

Note

First example of a borate-bridged dimeric aluminum Schiff-base complex containing five-coordinate metal centers

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The formation of a borate-bridged dimeric aluminum Schiff-base compound [salen(^tBu)Al]₂O₂BOMe [salen = *N,N'*-ethylenebis(salicylideneimine) (**1**)] has been reported. Complex **1** crystallizes in a triclinic *P* $\bar{1}$ space group with $a = 14.57$, $b = 15.15$, $c = 15.84$ Å and $\alpha = 96.92$, $\beta = 90.82$, $\gamma = 105.53^\circ$. The crystal structure shows the presence of a metaborate (MeOBO₂²⁻) bridge between two five-coordinate aluminum atoms with a bridging OBO angle of 123.25°. The compound has been characterized by ¹H, ¹³C, ¹¹B, ²⁷Al NMR, IR and mass spectroscopies and melting point measurements. ¹H NMR shows two complex multiplets for the ^tBu groups and two different environments for the imine protons. ¹¹B NMR shows a peak at 18 ppm characteristic of three-coordinate boron and ²⁷Al NMR shows a peak at 29 ppm characteristic of five-coordinate aluminum.

Keywords: Aluminum; Borate; Boroaluminate; Five-coordinate; Salen

1. Introduction

The Al–O–B–O–Al linkage is common in various boroaluminate compounds where the borate group acts as a bridging group between aluminum centers [1–8]. In most cases the trigonal metaborate connects to AlO₄ tetrahedra and Al is four-coordinate. Four-coordinate BO₄ units and five- and six-coordinate AlO₅ and AlO₆ units are also observed [1,8]. A bridging metaborate is fairly common in boroaluminate glasses but is rarely observed in chelated main group or transition metal compounds. Although there are several examples of carboxylate [9,10], phosphinate [11,12], sulfate [13] and nitrate [14] bridges between two metal centers in dinuclear compounds, examples of bridging borates between two chelated metal centers are rare. In one example, [(THF)₂Na{-B(OPh)₃H}]₂ [15], tetrahedral [B(OPh)₃H]– groups bridge two five-coordinate sodium atoms.

In the course of our work with aluminum compounds with *N,N'*-ethylenebis(salicylideneimine) (salen) ligands, we have discovered a series of salen–aluminum

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compounds with bridging phosphinate ligands [11,12] that are either dimeric or polymeric with two μ -phosphinate bridging groups. Some of the compounds revealed unique coupling of the salen ligand with THF. We have also reported salen compounds with bridging siloxides Ph_2SiO_2 between two boron centers [16]. We report here the fortuitous finding of a dimeric aluminum salen complex having only one bridging metaborate (MeOBO_2^{2-}) group between two Al centers. This is the first example of a single borate bridging two aluminum atoms. Indeed, this is the only example of a bridged five-coordinate Schiff-base compound.

2. Discussion

2.1 Synthesis

The compound $[\text{salen}(\text{tBu})\text{Al}]_2\text{O}_2\text{BOMe}$ (**1**) was not the desired product from the reaction attempted. The reaction involved the combination of $\text{salen}(\text{tBu})\text{AlBr}$ and piperazine in a 1:2 ratio under reflux in toluene. Compound **1** was collected from the filtrate, where no piperazine was found (which means the piperazine remained in the residue). The borate seems to have been incorporated into the compound from the borosilicate glassware used to run the reaction. We surmised that this was the only source of boron in the reaction. The boron from the borosilicate glassware may have been leached by a strong base used to clean the glassware. The leaching of boron from borosilicate glass under the influence of alkali is known [17,18]. However, we have not been able to determine the source of the methoxy group on boron.

2.2 Characterization

Compound **1** crystallizes as a dimer with Al–O–B–O–Al linkage (figure 1). There are two five-coordinate Al atoms in a distorted square-pyramidal geometry. The square-pyramidal geometry around the aluminum center is consistent with other five-coordinate monomeric aluminum salen compounds [19]. Salen, because of its rigid backbone, tends to adopt a square-pyramidal geometry whereas the more flexible ligand backbone in salpen and salben causes a trigonal planar geometry [20].

We have previously reported dimeric and polymeric salen complexes in which Al centers are linked by bridging phosphinate $[\text{Ph}(\text{H})\text{PO}_2]$ groups [11,12]. In all these compounds the aluminum atoms are six-coordinate and connected by two bridging phosphinate groups. Similar bridging is found in the acetate-bridged compound, $[\text{Mn}(\text{salpen})(\text{OAc})]_{2n}(\text{H}_2\text{O})_{3n}$, in which two acetate groups link six-coordinate Mn centers [10]. However, in the borate-bridged compound **1** reported here, the Al centers are five-coordinate and there is only one borate-bridging group. In addition, the phosphinate-bridged salen aluminum compounds were polymeric for salen and dimeric for salpen and salben. It was thought that the flexible backbone of the latter two compounds allows the dimer formation whereas the rigid backbone in salen led to a polymeric structure. $[\text{Mn}(\text{salpen})(\text{OAc})]_{2n}(\text{H}_2\text{O})_{3n}$ was also found to be polymeric, but $[\text{Mn}_2(\text{salen})_2(\text{O}_2\text{CPr})(\text{EtOH})(\text{H}_2\text{O})][\text{O}_2\text{CPr}]$ is dimeric and $\text{Mn}(\text{O}_2\text{CBu})(\text{salpen})$ is monomeric [9]. In comparison to these previously reported results, the borate-bridged salen aluminum compound **1** reported here is dimeric.

Crystal data and structure refinement details are shown in table 1 and important bond distances and angles are shown in table 2. The Al–O–B–O linkage is bent with an

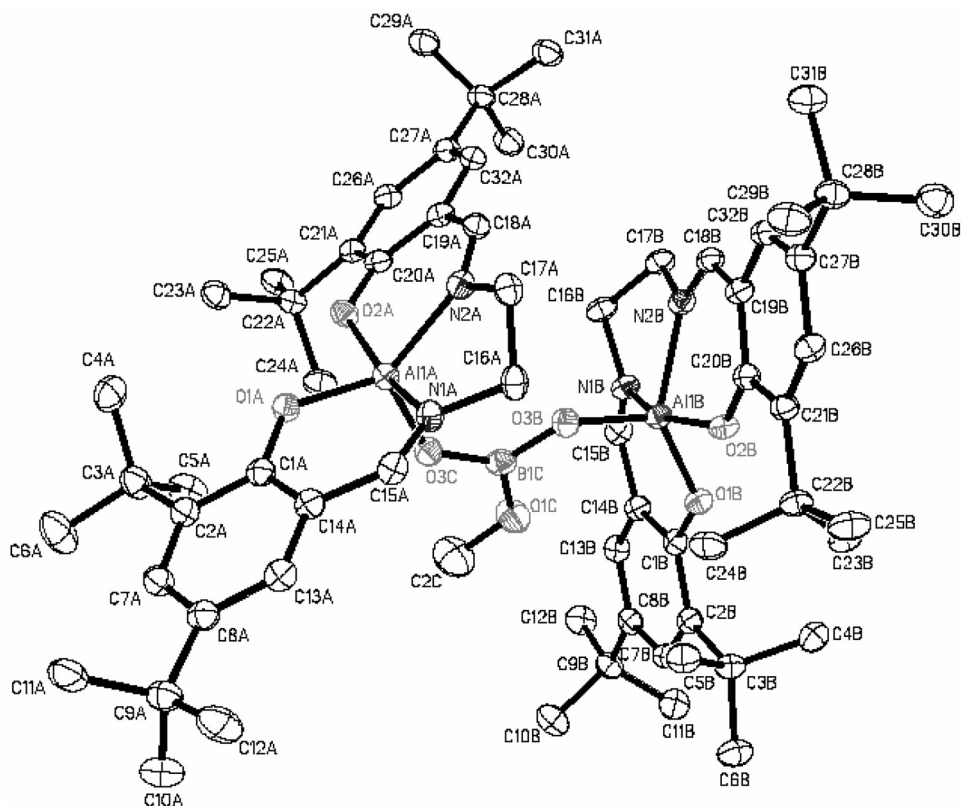


Figure 1. Crystal structure of $[\text{salen}^t\text{Bu}]\text{Al}_2\text{O}_2\text{BOMe}$ (**1**).

OBO angle of 123.25° , which is more obtuse than the O–P–O bond angle (119.1°) in $[\text{salen}^t\text{Bu}]\text{AlO}_2\text{P}(\text{H})\text{Ph}]_\infty$ [12]. However, the O–B–O bond angle in **1** is similar to that in borooaluminate compounds. For example, the O–B–O angle is *ca* 120° in $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ [5], 119 – 123° in $\text{Rb}_2\text{Al}_2\text{O}_7$ [2] and 118 – 121° in PbAlO_4 [3]. The Al–O bond distances in the Al–O–B–O linkages are *ca* 1.74 \AA , which is much shorter than the Al–O distance (*ca* 1.90 \AA) in the Al–O–P linkage in $[\text{salen}^t\text{Bu}]\text{AlO}_2\text{P}(\text{H})\text{Ph}]_\infty$ [12]. They are also shorter than the Al–O (ligand) bond distances (Al1A–O1A = 1.78 \AA , Al1A–O2A = 1.82 \AA , Al1B–O1B = 1.79 \AA , Al1B–O2B = 1.81 \AA).

The B–O bond distances are *ca* 1.35 \AA and fall in the range of B–O bond distances in known aluminoborate compounds. For example, the B–O distance is *ca* 1.36 \AA in $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ [5]. However, this distance is smaller than the B–O distance in the borate-bridged compound $[(\text{THF})_2\text{Na}\{\text{B}(\text{OPh})_3\text{H}\}]_2$ in which the bridging B–O bond distance is 1.41 – 1.52 \AA . This is understandable because the boron in the latter compound is four-coordinate and is expected to have longer bond distances. The bond angles around boron (121° , 123° and 115°) are indicative of a trigonal planar geometry.

^1H NMR shows two complex multiplets for the ^tBu groups and there are two different environments for the imine protons, in support of the dimeric structure. ^{27}Al NMR shows a peak at 29 ppm characteristic of five-coordinate aluminum. ^{11}B NMR

shows a peak at 18 ppm consistent with the presence of three-coordinate boron. For example, this value also falls in the range of the three-coordinate ^{11}B NMR shift in boronaluminate glass (17–19 ppm) [1].

No molecular ion peak was found in mass spectra of the compound. However, the most abundant ion was molecular ion minus one $t\text{Bu}$ (100%). Molecular ion minus OCH_3 was found in 8% abundance. IR spectra show several bands in the region of 1200–1500 cm^{-1} that are characteristic of B–O stretching for three-coordinate boron [21].

3. Conclusion

We have synthesized the first borate-bridged dimeric Schiff-base complex. The presence of five-coordinate metal centers is unprecedented in such dimeric bridged compounds.

4. Experimental

4.1 General remarks

Air-sensitive manipulations were conducted using a standard benchtop Schlenk line technique in conjunction with an inert atmosphere glove-box. Solvents were rigorously dried before use. Glassware was cleaned with a base and dried in an oven at 130°C overnight before use. $\text{Salen}(t\text{Bu})\text{AlBr}$ was synthesized from $\text{salen}(t\text{Bu})\text{H}_2$ and Me_2AlBr by a method to be reported elsewhere. NMR data were obtained on Varian Gemini-200 and VXR-400 instruments. Chemical shifts were reported relative to SiMe_4 for ^1H and ^{13}C , $\text{BF}_3\cdot\text{Et}_2\text{O}$ for ^{11}B and AlCl_3 in D_2O for ^{27}Al and are reported in ppm. Infrared transmission spectra were recorded at room temperature using the KBr pellet technique on a Fourier-transform Magna-IR ESP 560 spectrometer. X-ray data were collected on a Nonius Kappa-CCD unit using $\text{Mo K}\alpha$ radiation. Crystal data are summarized in table 1. All calculations were performed using the Siemens software package SHELXTL-Plus. The structure was solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

4.2 Synthesis

Piperazine (0.156 g, 1.81 mmol) was added to a rapidly stirred solution of $\text{salen}(t\text{Bu})\text{AlBr}$ (0.538 g, 0.90 mmol) in diethylether. The reaction mixture was refluxed under nitrogen for 22 h. Then it was cannula filtered and the volatiles were removed under vacuum from the filtrate to give a pale yellow solid, which was washed with toluene and dichloromethane and recrystallized from acetonitrile to give pale yellow crystals. Yield: 0.20 g (41%). Mp: 320–322°C (dec.). ^1H NMR (CDCl_3): δ 1.27 (m, 36H, $\text{C}(\text{CH}_3)_3$), 1.5 (m, 36H, $\text{C}(\text{CH}_3)_3$), 3.15 (s, 3H, OCH_3), 3.59–3.73 (m, 8H, NCH_2), 4.17 (m, 8H, NCH_2), 6.96–7.08 (m, 4H, PhH), 7.46–7.54 (d, 2H, PhH), 8.18 (s, 2H, $\text{N} = \text{CH}$), 8.31 (s, 2H, $\text{N} = \text{CH}$). ^{13}C NMR (CDCl_3): δ 29.5 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{C}(\text{CH}_3)_3$), 34.0 ($\text{C}(\text{CH}_3)_3$), 35.5 ($\text{C}(\text{CH}_3)_3$), 54.7 (OCH_3), 55.0 (NCH_2), 118.3 (Ph), 129.9 (Ph), 130.3 (Ph), 130.8 (Ph), 137.5 (Ph), 137.9 (Ph), 140.5 (Ph), 140.9 (Ph), 163.1 (Ph), 169.2 (NCH), 169.7 (NCH). ^{11}B NMR (CDCl_3): δ 18 ($W_{1/2} = 606$ Hz). ^{27}Al NMR (CDCl_3): δ 29

Table 1. Crystal data and structure refinement details.

Empirical formula	$C_{67}H_{98}Al_{12}BN_5O_7$
$M/g\ mol^{-1}$	2030.67
Color	Colorless to pale yellow
Crystal size/mm	$0.25 \times 0.20 \times 0.15$
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	14.57050(10)
$b/\text{\AA}$	15.15320(10)
$c/\text{\AA}$	15.8361(2)
$\alpha/^\circ$	96.9214(4)
$\beta/^\circ$	90.8234(4)
$\gamma/^\circ$	105.5278(4)
$V/\text{\AA}^3$	3340.30(5)
$\rho_{\text{calc}}/g\ cm^{-3}$	1.144
Z	2
$F(000)$	1244
$\mu(\text{Mo K}\alpha)/mm^{-1}$	0.097
T/K	90.0(2)
hkl range	$-18 \leq h \leq 18, -19 \leq k \leq 19, -20 \leq l \leq 20$
Θ range/ $^\circ$	$1.30 - 27.49$
Reflections measured	30 396
Unique reflections (R_{int})	15 307 (0.0374)
Observed reflections, $n [F \geq 4\sigma(F)]$	10 740
Refinement method	Full-matrix least-squares on F^2
Refined parameters/restraints	765/0
$R1 [I > 2\sigma]$	0.0486, $wR2 = 0.1282$
$R1$ (all data)	0.0793, $wR2 = 0.1434$
Goodness-of-fit on F^2	1.044
Largest diff. peak and hole/ $e\ \text{\AA}^{-3}$	0.381 and 0.402

Table 2. Selected bond distances (\AA) and angles ($^\circ$).

Al1A–N1A	2.0216(14)	Al1B–N1B	2.0108(14)
Al1A–N2A	2.0009(14)	Al1B–N2B	2.0107(14)
Al1A–O1A	1.7841(12)	Al1B–O1B	1.7929(12)
Al1A–O2A	1.8156(12)	Al1B–O2B	1.8104(12)
Al1A–O3C	1.7381(12)	Al1B–O3B	1.7352(12)
B1C–O1C	1.389(2)	O1C–C2C	1.398(2)
B1C–O3B	1.349(2)		
B1C–O3C	1.350(2)		
O1A–Al1A–O2A	91.56(5)	O1B–Al1B–O2B	90.58
O1A–Al1A–O3C	109.29(6)	O1B–Al1B–O3B	118.31(6)
O1A–Al1A–N1A	88.04(6)	O1B–Al1B–N1B	87.61(6)
O2A–Al1A–N2A	88.26(6)	O2B–Al1B–N2B	88.21(6)
O2A–Al1A–O3C	101.64(6)	O2B–Al1B–O3B	101.32(6)
O3C–Al1A–N1A	96.37(6)	O3B–Al1B–N1B	98.03(6)
O3C–Al1A–N2A	115.29(6)	O3B–Al1B–N2B	103.71(6)
N1A–Al1A–N2A	78.63(6)	N1B–Al1B–N2B	79.03(6)
Al1A–O3C–B1C	133.19(12)	Al1B–O3B–B1C	132.39(12)
O3C–B1C–O1C	121.15(17)		
O3C–B1C–O3B	123.25(16)		
O3B–B1C–O1C	115.59(16)		

($W_{1/2} = 1158\ \text{Hz}$). IR ν/cm^{-1} : 2955s, 2909s, 2866m, 1654s, 1629s, 1557s, 1542m, 1444s, 1390s, 1262m, 1176m, 1107w, 1056w, 834m, 792m, 753m, 594m, 497w. MS (MALDI-TOF): 1078 ($M^+ - \text{OCH}_3$, 8%), 1052 ($M^+ - t\text{Bu}$, 100%).

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