Tetradentate Schiff base Beryllium complexes.

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Salen: N,N'-Bis(salicylidene)ethylenediamine

Salbut: N,N'-Bis(salicylidene)butylenediamine

BeSalen: Bis(salicylidene)ethylenediamine beryllium

BeSalbut   Bis(salicylidene)butylenediamine beryllium

Abstract

The structure of (BeSalen)$_2$ is reported. The incompatibility of the geometry of the beryllium with the inflexibility of the Salen ligand gives rise to a rare dimeric bis-didentate motif.

Symmetric tetradentate ligands such as Salen are typically used to occupy the four coordination sites of the meridial plane of a given metal centre.[1-3] Of all the structures in the CCDC database involving a Salen moiety remarkably few (~6) have the ligand coordinated bis-didentate to two metal centres. The ability to coax Salen out of its natural planar tetradentate motif requires a partner metal which is limited in its geometric preferences. Over 50 years ago two studies indicated that beryllium and Salen might have just such an interesting relationship.[4,5] Considering our interest in the structures of complexes which arise from a mismatch of the geometric preferences of the ligand and metal we have chosen to re-visit the synthesis of beryllium Schiff bases and structurally characterise the compound first described over 50 years ago.[4-7]
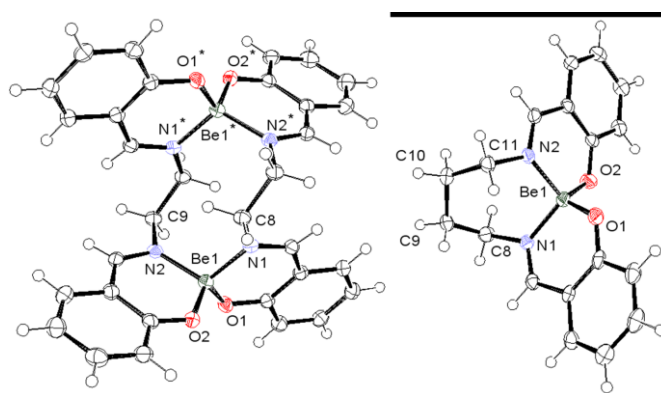

Fig. 1. X-ray structures of (BeSalen)$_2$ and BeSalbut. The thermal ellipsoids are drawn at 50%. Crystallographic data can be found in the table 1

(BeSalen)$_2$ and BeSalbut were prepared from beryllium sulphate as previously described.[4,5] Both compounds were crystallised and subjected to analysis by XRD methods (Fig. 1). The structure of (BeSalen)$_2$ obtained confirmed that the species is dimeric in nature. The tetrahedral nature of beryllium forces the Salen ligand to re-arrange such that the two phenolate/imine pairs coordinate to different metal centres. This simple motif is extremely rare and has only been observed in species where groups are present which affect the ability of the ligand to occupy the meridial plane.[1-3] Consistent with previous studies extending the di-imine chain to four carbons affords the ligand freedom to generate a tetrahedral environment thus allowing it to satisfy the needs of a single metal centre (Fig. 1).

The characterisation of these species completes a structural profile of Salen with the early metals (Fig.2). The Salen complexes of lithium and sodium are based on a M$_4$O$_4$ core.[8] For divalent beryllium a simpler dimeric structure is obtained (Fig. 1). With the larger group II metals or by affording the ligand greater flexibility (e.g. BeSalbut) we observe a move to

monomeric behaviour.[9] In short we see clusters and cages giving way to polymers and dimers, concluding with simple monomeric species.
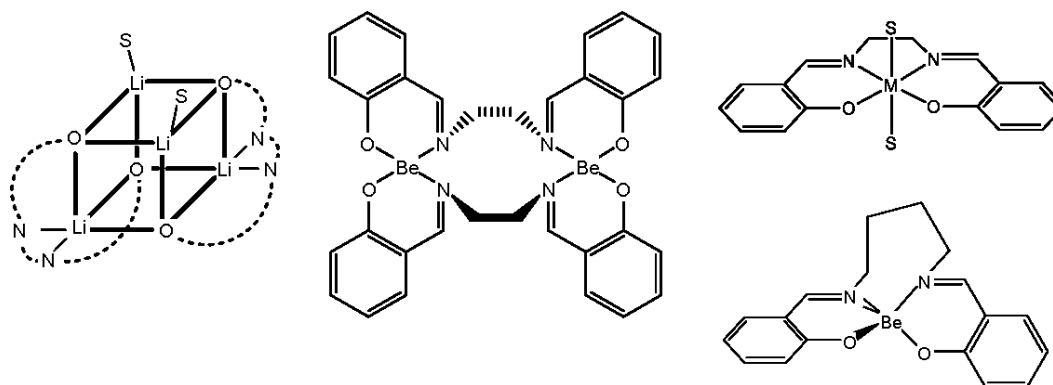

Fig. 2. An overview of the structural progression of simple Salen complexes

The metrical parameters for the two tetradentate Schiff base compounds show great uniformity between the two structures and with other beryllium didentate Schiff base compounds (Table 1, Fig. 2).[11-13] The flexibility of Salbut allows the ligand to position itself in a tetrahedral motif. Salen achieves the same result by adopting a di-dentate motif with the ligands operating in concert.

Bond distances d/Å	(BeSalen)$_2$	BeSalbut	CASDIK	CASDIP	NETCIY	QAQFIY	QAQFOE	SEWPAN	(BeSalen)$_2$ Calc	BeSalen Calc
Be-O1	1.5794(17)	1.582(4)	1.560	1.564	1.583	1.598	1.572	1.573	1.593	1.591
Be-O2	1.5861(18)	1.583(4)	1.578	1.573	1.570	1.598	1.575	1.573	1.589	1.591
Be-N1	1.7331(18)	1.722(4)	1.754	1.748	1.777	1.698	1.726	1.747	1.755	1.750
Be-N2	1.7413(18)	1.727(4)	1.750	1.744	1.776	1.698	1.730	1.747	1.746	1.750
Bond angles (°)										
O1-Be-O2	113.60(10)	113.7(2)	116.07	116.31	115.12	115.28	117.86	114.33	117.56	110.77
O1-Be-N1	106.25(10)	106.2(2)	105.63	105.36	104.32	103.87	103.54	104.52	105.09	102.15
O1-Be-N2	110.63(10)	112.0(2)	112.02	112.10	109.93	110.59	109.08	111.17	106.69	125.92
O2-Be-N1	108.24(10)	115.5(2)	111.20	111.81	108.05	110.59	110.71	111.17	107.99	125.91
O2-Be-N2	105.62(10)	105.4(2)	103.92	105.4	104.55	103.87	104.00	104.52	105.27	102.15
N1-Be-N2	112.62(9)	103.8(2)	107.86	107.19	115.21	112.93	111.83	111.30	114.60	90.89

Table S2 The bond distances (d/Å) and angles (°) for (BeSalen)$_2$, BeSalbut, Beryllium didentate Schiff base complexes and the calculated BeSalen species.[11-13]
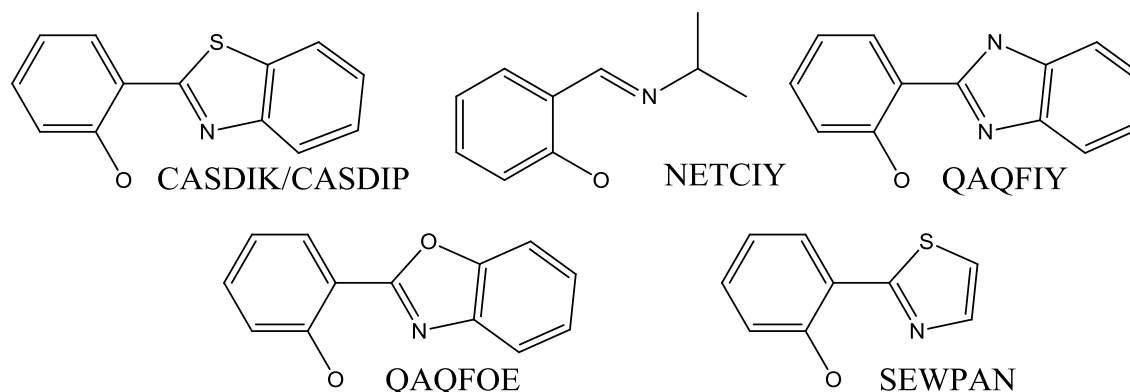

Fig 2. Ligand motifs of the structurally characterised beryllium Schiff base compounds. [11-13]

In an attempt to understand the stability of the various forms of BeSalen (dimer vs monomer) we subjected the compound to analysis by *ab-initio* DFT calculations. We used the isolated dimer (Fig. 1) as a model of the dimeric form. On refinement the total energy of (BeSalen)$_2$ was calculated to be -1786. 16016811 a.u. Two monomers were also constructed. A tetrahedral form, M$_T$, was generated from the XRD structure of BeSalbut (Fig. 1). For this model the two carbons (C9, C10) were deleted in Gauss-View and C8 & C11 connected and moved to a distance commensurate with a single bond. A second, planar model (M$_P$) was constructed from the XRD structure of NiSalen, using the atomic coordinates obtained from the ccdc (FEYWEM) and by subsequently replacing the nickel by beryllium.[14] These two models represent the geometric extremes of BeSalen. The two monomers, M$_T$ and M$_P$, both refined to an identical tetragonally distorted structure (table 1) of total energy -893.06173121 a.u. For the necessary comparison the value of the energy obtained for the (BeSalen)$_2$ must be halved (i.e. -893.08008405 a.u.) to reflect the number of atoms present in the monomer. After this adjustment we can see that the observed dimeric structure is preferred over the monomeric form by 11.52 kcal/mole.

Experimental

Synthesis: Salen, Salbut, (BeSalen)$_2$ and BeSalbut were prepared using established methods.[4, 5, 15]

BeSalbut crystallised directly from the cooling filtrate and was analysed as received. Expected for $C_{18}H_{18}N_2BeO_2.H_2O$: C, 67.28; H, 6.27; N 8.71% Found: C, 67.60; H, 6.13; N 9.27% ESI-MS [(BeSalbut)Na]$^+$: 526 (90%), [(BeSalbut)$_2$H]$^+$: 304 (100%), [(BeSO$_4$)$_2$]$^+$: 210 (30%). ^{1}H NMR spectrum [400 MHz, DMSO, 25 °C] δ: 1.47 (br m, 2H, -CH$_2$), 2.08 (br m, 2H, -CH$_2$), 3.59 (br m, 4H, N-CH$_2$), 6.60 (br d 2H, arom J = 8 Hz: Influence of the ^{9}Be centre: 100% abundant, I = 3/2), 6.64 (dt, 2H, arom J = 7 Hz; 1 Hz), 7.31 (dt, 2H, arom, J = 7.6 Hz; 2 Hz) 7.40 (dd, 2H, arom, J = 7.6 Hz; 2 Hz), 8.52 (s, 2H, -CH=N), XRD data: Monoclinic c1c1, a = 7.6771(10) Å, b = 17.9229(10) Å, c = 11.3182(12) Å, β = 98.385(14)°, V (Å^3) 1540.69(32), Z = 4, r$_{obs}$ = 0.0445, wR$_2$ = 0.0932.

(BeSalen)$_2$ was obtained directly from the cooling filtrate as a powder and was analysed as received. Crystals were grown from the slow evaporation of a dilute solution of (BeSalen)$_2$ in DMF. Expected for $C_{32}H_{28}N_4Be_2O_4.H_2O$: C, 67.60; H, 5.32;

N 9.85% Found: C, 68.33; H, 5.36; N 9.93% ESI-MS [(BeSalen)$_2$Na]$^+$: 573 (40%), [(BeSO$_4$)$_3$]$^+$: 315 (100%), [(BeSalen)$_2$Na]$^+$: 298 (25%), [(BeSalen)]$^+$: 276 (15%). XRD data: Triclinic P-1, a = 8.5367(6) Å, b = 8.8067(6) Å, c = 10.1596(7) Å, α = 106.505(6)º, β = 92.538(6)º, γ = 97.889(6)º, V (Å^3) 772.60(16), Z = 1, r$_{obs}$ = 0.0361, wR$_2$ = 0.0935. Solubility insufficient for ^{1}H NMR spectroscopy

All DFT calculations were performed using the Gaussian09 program[16] employing the B3LYP[17, 18] functional using the 6-31++G(d, p) basis set. Geometry optimisations were performed with no symmetry constraints and vibrational mode analysis used to confirm the ground state of the monomeric species.

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