Instrumental Achievements

Crystal Structure of {[μ-Bis(salicylidene)-1,3-propanediaminato]-copper(II)}dibromozinc(II)

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The title compound is a double oxygen-bridged dimeric heteronuclear metal complex. The coordination around the Cu atom is distorted square-planar involving two O and two N atoms from the bis(salicylidene)-1,3-propanediamine ligand. The Zn atom in the molecule has a distorted tetrahedral coordination sphere consisting of the two O atoms of the ligand and the two Br atoms. The bridging plane between the metal atoms is not planar.

(Received November 22, 2001; Accepted July 12, 2002)

The structure and properties of double oxygen-bridged dimeric homo- or heteronuclear metal complexes of general formulae (MM′X_2 SALPD), where (M = Cu, Zn, Ni; M′ = Zn, Hg; X = Cl, Br, I and SALPD = bis(salicylidene)-1,3-propanediamine), have been subjects of considerable interest in this laboratory.[1-4] Unusual magnetic properties due to superexchange interactions over the O atoms make these structures with double oxygen bridges interesting. Similar dimeric complexes have also been reported previously.[5-7]

We report here on a new member in a family of double oxygen-bridged dimeric heteronuclear metal complex [$CuZnBr_2$(SALPD)], which is isostructural with the two complexes, [$CuZnCl_2$(SALPD)] and [$CuZnI_2$(SALPD)], mentioned above.

To synthesize the title complex, bis(salicylidene)-1,3-diaminopropane (1.410 g, 0.005 mol) was dissolved in hot ethanol (50 ml), and an ammonia solution (10%, 10 ml) was added. To this mixture, a solution of $CuCl_2 \cdot 2H_2O$ (0.850 g, 0.005 mol) in hot water (20 ml) was added. After 24 h, $C_{17}H_{16}CuN_2O_2$ crystals were filtered off and 0.343 g (0.001 mol) of these crystals were dissolved in 1,4-dioxane (50 ml) and heated to the boiling point. To this solution, $ZnBr_2$ (0.225 g, 0.001 mol) in methanol (20 ml) was added, and the resulting solution set aside for 4 d. The crystals were filtered off and dried in air.

The crystal and experimental data are given in Table 1 and the final atomic parameters are presented in Table 2; selected bond distances and angles are given in Table 3.

The coordination around the copper atom is distorted square-planar involving two O and N atoms from the $SALPD^{2-}$ ligand. The CuN1 and CuN2 bond lenghts [1.970(8) – 1.969(8)Å] are equal among themselves within the experimental error. The irregularity of the square-planar coordination is mainly due to the different bond angles around the copper atom. Although the

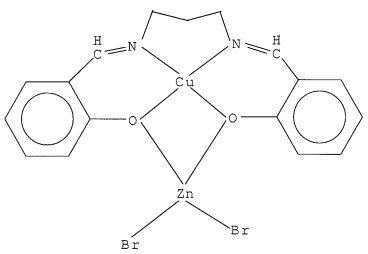

Fig. 1 Chemical diagram of the title molecule.

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Table 1 Crystal and experimental data

Formula: [$CuZnBr_2(C_{17}H_{16}N_2O_2)$]	
Formula weight = 569.06	
Space group: $P2_1/c$	
Crystal system: monoclinic	$Z = 4$
a = 11.6988(8)Å	
b = 8.3833(10)Å	
c = 18.7203(13)Å	β = 101.197(5)°
V = 1808.0(3)Å^3	
D_x = 2.092 g/cm^3	
μ(Mo K$_\alpha$) = 6.93 mm^{-1}	
θ_{max} = 27.2° with Mo K$_\alpha$	
T = 295 K	
Color = black	
F(0 0 0) = 1108.0	
Crystal size: 0.35 × 0.30 × 0.20	
Radiation Mo K$_\alpha$ (λ = 0.71073 Å)	
R = 0.0528	
Rw = 0.0518	
No. of reflections used = 2265	
No. of parameters = 226	
Goodness-of-fit = 1.06	
(Δ/σ) = 0.001	
$(\Delta\rho)_{max}$ = 0.723 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –1.062 eÅ^{-3}	
Measurement: Enraf-Nonius CAD-4 diffractometer	
Program system: Enraf-Nonius MolEN	
Structure determination: Simpel-MolEN	
Treatment of hydrogen atoms: All H atoms were placed geometrically 0.95 Å from their parent atoms and a riding model was used with U_{iso} (H) = 1.3U_{eq} (C).	
Refinement: full-matrix	

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

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Cu	0.7205(1)	0.0380(2)	0.96470(6)	2.80(2)
Zn	0.7491(1)	0.0988(2)	1.12872(6)	3.10(2)
Br1	0.6897(1)	-0.0349(2)	1.22592(6)	4.09(2)
Br2	0.8487(1)	0.3392(2)	1.15795(6)	4.18(2)
N1	0.8180(7)	-0.079(1)	0.9068(4)	2.7(2)
N2	0.6178(7)	0.149(1)	0.8855(4)	3.2(2)
O1	0.8151(6)	-0.0311(9)	1.0555(3)	3.2(1)
O2	0.6360(6)	0.1287(9)	1.0354(3)	3.4(2)
C1	0.9004(8)	-0.137(1)	1.0675(5)	2.6(2)
C2	0.9454(9)	-0.189(1)	1.1375(5)	3.5(2)
C3	1.035(1)	-0.298(1)	1.1499(6)	4.0(3)
C4	1.084(1)	-0.356(1)	1.0937(7)	4.3(3)
C5	1.0418(9)	-0.306(1)	1.0240(6)	3.9(3)
C6	0.9486(8)	-0.200(1)	1.0090(5)	2.6(2)
C7	0.9044(9)	-0.163(1)	0.9344(5)	3.2(2)
C8	0.7976(9)	-0.075(1)	0.8265(5)	3.7(2)
C9	0.6758(9)	-0.028(1)	0.7923(5)	3.7(2)
C10	0.643(1)	0.137(1)	0.8118(5)	4.1(3)
C11	0.5289(9)	0.227(1)	0.8934(6)	3.8(3)
C12	0.4819(9)	0.264(1)	0.9576(5)	3.0(2)
C13	0.382(1)	0.355(1)	0.9518(6)	3.9(3)
C14	0.335(1)	0.398(2)	1.0104(6)	4.2(3)
C15	0.3924(9)	0.354(1)	1.0786(6)	3.9(2)
C16	0.4927(9)	0.264(1)	1.0866(6)	3.7(2)
C17	0.5390(8)	0.218(1)	1.0270(5)	2.6(2)

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

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

Cu...Zn	3.073(3)	Cu - O1	1.945(6)
Br1 - Zn	2.346(2)	Cu - O2	1.943(7)
Br2 - Zn	2.343(2)	Cu - N1	1.970(8)
Zn - O1	2.010(7)	Cu - N2	1.969(8)
Zn - O2	2.012(6)	O1 - C1	1.33(1)
O2 - C17	1.34(1)	N1 - C7	1.27(1)
N2 - C11	1.36(1)		
Br1- Zn-Br2	115.66(6)	O1-Cu-N1	92.2(3)
Br1- Zn-O1	118.3(2)	O2-Cu-N1	170.0(3)
Br1- Zn-O2	119.6(2)	O2-Cu-N2	90.7(3)
Br2- Zn-O1	113.0(2)	N1-Cu-N2	99.0(3)
Br2- Zn-O2	108.6(2)	Zn- O1-Cu	102.0(3)
O1-Zn-O2	75.4(3)	Zn- O2-Cu	102.0(3)
O1-Cu-O2	78.5(3)		

O1–Cu–N1 [92.2(3)˚] and O2–Cu–N2 [90.7(3)˚] bond angles are close to each other, the O1–Cu–O2 [78.5(3)˚] and N1–Cu–N2 [99.0(3)˚] bond angle values are clearly different. This is caused by the steric limitations in the propanediamine chelate ring as well as in the bridging plane. The copper atom is located at a distance of 0.027(1)Å from the coordination plane defined by the atoms N1, O1, O2, N2.

The second metal atom, zinc, in the molecule has a distorted tetrahedral environment, and is coordinated by the two O atoms of the $SALPD^{2-}$ ligand and the two Br atoms. The two O atoms also constitute the bridge between the Cu and Zn atoms. The

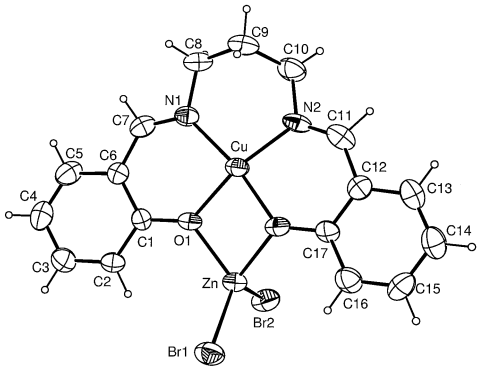

Fig. 2 ORTEP drawing of the asymmetric unit of the title compound with the atomic numbering of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

bond angles around the Zn atom range from 75.4(3)˚ (O1–Zn–O2) to 118.3(2)˚ (O1–Zn–Br1), which indicates a serious deviation from the ideal tetrahedral angle. The two Zn–O [2.010(7) – 2.012(6)Å] and the Zn–Br [2.346(2) – 2.343(2)Å] distances are mutually equal within the experimental error.

The bridging plane (Cu, O1, Zn, O2) is not completely planar. The distances of the two metal atoms, Cu and Zn, from the respective best plane are 0.098(1) and 0.093(1), while the corresponding distances for O1 and O2 have equal values of –0.096(7)Å. The six-membered chelate ring (Cu, N1, C8, C9, C10, N2) has a chair conformation. The distances of two para-positioned chair atoms, Cu and C9, from the best plane through the other four atoms of the ring, are 0.031(1) and –0.707(11)Å, respectively. The diherdal angle between the coordination plane around Cu(O1, O2, N2, N1) and the bridging plane (Cu, O1, Zn, O2) is 9(1)˚. The maximum and minimum residual electron densities were observed within 1.0 Å of the Br atom.

Acknowledgements

The partial support of The Turkish Academy of Science is acknowledged.

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