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Divalent tin and lead complexes of a bulky salen ligand: the syntheses and structures of [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb

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The divalent tin and lead complexes, [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb, have been synthesized by the reactions of $[(Me_3Si)_2N]_2M$ (M = Sn, Pb) with the substituted Salen compound, [Salen$^{Bu^t,Me}$]H_2. [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb have been characterized by X-ray diffraction, which demonstrates that the complexes are structurally similar, with the metal atom located above the $[N_2O_2]$ plane. Despite their similar structures, however, ^{1}H NMR spectroscopy demonstrates that the barrier for the formal transfer of the metal from one face of the ligand to the other is significantly greater for the tin derivative.

Introduction

We are presently interested in the chemistry of divalent complexes of the Group 14 elements, germanium, tin and lead, supported by tetradentate nitrogen and oxygen donor ligands. For example, we have used the $[N_4]$ octamethyldibenzotetraaza[14]annulene dianion $[\eta^4\text{-}Me_8taa]^{2-}$ to prepare a series of subvalent complexes, $[\eta^4\text{-}Me_8taa]M$ (M = Ge, Sn, Pb), of which the germanium and tin derivatives undergo oxidative addition with the elemental chalcogens producing terminal chalcogenido complexes $[\eta^4\text{-}Me_8taa]ME$ (M = Ge, E = S, Se, Te; M = Sn, E = S, Se).[1–3] In addition, the X-ray diffraction data for the lead complex $[\eta^4\text{-}Me_8taa]Pb$ were found to be capable of being refined into a well-behaved false minimum, the result of which is the generation of a non-macrocyclic structure for a compound that is actually macrocyclic.[4] More recently, we have used the $[O_4]$ donor calix[4]arene ligand system to synthesize related subvalent complexes of germanium and tin, namely [Bu^{t}calix$^{(TMS)_2}$]M (M = Ge, Sn).[5] To complement the above studies using $[N_4]$ and $[O_4]$ donor ligands, we have started to explore the subvalent chemistry of these elements using hybrid $[N_2O_2]$ donor ligands, and in this paper we describe the syntheses and structures of divalent tin and lead complexes supported by a bulky Salen ligand, namely [Salen$^{Bu^t,Me}$]M (M = Sn, Pb).

Results and discussion

The [Salen$^{R,R'}$] ligand system (Fig. 1), obtained by condensation of a salicylaldehyde derivative with 1,2-ethylenediamine, has proved to be very useful in coordination chemistry. Historically, however, the vast majority of studies using [Salen$^{RR'}$] ligands has focussed on transition metal chemistry,[6] with the interest in main group [Salen$^{RR'}$] complexes being more recent. Furthermore, to date, most applications in main group chemistry have been concerned with the Group 13 elements.[7,8] The specific ligand that we chose to use for studying divalent compounds of the heavy Group 14 elements is [Salen$^{Bu^t,Me}$], in which Bu^t and Me substituents occupy the 4- and 6-positions of the aryl-ring, respectively.[9] As a consequence of these substituents, the [Salen$^{Bu^t,Me}$] ligand provides both a greater steric bulk and a simpler ^{1}H NMR spectroscopic probe as compared to the parent [Salen] ligand.

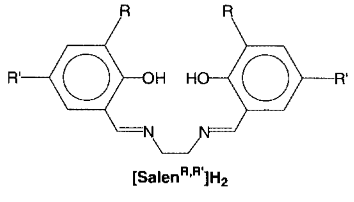
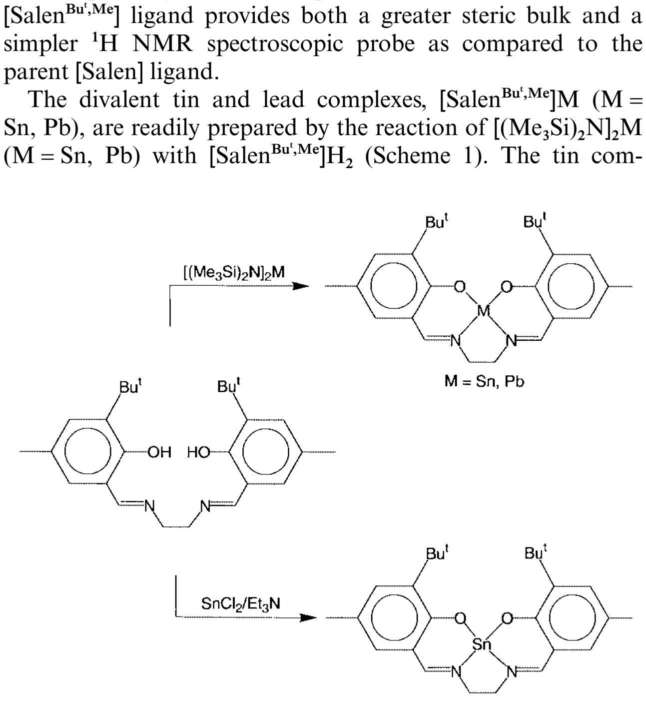


Fig. 1 The [Salen$^{R,R'}$]H_2 system.

The divalent tin and lead complexes, [Salen$^{Bu^t,Me}$]M (M = Sn, Pb), are readily prepared by the reaction of $[(Me_3Si)_2N]_2M$ (M = Sn, Pb) with [Salen$^{Bu^t,Me}$]H_2 (Scheme 1). The tin complex, [Salen$^{Bu^t,Me}$]Sn, may also be prepared by the reaction of $SnCl_2$ with [Salen$^{Bu^t,Me}$]H_2 in the presence of Et_3N.[10] Divalent tin and lead complexes of [Salen] and its derivatives are rare,[11] with only one structurally characterized example, [Saldph]-Sn,[10,12] being listed in the Cambridge Structural Database.[13,14] Other reports of [Salen$^{R,R'}$] tin[15] and lead[16] complexes have been made, but these deal almost exclusively with tetravalent complexes, *e.g.* [Salen$^{R,R'}$]MR_2.[17]



Scheme 1

The molecular structures of [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb have been determined by X-ray diffraction, as illustrated in Fig. 2 and 3; selected metrical data are listed in Table 1. As would be expected, their structures are very similar. Thus, the metal atoms in [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb are located above the "$[N_2O_2]$ coordination plane" (*vide infra*), with the only significant difference being that the Sn–X (X = O, N) distances are *ca.* 0.1 Å shorter than the corresponding Pb–X lengths, a difference which is comparable to the variation in covalent radii of Sn (1.40 Å) and Pb (1.54 Å).[18] For comparison

Table 1 Selected bond lengths (Å) and angles (°) for $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{M}$ (M = Sn, Pb)

	$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$	$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$
M–O1	2.137(3)	2.255(7)
M–O2	2.091(2)	2.206(5)
M–N1	2.347(3)	2.455(7)
M–N2	2.351(3)	2.443(7)
O1–M–O2	80.6(1)	81.0(2)
N1–M–N2	68.5(1)	66.5(3)
O1–M–N1	77.6(1)	75.2(2)
O1–M–N2	130.7(1)	126.6(2)
O2–M–N1	107.7(1)	104.4(2)
O2–M–N2	77.1(1)	74.3(2)

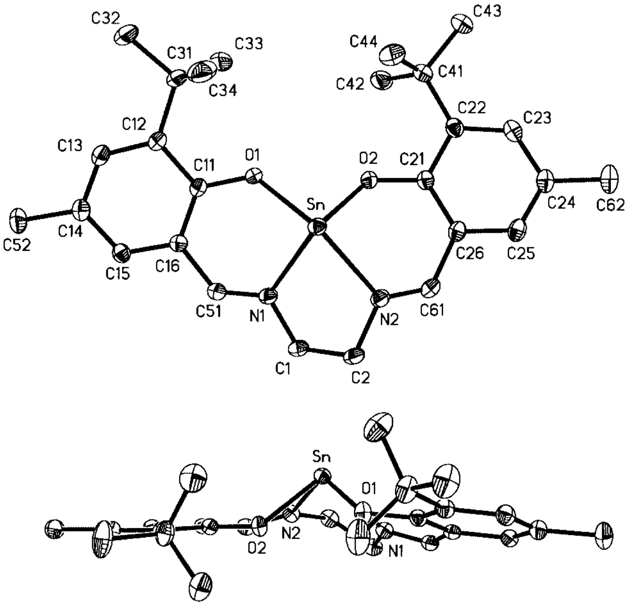


Fig. 2 Two views of the molecular structure of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$.

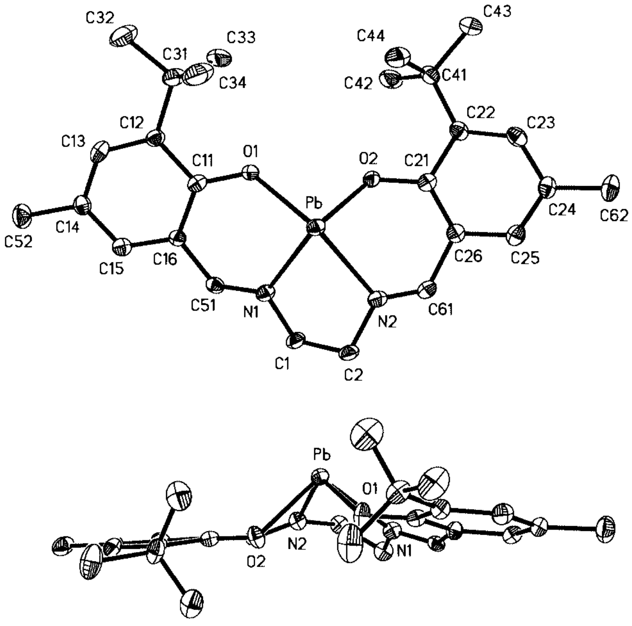


Fig. 3 Two views of the molecular structure of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$.

purposes, salient average metrical data are presented in Table 2, which also includes the data for [Saldph]Sn.[12] There are, however, no structurally characterized divalent $[\mathrm{Salen}^{\mathrm{R,R'}}]\mathrm{Pb}$ complexes listed in the Cambridge Structural Database for comparison with $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$.[19]

Table 2 Comparison of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{M}$ (M = Sn, Pb) and [Saldph]Sn

	$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$	$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$	[Saldph]Sn[a]
d(M–O)/Å	2.11	2.23	2.14
d(M–N)/Å	2.35	2.45	2.38
$d(\mathrm{M{-}N_2O_2})$/Å[b]	1.11	1.22	1.13
O–M–O/°	80.6	81.0	78.1
N–M–N/°	68.5	66.5	68.0
$(\mathrm{O{-}M{-}N})_{cis}$/°	77.4	74.8	77.7
$(\mathrm{O{-}M{-}N})_{trans}$/°	107.7 & 130.7	104.4 & 126.6	119.4

[a] Data taken from ref. 10. [b] $d(\mathrm{M{-}N_2O_2})$ is the distance of the metal from the mean plane defined by the coordinating oxygen and nitrogen atoms.

Table 3 ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic data

Assignment	δ (ppm) and coupling (Hz) $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$	δ (ppm) and coupling (Hz) $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$
$^1\mathrm{H(CDCl_3)}$		
$\mathrm{C(C}H_3)_3$	1.48, s	1.49, s
$\mathrm{C}H_3$	2.24, s	2.27, s
$\mathrm{C}H_2\mathrm{C}H_2$	3.72, m (2H) 3.87, m (2H)	3.87, s, $J_{\mathrm{Pb-H}} = 14$
$\mathrm{C}H$	6.73, d, 2	6.73, d, 2
$\mathrm{C}H$	7.18, d, 2	7.23, d, 2
$H\mathrm{C{=}N}$	8.05, s, $^3J_{\mathrm{Sn-H}} = 21$	7.98, s, $^3J_{\mathrm{Pb-H}} = 46$
$^{13}\mathrm{C(CDCl_3)}$		
$2\mathrm{C(}C\mathrm{H_3)_3}$	20.5, q, $J_{\mathrm{C-H}} = 125$	20.5, q, $J_{\mathrm{C-H}} = 126$
$2C\mathrm{H_3}$	29.8, q, $J_{\mathrm{C-H}} = 126$	29.9, q, $J_{\mathrm{C-H}} = 126$
$2C\mathrm{(CH_3)_3}$	35.1, s	35.1, s
$\mathrm{N}C\mathrm{H_2}C\mathrm{H_2N}$	55.7, t, $J_{\mathrm{C-H}} = 141$	57.9, t, $J_{\mathrm{C-H}} = 139$
2C	120.3, s	122.1, s
2C	123.7, s	122.7, s
2CH	131.4, d, $J_{\mathrm{C-H}} = 153$	131.2, d, $J_{\mathrm{C-H}} = 154$
2CH	133.0, d, $J_{\mathrm{C-H}} = 151$	132.3, d, $J_{\mathrm{C-H}} = 151$
2C	142.7, s	143.1, s
2C	163.4, s	164.7, s
$2\mathrm{(H)}C\mathrm{{=}N}$	167.2, d, $J_{\mathrm{C-H}} = 158$	167.1, d, $J_{\mathrm{C-H}} = 159$
$^{119}\mathrm{Sn(CDCl_3)}$	−518, s	

A notable feature of the structures of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ is that the $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]$ ligand is not flat but adopts a slightly twisted conformation, such that the four coordinating atoms of the $[\mathrm{N_2O_2}]$ core are not coplanar but deviate significantly from their mean-plane (Fig. 2 and 3).[20] A further manifestation of the twisting is the observation that the two $(\mathrm{O{-}M{-}N})_{trans}$ angles in $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{M}$ (M = Sn, Pb) differ by more than 20°. In contrast, the $[\mathrm{N_2O_2}]$ atoms in [Saldph]Sn are coplanar with identical $(\mathrm{O{-}M{-}N})_{trans}$ angles (119.4°), as compared to the two distinct values for $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ (107.7 and 130.7°).

$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ have also been characterized by multinuclear NMR spectroscopy (Table 3). For example, the tin complex is characterized by a ^{119}Sn signal at δ −518, a value which is comparable to those of the related divalent derivatives, [Salen]Sn (δ −564), [Saldph]Sn (δ −543), [Salph]Sn (δ −559), $[\mathrm{SaleanH_2}]\mathrm{Sn}$ (δ −524), and $[\mathrm{SalpanH_2}]\mathrm{Sn}$ (δ −521).[10,14] The most interesting spectroscopic features, however, are concerned with the ^{1}H NMR spectroscopic signals for the [CH=N] and $[\mathrm{NCH_2CH_2N}]$ moieties of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$. In particular, the signals for the $[\mathrm{NCH_2CH_2N}]$ groups are substantially different for $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$, as shown in Fig. 4. Thus, the $[\mathrm{NCH_2CH_2N}]$ moiety of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ is observed as a singlet with ^{207}Pb[21] satellites $[{}^3J({}^{207}\mathrm{Pb{-}H}) = 14\ \mathrm{Hz}]$, whereas that for $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ is observed as two complex multiplets. The complex nature

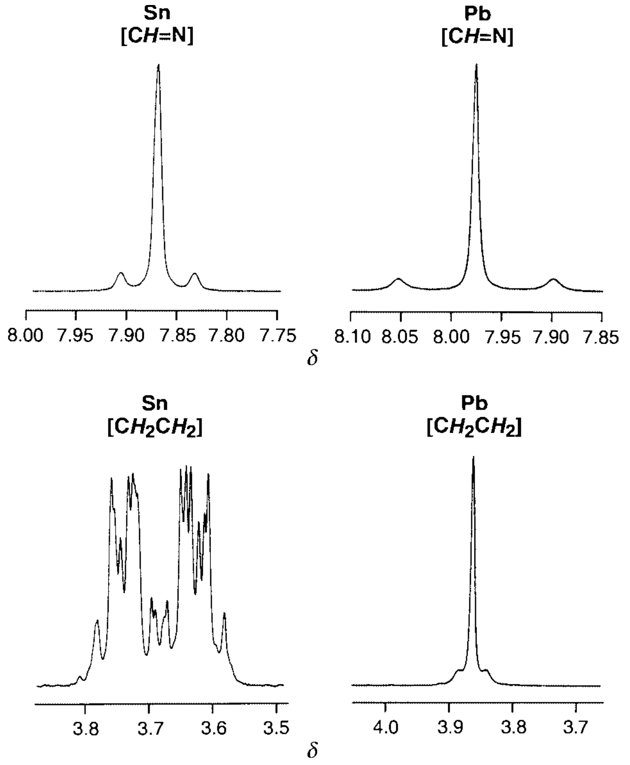


Fig. 4 ^{1}H NMR signals (300 MHz) for the [CH=N] (upper) and [NCH$_2$CH$_2$N] (lower) moieties of [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb in CDCl$_3$.

of the spectrum for [Salen$^{Bu^t,Me}$]Sn is that which would be expected for the solid state structure which has only C_1 symmetry.[22] In view of the chemical inequivalence of the [NCH$_2$CH$_2$N] protons in [Salen$^{Bu^t,Me}$]Sn, the observation of a singlet for the lead complex [Salen$^{Bu^t,Me}$]Pb may be explained by the formal translation of the lead atom from one side of the ligand to the other, thereby resulting in all of the [NCH$_2$CH$_2$N] hydrogen atoms becoming equivalent on the NMR timescale.[23] Variable temperature ^{1}H NMR spectroscopic studies confirm this suggestion, with decoalescence of the [NCH$_2$CH$_2$N] proton signals for [Salen$^{Bu^t,Me}$]Pb being observed at 260 K (Fig. 5).[24] The tin complex, however, is still static at 353 K, so that the barrier for exchange within [Salen$^{Bu^t,Me}$]Sn is considerably greater than that within [Salen$^{Bu^t,Me}$]Pb. Since Pb is slightly larger than Sn, the latter observation is interesting because it suggests that the exchange mechanism for lead does not involve a simple passage of the metal through the [N$_2$O$_2$] plane, since the barrier for Sn would be expected to be lower than that for Pb.

Finally, both [Salen$^{Bu^t,Me}$]Sn and [Salen$^{Bu^t,Me}$]Pb exhibit coupling, in the form of satellites ($^{119/117}$Sn[25] and ^{207}Pb[21]), between the central metal atom and the hydrogen of the [CH=N] moiety, as illustrated in Fig. 4: $J(^{119/117}\mathrm{Sn–H}) = 21$ Hz and $J(^{207}\mathrm{Pb–H}) = 46$ Hz. The $J(^{119/117}\mathrm{Sn–H})$ coupling constant is similar in magnitude to that reported for the tetravalent tin complex, [Salen]SnCl$_2$, $J(^{119/117}\mathrm{Sn–H}) = 36$ Hz.[26]

Experimental

General considerations: techniques and reagents

All manipulations were performed using a combination of glovebox, high vacuum or Schlenk techniques.[27] Solvents were purified and degassed by standard procedures and all commercially available reagents were used as received. [(Me$_3$Si)$_2$N]$_2$Sn and [(Me$_3$Si)$_2$N]$_2$Pb were prepared by the literature method.[28] [Salen$^{Bu^t,Me}$]H$_2$ was prepared by condensation of ethylenediamine with 4-methyl-6-*tert*-butylsalicylaldehyde[29] using a procedure analogous to that for other Salen ligands.[30]

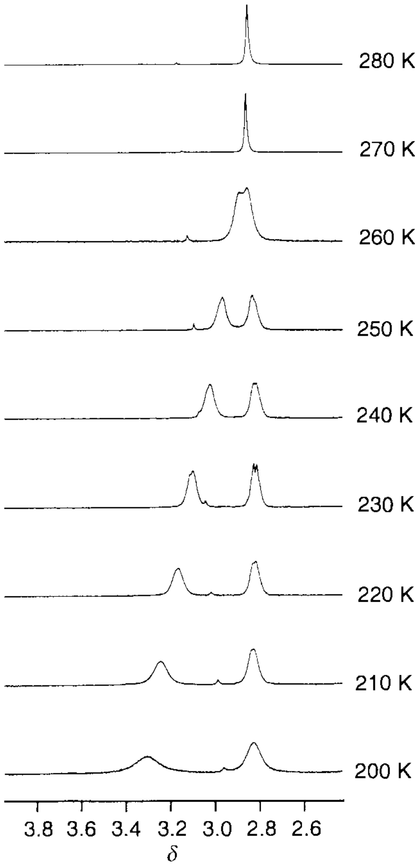


Fig. 5 Variable temperature ^{1}H NMR spectra (500 MHz) of the [NCH$_2$CH$_2$N] moiety of [Salen$^{Bu^t,Me}$]Pb in C$_6$D$_5$CD$_3$.

IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer and are reported in cm^{-1}. Carbon, hydrogen and nitrogen elemental analyses (CHN) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. ^{1}H NMR spectra were recorded on Varian VXR-300 and VXR-400 spectrometers operating at 299.924 and 399.95 MHz, respectively, and Bruker DMX-500 and DPX-300 spectrometers operating at 500.133 and 300.132 MHz, respectively. ^{13}C and ^{119}Sn spectra were recorded on the Varian VXR-300 operating at 75.429 and 111.800 MHz, respectively. ^{1}H and ^{13}C NMR spectra are reported in ppm relative to SiMe$_4$ and were referenced internally to the residual protio solvent (δ 7.15 for C$_6$D$_5$H and δ 7.26 for CHCl$_3$) and the ^{13}C resonances of the solvents (δ 128 for C$_6$D$_6$ and δ 77 for CDCl$_3$). ^{119}Sn spectra were referenced externally to a CDCl$_3$ solution of SnMe$_4$.[31]

Synthesis of [Salen$^{Bu^t,Me}$]H$_2$

Ethylenediamine (0.77 mL, 11.43 mmol) was added to a solution of 4-methyl-6-*tert*-butylsalicylaldehyde (4.42 g, 22.9 mmol) in ethanol (*ca.* 50 mL) and the mixture was heated at *ca.* 85–90 °C in an ampoule for 1 hour, thereby depositing a yellow solid. The mixture was cooled to room temperature and filtered giving [Salen$^{Bu^t,Me}$]H$_2$ as a yellow solid (2.5 g, 53%).

Synthesis of [Salen$^{Bu^t,Me}$]Sn

Method A. Benzene (*ca.* 5 mL) was added to a mixture of [(Me$_3$Si)$_2$N]$_2$Sn (0.39 g, 0.89 mmol) and [Salen$^{Bu^t,Me}$]H$_2$ (0.30 g, 0.73 mmol). The resulting mixture was stirred for *ca.* 4 hours at room temperature to give a yellow precipitate. The mixture was filtered and the yellow solid was washed with benzene (*ca.* 3 mL) and pentane (*ca.* 10 mL) and dried under vacuum giving [Salen$^{Bu^t,Me}$]Sn (0.30 g, 78%). Analysis calcd. for C$_{26}$H$_{34}$N$_2$O$_2$Sn: C, 59.5; H, 6.5; N, 5.3. Found: C, 59.5; H, 6.3; N, 4.7%. IR data: 2937(s), 2862(s), 1650(vs), 1621(vs), 1545(vs), 1460(m),

Table 4 Crystal, intensity collection and refinement data

	$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$	$[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$
Lattice	Triclinic	Triclinic
Formula	$C_{26}H_{34}N_2O_2Sn$	$C_{26}H_{34}N_2O_2Pb$
Formula weight	525.2	613.7
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	7.765(2)	7.720(2)
b/Å	12.812(3)	12.880(3)
c/Å	14.187(3)	14.316(4)
α/°	110.12(2)	111.05(2)
β/°	97.67(2)	97.02(2)
γ/°	97.45(2)	98.52(2)
V/Å^3	1269.7(6)	1297.0(7)
Z	2	2
T/K	296	296
Radiation (λ/Å)	0.71073	0.71073
ρ (calcd.)/g cm^{-3}	1.374	1.571
μ(Mo-Kα)/mm^{-1}	1.029	6.526
θ max/°	22.5	22.5
No. of data	3346, 3119 [$F > 2\sigma(F)$]	3396, 3018 [$F > 2\sigma(F)$]
No. of parameters	281	281
R	0.0247	0.0345
R_w	0.0360	0.0448
GOF	1.09	1.20

1410(s), 1380(s), 1351(m), 1334(m), 1282(s), 1262(vs), 1237(s), 1203(s), 1164(s), 1097(s), 1027(s), 970(m), 927(w), 868(m), 796(s), 689(w), 599(w), 497(m).

Method B. Ethanol (*ca.* 10 mL) was added to a mixture of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{H}_2$ (0.20 g, 0.49 mmol) and $SnCl_2$ (0.09 g, 0.49 mmol) in a glass ampoule. Et_3N (0.15 mL, 0.99 mmol) was added and the mixture was heated at *ca.* 80 °C for 3 hours after which time it was cooled to room temperature giving a yellow precipitate. The mixture was filtered, and the yellow solid was washed with ethanol (2 × 7 mL) and dried *in vacuo* giving $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ (0.15 g, 57%).

Synthesis of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$

Benzene (*ca.* 10 mL) was added to a mixture of $[(Me_3Si)_2N]_2Pb$ (1.00 g, 1.89 mmol) and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{H}_2$ (0.70 g, 1.71 mmol). The resulting mixture was stirred for *ca.* 3 days at room temperature to give a yellow precipitate. The mixture was filtered and the yellow solid was washed with benzene (2 × 2 mL) and dried *in vacuo* giving $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ (0.80 g, 76%). Analysis calcd. for $C_{26}H_{34}N_2O_2Pb$: C, 50.9; H, 5.6; N, 4.6. Found: C, 49.9; H, 5.3; N, 4.3%. IR data: 2940(s), 2903(s), 2864(s), 1643(vs), 1615(vs), 1542(s), 1472(m), 1460(m), 1408(s), 1376(s), 1348(m), 1308(m), 1285(s), 1262(s), 1237(s), 1201(m), 1161(m), 1095(m), 1027(w), 969(w), 927(vw), 869(w), 840(w), 793(m), 597(vw), 569(vw), 531(vw), 490(m).

Crystal structure determinations

Crystallographic data for $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ were collected on a Siemens P4 diffractometer using graphite monochromated Mo-Kα X-radiation (λ = 0.71073 Å). The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures using SHELXTL.[32] Hydrogen atoms attached to carbon were included in calculated positions. Crystal data, data collection and refinement parameters are summarized in Table 4.

CCDC reference number 186/1620.

Conclusion

In conclusion, $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ are the sole pair of divalent Group 14 [Salen] complexes to have been structurally characterized. The molecular structures of $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Sn}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{Pb}$ are very similar, both featuring non-planar geometries, but ^{1}H NMR spectroscopy demonstrates that the barrier for the formal transfer of the metal from one face of the ligand to the other is significantly greater for the tin derivative.

Acknowledgements

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9 Aluminium complexes of this ligand, namely, $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{AlCl}$ and $[\mathrm{Salen}^{\mathrm{Bu^t,Me}}]\mathrm{AlR}$ (R = Me, Et), have been prepared. See: I. Taden, H.-C. Kang, W. Massa and J. Okuda, *J. Organomet. Chem.*, 1997, **540**, 189.

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23 Although the precise mechanism of the exchange process is unknown, the observation that the [*H*C=N] group exhibits $^3J(^{207}\mathrm{Pb}\text{–}\mathrm{H})$ coupling at high temperatures suggests that dissociation of lead is not involved and that the exchange is intramolecular.

24 Due to the complex nature of the ABCD pattern of the stereochemically rigid structure, a detailed analysis of the dynamics was not performed. Nevertheless, an upper limit for the exchange barrier at 270 K can be estimated as 13 kcal mol^{-1}.

25 The coupling to tin is an unresolved composite of coupling to both ^{117}Sn ($I = 1/2$, 7.68%) and ^{119}Sn ($I = 1/2$, 8.58%) where $J(^{119}\mathrm{Sn})/J(^{117}\mathrm{Sn}) = 1.05$, due to the ratio of the respective magnetogyric ratios. See ref. 21.

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