КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A TRINUCLEAR Zn(II) COMPLEX:
[Zn₃L₂(μ₁,₁-N₃)₂I₂] [L = 2-[(3-DIMETHYLAMINOPROPYLIMINO)METHYL]-6-ETHOXYPHENOLATE]

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Reaction of zinc iodide, sodium azide and 2-[(3-dimethylaminopropylimino)methyl]-6-ethoxy-phenol (HL) results in the formation of a trinuclear complex $[Zn_3L_2(\mu_{1,1}-N_3)_2I_2]$. The complex is characterized by elemental analysis, IR spectroscopy, and X-ray crystallography. The complex possesses crystallographic two-fold rotation axis symmetry and crystallizes in the mono-clinic system, $C2/c$ space group, $a = 23.241(2)$ Å, $b = 10.849(1)$ Å, $c = 17.384(2)$ Å, $\beta = 120.868(1)°$, $V = 3762.4(6)$ Å^3, $Z = 4$. The molecule consists of two $[ZnL(N_3)I]$ units connected together by a central Zn atom. The terminal Zn atom is five-coordinated in a trigonal-bipyramidal geometry, and the central Zn atom is six-coordinated in an octahedral geometry. The Zn···Zn separation between the terminal and the central Zn atoms is 3.257(2) Å.

K e y w o r d s: Schiff base, azide, trinuclear, zinc, crystal structure.

Polynuclear zinc complexes have attracted much attention for their potential relevance as models of zinc-containing enzymes [1—4]. A number of hydrolases are known to contain two or more zinc atoms in close proximity at their respective active sites [5, 6]. Polynuclear zinc complexes with N- and O-donor ligands, with the Zn···Zn separation being less than 3.4 Å, are known to exist at the active sites of some enzymes, such as phospholipase *C* from *Bacillus cereus* and bovine lens leucine amin-opeptidase [7, 8]. A number of polynuclear zinc complexes have recently been reported, however, the azide-bridged polynuclear zinc complexes are very few [9—12]. The search in the Cambridge Crystallographic Database (version 5.31 with addenda up to February 26, 2010) [13] has revealed that azide-bridged trinuclear zinc complexes with Schiff bases have never been reported. In this paper, the synthesis and structure of a new azide-bridged trinuclear zinc complex with the Schiff base 2-[(3-dimethylaminopropylimino)methyl]-6-ethoxyphenol (HL, Scheme 1) is reported.
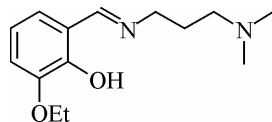
Scheme 1. Structural formula of HL

Experimental. Materials and methods. All chemicals were available commercially as analytical grade from Aldrich and were used without further purification. The C, H and N microanalyses were carried out using a Perkin-Elmer 240Q elemental analyzer. FT—IR spectra were recorded using KBr pellets with a Bio-Rad Digilab FTS-40 spectrometer.

Synthesis of HL. 3-Ethoxysalicylaldehyde (1.0 mmol, 166.2 mg) and *N,N*-dimethylpropyl-1,3-diamine (1.0 mmol, 102.2 mg) were mixed in 50 ml of the methanol solution and then stirred and re-

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fluxed for 30 min. The solvent was removed by distillation to give yellow oil of HL. Anal. Calcd. (%) for $C_{14}H_{22}N_2O_2$: C, 67.2; H, 8.9; N, 11.2. Found (%): C, 66.9; H, 8.9; N, 11.3. Characteristic IR data (cm^{-1}): 3450 (br, w, O—H), 1643 (s, C=N).

Synthesis of $[\mathbf{Zn_3L_2(\mu_{1,1}\text{-}N_3)_2I_2}]$. To a methanol solution (20 ml) containing HL (0.2 mmol, 50.0 mg) and sodium azide (0.2 mmol, 13.0 mg) ZnI_2 (0.2 mmol, 63.8 mg) was added. The mixture was stirred for 30 min at room temperature. The resulting clear solution was slowly evaporated to give colorless block-shaped crystals. Yield: 82 %. Anal. Calcd. (%) for $C_{28}H_{42}I_2N_{10}O_4Zn_3$: C, 32.6; H, 4.1; N, 13.6. Found (%): C, 32.2; H, 4.3; N, 13.8. Characteristic IR data (cm^{-1}): 2094 (vs, N_3), 1635 (s, C=N).

Caution! Azide salts are potentially explosive. Only small quantities of material should be prepared and handled with great care.

X-ray crystallography. The suitable single crystal of the complex was mounted on a glass fiber for data collection performed on a Bruker SMART 1000 CCD area diffractometer equipped with a graphite-monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) at 298 K. The unit cell dimensions were obtained with the least-squares refinements and the structure was solved by direct methods using the SHELXTL-97 program [14]. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. Hydrogen atoms in the complex were placed in the calculated positions and constrained to ride on their parent atoms. Multi-scan absorption correction was applied by using the SADABS program [15]. The crystallographic data and experimental details for structural analysis of the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2. CCDC-772557 for the complex contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: data_request@ccdc.cam.ac.uk.

Results and discussion. The molecular structure of the complex possesses crystallographic two-fold rotation axis symmetry. As shown in Fig. 1, three Zn centers [Zn2, Zn1, and Zn2A, symmetry code for A: 2–x, y, 1/2–z] are bridged by a total of two end-on azide ligands and two phenolate O atoms from two Schiff base ligands. The intramolecular Zn1···Zn2 distance is 3.257(2) Å.

T a b l e   1

Crystal Data and Structure Refinement for the Complex

Empirical formula	$C_{28}H_{42}I_2N_{10}O_4Zn_3$	D_c (g/cm^3)	1.823
Formula weight	1032.6	Absorption coefficient, mm^{-1}	3.585
Temperature, K	298(2)	$F(000)$	2032
Wavelength, Å	0.71073	θ range, deg.	2.04/27.00
Crystal shape/color	Block/colorless	Index ranges (h, k, l)	–29/29, –13/13, –22/22
Crystal size, mm	$0.27 \times 0.23 \times 0.23$	R_{int}	0.0333
Crystal system	Monoclinic	Reflections collected	15239
Space group	$C2/c$	Independent reflections	4073
a, Å	23.241(2)	Observed reflections with $I > 2\sigma(I)$	3319
b, Å	10.849(1)	Min. and max. transmission	0.444/0.493
c, Å	17.384(2)	Goodness-of-fit on F^2	1.039
β, deg.	120.868(1)	R_1, wR_2 [$I > 2\sigma(I)$)^a	0.0305, 0.0691
V, Å^3	3762.4(6)	R_1, wR_2 (all data)^a	0.0413, 0.0738
Z	4	Large diff. peak and hole, e/Å^3	0.684 and –0.577

$^aR_1 = \sum||F_0| - |F_c||/\sum|F_0|$, $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

Selected Bond Distances and Angles

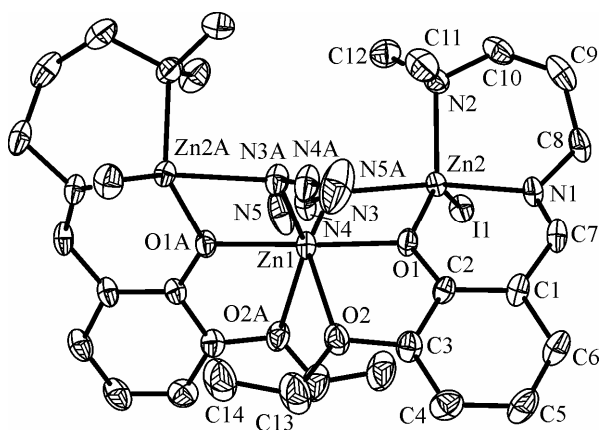| Distances, Å		Angles, deg.					
Zn1—O1	2.017(2)	O1—Zn1—O1A	177.9(1)	N2—Zn2—N3	95.0(1)	N3—Zn1—O2	146.2(1)
Zn1—N3	2.058(3)	O1—Zn1—N3	78.9(1)	N1—Zn2—I1	99.0(1)	O1—Zn2—N1	84.5(1)
Zn2—N1	2.108(3)	O1A—Zn1—O2	108.6(1)	N3—Zn2—I1	97.6(1)	N1—Zn2—N2	90.7(1)
Zn2—N3	2.184(3)	N3A—Zn1—O2	92.8(1)	O1—Zn1—N3A	99.9(1)	N1—Zn2—N3	159.2(1)
Zn1—O2	2.360(2)	O2—Zn1—O2A	78.9(1)	N3—Zn1—N3A	110.5(2)	O1—Zn2—I1	133.3(1)
Zn2—O1	2.070(2)	O1—Zn2—N2	115.7(1)	O1—Zn1—O2	73.1(1)	N2—Zn2—I1	110.8(1)
Zn2—N2	2.118(3)	O1—Zn2—N3	74.9(1)				
Zn2—I1	2.6145(10)						

Symmetry code for A: 2–*x*, *y*, 1/2–*z*.

The Zn1 atom is coordinated by two phenolate O and two ether O atoms from two Schiff base ligands and by two N atoms from two bridging azide ligands, forming a distorted octahedral geometry. The distortion of the coordination can be observed from the coordinate bond angles ranging from 73.1(1)° to 110.5(2)°. Three *trans* angles also deviate from the ideal value of 180° for a perfect octahedral geometry, ranging from 146.2(1) to 177.9(1)°. The distortion is mainly caused by the strain created by the five- and four-membered chelate rings (Zn1—O1—C2—C3—O2 and Zn1—O1—Zn2—N3).

The Zn2 atom is coordinated in a trigonal bipyramidal geometry with one phenolate O and one amine N atoms of a Schiff base ligand, one I atom defining the basal plane, one imine N atom of the Schiff base ligand, and one N atom of an azide ligand occupying the axial positions. The distortion of the trigonal bipyramidal coordination can also be observed from the coordinate bond angles. The three coordinate bond angles at the basal plane are 115.7(1)°, 133.3(1)°, and 110.8(1)° respectively, which deviate from the ideal values for a perfect trigonal bipyramidal geometry of 120°. The N1—Zn2—N3 bond angle of 159.2(1)° also deviates from the ideal value of 180°.

A close examination of the structure reveals that the Zn—O and Zn—N bond lengths can be considered as normal in comparison with similar few examples reported in the literature [9—12].

Molecular packing of the complex is shown in Fig. 2. There is a weak π···π stacking interaction between the adjacent benzene rings and the relevant distances are $Cg1 \cdots Cg1^i = 5.622$ Å and $Cg1 \cdots Cg1^i_{perp} = 4.392$ Å [symmetry code (i): 1/2–*x*, 1/2–*y*, 1–*z*; Cg1 is the centroid of the C1—C6 benzene ring and $Cg1 \cdots Cg1^i_{perp}$ is the perpendicular distance from the Cg1 ring plane to the Cg1^i ring plane] [16]. There are no other obvious contacts among the molecules.

Conclusions. Metalloenzymes with zinc-containing polymetallic centers have attracted much attention in coordination chemistry and bioinorganic chemistry. A new trinuclear zinc complex has been prepared and characterized. It contains a rarely reported linear array of zinc atoms

Fig. 1. View of the molecular structure of the complex with 30 % thermal ellipsoids. Atoms labeled with the suffix A or unlabeled are at the symmetry position 2–*x*, *y*, 1/2–*z*
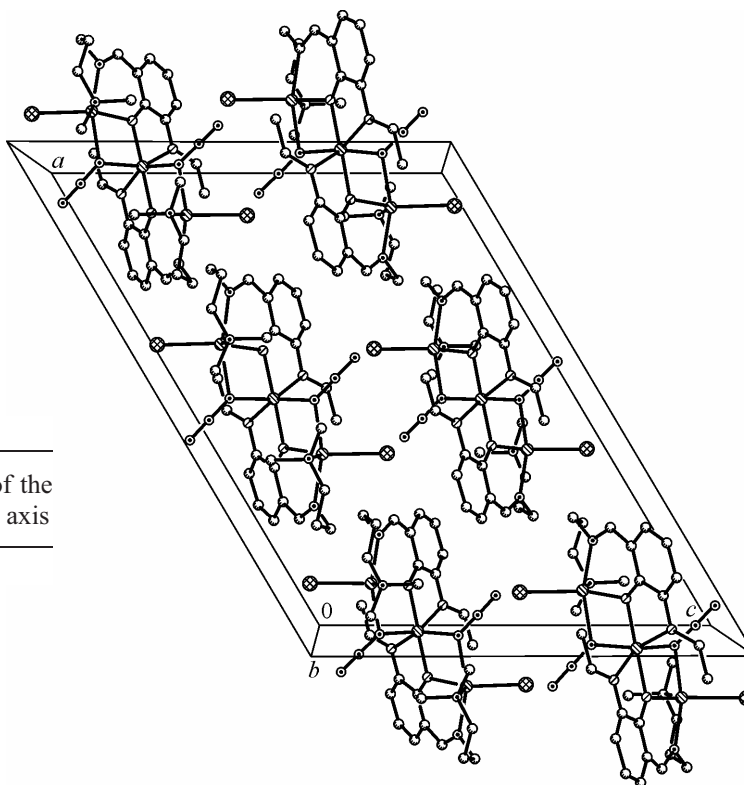
Fig. 2. Molecular packing of the complex viewed along the *b* axis

with phenolate and azide bridges. The complex may be used to mimic the active site of phospholipase *C* from *Bacillus cereus* and bovine lens leucine aminopeptidase.

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