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Synthesis and Crystal Structure of Salen Ligands Derived from Unsymmetrical Vicinal Diamine

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ABSTRACT

Salen type Schiff bases possessing an unsymmetrical vicinal diamine backbone are promising nominees in view of their diversified applications. Synthesis of such Schiff bases *viz*., 2'-((1E,1'E)-((1-phenylpropane-1,2-diyl)bis(azanylylidene)) bis(methanylylidene))diphenol and 2,2'-((1E,1'E)-((1-(*p*-tolyl)propane-1,2-diyl) bis (azanylylidene))bis(methanylylidene))diphenol were achieved. Their single crystals were developed using ethanol as solvent by slow evaporation technique and subjected for XRD-studies. Interestingly, both the crystals crystallize with similar pattern *i.e*., in triclinic crystal system with space group P-1 and both found to have E-configuration at each imine bond. XRD data reveals the molecular structure of both the compounds exhibit similar intra & inter- molecular hydrogen bonding interactions.

Keywords: Crystal structure, Unsymmetrical vicinal diamines, Salen ligand, Schiff base, CCDC: 1448832 & 1448833.

INTRODUCTION

Salen ligands are privileged entrants both in synthetic and medicinal fields. Though Schiff bases are known for several decades[1-5], chemists are still interested in design and synthesis of new Schiff bases[6,7], as these are capable of coordinating with various metals, which find applications in fields of synthesis[8], medicine[9] and material study.[10] Numerous studies were conducted in order to understand the properties of salen and its derivatives.[11-14] Owing to the importance of salen type ligands, the understanding of their structure becomes significant. Hence, the present report adds one more feather on the crown to the world of single crystals of salen ligands.

EXPERIMENTAL

Synthesis and Crystallization

2,2'-((1E,1'E)-((1-phenylpropane-1,2-diyl)bis(azanylylidene))bis(methanylylidene)) diphenol: Synthesis of salen ligand **1**, ($C_{23}H_{21}ClN_2O_2$), was achieved from the condensation 2-hydroxybenzaldehyde (0.02 mol) and 1-phenylpropane-1,2-diamine (0.01 mol) in ethanol (25 ml, 99%). The mixture was refluxed for 3h and the resulting solid product was collected by filtration. The solid was purified by recrystallization using ethanol which afforded yellow needles of pure salen ligand. Single crystal of the compound was developed using ethanol as solvent by slow evaporation technique.

2,2'-((1E,1'E)-((1-(*p*-tolyl)propane-1,2-diyl)bis(azanylylidene))bis(methanylylidene)) diphenol: The above procedure was repeated for the synthesis of salen ligand **2**, ($C_{24}H_{24}N_2O_2$) with 2-hydroxybenzaldehyde(0.02 mol) and 1-(*p*-tolyl)propane-1,2-diamine (0.01 mol) as reagents. The single crystal was developed from ethanol by slow evaporation technique.

XRD study

For Salens 1 & 2 the crysatal data were collected on a Bruker Proteum 2CCD diffractometer with X-ray generator operating at 45 kV and 10 mA using CuKα radiation of wavelength 0.71073 Å. The cell refinement and data thus obtained were processed using *APEX2* and *SAINT* [15]; Data reduction by *SAINT* and *XPREP*.[16] The structure was solved by direct method and refined by full-matrix least squares on F^2 using SHELXS and SHELXL programs.[17] The geometrical parameters were calculated by using PLATON.[18] Crystal Data, collection procedure and refinement results were summarized in **Table 1.** Supplementary crystallographic data can be obtained from CCDC using numbers:1448833 (salen**1**) & 1448832 (salen **2**).

RESULT AND DISCUSSION

Salen ligands **1** and **2** were synthesized by the condensation of salicylaldehyde with corresponding 1,2-diamines in ethanolic medium. Both **1** and **2** were subjected for single crystal growth using ethanol as solvent by slow evaporation technique. The single crystals of **1** as well as **2** were subjected for XRD study [Salen**1**: CCDC: **1448833** & Salen**2**: CCDC: **1448832**]. The Crystal Data for salens **1** and **2** were presented in **Table 1**.The ORTEP of salens **1** and **2** were presented in **Fig.1** & **2**, respectively. The packing diagrams for both were given in **Fig.3** & **4**. In salen **1**, the bonding parameters of C=N [C7-N1(1.272 Å), C17-N2 (1.268 Å)] & C-O [C1-O1(1.352 Å), C23-O2(1.355 Å)] signify an exclusive formation of enol-imine form over the other tautomeric forms(keto-amine) of Schiff base. It is observed that, the C-N & C-O bond lenths are consistent with normal C=N & C-O bond lengths, respectively. Similarly, from the crystal data of salen **2**, C=N [C7-N1(1.26Å), C18-N2 (1.268Å)] & C-O [C1-O1(1.34 Å), C24-O2(1.346 Å)] the existence of its enol-imine form are established. Inter- and intra- molecular interactions observed from the crystal data of Salen **1** & **2** are presented in **Table 2** & **3**, respectively. Both Salens exhibit N….H-O type hydrogen bonding.

Table 1. The Crystal Data for salens1 and 2

Salen	**1**	**2**
CCDC	**1448833**	**1448832**
Empirical formula	C23H22N202	C24H24N202
Formula weight	358.42	372.45
T (K)	296(2)	296(2)
Wavelength (Å)	0.71073 A°	0.71073 A°
Crystal system, space group	Triclinic P-1	TriclinicP-1
Unit-cell		
a (Å)	9.6534(2	9.5158(2)
b (Å)	10.1308(3)	11.0960(3)
c (Å)	10.6936(3)	11.1132(2)
α(°)	85.985(3)	97.9510(10)
β (°)	79.586(3)	94.7630(10)
γ(°)	66.714(2)	112.081(2)
Volume ($Å^3$)	944.79	1065.17
Z, Calculated density D (Mg/m^3)	2,1.260	2,1.161
F(000)	380	396
Absorption coefficient μ (mm^{-1})	0.081	0.074
h range for data collection (°)	2.189 to 25.000	2.015 to 24.998
hkl range	-11<=h<=11/-12<=k<=12/ -12<=1<=12	11<=h<=11/-13<=k<=13 -13<=1<=13
Reflections collected	17130	19711
Unique R_{int}	3323(0.0320)	3743(0.0270)
Crystal size	0.300×0.200× 0.200	0.350×0.300×0.250
Data / restraints / parameters	3323/0/245	3743/0/254
Goodness-of-fit on F^2	1.015	1.102
Absolute structure parameter R(F) (I > 2σ(I))	0.1(7)	0.1
Extinction coefficient wR(F^2)(all data)	0.015(3)	0.010(3)
Largest diff. peak and hole max/min. △σ(e/$Å^3$)	0.137/-0.212	0.264/-0.180

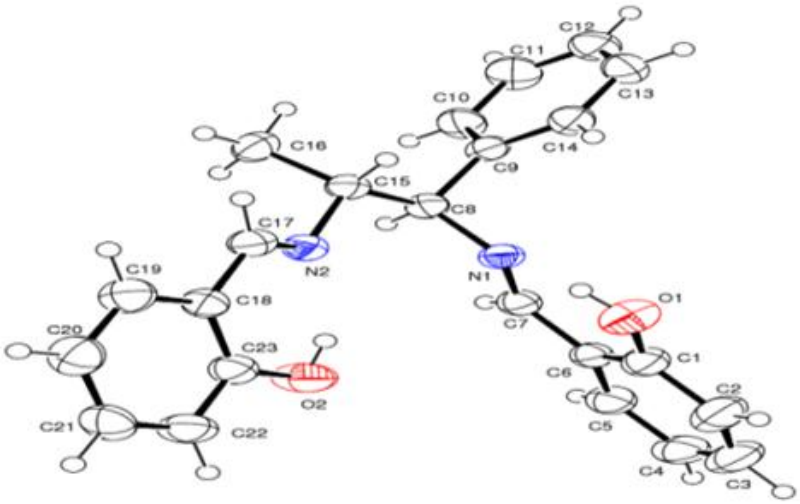

Fig. 1. ORTEP of compound 1

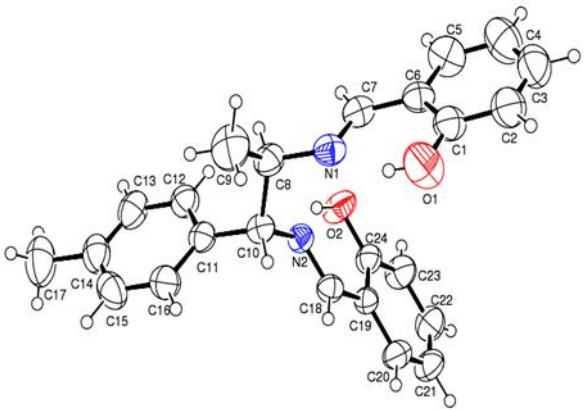

Fig. 2. ORTEP of compound 2

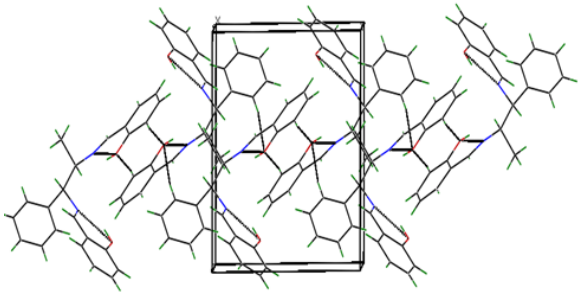

Fig. 3 Packing diagram of compound 1

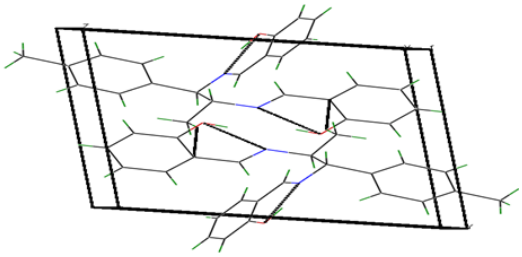

Fig. 4 Packing diagram of compound 2

Table 2. Hydrogen bonds [Å and °] of Salen 1

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(22)-H(22)...O(2)#1	0.93	2.64	3.556(3)	169.5
O(1)-H(1A)...N(1)	0.82	1.88	2.600(2)	146.2
O(2)-H(2A)...N(2)	0.82	1.87	2.596(2)	146.5

Symmetry transformations used to generate equivalent atoms / #1 -x+1,-y+1,-z+1

Table 3. Hydrogen bonds [Å and °] of Salen 2

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(1)	0.82	1.85	2.584(3)	148.3
O(2)-H(2A)...N(2)	0.82	1.83	2.563(3)	147.6

Symmetry transformations used to generate equivalent atoms

The selected bond length (A°), bond angle (°) and Torsion angles (°) of salens **1**and **2** are presented in **Table 4** & **5**, respectively. From the torsional angles of salens **1** & **2**, it is observed that both the salens, exist in E-configuration at each imine bonds.

Table 4: Selected bond length (A°), bond angle (°) and Torsion angles (°) of salen 1

Bond length (A°)	(A°)	Bond angle	(°)	Torsion angle	(°)
C1-O1	1.352	O2-C23-C18	121.2	C2-C1-C6-C7	-178.79
C23-O2	1.355	O1-C1-C2	118.5	C9-C8-C15-C16	70.3
C15-C16	1.521	O1-C1-C6	121.3	N1-C8-C15-C16	-167.09
C8-C9	1.512	O2-C23-C22	118.6	N2-C15-C8-C9	-167.88
C8-N1	1.465	N2-C15-C16	110.6	N2-C17-C18-C23	10.2
C15-N2	1.468	N2-C15-C8	109.3	N2-C17-C18-C19	-170.24
C17-N2	1.268	N1-C8-C9	110.5	C16-C15-C8-C9	70.3
C15-C8	1.530	C16-C15-C8	110.24	C15-C8-N1-C7	136.2
C9-C14	1.387	C8-C9-C14	121.54	C17-N2-C18-C23	10.2
C12-C13	1.366	N2-C17-C18	118.8	C8-C9-C14-C13	179.7
C18-C23	1.392	N1-C7-C6	122.5	C8-C9-C10-C11	179.5
C7-N1	1.272	C12-C11-C10	120.4	C16-C15-N2-C17	-73.4

Table 5: Selected bond length (A°), bond angle (°) and Torsion angles (°) of salen 2

Bond length	(A°)	Bond angle	(°)	Torsion angle	(°)
C8-C10	1.527	C10- C8-N1	110.0	C8-N1-C7-C6	178.7
C8-N1	1.458	C10-N2-C18	109.2	C10-N2-C18-C19	176.8
C10-N2	1.459	C8-N1-C7	118.1	C10-C11-C16-C15	-178.9
N2-C18	1.26	N1-C7-C6	122.7	C9-C8-N1-C7	-127.7
N1-C7	1.26	C6-C1-O1	120.8	C17-C14-C15-C16	-179.1
O1-C1	1.34	C23-C24-O2	118.6	C3-C2-C1-O1	-179.6
C24-O2	1.346	C10-C11-C12	121.2	N1-C7-C6-C5	179.6
C17-C14	1.514	C13-C14-C17	120.4	N2-C18-C19-C20	-179.6
C9-C8	1.517	N1-C8-C9	109.0	C17-N2-C18-C23	179.5
C10-C11	1.500	C10-C11-C16	120.8	C8-C9-C14-C13	179.5

CONCLUSION

Salen ligands **1** and **2** were synthesized by the condensation of salicylaldehyde with corresponding 1,2-diamines in ethanolic medium. Single crystals of both were achieved by slow evaporation method. Surprisingly, both the crystals crystallize with similar pattern, in triclinic crystal system with space group P-1, exhibiting N….H-O type hydrogen bonding interaction. Both salens found to have E-configuration at each imine bonds. The bonding parameters of C=N & C-O signify an exclusive formation of enol-imine form over the other tautomeric forms of Schiff base.

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