КРАТКИЕ СООБЩЕНИЯ

CRYSTAL STRUCTURE OF A NOVEL PHENOLATO, AZIDO, AND ACETATO Co-BRIDGED TRINUCLEAR ZINC(II) COMPLEX DERIVED FROM 4-CHLORO-2-[(2-DIETHYLAMINOETHYLIMINO)METHYL]PHENOL

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A novel phenolato, azido, and acetato co-bridged trinuclear zinc(II) complex [Zn$_3$L$_2$(μ_2-CH$_3$COO)$_2$($\mu_{1,1}$-N$_3$)(N$_3$)], where L is the deprotonated form of 4-chloro-2-[(2-diethylamino-ethylimino)methyl]phenol, is prepared and characterized by elemental analysis, infrared spectrum, and single crystal X-ray determination. The complex crystallizes in the triclinic space group $P\bar{1}$, with unit cell dimensions $a = 12.7196(5)$ Å, $b = 13.6597(6)$ Å, $c = 13.7214(5)$ Å, $\alpha = 65.700(1)°$, $\beta = 83.429(1)°$, $\gamma = 63.545(1)°$, $V = 1938.4(1)$ Å^3, $Z = 2$, GOOF = 1.013, $R_1 = 0.0456$, and $wR_2 = 0.1032$. Structural analysis shows that the distances among the adjacent zinc atoms are 3.282(1) Å and 3.213(1) Å. The zinc atoms are in distorted square pyramidal and trigonal bipyramidal coordinations.

K e y w o r d s: Schiff base, trinuclear complex, zinc complex, crystal structure, X-ray crystallography.

Polynuclear complexes containing bridging ligands are of great interest because of their interesting molecular topologies as well as the fact that they may be designed with specific functionalities [1—3]. Due to versatile coordination modes of the azide ligand, it has become the most extensively studied building block in the construction of various polynuclear complexes [4, 5]. In general, the modes observed for the azide bridges contain end-on ($\mu_{1,1}$) and end-to-end ($\mu_{1,3}$). In addition, acetate is also a fascinating ligand which can coordinate to metal atoms through monodentate chelating, bidenate bridging, monoatomic bridging, and chelating bridging modes [6].

Schiff bases, especially those prepared from the salicylaldehyde derivatives, have been extensively studied for their coordination chemistry. The adjacent deprotonated hydroxyl groups of the Schiff base ligands usually coordinate to different metal atoms, generating polynuclear complexes [7, 8]. To our knowledge, complexes simultaneously bearing phenolate, azide, and acetate bridging ligands are very rare [9]. Based on the above considerations, we report in this paper a novel phenolato, azido, and acetato co-bridged trinuclear zinc(II) complex [Zn$_3$L$_2$(μ_2-CH$_3$COO)$_2$($\mu_{1,1}$-N$_3$)(N$_3$)], where L is the deprotonated form of 4-chloro-2-[(2-diethylaminoethylimino)methyl]phenol (HL).

Experimental. Materials and measurements. 5-Chlorosalicylaldehyde and *N,N*-diethylethane-1,2-diamine were purchased from Lancaster. All other chemicals (reagent grade) were commercially available and used without further purification. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR 360 spectrophotometer as KBr pellets in the range 4000—400 cm^{-1}.

Synthesis of [Zn$_3$L$_2$(μ_2-CH$_3$COO)$_2$($\mu_{1,1}$-N$_3$)(N$_3$)] (I). 5-Chlorosalicylaldehyde (1.0 mmol, 0.158 g) and *N,N*-diethylethane-1,2-diamine (1.0 mmol, 0.116 g) were mixed and stirred in methanol (30 ml)

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Crystallographic data and refinement parameters for **I**

Molecular formula	$C_{30}H_{42}Cl_2N_{10}O_6Zn_3$
Molecular weight	905.8
Temperature, K	298(2)
Crystal shape / colour	Block / colorless
Crystal dimensions, mm	0.18×0.17×0.17
Crystal system	Triclinic
Space group	$P\bar{1}$
$a, b, c, \text{Å}$	12.7196(5), 13.6597(6), 13.7214(5)
$\alpha, \beta, \gamma,$ deg.	65.700(1), 83.429(1), 63.545(1)
$V, \text{Å}^3$	1938.4(1)
Z	2
d_{calc}, g/cm^{-3}	1.552
Absorption coefficient, mm^{-1}	2.032
$F(000)$	928
θ range, deg.	2.32 / 25.50
Range / indices (h, k, l)	−15/15, −16/16, −16/16
Absorption correction	Multi-scan
T_{min} / T_{max}	0.7111 / 0.7238
Reflections / parameters	7212 / 465
Observed reflections [$I \geq 2\sigma(I)$]	5187
Restraints	6
Goodness of fit on F^2	1.013
$R_1, wR_2 [I \geq 2\sigma(I)]^a$	0.0456, 0.0765
R_1, wR_2 (all data)^a	0.1032, 0.1185

$^a R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, \ wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2},$

$w = [\sigma^2 F_0^2 + (0.0514(F_0^2 + 2F_c^2)/3)^2 + 2.5066(F_0^2 + 2F_c^2)/3]^{-1}.$

at room temperature for 30 min. Then, a methanol solution containing sodium azide (1.0 mmol, 0.065 g) and zinc acetate dihydrate (1.0 mmol, 0.220 g) were added to the solution. The final mixture was further stirred at room temperature for 30 min to give a colorless solution. Upon keeping the solution in air for a few days, colorless block-shaped single crystals of the complex, suitable for X-ray crystal structure determination, were formed at the bottom of the vessel. The crystals were isolated by filtration, washed three times with methanol, and dried in a vacuum desiccator containing anhydrous CaCl$_2$. Yield 45 % on the basis of zinc acetate. *Anal.* Calc. for $C_{30}H_{42}Cl_2N_{10}O_6Zn_3$: C 39.8; H 4.7; N 15.5. Found: C 39.6; H 4.8; N 15.4. %.

X-ray crystallography. Diffraction intensities for **I** were collected at 298(2) K using a Bruker SMART 1K area-detector with MoK_α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [10], and multi-scan absorption corrections were performed using the SADABS program [11]. The structure was solved by a direct method and refined against F^2 by the full-matrix least-squares method using SHELXTL [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Selected bond distances (Å) *and angles* (deg.) *for* **I**

Bond distances					
Zn1—O1	2.155(3)	Zn3—O2	2.094(3)	Zn2—O1	2.006(3)
Zn1—N2	2.222(3)	Zn3—O6	1.962(3)	Zn2—O3	2.036(3)
Zn1—N8	2.016(4)	Zn3—N4	2.257(4)	Zn2—N8	2.174(4)
Zn2—O2	1.999(3)	Zn1—N1	2.058(3)	Zn3—O4	1.979(3)
Zn2—O5	2.011(3)	Zn1—N5	1.968(4)	Zn3—N3	2.033(4)

Bond angles					
N5—Zn1—N8	123.62(18)	O6—Zn3—O4	111.52(17)	O2—Zn2—O5	96.90(13)
N8—Zn1—N1	126.41(15)	O4—Zn3—N3	104.71(15)	O2—Zn2—O3	106.88(12)
N8—Zn1—O1	76.44(13)	O4—Zn3—O2	97.94(13)	O5—Zn2—O3	93.20(14)
N5—Zn1—N2	96.86(16)	O6—Zn3—N4	89.08(15)	O1—Zn2—N8	76.20(12)
N1—Zn1—N2	82.43(13)	N3—Zn3—N4	81.08(14)	O3—Zn2—N8	86.70(14)
O2—Zn2—O1	125.50(12)	N5—Zn1—N1	108.39(17)	O6—Zn3—N3	143.64(16)
O1—Zn2—O5	94.02(12)	N5—Zn1—O1	99.49(15)	O6—Zn3—O2	91.23(14)
O1—Zn2—O3	125.61(12)	N1—Zn1—O1	83.77(12)	N3—Zn3—O2	86.69(13)
O2—Zn2—N8	94.90(14)	N8—Zn1—N2	101.89(14)	O4—Zn3—N4	100.89(15)
O5—Zn2—N8	167.70(13)	O1—Zn1—N2	161.27(12)	O2—Zn3—N4	159.62(13)

Results and discussion. Crystal structure description of I. The molecular structure of **I** to-gether with the atom numbering scheme is shown in Fig. 1. The compound **I** is a $\mu_{1,1}$-azido, μ_2-acetato, and phenolato co-bridged trinuclear zinc(II) complex. The Zn1 and Zn2 atoms are bridged by one phe-nolate group and one end-on azide ligand with a distance of 3.282(1) Å. The Zn2 and Zn3 atoms are bridged by one phenolate group and two acetate ligands with a distance of 3.213(1) Å. The Schiff base ligands coordinate to the Zn atoms through phenolate O, imine N, and amine N atoms. One azide lig-and coordinates to the Zn atoms through an end-on bridging mode, while the other through a terminal coordination mode. Both acetate ligands coordinate to the Zn atoms through a bidentate bridging mode. The dihedral angle between the two benzene rings of the Schiff base ligands is 90.2(3)°.
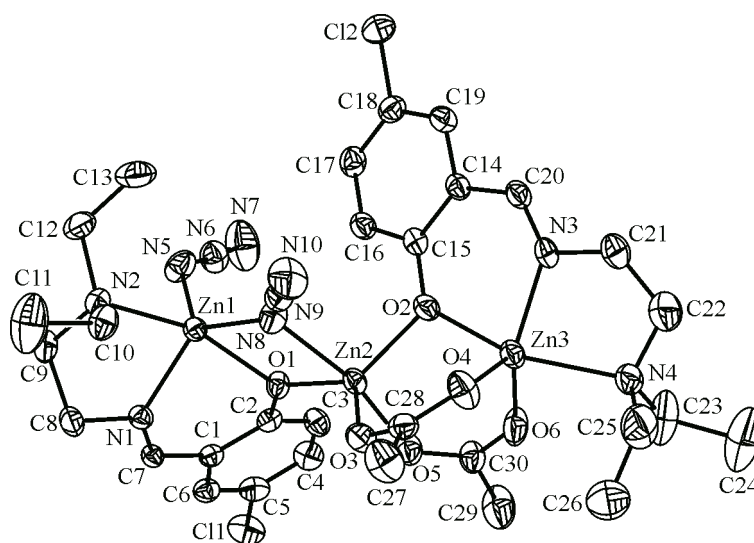

Fig. 1. Molecular structure of **I** at a 30 % probability displacement. Hydrogen atoms are omitted for clarity

The Zn1 atom is in a distorted trigonal bipyramidal coordination configuration, with N1, N5 and N8 atoms defining the basal plane and with O1 and N2 atoms occupying the axial positions. The distortion of the coordination is revealed by the bond angles, ranging from 108.39(17) to 126.41(15)° for the basal plane. The diagonal O1—Zn1—N2 angle of 161.27(12)° is also much deviated from the ideal value of 180°. The Zn1 atom deviates from the least-squares plane defined by three basal donor atoms by 0.145(1) Å. The Zn2 atom is also in a distorted trigonal bipyramidal coordination configuration, with O1, O2 and O3 atoms defining the basal plane and with O5 and N8 atoms occupying the axial positions. The distortion of the coordination is revealed by the bond angles ranging from 106.88(12)° to 125.61(12)° for the basal plane. The diagonal O5—Zn2—N8 angle of 167.70(13)° is also much deviated from the ideal value of 180°. The Zn2 atom deviates from the least-squares plane defined by the three basal donor atoms by 0.164(1) Å. The Zn3 atom is in a distorted square pyramidal coordination configuration, with N3, N4, O2, and O6 atoms defining the basal plane and with the O4 atom occupying the apical position. The distortion of the coordination is also revealed by the bond angles, ranging from 81.08(14)° to 91.23(14)° for the perpendicular angles and from 143.64(16)° to 159.62(13)° for the *trans* angles of the basal plane. The angles between the apical donor and basal donor atoms range from 97.94(13)° to 111.52(17)°, which are much deviated from the ideal value of 90°. The Zn3 atom deviates from the least-squares plane defined by the four basal donor atoms by 0.491(2) Å. The distortion of the coordination configurations are mainly caused by the strain created by the four- and five-membered chelate rings. The Zn—O and Zn—N bond lengths are comparable to the corresponding values observed in other Schiff base zinc(II) complexes [13—15]. Both bridging and terminal azide ligands are nearly linear and show bent coordination modes with the metal atoms [N5—N6—N7/Zn1—N5—N6 = 175.8(6)°/128.5(4)°;   N8—N9—N10/Zn1—N8—N9/Zn2—N8—N9 = 177.1(5)°/136.1(3)°/118.4(3)°].

The question arises as to whether the coordination polyhedra around the Zn atoms can be described as a distorted square pyramid or a trigonal bipyramid. Further information can be obtained by determining the structural index τ [16] which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$); $\tau = (\beta - \alpha)/60°$, α and β being the two largest angles around the central atom. The τ values are 0.58 for Zn1, 0.70 for Zn2, and 0.27 for Zn3. Thus, the coordination geometries of Zn1 and Zn2 are best described as a severely distorted trigonal bipyramid, and that of Zn3 is best described as a distorted square pyramid.

IR spectra. The bands in the range 2870—2980 cm^{-1} are characteristic of aliphatic ν(C—H) vibrations for **I** and those observed at about 3057 cm^{-1} are attributed to the aromatic ν(C—H) vibrations. The intense absorption bands at 2099 cm^{-1} and 2070 cm^{-1} are assigned to the azide ligands [17]. There are two different peaks in the spectrum, which are in accordance with the X-ray structure indicating that there are one bridging azide ligand and one termial azide ligand. The strong absorption band at 1644 cm^{-1} can be attributed to ν(C=N) [18]. The spectrum of **I** revealed an intense band at 1596 cm^{-1} for ν_{asym}(COO) and an intense band at 1460 cm^{-1} for ν_{sym}(COO). The $\Delta\nu$ value of 136 cm^{-1} is in accordance with the bidentate acetate bridging ligands [6].

CCDC–929003 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: deposit@ccdc.cam.ac.uk.

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