ANALYTICAL SCIENCES JUNE 2002, VOL. 18

Instrumental Achievements

Crystal Structure of {[μ-*N*,*N*′-Bis(salicylidene)-1,3-propanediaminatodimethylformamide]zinc(II)}diiodozinc(II)

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(Received June 11, 2001; Accepted December 18, 2001)

Zinc(II) ion is the first in a row of essential rare elements for living beings. It has been recognized to be an activator for more than 120 hydrolytic enzymes.[1]

A quantity of ligand [L = *N*,*N*′-bis(salicylidene)-1,3-propane] (0.282 g, 0.001 mol) was dissolved in 30 ml hot DMF by warming and was mixed with 30 ml hot MeOH containing either ZnI_2 (0.639 g, 0.002 mol). The mixtures were set aside for one week. The resulting yellow crystals were filtered with a Büchner funnel and dried in ambient air. The chemical diagram of the complex is shown in Fig. 1.

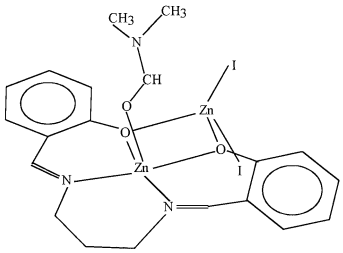

Fig. 1 Chemical diagram.

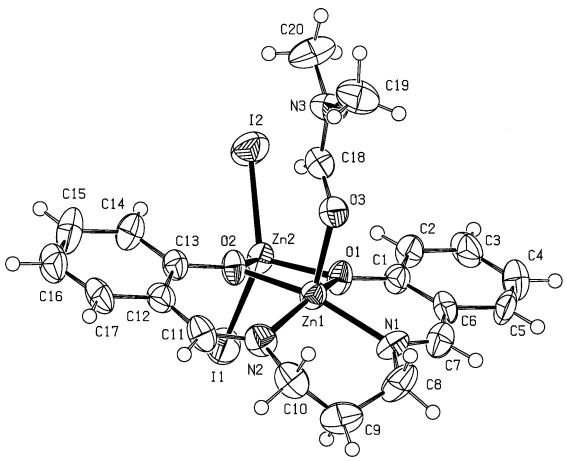

Fig. 2 The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

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Structures with double oxygen bridges are of interest because they have unusual magnetic moments due to the superexchange interactions over the O atoms.[2] The crystal structure of the title compound, $[ZnI_2(C_{17}H_{12}N_2O_2)(C_3H_7NO)]$, consists of a doubly oxygen-bridged homonuclear dimeric complex. The Zn1 atom has a square-pyramidal environment involving two O and two N atoms of the $SALPD^{2-}$ [$C_{17}H_{12}N_2O_2$, *N*,*N*′-bis(salicylidene)-1,3-propane] ligand, and an O atom from DMF [C_3H_7NO, dimethyformamide] group. As can be seen in Fig. 2, the coordination around terminal Zn atom is distorted tetrahedral, involving two bridging oxygen atoms and two iodine atoms. The bond lengths of the Zn–I_1 and Zn–I_2 are 2.5373(14) and 2.5527(14)Å, respectively.

Similar dimeric complexes have been investigated

Table 1 Crystal and experimental data

Formula: $[ZnI_2(C_{17}H_{12}N_2O_2)(C_3H_7NO)]$
Formula weight = 737.95
Space group: $P2_12_12_1$
Crystal system: orthorhombic $Z = 4$
a = 10.5599(12)Å
b = 14.9004(11)Å
c = 16.1511(12)Å
V = 2541.3(4)Å^3
D_x = 1.929 g/cm^3
μ(Mo K$_\alpha$) = 4.341 mm^{-1}
T = 295 K
Color = yellow
Radiation Mo K$_\alpha$ (λ = 0.71073 Å)
Crystal size: 0.20 × 0.15 × 0.10
$2\theta_{max}$ = 52.58°
No. of reflection = 5650
No. of reflection used = 2824($I > 2\sigma(I)$)
No. of parameters = 272
R = 0.053
Rw = 0.133
Goodness-of-fit = 1.09
$(\Delta\rho)_{max}$ = 1.40 eÅ^{-3} (0.92 Å from I2 atom)
$(\Delta\rho)_{min}$ = –0.64 eÅ^{-3}
Measurement: Enraf-Nonius CAD-4
Program system: SHELX97
Structure determination: SHELXS97
Refinement: full matrix least-square SHELXL97
Treatment of hydrogen atoms: geometric calculation

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

Atom	*x*	*y*	*z*	B_{eq}
Zn1	0.67115(11)	0.93771(7)	0.12385(7)	2.95(3)
Zn2	0.38311(10)	0.99164(8)	0.12118(7)	3.16(3)
I1	0.22475(8)	0.86403(6)	0.13130(5)	4.85(3)
I2	0.29291(10)	1.15020(6)	0.11108(6)	5.57(3)
O1	0.5247(7)	0.9629(5)	0.0445(4)	3.24(16)
O2	0.5265(7)	0.9780(5)	0.1996(4)	3.38(17)
O3	0.7644(7)	1.0584(5)	0.1196(4)	3.72(17)
N1	0.7573(9)	0.8651(6)	0.0317(5)	3.47(2)
N2	0.7492(9)	0.8725(6)	0.2221(6)	3.86(2)
N3	0.7494(10)	1.2097(7)	0.1223(7)	4.33(2)
C1	0.5266(11)	0.9612(7)	-0.0385(6)	3.08(2)
C2	0.4280(11)	1.0015(9)	-0.0843(6)	3.55(3)
C3	0.4252(14)	1.0034(10)	-0.1684(7)	4.65(3)
C4	0.5240(13)	0.9591(10)	-0.2127(7)	4.49(3)
C5	0.6185(13)	0.9194(8)	-0.1708(6)	4.18(3)
C6	0.6226(11)	0.9194(8)	-0.0824(6)	3.31(2)
C7	0.7278(12)	0.8722(8)	-0.0452(7)	3.94(3)
C8	0.8692(13)	0.8106(9)	0.0535(8)	4.97(4)
C9	0.8544(12)	0.7599(8)	0.1335(9)	4.81(3)
C10	0.8614(11)	0.8147(8)	0.2079(7)	4.26(3)
C11	0.7153(11)	0.8824(8)	0.2988(6)	3.94(3)
C12	0.6124(13)	0.9343(7)	0.3298(6)	3.55(3)
C13	0.5213(11)	0.9819(7)	0.2839(5)	3.08(2)
C14	0.4291(12)	1.0302(10)	0.3242(7)	4.26(3)
C15	0.4187(13)	1.0316(12)	0.4094(8)	5.60(5)
C16	0.5061(14)	0.9843(11)	0.4575(7)	4.73(4)
C17	0.6046(13)	0.9372(8)	0.4173(6)	4.02(3)
C18	0.7016(10)	1.1293(7)	0.1224(6)	3.31(2)
C19	0.8843(14)	1.2251(9)	0.1175(10)	5.60(4)
C20	0.6661(17)	1.2895(8)	0.1237(10)	6.31(4)

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

Table 3 Selected bond distances (Å) and angles (˚)

Zn1-Zn2		3.1464(16)		Zn2-I1		2.5373(14)	
Zn2-I2		2.5527(14)		Zn2-O1		1.988(7)	
Zn1-O1		2.043(7)		Zn2-O2		1.985(7)	
Zn1-O2		2.047(7)		Zn1-N1		2.052(8)	
Zn1-O3		2.051(8)		Zn1-N2		2.034(9)	
O1	Zn1	O2	75.9(2)	O1	Zn1	O3	100.4(3)
O1	Zn1	N1	88.7(3)	O2	Zn1	O1	97.0(3)
O2	Zn1	N1	156.7(3)	O3	Zn1	N1	103.0(3)
N2	Zn1	O3	104.5(3)	N2	Zn1	O2	88.6(3)
N2	Zn1	O1	152.0(4)	N2	Zn1	N1	97.7(4)
I1	Zn2	I2	116.86(5)	Zn2	O1	Zn1	102.6(3)
O1	Zn2	I2	116.1(2)	O1	Zn2	I1	112.0(2)
O2	Zn2	I2	112.6(2)	O2	Zn2	I2	114.9(2)
O2	Zn2	O1	78.5(3)				

previously.[3,4] {[μ-*N*,*N*′-Bis(salicylidene)-1,3-propanediaminato-dimethylformamide]zinc(II)}diiodozinc(II) [ZnL·ZnI_2·DMF] and {[μ-*N*,*N*′-bis(salicylidene)-1,3-propanediaminatodimethyl-formamide]zinc(II)}dibromozinc(II) [ZnL·$ZnBr_2$·DMF][3] are almost identical. The corresponding bond distances and angles have almost the similar values in these two complexes. The Zn··Zn bond distances are 3.1464(16) and 3.1480(7)Å for the present work and ZnL·$ZnBr_2$·DMF, respectively. The crystal and experimental data are given in Table 1, the final atomic parameters are presented in Table 2 and the selected bond distances and angles are in Table 3.

Acknowledgements

The authors wish to acknowledge the purchase of the CAD4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

References

1. I. Bertini, H. B. Gray, S. J. Lippard, and J. S. Valentine, *Bioinorg. Chem*., **1994**, 37.
2. M. Kato, H. B. Jonassen, and J. C. Fanning, *J Chem. Rev*., **1964**, *64*, 99.
3. O. Atakol, H. Nazır, M. Aksu, C. Arıcı, F. Ercan, and B. Çiçek, *Synth. React. Inorg. Met.-Org. Chem*., **2000**, *30*, 709.
4. O. Atakol, L. Tatar, M. A. Akay, and D. Ülkü, *Anal. Sci*., **1999**, *15*, 199.