

# Six-coordinated zinc complexes: $[\text{Zn}(\text{H}_2\text{O})_4(\text{phen})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $[\text{ZnNO}_3(\text{H}_2\text{O})(\text{bipy})(\text{Him})]\text{NO}_3$ (phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine, and Him = imidazole)

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Two novel six-coordinated zinc complexes, tetra-aqua(1,10-phenanthroline)zinc dinitrate monohydrate,  $[\text{Zn}(\text{H}_2\text{O})_4(\text{phen})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (**1**) and aqua(2,2'-bipyridine)(imidazole)-nitratozinc nitrate,  $[\text{ZnNO}_3(\text{H}_2\text{O})(\text{bipy})(\text{Him})]\text{NO}_3$  (**2**) were prepared. Compound **1** crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 8.780(4)$ ,  $b = 13.609(4)$ ,  $c = 15.368(5)$  Å,  $\beta = 93.86(2)^\circ$ ,  $V = 1832.1(12)$  Å<sup>3</sup>. In **1**, a phenanthroline molecule chelates the zinc atom and four water molecules complete the octahedral geometry around the metal. Compound **2** crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 7.250(1)$ ,  $b = 24.554(4)$ ,  $c = 10.258(2)$  Å,  $\beta = 107.880(10)^\circ$ ,  $V = 1737.9(5)$  Å<sup>3</sup>. In **2**, a bipyridine molecule and a nitrate anion chelate the zinc atom. An imidazole molecule and a water molecule then complete the six-coordinated geometry around zinc. The intermolecular packing is controlled by hydrogen bonding, especially in **1** and by  $\pi$  stacking. The thermal stability of the compounds and the loss of water molecules and ligands was monitored by a thermogravimetric study.

**KEY WORDS:** Zinc; phenanthroline; 2,2'-bipyridine; imidazole; hydrogen bonding;  $\pi$  stacking.

## Introduction

In the past 20 years, a number of mononuclear zinc enzymes, such as phospholipase C,<sup>1</sup> bovine lens leucine aminopeptidase,<sup>2</sup> ATPases,<sup>3,4</sup> carbonic anhydrases,<sup>5-7</sup> and peptide deformylase,<sup>8</sup> have been found and some of these have been determined by X-ray crystallography.

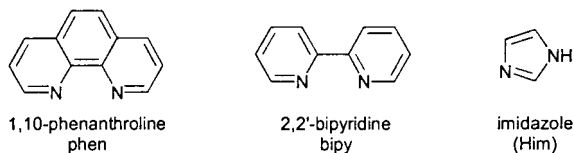
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They play a number of diverse and important roles in biological systems and have received considerable attention from inorganic chemists. Since mononuclear zinc complexes may serve as model compounds for these enzymes, a number of these complexes have been prepared in recent years for this purpose.<sup>9</sup>

1,10-Phenanthroline (phen) and 2,2'-bipyridine (bipy) have extended planar  $\pi$  systems and can be used in model compounds to mimic the noncovalent interactions in biological processes.<sup>1</sup> A few phenanthroline and bipyridine-containing zinc complexes have been described recently.<sup>6,10-12</sup> We report here the



Scheme 1.

preparation and characterization of two novel six-coordinated zinc complexes, tetra-aqua(1,10-phenanthroline)zinc dinitrate monohydrate,  $[\text{Zn}(\text{H}_2\text{O})_4(\text{phen})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (**1**) and aqua(2,2'-bipyridine)(imidazole)nitratozinc nitrate,  $[\text{Zn}(\text{NO}_3)(\text{H}_2\text{O})(\text{bipy})(\text{Him})]\text{NO}_3$  (**2**).

## Experimental

### Physical measurements

Elemental analyses were carried out with a Perkin-Elmer CHN Analyser Model 240. IR spec-

tra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer with KBr discs. Thermochemical studies were made on a Perkin-Elmer 7 Series System under a nitrogen atmosphere (20 mL  $\text{min}^{-1}$ ) and a temperature increase of  $20^\circ\text{C min}^{-1}$ .

### Preparation of $[\text{Zn}(\text{H}_2\text{O})_4(\text{phen})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**1**)

To an aqueous solution (20 mL) of zinc nitrate (3.0 g, 10 mmol) was added an aqueous solution (10 mL) of 1,10-phenanthroline (2.0 g, 10 mmol) and a solution of imidazole (0.67 g, 10 mmol) with stirring. The mixture was heated to  $60^\circ\text{C}$  and stirred for 2 h. A white crystalline solid was obtained by slow evaporation of the solvent. Yield: 4.1 g, 90%. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_{11}\text{Zn}$  (mol. wt. 459.67): C, 31.35;

Table 1. Crystal Data and Structure Refinement for **1** and **2**

Compound	$[\text{Zn}(\text{phen})(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ( <b>1</b> )	$[\text{ZnNO}_3(\text{H}_2\text{O})(\text{bipy})(\text{Him})]\text{NO}_3$ ( <b>2</b> )
CCDC deposit no.	CCDC-1003/5992	CCDC-1003/5993
Color/shape	colorless/prismatic	colorless/prismatic
Empirical formula	$\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_{11}\text{Zn}$	$\text{C}_{13}\text{H}_{14}\text{N}_6\text{O}_7\text{Zn}$
Formula weight, $\text{g mol}^{-1}$	459.67	431.67
Temperature, K	288(2)	288(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
No. of reflections used for cell determination ( $\theta$ range)	25 (2.74–13.81°)	25 (2.66–15.76°)
Unit cell dimensions		
$a$ , Å	8.780(4)	7.250(1)
$b$ , Å	13.609(4)	24.554(4)
$c$ , Å	15.368(5)	10.258(2)
$\beta$ , deg	93.86(2)	107.88(1)
Volume, Å <sup>3</sup>	1832.1(12)	1737.9(5)
$Z$	4	4
Density (calculated), $\text{g cm}^{-3}$	1.667	1.650
$\mu$ (Mo $K\alpha$ ), $\text{cm}^{-1}$	14.07	14.65
$F(000)$	944	880
Crystal size, $\text{mm}^3$	$0.30 \times 0.20 \times 0.16$	$0.32 \times 0.28 \times 0.22$
$2\theta$ max, deg	50	51
Reflections collected	3734	3710
Independent reflections	3227 ( $R_{\text{int}} = 0.0219$ )	3234 ( $R_{\text{int}} = 0.0208$ )
Absorption correction	Empirical	Empirical
Max./min. transmission	0.8091/0.7453	0.7836/0.7061
Data/restraints/parameters	3227/15/293	3234/0/253
Goodness of fit on $F^2$	0.872	0.918
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0390$ , $wR2 = 0.0774$	$R1 = 0.0381$ , $wR2 = 0.0835$
$R$ indices (all data)	$R1 = 0.0664$ , $wR2 = 0.0828$	$R1 = 0.0658$ , $wR2 = 0.0915$
Largest diff. peak and hole, $\text{e Å}^{-3}$	0.412 and $-0.396$	0.586 and $-0.337$

**Table 2.** Atomic Coordinates ( $10^4$ ) and Equivalent Isotropic Thermal Parameters for **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Zn	2547(1)	12679(1)	-260(1)	33(1)
O(1)	763(3)	12308(2)	-1157(2)	47(1)
O(2)	2338(4)	14160(2)	-575(2)	44(1)
O(3)	4024(3)	12636(2)	-1323(2)	40(1)
O(4)	859(3)	12946(2)	680(2)	43(1)
O(5)	2156(3)	11726(2)	2233(2)	55(1)
O(6)	76(4)	11196(2)	1579(2)	65(1)
O(7)	964(4)	10508(2)	2771(2)	80(1)
O(8)	3657(3)	5910(2)	830(2)	53(1)
O(9)	2208(3)	7172(2)	875(2)	66(1)
O(10)	1370(3)	5871(2)	211(2)	57(1)
O(11)	1001(5)	13870(3)	2470(2)	67(1)
N(1)	4389(3)	12821(2)	690(2)	31(1)
N(2)	2867(3)	11187(2)	124(2)	31(1)
N(3)	1080(4)	11141(3)	2191(2)	44(1)
N(4)	2423(4)	6312(2)	637(2)	39(1)
C(1)	5109(5)	13619(3)	971(2)	42(1)
C(2)	6337(5)	13601(3)	1598(3)	47(1)
C(3)	6830(5)	12721(3)	1944(2)	47(1)
C(4)	6065(4)	11859(3)	1678(2)	36(1)
C(5)	6460(5)	10906(3)	2023(2)	45(1)
C(6)	5672(5)	10099(3)	1761(2)	42(1)
C(7)	4414(4)	10164(2)	1119(2)	34(1)
C(8)	3540(5)	9350(3)	823(2)	40(1)
C(9)	2383(5)	9469(3)	203(3)	46(1)
C(10)	2073(4)	10407(3)	-135(2)	39(1)
C(11)	4011(4)	11079(2)	753(2)	29(1)
C(12)	4846(4)	11941(2)	1038(2)	29(1)

<sup>a</sup> $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

H, 3.95; N, 12.19. Found: C, 31.01; H, 4.22; N, 12.31. IR ( $\text{cm}^{-1}$ ): 3445 (br, s), 3049 (m), 1828 (w), 1762 (m), 1622 (m), 1603 (m), 1583 (s), 1522 (m), 1493 (m), 1431 (s), 1385 (s), 1224 (w), 1147 (m), 1106 (m), 1091 (m), 1034 (w), 1000 (w), 872 (s), 851 (s), 825 (s), 788 (s), 725 (s), 646 (s), 507 (s).

#### Preparation of $[\text{ZnNO}_3(\text{H}_2\text{O})(\text{bipy})(\text{Him})]\text{NO}_3$ (**2**)

The procedure for **2** identical to **1** except that 2,2'-bipyridine instead of phenanthroline was used. Yield: 3.71 g, 86%. Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{N}_6\text{O}_7\text{Zn}$  (mol. wt. 431.67): C, 36.17; H, 3.27; N, 19.47. Found: C, 36.50; H, 3.61; N, 19.81. IR ( $\text{cm}^{-1}$ ): 1736 (m), 1608 (s), 1598 (s), 1578 (m),

**Table 3.** Atomic Coordinates ( $10^4$ ) and Equivalent Isotropic Thermal Parameters for **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Zn	1229(1)	1193(1)	7427(1)	44(1)
O(1)	208(4)	954(1)	9181(3)	67(1)
O(2)	-1705(4)	760(1)	7197(2)	65(1)
O(3)	-2401(5)	492(1)	8979(4)	112(1)
O(4)	-559(5)	1870(1)	7041(4)	73(1)
O(5)	-183(7)	2848(1)	8280(3)	131(2)
O(6)	1030(5)	3314(1)	10070(3)	105(1)
O(7)	111(5)	2513(1)	10234(4)	95(1)
N(1)	2348(4)	404(1)	7328(3)	42(1)
N(2)	1291(4)	1150(1)	5390(3)	46(1)
N(3)	3597(4)	1580(1)	8612(3)	46(1)
N(4)	6526(5)	1910(1)	9343(4)	70(1)
N(5)	-1343(5)	725(1)	8469(3)	58(1)
N(6)	341(5)	2880(1)	9509(3)	60(1)
C(1)	2870(5)	50(1)	8368(3)	51(1)
C(2)	3512(5)	-469(2)	8224(4)	56(1)
C(3)	3614(5)	-628(2)	6980(4)	57(1)
C(4)	3098(5)	-265(1)	5903(4)	54(1)
C(5)	2466(4)	250(1)	6105(3)	41(1)
C(6)	1864(5)	668(1)	5010(3)	44(1)
C(7)	1874(5)	578(2)	3686(3)	57(1)
C(8)	1308(6)	993(2)	2741(4)	68(1)
C(9)	767(6)	1484(2)	3131(4)	67(1)
C(10)	766(5)	1549(2)	4464(4)	58(1)
C(11)	3995(5)	1741(1)	9948(4)	54(1)
C(12)	5800(6)	1949(2)	10394(4)	63(1)
C(13)	5173(6)	1692(2)	8290(4)	65(1)

<sup>a</sup> $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

1568 (m), 1544 (m), 1495 (s), 1478 (s), 1445 (s), 1385 (s), 1318 (s), 1295 (s), 1265 (s), 1179 (s), 1159 (s), 1137 (w), 1122 (w), 1096 (s), 1070 (s), 1027 (s), 985 (s), 952 (w), 907 (m), 854 (s), 832 (w), 815 (w), 774 (s), 740 (s), 656 (s), 632 (s), 620 (s).

#### X-ray structure determination

Data were collected by the  $\omega$ -scan method with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and the use of a graphite monochromator on a Siemens-Bruker P4 four-circle diffractometer. The structures were solved by direct methods (SHELXS-97)<sup>13</sup>; refinement was done by full-matrix least-squares on  $F^2$  using the SHELXL-97 program suite.<sup>14</sup> All non-hydrogen

**Table 4.** Selected Bond Lengths (Å) and Angles (°) for **1**

Bond lengths	
Zn—O(2)	2.077(3)
Zn—O(1)	2.078(3)
Zn—N(1)	2.113(3)
Zn—N(2)	2.127(3)
Zn—O(3)	2.154(3)
Zn—O(4)	2.169(3)
Bond angles	
O(2)—Zn—O(1)	91.74(12)
O(2)—Zn—N(1)	97.10(11)
O(1)—Zn—N(1)	171.15(12)
O(2)—Zn—N(2)	176.43(12)
O(1)—Zn—N(2)	91.82(12)
N(1)—Zn—N(2)	79.33(11)
O(2)—Zn—O(3)	84.12(11)
O(1)—Zn—O(3)	87.42(12)
N(1)—Zn—O(3)	93.13(12)
N(2)—Zn—O(3)	96.29(11)
O(2)—Zn—O(4)	86.51(12)
O(1)—Zn—O(4)	87.98(12)
N(1)—Zn—O(4)	92.88(11)
N(2)—Zn—O(4)	93.37(11)
O(3)—Zn—O(4)	169.42(11)

positions were located and refined. The atoms were refined with anisotropic temperature factors. The hydrogen atoms on phen for **1** and those on bipy and Him for **2** were placed

at calculated positions using appropriate riding models and an isotropic temperature factor of  $B_{\text{eq}}(\text{H}) = 1.2B_{\text{eq}}$  (C or N). The H atoms on the water molecules for both complexes were located from a difference Fourier synthesis and refined isotropically with free temperature factors. The O—H bond distances of the five water molecules in **1** were restrained to the target values  $>0.8 \text{ \AA}$  with DFIX. Crystal data are listed in Table 1. The final atomic positional parameters, selected bond lengths and bond angles are given in Tables 2–6. Graphics were obtained with ORTEP-III for Windows.<sup>15</sup> Hydrogen bonding computations for the crystal structure discussion were carried out with SHELXL and PLATON for Windows.<sup>16</sup> The structural data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-1003/XXXX for **1**, CCDC-1003/XXXX for **2**).

## Results and discussion

For compound **1**, we tried to prepare a zinc complex that would contain both the phenanthroline and the imidazole ligand. However, only the

**Table 5.** Hydrogen Bonding Interactions in **1** and **2**

D—H...A	D—H	H...A	D...A	D—H...A
Compound <b>1</b>				
O(1)—H(1A)...O(9) <sup>3</sup> <sub>-</sub>	0.822(10)	1.947(12)	2.766(4)	173(5)
O(1)—H(1B)...O(11) <sup>4</sup> <sub>-</sub>	0.823(10)	1.851(11)	2.668(4)	172(4)
O(2)—H(2A)...O(10) <sup>1</sup> <sub>-</sub>	0.815(10)	1.996(17)	2.782(4)	162(4)
O(2)—H(2B)...O(7) <sup>4</sup> <sub>-</sub>	0.819(10)	1.960(12)	2.778(4)	176(5)
O(3)—H(3A)...O(8) <sup>3'</sup> <sub>-</sub>	0.817(10)	2.091(12)	2.903(4)	173(5)
O(3)—H(3B)...O(5) <sup>4</sup> <sub>-</sub>	0.817(10)	1.995(12)	2.807(4)	173(5)
O(4)—H(4A)...O(6)	0.816(10)	2.048(13)	2.860(4)	173(4)
O(4)—H(4B)...O(10) <sup>3</sup>	0.817(10)	2.028(13)	2.817(4)	162(3)
O(11)—H(11A)...O(4)	0.818(10)	2.212(15)	3.020(5)	170(4)
O(11)—H(11B)...O(7) <sup>2</sup> <sub>-</sub>	0.821(10)	2.007(12)	2.827(5)	176(5)
Compound <b>2</b>				
O(4)—H(4A)...O(5)	0.85(5)	1.85(5)	2.691(5)	169(5)
O(4)—H(4B)...O(6) <sup>4''</sup> <sub>-</sub>	0.78(4)	1.94(5)	2.708(5)	172(5)
N(4)—H(41)...O(7) <sup>1''</sup> <sub>-</sub>	0.86	2.12	2.884(4)	147.4

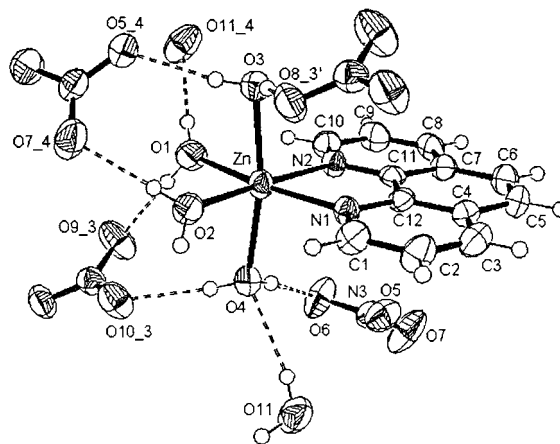
*Note.* D = Donor, A = acceptor. Symmetry transformations for compound **1**: <sub>-1</sub>  $x, 1 + y, z$ ; <sub>-2</sub>  $-x, 0.5 + y, 0.5 - y$ ; <sub>-3</sub>  $-x, 2 - y, -z$ ; <sub>-3'</sub>  $1 - x, 2 - y, -z$ ; <sub>-4</sub>  $x, 2.5 - y, -0.5 + z$ ; symmetry transformations for compound **2**: <sub>-1</sub>  $1 + x, y, z$ ; <sub>-4</sub>  $-0.5 + x, 0.5 - y, -0.5 + z$ .

**Table 6.** Selected Bond Lengths (Å) and Angles (°) for **2**

Bond lengths	
Zn–N(3)	2.011(3)
Zn–O(4)	2.070(3)
Zn–N(2)	2.106(3)
Zn–N(1)	2.116(3)
Zn–O(1)	2.224(3)
Zn–O(2)	2.324(3)
O(1)–N(5)	1.268(4)
O(2)–N(5)	1.252(4)
O(3)–N(5)	1.200(4)
Bond angles	
N(3)–Zn–O(4)	96.03(13)
N(3)–Zn–N(2)	110.45(11)
O(4)–Zn–N(2)	93.06(13)
N(3)–Zn–N(1)	101.11(11)
O(4)–Zn–N(1)	162.41(13)
N(2)–Zn–N(1)	77.34(10)
N(3)–Zn–O(1)	94.02(11)
O(4)–Zn–O(1)	91.30(12)
N(2)–Zn–O(1)	154.50(11)
N(1)–Zn–O(1)	91.39(10)
N(3)–Zn–O(2)	149.56(10)
O(4)–Zn–O(2)	81.26(12)
N(2)–Zn–O(2)	99.99(9)
N(1)–Zn–O(2)	85.89(10)
O(1)–Zn–O(2)	55.94(9)

phenanthroline complex was obtained despite the presence of imidazole. The zinc atom in **1** has a six-coordinate geometry with phen acting as a chelating ligand via both N atoms. Four water molecules coordinate to Zn in order to complete its coordination sphere (Fig. 1).

The bond lengths and angles for phenanthroline–zinc in **1** (Table 4) are in good agreement with those reported for the free ligand as well as the related zinc complexes. The Zn–N distances of 2.113(3) and 2.127(3) Å are comparable to some other six-coordinate zinc–phen complexes, e.g. [Zn(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (2.17(1) Å)<sup>17</sup> but somewhat longer than those found in [Zn(phen)Cl<sub>2</sub>] (2.061(7) Å)<sup>18</sup> because of the change of the coordination number from six to four. The bond angle of 79.33(11)° in **1** is a little bit larger than those found in [Zn(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (average 76.8(1)°)<sup>17</sup> but similar to that in [Zn(phen)Cl<sub>2</sub>] (80.4(3)°).<sup>18</sup> There is an extensive hydrogen bonding network

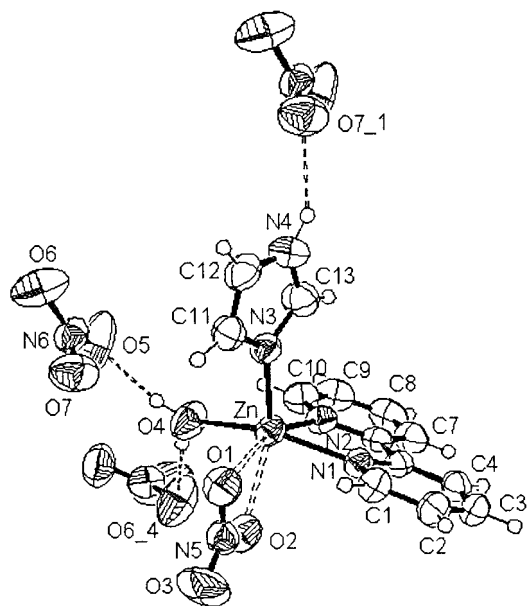


**Fig. 1.** Molecular structure of **1** with most of the hydrogen bonding interactions. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

involving the aqua ligands and the nitrate anions. Most of this network was included in Fig. 1. The distances and angles of the hydrogen bonding network are listed in Table 5.

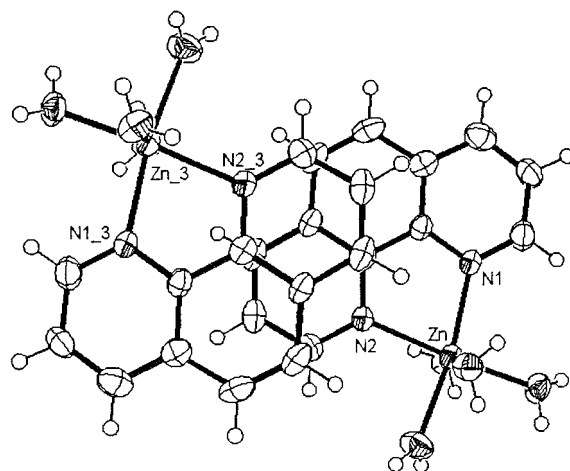
The aqua ligands and the lattice water molecule interact with the uncoordinated NO<sub>3</sub><sup>−</sup> anions via hydrogen bonding. All hydrogen atoms are involved in hydrogen bonding. This makes the crystal stable in air under ambient pressure for a long time. The IR spectrum of **1** shows a broad peak at 3445 cm<sup>−1</sup> which is due to the coordinated and the lattice water molecules in the crystal. For other recent examples of metal complexes with incorporation of water molecules and extensive hydrogen bonding networks see Ref. 19. A thermogravimetric study of **1** shows that the complex begins to lose two water molecules from 40 up to 130°C which corresponds to a weight loss of 8.15%. The residue remained stable until the temperature rose to 320°C. Then followed a sharp weight loss of 46% indicating the loss of the remaining three water molecules together with the phenanthroline ligand.

For compound **2**, the coordination geometry is pseudo-octahedral with bipyridine and a nitrate group acting as two chelate ligands. An imidazole molecule and a water molecule complete the six-coordinate geometry as shown in Fig. 2.



**Fig. 2.** Molecular structure of **2** also showing the hydrogen bonding interactions. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

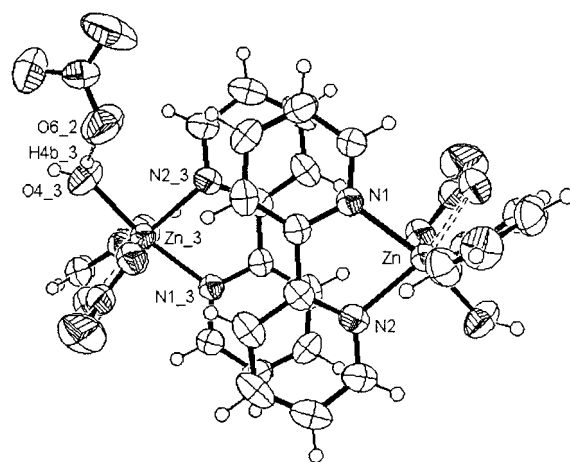
It can be noted that in **2** only one of the nitrate groups interacts with the metal atom, while the other one remains uncoordinated. The two Zn—O(NO<sub>3</sub><sup>-</sup>) bond distances vary somewhat (2.224(3) Å vs. 2.324(3) Å) and are considerably longer than the Zn—N or the Zn—O(OH<sub>2</sub>) contacts (Table 6). The Zn—N(Him) bond length of 2.011(3) Å is comparable to those found in [Zn(maleato)(Him)<sub>3</sub>] (1.990(3), 2.013(3) and 2.016(3) Å).<sup>5</sup> The Zn—N(bipy) bond distances of 2.106(3) and 2.116(3) Å are similar to those found in [Zn(maleato)(H<sub>2</sub>O)(bipy)]<sub>2</sub> (2.1021(15) and 2.120(2) Å).<sup>12</sup> The bond angle of 77.34(10)° for bipy in **2** is also similar to that in [Zn(maleato)(H<sub>2</sub>O)(bipy)]<sub>2</sub> (77.20(6)°). The hydrogen atoms of the aqua ligand and also the N-H group of the imidazole are engaged in hydrogen bonding to the uncoordinated nitrate anions as was also shown in Fig. 2. The distances and angles of the hydrogen bonds are included in Table 5. A thermogravimetric study of **2** shows that this complex is stable up to 100°C. With the increase in temperature, the coordinated water molecule is lost at ca



**Fig. 3.**  $\pi$  Stacking in **1**. Symmetry transformation:  $\_3 1 - x, 2 - y, -z$ . The nitrate anions and the water of crystallization have been omitted for clarity.

114°C as evidenced by the weight loss of 4.4%. At ca 200°C, the loss of the organic ligand starts and proceeded continuously up to 500°C.

In addition to hydrogen bonding the intermolecular packing in **1** and **2** is also determined by  $\pi$  stacking between the aromatic ligands. Figs. 3 and 4 visualize the  $\pi$  stacking with a view perpendicular to the  $\pi$  planes. Multidentate nitrogen heterocycles are used prominently as building blocks in the design of metal-ligand networks and  $\pi$ - $\pi$



**Fig. 4.**  $\pi$  Interactions in **2**. Symmetry transformations:  $\_2 0.5 - x, 0.5 - y, 1.5 - z; \_3 -x, -y, 1 - z$ .

stacking is an increasingly noted feature in their structural description.<sup>20</sup> The  $\pi$  arrangement in **1** and **2** shows the expected offset or slipped stacking with a parallel displacement of the  $\pi$  planes. Shortest intermolecular C...C contacts are 3.362 Å in **1** and 3.567 Å in **2**. It is a noted trend that  $\pi$  stacking becomes more favorable with increased aromatic ring numbers. Shorter  $\pi$  contacts are usually found between extended, anellated  $\pi$  systems, such as phenanthroline, in comparison to monoaromatic rings, e.g. (bi)pyridine.<sup>20</sup>

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### References

1. Barton, J.K. *Pure Appl. Chem.* **1989**, *61*, 563.
2. Burley, S.K.; David, P.R.; Sweet, R.M.; Taylor, A.; Lipscomb, W.N. *J. Mol. Biol.* **1992**, *124*, 113.
3. Müller-Hartmann, A.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2000**, 2355.
4. Strager, N.; Lipscomb, W.N.; Klabunde, T.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2024.
5. Zhang, C.; Du, W.; Mei, Y. *J. Chem. Res., Synop.* **2000**, 214.
6. Chen, X.M.; Xu, Z.T.; Huang, X.C. *J. Chem. Soc., Dalton Trans.* **1994**, 2331.
7. Vallee, B.L.; Auld, D.S. *Acc. Chem. Res.* **1993**, *26*, 543.
8. Chang, S.; Karambelkar, V.V.; diTargiani, R.C.; Goldberg, D.P. *Inorg. Chem.* **2001**, *40*, 194.
9. Lipscomb, W.N.; Strager, N. *Chem. Rev.* **1996**, *96*, 2375.
10. Uhlenbrock, S.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1451.
11. Zhang, C.; Yu, K.; Wu, D.; Zhao, C. *Acta Crystallogr., Sect. C*, **1999**, *55*, 1815.
12. Zhang, C.; Yu, K.; Wu, D.; Zhao, C. *Acta Crystallogr., Sect. C*, **1999**, *55*, 1470.
13. Sheldrick, G.M. *SHELXS-97, Programs for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.
14. Sheldrick, G.M. *SHELXL-97, Programs for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
15. (a) Burnett, M.N.; Johnson, C.K. *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*; Report ORNL-6895; Oak Ridge National Laboratory: Oak Ridge, TN, 1996; (b) Farrugia, L.J. *ORTEP-III for Windows*, version 1.0.1 $\beta$ ; University of Glasgow, 1997; (c) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
16. (a) Spek, A.L. *Acta Crystallogr. Sect. A* **1990**, *46*, C34; (b) Farrugia, L.J. *PLATON*, version 29-11-98; Windows implementation; University of Glasgow, 1998.
17. Hu, N.H.; Liu, Y.S. *Acta Crystallogr., Sect. C*, **1991**, *47*, 2324.
18. Khan, M.A.; Tuck, D.G. *Acta Crystallogr., Sect. C*, **1984**, *40*, 60.
19. (a) Janiak, C.; Deblon, S.; Wu, H.-P.; Kolm, M.J.; Klüfers, P.; Piotrowski, H.; Mayer, P. *Eur. J. Inorg. Chem.* **1999**, 1507; (b) Janiak, C.; Temizdemir, S.; Scharmann, T.G.; Schmalstieg, A.; Demtschuk, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2053; (c) Burrows, A.D.; Harrington, R.W.; Mahon, M.F.; Price, C.E. *J. Chem. Soc., Dalton Trans.* **2000**, 3845; (d) Plater, J.M.; Foreman, M.R. St. J.; Gelbrich, T.; Coles, S.J.; Hursthouse, M.B. *J. Chem. Soc., Dalton Trans.* **2000**, 3065; (e) Janiak, C.; Scharmann, T.G.; Hemling, H.; Lentz, D.; Pickardt, J. *Chem. Ber.* **1995**, *128*, 235; (f) Janiak, C.; Scharmann, T.G.; Günther, W.; Girgsdies, F.; Hemling, H.; Hinrichs, W.; Lentz, D. *Chem. Eur. J.* **1995**, *1*, 637.
20. (a) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885; and references therein; (b) Blake, A.J.; Champness, N.R.; Cooke, P.A.; Nicolson, J.E.B.; Wilson, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3811; (c) Nakash, M.; Clyde-Watson, Z.; Feeder, N.; Teat, S.J.; Sanders, J.K.M. *Chem. Eur. J.* **2000**, *6*, 2112.