

## MODELS OF THE ACTIVE SITES OF ZINC CONTAINING ENZYMES: THE CRYSTAL STRUCTURES OF TWO BIS(TRIPOD)ZINC(II) COMPLEXES

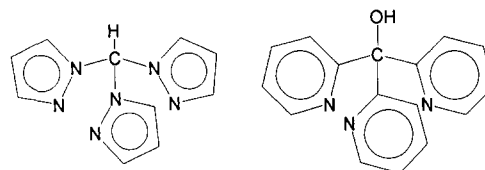
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**Abstract**—Attempts to prepare complexes of the type  $[\text{Zn}(\text{tripod})\text{L}]^{x+}$ , where L is a uni-negative anion, yielded only bis(tripod)zinc(II) complexes. The crystal structures of two of these bis(tripod)zinc(II) complexes, bis(tris(pyrazolyl)methane)zinc(II) nitrate (**I**) and bis(tris(pyridine)methanol)zinc(II) nitrate-4-hydrate (**II**) are described. The geometries about the zinc atoms are close to octahedral and average Zn—N distances are 2.136 and 2.148 Å for **I** and **II**, respectively. There are no significant interligand interactions which might mitigate against the formation of the bis(tripod)zinc(II) complexes. The reasons for the preference for these complexes over those sought are discussed.

Tripodal ligands with three pyridine, pyrazolyl or imidazole groups are increasingly being used in the small molecule modelling of the active sites of metallo-enzymes in which the metal is coordinated to two or three imidazole groups from histidine.<sup>1–4</sup> In most of these studies the aromatic group carries bulky substituents, added to prevent the formation of bis(ligand) complexes and to modify the metal environment. We are employing such substituted tripod ligands in modelling of the active site of the enzyme dihydroorotase. However, in order to establish whether it is possible to form  $[\text{Zn}(\text{tripod})\text{L}]^{x+}$  complexes, with unsubstituted tripodal ligands and, in so doing, to more closely model the active site, we undertook the preparation of a number of complexes in which the tripod was either tris(pyrazol-1-yl)methane ( $L_1$ ) or tris(pyridine)methanol ( $L_2$ ) (Scheme 1) and L was one of a number of ligands including natural substrates of dihydroorotase. In all cases the result was formation of bis(tripod)zinc(II) complexes. In order to confirm this the products were structurally characterized and the structures are described herein. There have been relatively few bis(tripod)metal complexes so characterized and there have only



Scheme 1.

been two previous crystal structure analyses of bis(tripod)zinc(II) complexes.<sup>5,6</sup>

### EXPERIMENTAL

#### *Synthesis of bis{tris(pyrazol-1-yl)methane}zinc(II) nitrate (**I**)*

Zinc(II) nitrate-6-hydrate, tris(pyrazol-1-yl)methane and either acetate, dihydroorotate or carbamyl aspartate as their sodium salts were dissolved separately in the minimum amount of 2-propanol and combined in equimolar ratios. A white solid precipitated over a period of days. Recrystallization from ethanol yielded colourless crystals.

#### *Synthesis of bis{tris(pyridine)methanol}zinc(II) nitrate-4-hydrate (**II**)*

Zinc(II) nitrate-6-hydrate, tris(pyridine)methanol and either dihydroorotate or carbamyl

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aspartate as their sodium salts were dissolved separately in the minimum amount of ethanol and combined in equimolar ratios. A white solid precipitated over a period of days. Recrystallization from ethanol yielded colourless crystals.

### Crystal data

(I) Formula  $[\text{Zn}(\text{C}_{10}\text{H}_{10}\text{N}_6)_2](\text{NO}_3)_2$ ;  $M$  617.86, monoclinic, space group  $P2_1/n$ , with  $a = 9.974(3)$ ,  $b = 7.961(2)$ ,  $c = 17.050(2)$  Å,  $\beta = 102.13(2)^\circ$ ;  $V = 1323.6$  Å<sup>3</sup>,  $D_c(Z = 2) = 1.550$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 9.70$  cm<sup>-1</sup>,  $\lambda = 0.7107$  Å,  $F(000) = 632$  electrons. Specimen: colourless needles,  $0.11 \times 0.11 \times 0.24$  mm<sup>3</sup>,  $A_{\text{max,min}}^* = 1.15, 1.01$ ,  $N = 2609$ ,  $N_o = 1356$ ,  $hkl$  -12 to 12, 0 to 14, 0 to 20,  $R = 0.042$ ,  $R_w = 0.042$ ,  $w = 1.37[\sigma^2(F_o) + 0.00018F_o^2]$  (where  $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$  and  $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ ).

(II) Formula  $[\text{Zn}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ;  $M$  788.06, triclinic, space group  $P\bar{1}$ , with  $a = 10.825(2)$ ,  $b = 13.435(3)$ ,  $c = 13.549(2)$  Å,  $\alpha = 77.79(1)^\circ$ ,  $\beta = 71.26(1)^\circ$ ,  $\gamma = 67.01(1)^\circ$ ;  $V = 1709.4$  Å<sup>3</sup>,  $D_c(Z = 2) = 1.53$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 7.43$  cm<sup>-1</sup>,  $\lambda = 0.7107$  Å,  $F(000) = 816$  electrons. Specimen: colourless needles,  $0.025 \times 0.014 \times 0.11$  mm<sup>3</sup>,  $A_{\text{max,min}}^* = 1.12, 1.07$ ,  $N = 6290$ ,  $N_o = 4124$ ,  $hkl$  -12 to 12, -16 to 16, 0 to 16,  $R = 0.049$ ,  $R_w = 0.055$ ,  $w = 2.14[\sigma^2(F_o) + 0.00055F_o^2]$ .

### Structure determinations

For diffractometry crystals were mounted on glass fibres with cyanoacrylate resin. Lattice parameters at 21°C were determined by least-squares fits to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4F four-circle diffractometer employing graphite monochromated Mo-K $\alpha$  radiation. Intensity data were collected in the range  $1 < \theta < 25^\circ$ . Data reduction and application of Lorentz, polarization, numerical absorption and decomposition corrections were carried out using the Enraf-Nonius Structure Determination Package.<sup>7</sup>

The structures were solved by direct methods using SHELXS-86<sup>8</sup> and the solutions were extended by difference Fourier methods. Hydrogen atoms in **I** were included at calculated sites (C—H, 0.97 Å) with group isotropic thermal parameters; those in **II** were included at sites located in difference maps and were refined with individual isotropic thermal parameters. All other atoms in both structures were refined anisotropically.

Full-matrix least-squares methods for **I** and blocked-matrix least squares for **II** were used to

refine an overall scale factor, positional and thermal parameters. Scattering factors and anomalous dispersion terms for Zn were taken from International Tables<sup>9</sup> and for all other atoms the terms supplied in SHELX-76<sup>10</sup> were used. All calculations were carried out using SHELX-76 and plots were drawn using ORTEP.<sup>11</sup>

The atom numbering schemes are given in Figs 1 and 2 and bond lengths and angles are listed in Tables 1–4. Listings of final atomic coordinates, observed and calculated structure factors, non-hydrogen atom thermal parameters, hydrogen atom coordinates and thermal parameters, torsion angles, close non-bonded contacts and details of least-squares planes calculations (Tables S1–S14) are deposited as an accessory publication.

## RESULTS AND DISCUSSION

### Syntheses

In all cases the syntheses, in which Zn<sup>2+</sup>, a tripodal ligand and a uninegative anion were combined in 1:1:1 ratios, yielded  $[\text{Zn}(\text{tripod})_2]^{2+}$  complex cations rather than  $[\text{Zn}(\text{tripod})(\text{L})]^+$  (L = acetate, dihydroorotate or carbamyl aspartate) cations. Complexes similar to those sought,  $[\text{Zn}\{\text{HB}(\text{pz})_3\}(\text{NO}_3)]$  and  $[\text{Zn}\{\text{P}(\text{py})_3\}(\text{NO}_3)_2]$ , have been described recently so under some conditions they can be isolated.<sup>4,6</sup> In the first of these complexes the tripodal ligand is anionic rather than neutral as in the case of ligands L<sub>1</sub> and L<sub>2</sub> and the solvents used were tetrahydrofuran (THF) and methanol in place of the 2-propanol or ethanol we employed. However, no clear pattern emerges from these results.

### Description of the structures

The structure of **I** consists of the  $[\text{Zn}(\text{L}_1)_2]^{2+}$  cation located with the Zn atom lying at a centre of symmetry and a nitrate anion rotationally disordered over two equally occupied sites. There is a close contact between the methylene group and the nitrate anion (C(1)⋯O(3) 3.051 Å, H(1)⋯O(3) 2.13 Å). This C—H⋯O hydrogen bond, though weak, does indicate that the bridgehead group is unusually acidic. There are also a number of longer contacts (H⋯O ~ 2.4 Å) between nitrate oxygen atoms and hydrogen atoms of the pyrazolyl groups. The structure of **II** consists of two independent  $[\text{Zn}(\text{L}_2)_2]^{2+}$  cations, each located with the Zn atom lying on a centre of symmetry, two nitrate anions at general sites and four water molecules. There are a number of strong hydrogen bonds involving the

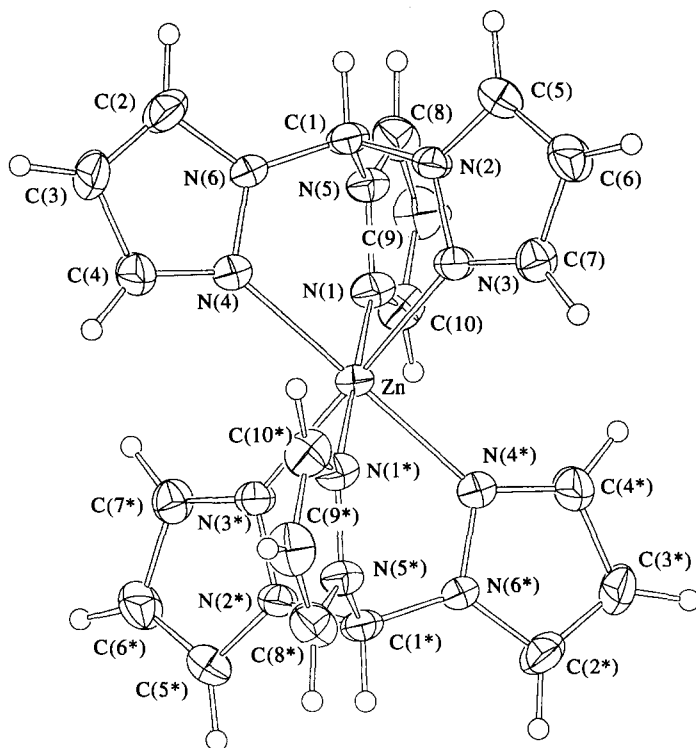


Fig. 1. ORTEP (30% probability) plot of **I** giving atom numbering.

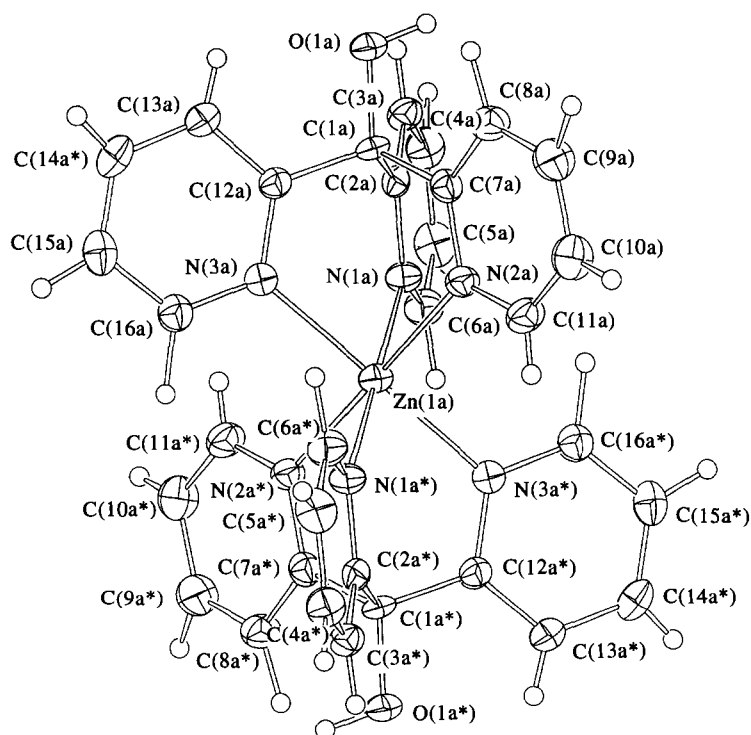


Fig. 2. ORTEP (30% probability) plot of **II** giving atom numbering. An ORTEP plot of the other independent molecule has been deposited.

Table 1. Bond lengths (Å) for **I**

N(2)—Zn	2.122(4)	N(4)—Zn	2.143(4)
N(6)—Zn	2.144(4)	N(2)—N(1)	1.352(5)
C(1)—N(1)	1.443(7)	C(2)—N(1)	1.333(6)
C(4)—N(2)	1.317(6)	N(4)—N(3)	1.357(5)
C(1)—N(3)	1.439(6)	C(5)—N(3)	1.346(6)
C(7)—N(4)	1.309(6)	N(6)—N(5)	1.358(5)
C(1)—N(5)	1.443(6)	C(8)—N(5)	1.354(6)
C(10)—N(6)	1.320(6)	C(3)—C(2)	1.345(8)
C(4)—C(3)	1.389(7)	C(6)—C(5)	1.352(7)
C(7)—C(6)	1.402(7)	C(9)—C(8)	1.336(8)
C(10)—C(9)	1.407(7)	O(1)—N(7)	1.075(31)
O(2)—N(7)	1.361(27)	O(3)—N(7)	1.226(24)
O(4)—N(7)	1.184(21)	O(5)—N(7)	1.252(24)
O(6)—N(7)	1.152(21)		

Table 2. Bond angles (°) for **I**

N(4)—Zn—N(2)	85.1(2)	N(6)—Zn—N(2)	84.4(2)
N(6)—Zn—N(4)	83.2(2)	C(1)—N(1)—N(2)	120.2(4)
C(2)—N(1)—N(2)	112.2(4)	C(2)—N(1)—C(1)	127.6(4)
N(1)—N(2)—Zn	117.5(3)	C(4)—N(2)—Zn	138.4(4)
C(4)—N(2)—N(1)	104.0(4)	C(1)—N(3)—N(4)	120.2(3)
C(5)—N(3)—N(4)	110.6(4)	C(5)—N(3)—C(1)	129.1(4)
N(3)—N(4)—Zn	116.9(3)	C(7)—N(4)—Zn	137.5(3)
C(7)—N(4)—N(3)	105.6(4)	C(1)—N(5)—N(6)	120.1(4)
C(8)—N(5)—N(6)	110.5(4)	C(8)—N(5)—C(1)	128.8(4)
N(5)—N(6)—Zn	116.9(3)	C(10)—N(6)—Zn	136.9(4)
N(2)—Zn—N(4) <sup>i</sup>	94.8(2)	N(2)—Zn—N(6) <sup>i</sup>	95.6(2)
N(4)—Zn—N(6) <sup>i</sup>	96.8(2)		

$$i = 1 - x, -y, -z.$$

hydroxyl groups of the ligands, the nitrate groups and the water molecules.

The coordination of the tripodal ligands in both structures is N, N', N''. An alternative N, N', O coordination for ligand L<sub>2</sub>, with two pyridyl N atoms and the hydroxyl O atom bound, has been reported for the bis(L<sub>2</sub>)ruthenium(II) complex.<sup>12</sup> In the cobalt(III) complex, both ligands adopt the N, N', N'' coordination mode observed in the present structures.<sup>13</sup>

The geometry about zinc is close to octahedral in each structure. The intraligand N—Zn—N angles average to 84.2° in **I** and to 84.6° in **II**. The Zn—N bond lengths are similar in the two structures, averaging 2.136 Å in **I** and 2.148 Å in **II**, though in each there is substantial variation in individual bond lengths, ranging over 2.122 to 2.144 Å in **I** and 2.122 to 2.174 Å in **II**. The bond lengths are

all substantially shorter than in hexakis(imidazole)zinc(II) where the average is 2.193 Å and the range 2.183–2.196 Å.<sup>14</sup> The shorter bonds probably result from the absence, in a tripodal ligand, of the interligand repulsion that occurs between three unidentate ligands. The aromatic rings do not deviate significantly from planarity in either structure but the Zn atoms lie up to 0.3 Å out of these planes. Similar bond lengths and angles were observed in the two other bis(tripod)zinc(II) complexes. In [Zn{(pz)<sub>2</sub>(py)CH<sub>2</sub>}(NO<sub>3</sub>)<sub>2</sub>], the monoclinic form of which is approximately isostructural with **I**, the Zn—N bond lengths range from 2.121 to 2.163 Å and average 2.141 Å,<sup>5</sup> and in [Zn{P(py)<sub>3</sub>}(NO<sub>3</sub>)<sub>2</sub>] the range is 2.152 to 2.178 Å and the average is 2.165 Å.<sup>6</sup> The bond lengths and angles and the variability in M—N bond lengths are also similar to those in the cobalt(II)

Table 3. Bond lengths (Å) for II

N(1a)—Zn(1a)	2.122(4)	N(2a)—Zn(1a)	2.174(3)
N(3a)—Zn(1a)	2.149(3)	C(2a)—N(1a)	1.343(4)
C(6a)—N(1a)	1.340(6)	C(7a)—N(2a)	1.334(4)
C(11a)—N(2a)	1.336(7)	C(12a)—N(3a)	1.343(4)
C(16a)—N(3a)	1.345(5)	C(2a)—C(1a)	1.542(6)
C(7a)—C(1a)	1.544(6)	C(12a)—C(1a)	1.518(5)
O(1a)—C(1a)	1.403(4)	C(3a)—C(2a)	1.376(7)
C(4a)—C(3a)	1.394(7)	C(5a)—C(4a)	1.356(6)
C(6a)—C(5a)	1.365(8)	C(8a)—C(7a)	1.385(5)
C(9a)—C(8a)	1.376(8)	C(10a)—C(9a)	1.367(7)
C(11a)—C(10a)	1.363(6)	C(13a)—C(12a)	1.379(5)
C(14a)—C(13a)	1.372(6)	C(15a)—C(14a)	1.352(6)
C(16a)—C(15a)	1.375(6)	N(1b)—Zn(1b)	2.136(3)
N(2b)—Zn(1b)	2.168(4)	N(3b)—Zn(1b)	2.140(3)
C(2b)—N(1b)	1.346(5)	C(3b)—N(1b)	1.326(6)
C(7b)—N(2b)	1.337(4)	C(11b)—N(2b)	1.348(7)
C(12b)—N(3b)	1.334(4)	C(16b)—N(3b)	1.345(5)
C(2b)—C(1b)	1.536(6)	C(7b)—C(1b)	1.524(7)
C(12b)—C(1b)	1.551(6)	O(1b)—C(1b)	1.400(4)
C(6b)—C(2b)	1.375(6)	C(4b)—C(3b)	1.365(7)
C(5b)—C(4b)	1.358(8)	C(6b)—C(5b)	1.382(9)
C(8b)—C(7b)	1.378(6)	C(9b)—C(8b)	1.369(9)
C(10b)—C(9b)	1.386(6)	C(11b)—C(10b)	1.349(7)
C(13b)—C(12b)	1.382(7)	C(14b)—C(13b)	1.383(7)
C(15b)—C(14b)	1.363(6)	C(16b)—C(15b)	1.379(7)
O(2a)—N(4a)	1.200(7)	O(3a)—N(4a)	1.189(8)
O(4a)—N(4a)	1.245(9)	O(2b)—N(4b)	1.245(7)
O(3b)—N(4b)	1.226(6)	O(4b)—N(4b)	1.229(6)

[Co{HB(pz)<sub>3</sub>}<sub>2</sub>] and [Co{HB(3-isopropyl-pz)(5-isopropyl-pz)<sub>2</sub>}<sub>2</sub>], as are the deviations of the metal from the pyrazol-1-yl planes.<sup>15,16</sup>

The closest contacts between the ligands within each complex are 3.83 Å (C···C) and 3.65 Å (C···H) for I and 3.41 Å (C···C) and 3.07 Å (C···H) for II, in each case substantially longer than the corresponding van der Waals radii sums of 3.00 Å (C···C) and 2.70 Å (C···H), respectively. Thus, there are no close contacts between the ligands that might mitigate significantly against formation of the bis(ligand) complexes. This is borne out by the observation of shorter Zn—N bond lengths in all of the bis(tripod)zinc(II) structures than are found for the hexakis(imidazole)zinc(II) complex. The substantially closer C···H contacts seen in II arise because the six-membered pyridine rings orient the hydrogen atom adjacent to the coordinated nitrogen atom more directly toward the other ligands.

### CONCLUSIONS

Trofimenko and colleagues have shown in a series of papers,<sup>16–18</sup> how substituents on the pyrazol-1-

yl rings can prevent formation of [M(tripod)<sub>2</sub>]<sup>x+</sup> complexes. It appears from the present study that in order to obtain complexes of the type [Zn(tripod)L]<sup>x+</sup>, where L is dihydrooroate or carbamyl aspartate, that substituted tripod ligands need to be employed. However, others have had success in producing similar complexes in which L is nitrate, a particularly poor ligand.<sup>4,6</sup> In one case the tripodal ligand was anionic rather than neutral,<sup>4</sup> as in the examples described above, and this may have a bearing on the relative stability of [M(tripod ligand)<sub>2</sub>]<sup>x+</sup> and [M(tripod ligand)L]<sup>x+</sup> complexes.

The solubility of different complexes may also have a bearing on the products obtained. Coordinate bonds to Zn are generally labile and, therefore, the least soluble products are generally those that are obtained. However, in the present study, tridentate ligands are used and the chelate effect would be expected to substantially decrease the lability of the complexes. Indeed, it would be anticipated that on this basis, and given the lack of strong interligand repulsions, that the bis(tripod)zinc(II) complexes would be the thermodynamically preferred products.

Table 4. Bond angles (°) for II

N(2a)—Zn(1a)—N(1a)	83.8(1)	N(3a)—Zn(1a)—N(1a)	84.5(1)
N(3a)—Zn(1a)—N(2a)	84.7(1)	C(2a)—N(1a)—Zn(1a)	120.1(3)
C(6a)—N(1a)—Zn(1a)	121.2(3)	C(6a)—N(1a)—C(2a)	118.6(4)
C(7a)—N(2a)—Zn(1a)	119.1(3)	C(11a)—N(2a)—Zn(1a)	122.1(2)
C(11a)—N(2a)—C(7a)	118.3(3)	C(12a)—N(3a)—Zn(1a)	121.0(2)
C(16a)—N(3a)—Zn(1a)	120.4(2)	C(16a)—N(3a)—C(12a)	118.6(3)
C(7a)—C(1a)—C(2a)	112.5(3)	C(12a)—C(1a)—C(2a)	110.0(3)
C(12a)—C(1a)—C(7a)	108.4(4)	O(1a)—C(1a)—C(2a)	110.0(3)
O(1a)—C(1a)—C(7a)	110.0(3)	O(1a)—C(1a)—C(12a)	105.7(3)
C(1a)—C(2a)—N(1a)	118.0(4)	C(3a)—C(2a)—N(1a)	121.6(4)
C(3a)—C(2a)—C(1a)	120.3(3)	C(4a)—C(3a)—C(2a)	118.4(3)
C(5a)—C(4a)—C(3a)	119.8(5)	C(6a)—C(5a)—C(4a)	118.7(5)
C(5a)—C(6a)—N(1a)	122.8(4)	C(1a)—C(7a)—N(2a)	118.0(3)
C(8a)—C(7a)—N(2a)	121.3(4)	C(8a)—C(7a)—C(1a)	120.5(3)
C(9a)—C(8a)—C(7a)	119.4(4)	C(10a)—C(9a)—C(8a)	119.0(4)
C(11a)—C(10a)—C(9a)	118.6(5)	C(10a)—C(11a)—N(2a)	123.3(4)
C(1a)—C(12a)—N(3a)	116.7(3)	C(13a)—C(12a)—N(3a)	120.9(3)
C(13a)—C(12a)—C(1a)	122.4(3)	C(14a)—C(13a)—C(12a)	119.5(3)
C(15a)—C(14a)—C(13a)	119.8(4)	C(16a)—C(15a)—C(14a)	118.7(4)
C(15a)—C(16a)—N(3a)	122.4(4)	N(2b)—Zn(1b)—N(1b)	85.9(1)
N(3b)—Zn(1b)—N(1b)	84.2(1)	N(3b)—Zn(1b)—N(2b)	84.3(1)
C(2b)—N(1b)—Zn(1b)	118.7(3)	C(3b)—N(1b)—Zn(1b)	122.0(3)
C(3b)—N(1b)—C(2b)	119.2(3)	C(7b)—N(2b)—Zn(1b)	120.2(3)
C(11b)—N(2b)—Zn(1b)	121.9(2)	C(11b)—N(2b)—C(7b)	117.9(4)
C(12b)—N(3b)—Zn(1b)	119.6(3)	C(16b)—N(3b)—Zn(1b)	121.0(3)
C(16b)—N(3b)—C(12b)	119.3(4)	C(7b)—C(1b)—C(2b)	110.0(4)
C(12b)—C(1b)—C(2b)	111.5(4)	C(12b)—C(1b)—C(7b)	109.4(3)
O(1b)—C(1b)—C(2b)	110.0(3)	O(1b)—C(1b)—C(7b)	106.1(4)
O(1b)—C(1b)—C(12b)	109.6(3)	C(1b)—C(2b)—N(1b)	118.7(3)
C(6b)—C(2b)—N(1b)	120.4(4)	C(6b)—C(2b)—C(1b)	120.9(4)
C(4b)—C(3b)—N(1b)	123.4(4)	C(5b)—C(4b)—C(3b)	117.7(6)
C(6b)—C(5b)—C(4b)	120.2(5)	C(5b)—C(6b)—C(2b)	119.1(4)
C(1b)—C(7b)—N(2b)	116.8(4)	C(8b)—C(7b)—N(2b)	122.2(5)
C(8b)—C(7b)—C(1b)	121.0(4)	C(9b)—C(8b)—C(7b)	118.9(4)
C(10b)—C(9b)—C(8b)	119.2(5)	C(11b)—C(10b)—C(9b)	118.7(6)
C(10b)—C(11b)—N(2b)	123.1(4)	C(1b)—C(12b)—N(3b)	117.9(4)
C(13b)—C(12b)—N(3b)	121.4(4)	C(13b)—C(12b)—C(1b)	120.7(3)
C(14b)—C(13b)—C(12b)	118.5(4)	C(15b)—C(14b)—C(13b)	120.5(5)
C(16b)—C(15b)—C(14b)	118.0(5)	C(15b)—C(16b)—N(3b)	122.3(4)
N(1a)—Zn—N(2a) <sup>i</sup>	96.2(1)	N(1a)—Zn—N(3a) <sup>i</sup>	95.6(1)
N(2a)—Zn—N(3a) <sup>i</sup>	95.3(1)	N(1b)—Zn—N(2b) <sup>ii</sup>	94.1(1)
N(1b)—Zn—N(3b) <sup>ii</sup>	95.8(1)	N(2b)—Zn—N(3b) <sup>ii</sup>	95.7(1)
O(3a)—N(4a)—O(2a)	121.7(7)	O(4a)—N(4a)—O(2a)	120.5(6)
O(4a)—N(4a)—O(3a)	117.8(6)	O(3b)—N(4b)—O(2b)	119.3(5)
O(4b)—N(4b)—O(2b)	119.9(4)	O(4b)—N(4b)—O(3b)	120.8(5)

$$i = 2 - x, 1 - y, 2 - z; ii = 2 - x, 1 - y, 3 - z.$$

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