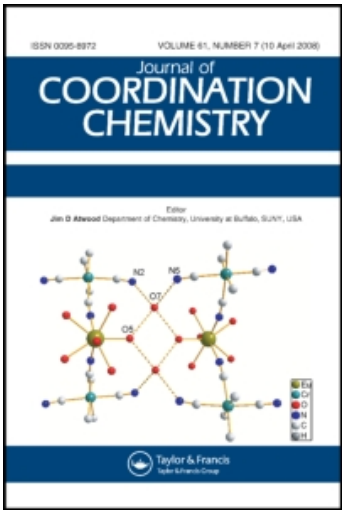

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Synthesis and Crystal Structures of Two Zinc(II) Complexes with the Tripodal Ligand Tris(2-Benzimidazolymethyl)Amine

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SYNTHESIS AND CRYSTAL STRUCTURES OF TWO ZINC(II) COMPLEXES WITH THE TRIPODAL LIGAND TRIS(2-BENZIMIDAZOLYMETHYL)AMINE

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This article reports the synthesis and crystal structures of two new mononuclear Zinc(II) complexes, $[Zn_2(NTB)_2(N_3)_2](NO_3)_2 \cdot 2CH_3OH$ (**1**) and $[Zn_2(NTB)_2(SCN)_2](NO_3)_2 \cdot 2CH_3OH \cdot H_2O$ (**2**). Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, $a = 13.743(4)$, $b = 14.374(4)$, $c = 14.443(5)$ Å; $\alpha = 77.053(5)$, $\beta = 81.824(5)$, $\gamma = 88.959(6)^\circ$; $Z = 2$; $R1 = 0.0418$, $wR2 = 0.0889$. Complex **2** also crystallizes in the triclinic system, space group $P\bar{1}$, $a = 12.203(10)$, $b = 14.430(12)$, $c = 18.541(15)$Å; $\alpha = 72.712(15)$, $\beta = 85.039(15)$, $\gamma = 73.610(14)$; $Z = 2$; $R1 = 0.0771$, $wR2 = 0.1288$. In both cases the central zinc(II) metal ions are coordinated to the four nitrogen atoms of NTB and a nitrogen atom of N_3^- (**1**) or SCN^- (**2**) to form distorted trigonal bipyramidal coordination spheres.

Keywords: Zinc; Tris(2-benzimidazolymethyl)amine; Crystal structure

INTRODUCTION

Zinc is the active metal in the largest number of metalloproteins found in Nature. While the biologically function of zinc in these proteins varies considerably, active sites exhibit a common structural motif [1]. Thus, most active sites are comprised of a pseudotetrahedral zinc centre containing a combination of nitrogen, oxygen, and/or sulfur donors, originating from solvent water, and/or histidine, tyrosine, aspartic or glutamic acids, and cysteine residues of the protein [2]. Histidine (imidazole) plays key roles in the catalytic functions of almost all of the metalloenzymes. Therefore, complexes with imidazole ligands are of interest as they may be good models for the active sites of zinc proteins. Here, the synthetically accessible polydentate benzimidazole ligand NTB (NTB = tris(2-benzimidazolymethyl)amine) is used to construct potential models of zinc proteins.

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EXPERIMENTAL

Starting Materials

NTB was synthesized by published procedure [3]. All other chemicals were of reagent grade and used as commercially obtained.

Synthesis of $[Zn_2(NTB)_2(N_3)_2](NO_3)_2 \cdot 2CH_3OH$ (1)

NTB (0.0610 g, 0.15 mmol) was dissolved in 10 mL of hot methanol and added to a solution of $Zn(NO_3)_2 \cdot 4H_2O$ (0.0392 g, 0.15 mmol) in 5 mL of methanol. To this solution was added an aqueous solution (1 mL) of NaN_3 (0.0098 g, 0.15 mmol). The resulting solution was allowed to stand for several days at room temperature, when crystals of Complex **1** were obtained as colourless prisms. *Anal*. found: C, 49.17; H, 4.30; N, 25.06. Calc. for $C_{50}H_{50}N_{22}O_8Zn_2$ (%): C, 49.31; H, 4.14; N, 25.30.

Synthesis of $[Zn_2(NTB)_2(SCN)_2](NO_3)_2 \cdot 2CH_3OH \cdot H_2O$ (2)

The synthesis method for **2** was similar to that of **1** except that NaN_3 was replaced by KSCN. *Anal*. found: C, 48.99; H, 4.36; N, 19.76. Calc. for $C_{52}H_{52}N_{18}O_9S_2Zn_2$ (%): C, 49.26; H, 4.13; N, 19.88.

Physical Measurements

Elemental analyses (C, H, N) were performed on a Perkin Elmer 240 instrument. Infrared spectra were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–600 cm^{-1} using KBr pellets.

X-ray Crystallography

The two complexes were mounted on a computer-controlled Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by a least-squares fit. For **1**, a total of 9153 independent reflections was collected, of which 7878 were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. For **2**, a total of 9065 independent reflections was collected, of which 8165 were considered as observed [$I > 2\sigma(I)$]. A SADABS absorption correction was applied. The structures was solved by direct methods (SHELXL-97 and SHELXS-97) [4], and refined by full matrix least-squares on F^2. Crystallographic data are listed in Table I. Final selected atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are listed in Table II.

RESULTS AND DISCUSSION

Crystal Structures

The structures of the two complexes are shown in Fig. 1. Selected bond distances and angles are listed in Table III. The two complexes are crystallographically

TABLE I Crystallographic data for the two complexes

Empirical formula	$C_{50}H_{50}N_{22}O_8Zn_2$	$C_{52}H_{52}N_{18}O_9S_2Zn_2$
Fw	1217.86	1267.98
Crystal dimensions (mm)	$0.30 \times 0.25 \times 0.20$	$0.30 \times 0.25 \times 0.20$
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.743(4)	12.203(10)
b (Å)	14.374(4)	14.430(12)
c (Å)	14.443(5)	18.541(15)
α (°)	77.053(5)	72.712(15)
β (°)	81.824(5)	85.039(15)
γ (°)	88.959(6)	73.610(14)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.470	1.408
λ (MoKα) (Å)	0.71073	0.71073
F (000)	1256	1308
R_1	0.0418	0.0771
wR_2	0.0889	0.1288

TABLE II Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^4$) (a) for Complex **1**; (b) for Complex **2**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
(a)				
Zn(1)	4319(1)	3001(1)	3360(1)	36(1)
N(1)	5112(3)	4283(2)	1976(2)	37(1)
N(2)	4969(2)	2296(2)	2390(2)	37(1)
N(3)	5849(3)	2194(3)	1013(3)	49(1)
N(4)	5238(3)	3724(2)	3934(2)	40(1)
N(5)	6251(3)	4906(3)	3908(3)	51(1)
N(6)	3199(3)	3856(2)	2895(2)	35(1)
N(7)	2614(3)	5129(2)	1982(2)	40(1)
N(17)	3645(3)	1920(3)	4379(3)	51(1)
N(18)	3291(3)	1912(3)	5135(4)	55(1)
N(19)	2894(4)	1859(4)	5938(4)	85(2)
C(1)	5855(3)	3783(3)	1467(3)	45(1)
C(2)	5550(3)	2754(3)	1616(3)	40(1)
C(3)	5441(3)	1294(3)	1409(3)	47(1)
C(4)	5488(4)	453(4)	1074(4)	68(2)
C(5)	4974(4)	− 315(4)	1665(5)	74(2)
C(6)	4451(4)	− 263(3)	2548(4)	63(2)
C(7)	4409(3)	567(3)	2866(3)	46(1)
C(8)	4902(3)	1356(3)	2278(3)	36(1)
C(9)	5512(3)	4976(3)	2430(3)	48(1)
C(10)	5672(3)	4526(3)	3426(3)	40(1)
C(11)	5551(3)	3582(3)	4838(3)	41(1)
C(12)	5327(4)	2879(3)	5664(3)	52(1)
C(13)	5755(4)	2948(4)	6454(4)	61(2)
C(14)	6412(5)	3683(4)	6415(4)	69(2)
C(15)	6647(4)	4384(4)	5599(4)	64(2)
C(16)	6196(4)	4326(3)	4821(4)	50(1)
C(17)	4319(3)	4653(3)	1436(3)	40(1)
C(18)	3377(3)	4544(3)	2106(3)	34(1)
C(19)	2244(3)	4001(3)	3308(3)	36(1)
C(20)	1683(3)	3517(3)	4138(3)	45(1)
C(21)	770(4)	3862(3)	4380(4)	54(1)
C(22)	407(4)	4673(4)	3817(4)	61(1)
C(23)	951(4)	5167(3)	2988(3)	52(1)
C(24)	1873(3)	4813(3)	2738(3)	38(1)

(*continued*)

TABLE II (Continued)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
(b)				
Zn(1)	2862(1)	2402(1)	763(1)	48(1)
S(1)	− 304(3)	1181(3)	1682(2)	117(2)
N(1)	4112(6)	1983(6)	1548(4)	46(2)
N(2)	5614(7)	2178(6)	1990(4)	54(2)
N(3)	2211(7)	3948(6)	424(4)	44(2)
N(4)	2261(7)	5447(7)	− 275(4)	55(2)
N(5)	3401(7)	1615(6)	− 18(4)	47(2)
N(6)	4592(7)	1128(6)	− 895(4)	55(2)
N(7)	4425(7)	3024(6)	76(4)	50(2)
N(8)	1560(8)	1887(6)	1325(5)	57(3)
C(1)	4273(9)	1382(7)	2311(5)	48(3)
C(2)	3674(9)	768(7)	2760(5)	55(3)
C(3)	4062(11)	269(8)	3460(6)	73(3)
C(4)	5010(12)	384(9)	3749(6)	79(4)
C(5)	5610(10)	1014(9)	3305(6)	69(3)
C(6)	5216(9)	1509(7)	2573(6)	49(3)
C(7)	4922(9)	2427(7)	1408(5)	45(2)
C(8)	5052(8)	3171(7)	664(5)	52(3)
C(9)	3832(9)	3969(8)	− 475(5)	63(3)
C(10)	2790(9)	4449(9)	− 109(5)	49(3)
C(11)	1303(9)	5618(8)	170(5)	47(3)
C(12)	488(10)	6491(9)	235(6)	65(3)
C(13)	− 354(10)	6365(9)	741(7)	71(3)
C(14)	− 424(9)	5406(10)	1168(5)	63(3)
C(15)	383(9)	4526(8)	1113(5)	48(3)
C(16)	1276(9)	4633(8)	606(5)	43(2)
C(17)	2995(10)	957(8)	− 282(5)	52(3)
C(18)	2031(10)	594(9)	− 91(6)	74(3)
C(19)	1878(10)	− 69(9)	− 467(6)	70(3)
C(20)	2623(11)	− 339(8)	− 1006(6)	69(3)
C(21)	3566(11)	13(8)	− 1217(6)	71(3)
C(22)	3755(10)	659(8)	− 842(6)	56(3)
C(23)	4337(9)	1691(8)	− 405(5)	55(3)
C(24)	5087(9)	2252(7)	− 274(5)	56(3)
C(25)	820(10)	1564(8)	1461(5)	58(3)

isostructural and present similar structures. It is interesting that the structure shows two crystallographically independent but chemical identical molecules. For clarity, we only label one zinc in every complex. In both cases the central zinc(II) ions are coordinated to four nitrogen atoms of NTB and a nitrogen atom of N_3^-(**1**) or SCN^-(**2**) to form a distorted trigonal bipyramid. NTB behaves as a tetradentate ligand where the three imidazolic nitrogen atoms are coordinated to the zinc(II) atom with Zn–N distances ranging from 2.010(4) to 2.046(3) Å for **1** and 2.037(7) to 2.064(8) Å for **2**. The bond distance between zinc and the tertiary nitrogen atom of NTB is 2.527(3) Å for **1** and 2.435(7) Å for **2**, respectively, much longer than normal bond distances. This significant elongation is also observed in other zinc complexes of NTB, i.e., 2.518 Å [5], 2.540 Å [6], 2.549 Å [7]. A nitrogen atom from N_3^-(**1**) or SCN^-(**2**) occupies the fifth position with a normal Zn–N distance. The average bond angle formed by the tertiary nitrogen atom (apical nitrogen), the zinc atom and the trigonal basal nitrogen atoms (the three imidazolic nitrogen atoms) is 74.61° for **1** and 74.97° for **2**. The zinc atom deviates 0.537 Å in **1** and 0.533 Å in **2** from the basal plane, repectively. Hydrogen bonds are located between the methanol (water) molecule and the ligand, as well as the NO_3^- anion and the ligand.

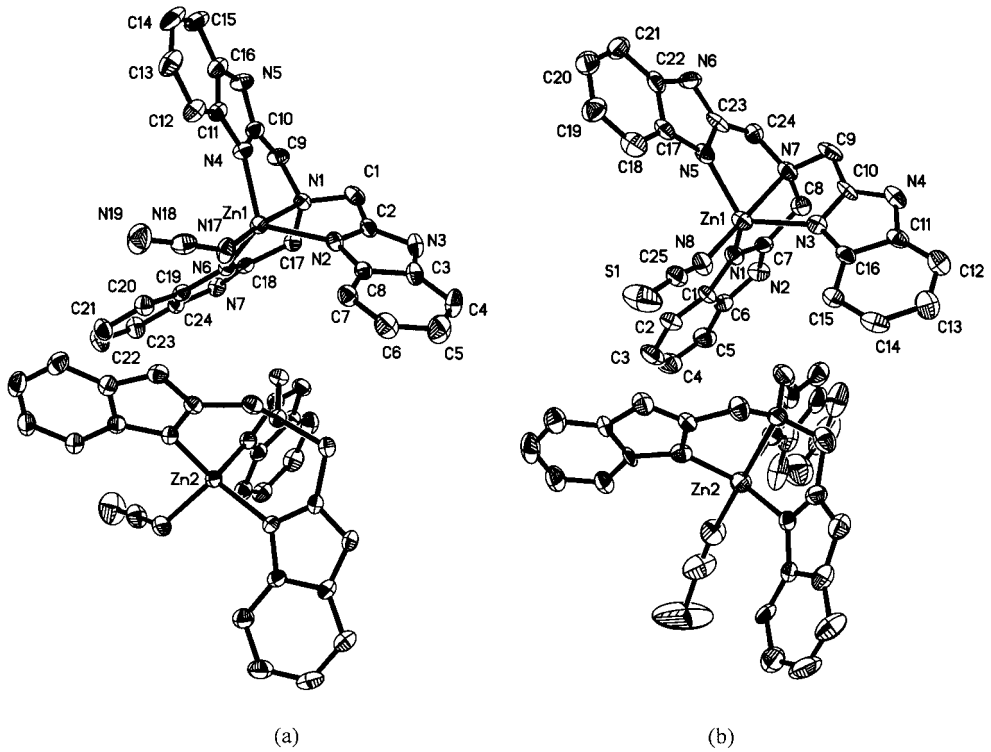

FIGURE 1 (a) ORTEP drawing of Complex **1**; (b) ORTEP drawing of Complex **2**.

TABLE III (a) Selected bond lengths (Å) and angles (°) for Complex **1**; (b) Selected bond lengths (Å) and angles (°) for Complex **2**

(a)			
Zn(1)–N(2)	2.010(4)	N(3)–C(3)	1.386(5)
Zn(1)–N(17)	2.019(4)	N(4)–C(10)	1.321(5)
Zn(1)–N(4)	2.023(3)	N(4)–C(11)	1.402(5)
Zn(1)–N(6)	2.046(3)	N(5)–C(10)	1.327(5)
Zn(1)–N(1)	2.527(3)	N(5)–C(16)	1.386(6)
N(1)–C(1)	1.448(5)	N(6)–C(18)	1.326(5)
N(1)–C(17)	1.454(5)	N(6)–C(19)	1.395(5)
N(1)–C(9)	1.462(5)	N(7)–C(18)	1.339(5)
N(2)–C(2)	1.326(5)	N(7)–C(24)	1.383(5)
N(2)–C(8)	1.402(5)	N(17)–C(18)	1.128(5)
N(3)–C(2)	1.332(5)	N(18)–C(19)	1.195(6)
N(2)–Zn(1)–N(17)	101.32(15)	C(1)–N(1)–Zn(1)	104.1(2)
N(2)–Zn(1)–N(4)	115.53(15)	C(17)–N(1)–Zn(1)	105.0(2)
N(17)–Zn(1)–N(4)	110.16(16)	C(9)–N(1)–Zn(1)	104.6(2)
N(2)–Zn(1)–N(6)	113.52(13)	C(2)–N(2)–Zn(1)	120.6(3)
N(17)–Zn(1)–N(6)	104.69(15)	C(8)–N(2)–Zn(1)	133.9(3)
N(4)–Zn(1)–N(6)	110.63(14)	C(10)–N(4)–Zn(1)	120.7(3)
N(2)–Zn(1)–N(1)	74.90(13)	C(11)–N(4)–Zn(1)	133.9(3)
N(17)–Zn(1)–N(1)	174.90(14)	C(18)–N(6)–Zn(1)	119.7(3)
N(4)–Zn(1)–N(1)	74.75(13)	C(19)–N(6)–Zn(1)	133.6(3)
N(6)–Zn(1)–N(1)	74.19(12)	N(18)–N(17)–Zn(1)	129.9(3)

(*continued*)

TABLE III Continued

(b)			
Zn(1)–N(8)	2.020(9)	N(3)–C(16)	1.372(11)
Zn(1)–N(1)	2.037(7)	N(4)–C(10)	1.354(11)
Zn(1)–N(5)	2.052(8)	N(4)–C(11)	1.378(11)
Zn(1)–N(3)	2.064(8)	N(5)–C(23)	1.309(11)
Zn(1)–N(7)	2.435(7)	N(5)–C(17)	1.403(11)
S(1)–C(25)	1.596(12)	N(6)–C(23)	1.353(12)
N(1)–C(7)	1.293(10)	N(6)–C(22)	1.357(12)
N(1)–C(1)	1.418(10)	N(7)–C(24)	1.464(11)
N(2)–C(7)	1.328(10)	N(7)–C(8)	1.482(10)
N(2)–C(6)	1.374(10)	N(7)–C(9)	1.473(11)
N(3)–C(10)	1.319(10)	N(8)–C(25)	1.107(11)
N(8)–Zn(1)–N(1)	105.2(3)	C(7)–N(1)–Zn(1)	118.7(6)
N(8)–Zn(1)–N(5)	105.6(3)	C(1)–N(1)–Zn(1)	135.4(7)
N(1)–Zn(1)–N(5)	109.0(3)	C(10)–N(3)–Zn(1)	116.0(7)
N(8)–Zn(1)–N(3)	104.4(3)	C(16)–N(3)–Zn(1)	136.0(7)
N(1)–Zn(1)–N(3)	110.7(3)	C(23)–N(5)–Zn(1)	119.7(7)
N(5)–Zn(1)–N(3)	120.7(3)	C(17)–N(5)–Zn(1)	135.4(7)
N(8)–Zn(1)–N(7)	179.5(3)	C(24)–N(7)–Zn(1)	106.7(5)
N(1)–Zn(1)–N(7)	75.3(3)	C(8)–N(7)–Zn(1)	104.0(5)
N(5)–Zn(1)–N(7)	74.1(3)	C(9)–N(7)–Zn(1)	103.2(6)
N(3)–Zn(1)–N(7)	75.5(3)	C(25)–N(8)–Zn(1)	162.0(10)

Spectroscopic Properties

IR spectra of **1** and **2** are similar and show strong absorption of NO_3^- at 1375 cm^{-1}. They both exhibit two absorption bands at 1610–1632 and 1590–1607 cm^{-1} which are assigned to the CN stretch of the imidazole ring. SCN^- (**1**) and N_3^- (**2**) are observed at 2100 and 2108 cm^{-1}, respectively.

Acknowledgments

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Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 185548 (**1**) and 185551 (**2**). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax:+44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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