Instrumental Achievements

Crystal Structure of a Tetramer Zinc Complex: Bis{μ-[*N*,*N*′-bis(salicylidene)-1,3-propanediaminato-zinc(II)]chloro-μ-azido)zinc(II)}

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There are two kinds of μ-bridges: the first is $\mu_{1,1}$, or end-on, where the same terminal atom coordinates two metal atoms; the second is $\mu_{1,3}$, or end-to-end, where both terminal N atoms each coordinate a metal atom.[1,2] Tetrahedral and square-pyramidal coordinations are most frequently encountered for the Zn(II) ion.[3,4] None of our previously reported structures dealing with the coordination of zinc have the azide anion in the coordination.[5-7] We report here on the structure of a tetranuclear Zn complex, which was obtained by combining two dinuclear Zn complexes *via* two end-on bridges.

To synthesize the title compound, 0.846 g (0.003 mol) of *N*,*N*′-bis(salicylidene)-1,3-propanediamine was dissolved in 100 ml of hot MeOH. After a solution of 0.816 g (0.006 mol) anhydrous $ZnCl_2$ in 30 ml of hot MeOH was added to this solution, the resulting mixture was set aside for 3 days. The precipitated crystals were filtered and dried under atmospheric conditions. Then, 0.449 (0.001 mol) of this complex was dissolved by heating in a mixture of 60 ml dioxane and 10 ml DMF. A solution of 0.130 g (0.002 mol) of NaN_3 in 5 ml of hot water was added to the mixture, and then set aside for one week. Crystals suitable for X-ray measurements were filtered and dried under atmospheric conditions.

The title compound $[(ZnC_{17}H_{16}N_2O_2)_2(ZnClN_3)_2]$ is a non-linear tetranuclear Zn(II) complex with C_i symmetry. As can be seen in Fig. 2, the 4-coordinate Zn1 ion has a distorted tetrahedral coordination involving one Cl atom, two phenolic O atoms of a *N*,*N*′-bis(salicylidene)-1,3-propanediaminato ($salpd^{2-}$) ligand as well as one N atom from an azide anion. The 5-coordinate Zn2 ion can be described as a distorted square *pyramid* or distorted trigonal bipyramid. A conclusive characterization may be obtained by determining the structural index (τ), which represents the relative amount of trigonality.[8] In the title complex, the calculated value of τ is 0.06 for Zn2, implying that the coordination around the Zn2 is a somewhat distorted square pyramid which involves two imine N atoms and two phenolate O atoms from the $salpd^{2-}$ ligand in the basal plane and one N atom from an azide anion in the axial position. The Zn2 ion is 0.4801(4)Å off the basal plane towards the $N3^{i}$

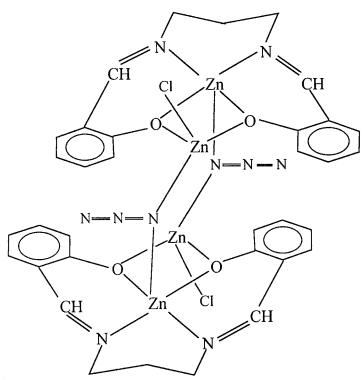

Fig. 1 Chemical structure.

Table 1 Crystal and experimental data

Formula: $C_{34}H_{32}Cl_2N_{10}O_4Zn_4$
Formula weight = 977.16
Crystal system: monoclinic
Space group: $P2_1/n$ $Z = 2$
a = 10.270(2)Å
b = 10.491(1)Å β = 92.436(10)°
c = 17.422(1)Å
V = 1875.4(4)Å^3
D_x = 1.73 g/cm^3
μ(Mo K$_\alpha$) = 2.72 mm^{-1}
T = 296 K
F(0 0 0) = 984
Crystal dimensions: 0.25 × 0.20 × 0.15 mm
Radiation = Mo K$_\alpha$ (λ = 0.71073 Å)
$2\theta_{max}$ = 50.8°
Number of reflections measured = 3855
No. of reflections used = 2982 [$F_0 > 1.0\sigma(F_0)$]
No. of parameters = 244
R = 0.032
Rw = 0.039
$(\Delta/\sigma)_{max}$ = 0.001
Goodness-of-fit = 1.00
Measurement: Enraf Nonius CAD-4
$(\Delta\rho)_{max}$ = 0.65 eÅ^3
$(\Delta\rho)_{min}$ = –0.19 eÅ^3
Structure determination: MolEN
Treatment of Hydrogen Atoms: All H atoms were placed geometrically 0.95 Å from their corresponding C atoms and a riding model was used.
Refinement: full matrix

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Table 2 Atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å
Zn1	0.61358(3)	0.11672(3)	0.42185(2)	3.315(7)
Zn2	0.67097(3)	-0.16990(3)	0.46217(2)	3.181(7)
C*l*	0.7278(1)	0.2312(1)	0.34212(6)	5.37(2)
O1	0.5596(2)	-0.0547(2)	0.3889(1)	3.87(5)
O2	0.7141(2)	0.0127(2)	0.4976(1)	3.56(4)
N1	0.6655(3)	-0.3045(3)	0.3767(2)	3.96(6)
N2	0.8457(3)	-0.2297(3)	0.5128(2)	3.73(6)
N3	0.4706(2)	0.2267(2)	0.4622(2)	3.27(5)
N4	0.4678(3)	0.3333(3)	0.4359(2)	3.75(6)
N5	0.4640(4)	0.4342(3)	0.4107(2)	6.29(9)
C1	0.4802(3)	-0.0878(3)	0.3300(2)	3.44(6)
C2	0.3897(4)	-0.0020(3)	0.2975(2)	4.28(7)
C3	0.3044(4)	-0.0377(4)	0.2384(2)	4.81(8)
C4	0.3063(4)	-0.1597(4)	0.2095(2)	5.05(9)
C5	0.3953(4)	-0.2445(4)	0.2390(2)	4.50(8)
C6	0.4842(3)	-0.2125(3)	0.2988(2)	3.63(6)
C7	0.5789(4)	-0.3084(3)	0.3214(2)	4.06(7)
C8	0.7571(4)	-0.4135(4)	0.3823(2)	5.24(9)
C9	0.7928(4)	-0.4488(4)	0.4624(3)	5.61(9)
C10	0.8906(4)	-0.3633(3)	0.5034(3)	4.80(8)
C11	0.9231(3)	-0.1592(3)	0.5530(2)	3.83(7)
C12	0.9079(3)	-0.0270(3)	0.5753(2)	3.59(6)
C13	1.0017(3)	0.0221(4)	0.6287(2)	4.42(8)
C14	0.9940(4)	0.1440(4)	0.6568(2)	5.13(9)
C15	0.8920(4)	0.2214(4)	0.6312(2)	4.89(8)
C16	0.8008(4)	0.1781(3)	0.5776(2)	4.19(7)
C17	0.8051(3)	0.0536(3)	0.5492(2)	3.39(6)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

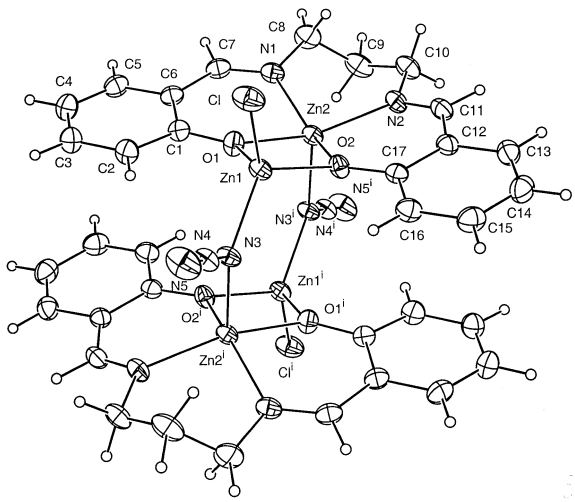

Fig. 2 ORTEP drawing of the title compound with atom labeling. Symmetry code: [(i) 1 – *x*, –*y*, 1 – *z*].

atom; the symmetry code is [(i): 1 – *x*, –*y*, 1 – *z*]. The four metal ions form a parallelogram with Zn–Zn corner angles of 80.27(1) and 99.73(1)° with non bonded Zn–Zn distances of 3.138(1) and 3.666(1)Å.

The six-membered Zn2, N1, C8, C9, C10 and N2 chelate ring has a boat conformation. The diagonally positioned Zn2 and C9 atoms are –0.2466(4) and –0.483(4)Å, off the least-squares plane through the other four atoms of the ring.

Table 3 Selected bond distances and bond angles of non-hydrogen atoms (Å, °)

Zn1 - Zn2		3.138(1)
Zn1 - Zn2^{i}		3.666(1)
Zn1 - C*l*		2.211(1)
Zn1 - O1		1.961(2)
Zn1 - O2		1.971(2)
Zn1 - N3		2.017(3)
Zn2 - O1		2.067(2)
Zn2 - O2		2.055(2)
Zn2 - N1		2.051(3)
Zn2 - N2		2.063(3)
Zn2 - N3^{i}		2.090(3)
N3 - N4		1.209(4)
N4 - N5		1.146(5)
Cl - Zn1 - O1		117.75(7)
Cl - Zn1 - O2		116.41(7)
Cl - Zn1 - N3		108.79(8)
O1 - Zn1 - N3		115.2(1)
O2 - Zn1 - N3		116.9(1)
O1 - Zn2 - O2		75.37(9)
O1 - Zn2 - N1		87.5(1)
O1 - Zn2 - N3^{i}		100.05(9)
O2 - Zn2 - N2		89.0(1)
O2 - Zn2 - N3^{i}		102.90(9)
N1 - Zn2 - N2		95.6(1)
N2 - Zn2 - N3^{i}		105.0(1)
Zn1 - O1 - Zn2		102.3(1)

Symmetry code (i) 1 – *x*, –*y*, 1 – *z*.

References

1. A. Escuer, R. Vicente, F. A. Mautner, and M. A. S. Goher, *Inorg. Chem*., **1997**, *36*, 1233.
2. P. Chaudhuri, T. Weyhermüller, E. Bill, and K. Wieghardt, *Inorg. Chim. Acta*, **1996**, *252*, 195.
3. M. Mikuriya, S. Ikenoue, R. Nukada, and J. Wan Lim, *Bull. Chem. Soc. Jpn*., **2001**, *74*, 101.
4. N. N. Greenwood and A. Earnshaw, "*Chemistry of Elements*", **1994**, Pergamon Press, Oxford, 1364.
5. O. Atakol, L. Tatar, M. A. Akay, and D. Ülkü, *Anal. Sci*., **1999**, *15*, 199.
6. L. Tatar, D. Ülkü, and O. Atakol, *Acta Crystallogr*., **1999**, *C55*, 508.
7. L. Tatar, E. Canel, O. Atakol, and D. Ülkü, *Anal. Sci*., **1999**, *15*, 103.
8. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, and G. C. Verschoor, *J. Chem. Soc. Dalton Trans*., **1984**, 1349.