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Synthesis and Crystal Structure of Five-Coordinated Cobalt(II) Dimer with Asymmetrical N_2O_2 Coordination Sphere

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A novel Co(II) dimer, $[Co(HL)]_2$, has been synthesized by the reaction of H_3L and $Co(CH_3COO)_2{\cdot}4H_2O$ in acetonitrile/methanol solution. X-Ray crystallographic analysis reveals that the Co(II) complex crystallizes in the triclinic system, space group P-1. The Co(II) atom is five-coordinated by four donor atoms of N_2O_2 coordination sphere and one O atom from other [Co(HL)] unit. Both of Co(II) atoms followed trigonal bipyramidal geometry. The complex molecule links with four other molecules into an infinite 2D-layer supramolecular structure on the *bc* crystallographic plane *via* intermolecular O-H···O, C-H···Br and C-H···O hydrogen-bonding interactions.

Keywords: Co(II) dimer, Synthesis, Characterization, Crystal structure.

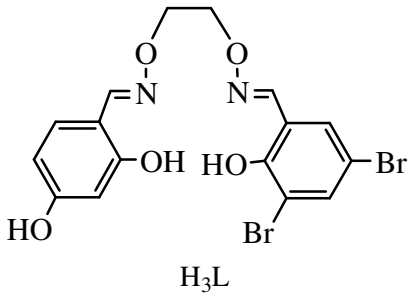
INTRODUCTION

H_2 salen complexes have been extensively investigated in the past decades since H_2salen (N,N'-*bis*(salicylaldehydo)-ethylenediamine) was first reported[1]. Salen and its derivatives are a class of versatile ligands, they can accommodate one, or more metal centers to form complexes. Three main structural types for H_2 salen and its analogues have been reported: (i) mononuclear [M(salen)]; (ii) binuclear $[M(salen)]_2$ and (iii) bridged trinuclear $\{[M(salen)]_2(OAc)_2M\}$. These complexes are used as catalysts in various organic reactions[2], models of reaction centers of metalloenzymes[3], non-linear optical materials[4,5] and exhibit interesting magnetic properties[6,7]. Herein, we report on the synthesis and crystal structure of a new Co(II) dimer with a asymmetrical Salen-type bisoxime chelating ligand based on O-alkyloxime instead of the imine moiety.

EXPERIMENTAL

3,5-Dibromo-2-hydroxybenzaldehyde and 2,4-dihydroxy-benzaldehyde were purchased from Aldrich and used without further purification. 1,2-*Bis*(aminooxy)ethane was synthesized according to an analogous method reported earlier[8-12]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. The analysis of Co was performed by an IRIS ER/S.WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-Ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

Synthesis of 7-hydroxy-4',6'-dibromo-2,2'-[ethylene-diyldioxy*bis*(nitrilomethylidyne)]diphenol (H_3L): H_3L was synthesized according to an analogous method reported earlier[13]. Yield: 67 %. m.p. 421-423 K. Anal. calcd. (%) for $C_{16}H_{14}Br_2N_2O_5$: C, 40.53; H, 2.98; N, 5.91. Found (%): C, 40.60; H, 2.89; N, 5.96.



H_3L

Scheme-I: Asymmetrical Salen-type ligand H_3L

Synthesis of Co(II) complex: A solution of cobalt(II) acetate tetrahydrate (2.48 mg, 0.010 mmol) in methanol (3 mL) was added dropwise to a solution of H_3L (4.75 mg, 0.010 mmol) in acetonitrile (3 mL) at room temperature. The colour of the solution turned to yellow immediately and the mixture was allowed to stand at room temperature for about 1 week.

After the solvent was partially evaporated, several brown block-shaped single crystals suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The single crystal of the Co(II) complex, with approximate dimensions of 0.31 mm × 0.20 mm × 0.12 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 293(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the Co(II) complex are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 938485.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR Co(II) COMPLEX

Empirical formula	$C_{32}H_{24}Br_4N_4O_{10}Co_2$
Formula weight	1062.05
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	a = 13.877(2), b = 14.261(2), c = 14.282(3), α = 83.537(2), β = 72.679(1), γ = 63.135(1)
Volume ($Å^3$)	2406.3(7)
Z	2
Density (calculated) (mg/m^3)	1.466
Absorption coefficient (mm^{-1})	4.057
$F_{(000)}$	1036
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	8483/8483 [R(int) = 0.0983]
Independent reflections	966
Data/restraints/parameters	8483/0/470
Goodness of fit indicator	1.084
R [I > 2σ(I)]	R_1 = 0.0397 wR_2 = 0.1632
Largest diff. peak and hole (e $Å^{-3}$)	0.622 and -0.674

RESULTS AND DISCUSSION

Crystal structure of Co(II) complex: Crystal struc-ture of the Co(II) complex is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. X-ray crystallography revealed that the Co(II) complex contains two Co(II) atoms

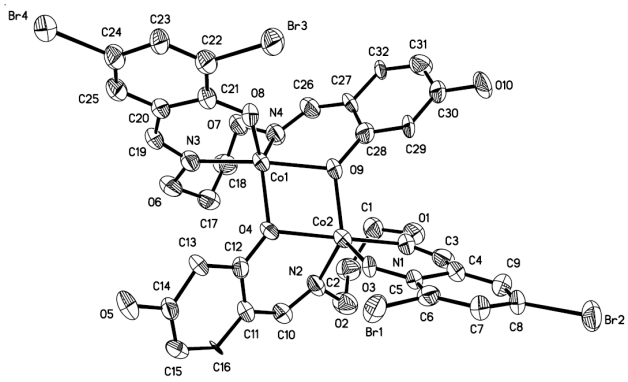


Fig. 1. Molecule structure of the Co(II) complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

and two deprotonated $(HL)^{2-}$ units. The structure can be described as two [Co(HL)] unit connected with a diphenoxy-bridge. Each of two Co(II) atoms sit in the N_2O_2 salen moieties. Two oxygen (O4 and O9) atoms site bridge two Co(II) atoms. Co1 adopts trigonal bipyramidal geometry with axial O9 and N3 (τ = 0.665)[14], which deviates from the mean plane (O4-N4-O8) by 0.135(3) Å. The distances of Co1 to the five donor atoms are all different (1.893-2.072 Å). The dihedral angle of N3-Co1-O8 and N4-Co1-O9 is 66.13(4)°, which indicates $(HL)^{2-}$ has serious distortion probably as a result of the asymmetry. The geometry of Co2 is similar to the Co1. The value of τ = 0.680 clearly shows that the environment of the Co2 atom is close to trigonal bipyramidal geometry in which the axial site is occupied by O4 and N1 atoms. This is different from the reported structures of its analogues Cu(salen)[14,15] and Cu(salamo)[16], which form slightly pyramidalized square planar geometries and be stabilized by the intermolecular contacts between copper and oxygen atoms to form a head-to-tail dimer.

Intermolecular interactions of the Co(II) complex: The hydrogen bond data are summarized in Table-3. In the crystal structure, two strong intermolecular O5-H5···O10 and O10-H10···O5 hydrogen bonds between the phenolic hydroxyl groups of the neighboring molecule link neighboring molecules into an infinite 1D chain supramolecular structure along the b axis, as illustrated in Fig. 2. Furthermore, this linkage is further stabilized *via* two pairs of intermolecular weak hydrogen bonds C25-H25···O6 and C1-H1A···Br2 to form the other infinite chain (Fig. 3). Thus, every complex molecule links four other molecules into an infinite 2D-layer supramole-

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR Co(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Co1-O8	1.89(1)	Co1-O9	2.07(1)	Co2-N2	2.04(2)
Co1-O4	2.02(1)	Co2-O3	1.90(1)	Co2-N1	2.05(2)
Co1-N4	2.03(2)	Co2-O9	1.97(1)	Co2-O4	2.12(1)
Co1-N3	2.065(16)	–	–	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
O8-Co1-O4	115.5(5)	O4-Co1-O9	77.6(4)	O9-Co2-N1	101.1(5)
O8-Co1-N4	114.2(6)	N4-Co1-O9	82.3(6)	N2-Co2-N1	90.5(7)
O4-Co1-N4	128.9(6)	N3-Co1-O9	168.8(7)	O3-Co2-O4	100.5(5)
O8-Co1-N3	89.7(6)	O3-Co2-O9	116.0(5)	O9-Co2-O4	77.6(4)
O4-Co1-N3	100.8(5)	O3-Co2-N2	113.9(6)	N2-Co2-O4	82.4(6)
N4-Co1-N3	90.4(6)	O9-Co2-N2	128.6(6)	N1-Co2-O4	169.4(7)
O8-Co1-O9	101.0(5)	O3-Co2-N1	89.6(7)	–	–

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, º)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A	Symmetry code
O5-H5···O10	0.82	2.25	3.07(2)	174	x, 1+y, z
O10-H10···O5	0.82	2.25	3.07(2)	172	x, -1+y, z
C25-H25···O6	0.93	2.57	3.09(3)	116	1-x, 1-y,1- z
C1-H1A···Br2	0.97	2.84	3.74(2)	154	1-x,- y, -z

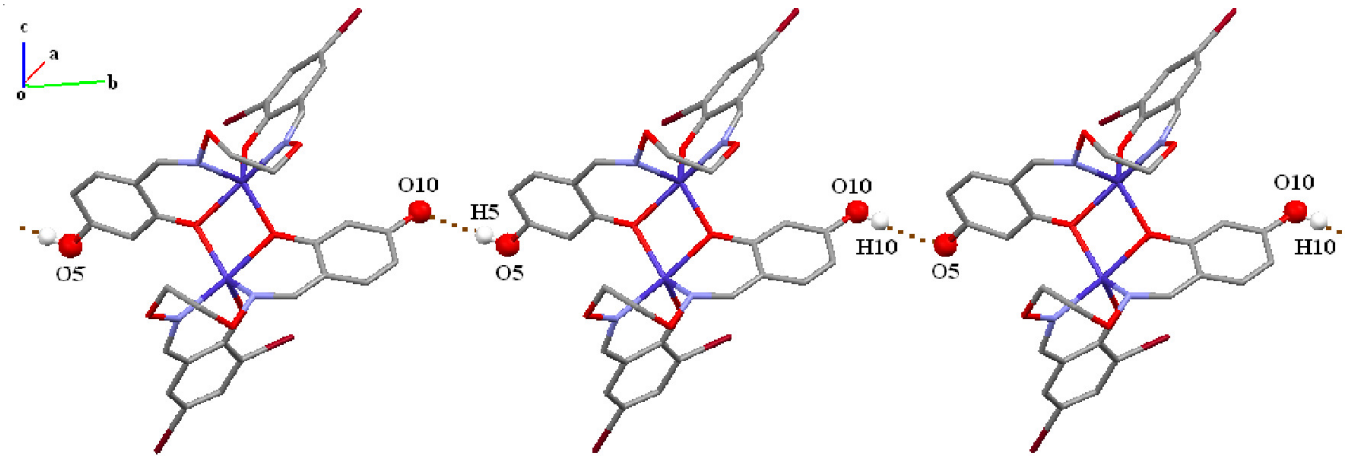


Fig. 2. (Colour online). View of the 1D chain motif of the Co(II) complex units along the b axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

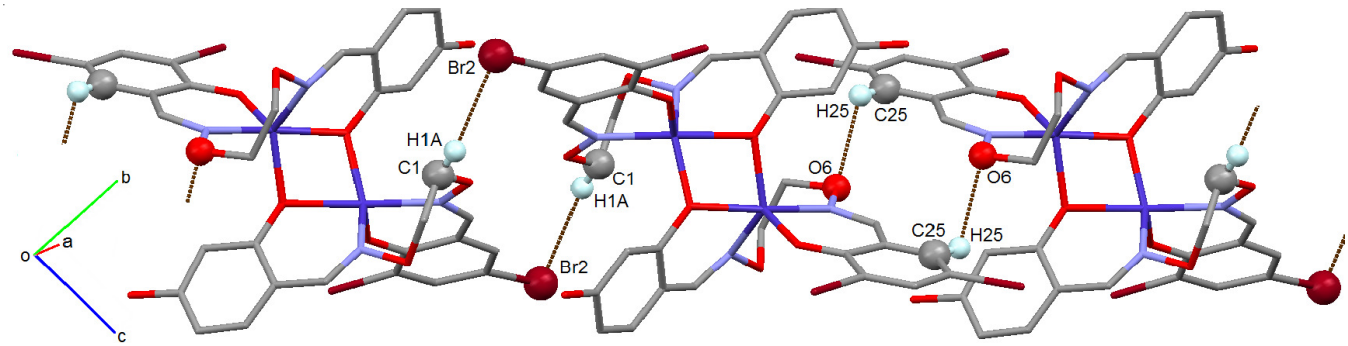


Fig. 3. (Colour online). View of the 2D-layer motif along the bc plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

cular structure on the bc crystallographic plane *via* intermolecular O-H···O, C-H···Br and C-H···O hydrogen-bonding interactions.

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