111.6(2)	N(3)—Zn(1)—N(8)	96.4(2)
Zn(1)—N(4)	0.2183(6)	N(7)—Zn(1)—N(5)	76.4(2)	N(7)—Zn(1)—N(8)	75.6(2)
Zn(1)—N(8)	0.2187(6)	N(1)—Zn(1)—N(5)	94.5(2)	N(1)—Zn(1)—N(8)	93.7(2)
		N(3—Zn(1)—N(4)	75.5(2)	N(5)—Zn(1)—N(8)	151.9(2)
				N(4)—Zn(1)—N(8)	91.1(2)

The distances from N(1) and N(4) to the equatorial plane are 0.208 nm and 0.212 nm, respectively.

Selected bond lengths and angles are given in Table 1. The Zn—N bond lengths are similar to those reported in the literature [14, 15]. The Zn—N bond lengths to the central pyridyl ring [0.2058(6)—0.2065(5) nm] are shorter than those to the terminal pyridyl rings [0.2146(5)—0.2187(6) nm] as anticipated from the constrained pytpy bite. All of the bond lengths and angles fall within the expected range.

The octahedral ZnN_6 unit is as expected, and there are no symmetry constraints on the N(2)...Zn(1)...N(6) vector. It is noteworthy that, in contrast to the structures mentioned above, the vector deviates from linearity (N(2)...Zn(1)...N(6) = 156.17°). Both pendant pyridine rings are twisted by approximately the same amount out of the plane of the pytpy unit (angles between the least squares planes of the rings containing N(2) and N(3), and N6 and N(7) are 28.68° and 25.99°, respectively). When viewed down the N(2)...Zn(1)...N6 axis, the two pendant pyridines exhibit approximately eclipsed conformation, in contrast to the staggered conformation observed in the reported complexes [16—18].

The notable feature of the solid-state structure of **I** is that all the cation, anions and solvent molecules are involved in the basic structural building block. There are $C—H_{aromatic}...O_{nitrate}$ and $O_{water}—H...O_{water}$ hydrogen bonds illustrated in Fig. 2 and Table 2. The neighbor cation motifs are linked by the $C—H...N_{py}$ hydrogen bond interactions which are shown in Fig. 3. Extensive $C—H...O_{nitrate}$ interactions operate between two neighbor cations, in addition to π-stacking between pairs of pendant pyridine rings containing atoms N6 (distance between least squares planes of rings = 0.350 nm) and between significantly offset pairs of tpy rings containing atoms N(1) (separation = 0.336 nm). The five-membered metallocycles of the same pytpy ligand are almost coplanar, with dihedral angles of 1.24° (Cg1—Cg2) and 1.29° (Cg3—Cg4). Two pytpy planes are almost perpendicular with dihedral angle of 87.10°.

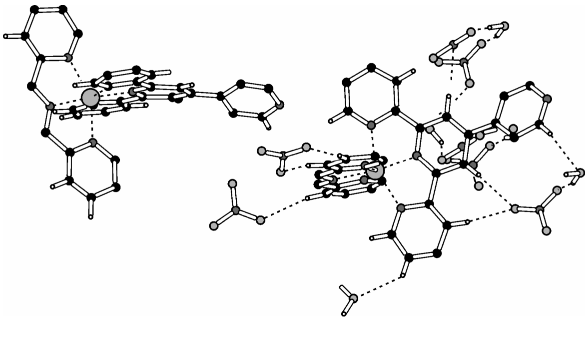

Fig. 2. Fragment of hydrogen-bonded chains of $[Zn(pytpy)_2]^{2+}$ cations in **I** (only H atoms participating in hydrogen bonding are shown)

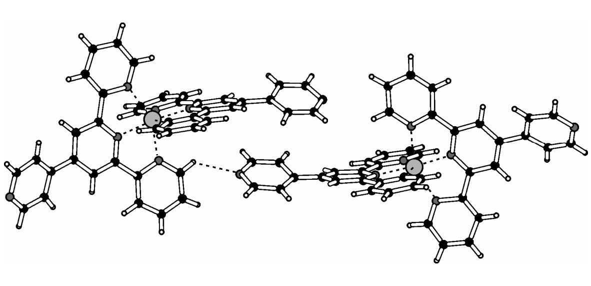

Fig. 3. Hydrogen bond between the cationic units in **I**

Table 2

Hydrogen-bonding Geometry (nm, deg.)

D—H...A	*d*(D—H)	*d*(H...A)	*d*(D...A)	∠D—H...A
O7—H7A...O1^{i}	0.085	0.218	0.2832	133
O7—H7B...O4^{i}	0.085	0.217	0.2986	161
O8—H8A...O6^{i}	0.083	0.2754	0.2754	137
O8—H8B...O2^{ii}	0.094	0.2654	0.3431	129
O8—H8B...O3^{ii}	0.094	0.2654	0.2729	134
C4—H4A...O2^{ii}	0.093	0.2654	0.3435	153
C17—H17A...O4^{iii}	0.093	0.2664	0.3266	131
C24—H24A...O5^{iv}	0.093	0.244	0.3368	173
C27—H27A...O5^{iv}	0.093	0.237	0.3299	177
C31—H31A...O8^{v}	0.093	0.2475	0.3469	131
C34—H34A...O3^{vi}	0.093	0.256	0.3485	174
C37—H37A...O3^{vi}	0.093	0.255	0.3442	162
C40—H40A...N6^{vii}	0.093	0.2764	0.3246	136

Symmetry codes: (i) $-x+2, -y, z-1/2$; (ii) $-x+1, -y, z-1/2$; (iii) $-x+1, -y+1, z-1/2$; (iv) $x-1, y, z$; (v) $y-1, -x+2, z+1/4$; (vi) $x, y+1, z$; (vii) $-x+2, -y+1, z-1/2$.

Also, there are present π—π stacking interactions between Cg2 and Cg5 (N(6)/C(31)—C(32) symmetry code: $-1+y$, $1-x$, $1/4+z$), Cg6 (N(1)/C(1)—C(5)) and Cg7 (N(15)/C(21)—C(25) symmetry code: $1+x$, y, z) , Cg(8) (N(8)/C(36)—C(40)) and Cg(5) (symmetry code: x, $1+y$, z) of neighboring molecules in an offset fashion, as shown in Fig. 3. The centroid-to-centroid distances are 0.4552(4) nm, 0.5027(4) nm and 0.5050(4) nm, and the dihedral angles are 8.31, 5.97 and 6.38°, respectively.

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