Triethyl-germanium, -tin and -lead complexes derived from internally functionalised oximes

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Reactions of triethylmetal(IV) chlorides with sodium salts of internally functionalised oximes in a 1:1 molar ratio in refluxing anhydrous benzene yield [$Et_3M\{ON{=}C(R)Ar\}$] [where R = H, Me; M = Ge **(1–5)**, Sn **(6,7)** or Pb **(8–12)**; Ar = 2-C_5H_4N, 2-C_4H_3O or 2-C_4H_3S]. All these derivatives have been characterised by elemental analysis and IR and NMR [^1H, $^{13}C\{^1H\}$, $^{119}Sn\{^1H\}$ and $^{207}Pb\{^1H\}$] spectroscopic studies. Absence of any significant shift in the hetero-aryl ring carbon / proton resonances and the presence of chemical shifts at ~δ110 ppm in ^{119}Sn NMR and at ~ δ 400 ppm in ^{207}Pb NMR spectra of these derivatives have been interpreted in terms of a tetrahedral geometry around the metal atom.

Keywords: sodium salt, internally functionalised oximes, ^{119}Sn and ^{207}Pb NMR

Organometallic compounds of heavy group 14 elements (Ge, Sn and Pb) have been the subject of considerable research interest due to their diverse structural features, wide range of applications in industry and catalytic and biocidal properties. In our earlier investigations on organotin(IV) compounds derived from internally functionalised oximes, it was reported that subtle change in the R groups on tin results in different structural motifs including metal-hetero atom interactions.[1-3]

In order to understand the effects on the structure of the corresponding derivatives when the central tin atom is being replaced by either germanium or lead, we synthesised some triethylgermanium(IV) and triethyllead(IV) complexes derived from internally functionalised oximes and the results are reported herein.

Results and discussion

Reactions of triethyl-germanium and –lead chlorides with the sodium salt of the internally functionalised oximes in refluxing benzene under anhydrous conditions gave complexes of the following type:

$$Et_3MCl + Na[ON{=}C(R)Ar\,] \rightarrow [Et_3M\{ON{=}C(R)Ar\}] + NaCl\downarrow$$

(where R = H, Me; M = Ge **(1–5)** or Pb **(8–12)**;
Ar = 2-C_5H_4N, 2-C_4H_3O or 2-C_4H_3S)

Triethylgermanium(IV) complexes are colourless liquids which can be distilled under vacuum in quantitative yields. They show higher volatility than their tin analogues.[2] Triethyllead(IV) complexes are golden yellow liquids which undergo decomposition to tetraethyllead (as confirmed by ^{1}H NMR spectrum) and a black residue, when subjected to distillation under reduced pressure:

$$2\ Et_3PbL \rightarrow Et_4Pb + \text{Black residue}$$

IR spectra

IR spectra of all these derivatives have been recorded from neat liquids in the range 4000–200 cm^{-1} and interpreted by comparing with the spectra of the free oximes as well as with other oxime-complexes.[2,4]. The hydroxy group absorption, which appears in the region 3100–3300 cm^{-1} in the free oximes, is absent in the IR spectra of all these complexes, indicating metal-ligand bond formation through the oxygen atom. A medium to weak intensity C=N absorption band in the region 1557–1666 cm^{-1} and a strong N-O absorption in the region 900–938 cm^{-1} for the free oximes are found to be shifted to the lower wave numbers on complexation and are observed in the regions 1541–1635 cm^{-1} and 887–930 cm^{-1}, respectively. The appearance of a new medium to strong intensity band in the IR spectra of triethylgermanium (IV) and triethyllead (IV) complexes in the regions 520–559 cm^{-1} and 406–439 cm^{-1}, respectively, may be assigned to the νM–O mode. Strong absorption in the region 583–593 cm^{-1} in triethylgermanium complexes may be assigned to νGe–C. Similarly, the presence of a strong to medium intensity band at 463 ± 3 cm^{-1} in triethyllead (IV) complexes may be assigned to νPb–C.

NMR spectra

^{1}H and $^{13}C\{^1H\}$ NMR spectra of all these complexes are summarised in Table 1. In the ^{1}H NMR spectra of the germanium complexes only a single large peak (centred at a point) has been observed for Ge–Et protons.[5] However, the Et_3Sn proton resonances appeared as a triplet and as a quartet.[2] In case of Et_3Pb complexes a set of triplets (7.8–7.9 Hz (t)) and quartets (7.7–7.9 Hz (q)) have been observed due to splitting of CH_3 and CH_2 group protons, respectively. This splitting is because of the presence of the lead isotope ^{207}Pb (natural abundance 21.11 % and spin ½).[6]

In the ^{13}C NMR spectra of these complexes, a slight down-field shift (δ 0.3–2.6 ppm) of the C=N carbon signal has been observed which is not affected by the change in the size of the central metal atom. No significant shift in the hetero-aryl ring carbon / proton resonances was observed, indicating that the metal-heteroatom interactions (which were present in the corresponding tetraorganodistannoxanes in the solid state[1,3]) are absent. In the $^{13}C\{^1H\}$ NMR spectra of all these complexes the M–CH_2 and M–CCH_3 carbons appeared as singlets and the Δ [$\delta(CH_3)$–$\delta(CH_2)$] increases with increasing size of the metal atom (~0.5 ppm for Ge, ~2.7 ppm for Sn and ~17.0 ppm for Pb). The Pb–CH_2CH_3 carbon resonances showed coupling with the ^{207}Pb isotope with $^1J(^{207}Pb–^{13}C)$ = 184 ± 4 Hz and $^2J\,(^{207}Pb–^{13}C)$ = ~ 35 Hz. When compared with ^nJ(Sn–C), it is found that ^1J(Pb–C) is always smaller than ^1J(Sn–C). The ^{119}Sn and ^{207}Pb NMR spectra of tin and lead (IV) compounds displayed single resonances at ~ 110 and ~ 400 ppm, respectively. These values are expected for four coordinate trialkyl tin and lead compounds.[6]

Experimental

All the reactions were carried out under anhydrous conditions using a methanol–benzene mixture as solvent. Et_3GeCl and Et_3SnCl were used as supplied while Et_3PbCl was prepared according to the literature method.[7]

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Table 1 NMR data in $CDCl_3$ for triethylgermanium, –tin and –lead oximates

Compound	^{1}H NMR δ ppm	^{13}C{^{1}H} NMR δ ppm	^{119}Sn{^{1}H}/ ^{207}Pb{^{1}H} NMR δ ppm
$Et_3Ge\{ON{=}C(Me)Py\}$	1.02–1.15; centred at 1.08 (Ge–CH_2CH_3); 2.34 (s, oxime–Me); 7.18 (td, 6.1 Hz (t), 1.8 Hz (d), H-5); 7.61 (m, H-4) 7.91 (dt, 8.1 Hz (d), 1.0 Hz (t), H-3); 8.57 (m, H-6).	7.1 (s, Ge–CH_2); 7.7 (Ge–CCH_3); 9.9 (oxime-Me); 120.0 (s, C-5); 122.6 (s, C-3); 135.5 (C-4); 148.4 (C-6); 155.8 (C-2); 157.8 (C=N).	–
$Et_3Ge\{ON{=}C(Me)C_4H_3O\}$	1.03–1.16; centred at 1.12 (Ge–CH_2CH_3); 2.16 (s, oxime–Me); 6.39 (dd, 3.3 and 1.7 Hz (d), H-4); 6.56 (d, 3.3 Hz (d), H-3); 7.42 (d, 1.1 Hz (d), H-5).	7.0 (s, Ge–CH_2); 7.7 (s, Ge–CCH_3); 10.7 (s, oxime-Me); 107.3 (s, C-4); 110.9 (s, C-3); 142.4 (s, C-5); 149.4 (s, C-2); 152.0 (s, C=N).	–
$Et_3Ge\{ON{=}C(Me)C_4H_3S\}$	1.11–1.21; centred at 1.17 (Ge–CH_2CH_3); 2.27 (s, oxime–Me); 7.01 (m, H-4); 7.17 (m, H-3); 7.20 (m, H-5).	7.2 (s, Ge–CH_2); 7.7 (s, Ge–CCH_3); 11.6 (s, oxime–Me); 124.5 (s, C-4); 125.5 (s, C-3); 126.5 (s, C-5); 142.5 (s, C-2); 152.1 (s, C=N).	–
$Et_3Ge\{ON{=}C(H)Py\}$	1.03–1.13; (centred at 1.12 (Ge–CH_2CH_3); 7.18 (td, 6.2 Hz (t), 1.1 Hz (d), H-4); 7.63 (td, 7.6 Hz (t), 1.7 Hz (d), H-5); 7.83 (d, 7.9 Hz (d), H-3); 8.26 (s, oxime-H); 8.55 (d, 5.4 Hz (d), H-6).	7.1 (s, Ge–CH_2); 7.7 (s, Ge–CCH_3); 120.1 (s, C-5); 123.1 (s, C-3); 136.0 (s, C-4); 149.2 (s, C-6); 151.9 (s, C-2); 152.7 (s, C=N).	–
$Et_3Ge\{ON{=}C(H)C_4H_3S\}$	1.17 (Ge–CH_2CH_3); 7.06 (t, 4.4 Hz (t), H-4); 7.31 (d, 3.7 Hz (d), H-3); 7.44 (dt, 5.1 Hz (d), 1.0 Hz, (t), H-5); 7.84 (s, oxime-H).	7.2 (s, Ge–CH_2); 7.8 (s, Ge–CCH_3); 125.5 (s, C-4); 129.7 (s, C-3); 131.5 (s, C-5); 141.2 (s, C-2); 142.9 (s, C=N).	–
$Et_3Sn\{ON{=}C(Me)Py\}$	1.16–1.44 (m, Sn–CH_2CH_3); 2.34 (s, oxime–Me); 7.17 (br, H-4); 7.60 (br, H-5); 7.88 (d, 7.8 Hz, H-3); 8.56 (s, H-6)	7.0 {$^1J(^{119/117}Sn–^{13}C)$ = 365 Hz, Sn–CH_2}; 9.7 (Sn–CCH_3); 9.8 (s, oxime–Me); 120.0 (C-5); 122.5 (C-3); 135.6 (C-4); 148.6 (C-6); 156.4 (C-2); 157.8 (C=N).	111.7
$Et_3Sn\{ON{=}C(Me)C_4H_3O\}$	1.09–1.46 (m, Sn–CH_2CH_3); 2.17 (s, oxime–Me); 6.38 (s, H-4); 6.51 (br s, H-3); 7.39 (s, H-5).	6.9 [$^1J(^{119/117}Sn–^{13}C)$ = 354 Hz, Sn–CH_2]; 9.6 (Sn–CCH_3); 10.3 (oxime–Me); 106.6 (C-4); 111.0 (C-3); 142.2 (C-5); 149.3 (C-2); 152.5 (C=N).	110.9
$Et_3Pb\{ON{=}C(Me)Py\}$	1.67 (t, 7.9 Hz, Pb–CCH_3); 2.04 (q, 7.9 Hz, Pb–CH_2); 2.31 (s, oxime–Me); 7.08 (t, 5.7 Hz, H-4); 7.55 (t, 6.4 Hz, H-5); 7.76 (br, H-3); 8.60 (br, H-6).	9.5 (s, oxime–Me); 12.3 {$^2J(^{207}Pb–^{13}C)$ = 34 Hz, Pb–CCH_3}; 29.1 {$^1J(^{207}Pb–^{13}C)$ = 188 Hz, Pb-CH_2}; 119.7 (s, C-5); 122.0 (s, C-3); 135.8 (s, C-4); 148.6 (s, C-6); 154.7 (s, C-2); 156.3 (s, C=N).	386.8
$Et_3Pb\{ON{=}C(Me)C_4H_3O\}$	1.66 (t, 7.8 Hz, Pb-CCH_3); 2.03 (q, 7.6 Hz, Pb-CH_2); 2.12 (s, oxime-Me); 6.32 (dd, 2.5 and 1.8 Hz, H-4); 6.42 (d, 3.2 Hz, H-3); 7.33 (br, H-5).	10.1 (s, oxime-Me); 12.2 {$^2J(^{207}Pb-^{13}C)$ = 34 Hz, Pb-CCH_3}; 28.8 {$^1J(^{207}Pb-^{13}C)$ = 186 Hz, Pb-CH_2}; 105.7 (s, C-4); 110.7 (s, C-3); 141.6 (s, C-5); 148.0 (s, C-2); 152.9 (s, C=N).	384.9
$Et_3Pb\{ON{=}C(Me)C_4H_3S\}$	1.75 (t, 7.9 Hz, Pb–CCH_3); 2.12 (q, 7.9 Hz, Pb–CH_2); 2.32 (oxime–Me); 6.93 (t, 4.7 Hz, H-4); 7.02 (t, 6.2 Hz, H-3); 7.25 (br, H-5).	11.0 (s, oxime–Me); 12.2 {$^2J(^{207}Pb–^{13}C)$ = 35 Hz, Pb–CCH_3}; 29.2 {$^1J(^{207}Pb–^{13}C)$ = 184 Hz, Pb–CH_2}; 123.0 (s, C-4); 124.1 (s, C-3); 126.2 (s, C-5); 144.0 (s, C-2); 150.6 (s, C=N).	395.4
$Et_3Pb\{ON{=}C(H)Py\}$	1.77 (t, 7.8 Hz, Pb–CCH_3); 2.16 (q, 7.7 Hz, Pb–CH_2); 7.13 (br, H-4); 7.57 (br, H-5); 7.75 (br, H-3); 8.15 (s, oxime–H); 8.65 (br, H-6).	12.5 (Pb–CCH_3); 31.1 (Pb–CH_2); 120.7 (s, C-5); 123.4 (s, C-3); 136.9 (s, C-4); 148.8 (s, C-6); 149.5 (s, C-2); 152.4 (s, C=N). ^nJ(Pb–C) not observed.	422.0
$Et_3Pb\{ON{=}C(H)C_4H_3S\}$	1.74 (t, 7.8 Hz, Pb–CCH_3); -2.11 (q, 7.9 Hz, Pb–CH_2); 6.99 (br, H-4); 7.21 (br, H-3); 7.26 (d, 4.7 Hz, H-5); 7.80 (oxime–H).	12.4 {$^2J(^{207}Pb–^{13}C)$ = 35 Hz, Pb–CCH_3}; 29.4 {$^1J(^{207}Pb–^{13}C)$ = 180 Hz, Pb–CH_2}; 125.0 (s, C-4); 128.2 (s, C-3); 132.1 (s, C-5); 142.4 (C-2, C=N).	–

CAUTION: All operations were carried out with due care because of the toxicity of triethyllead(IV) compounds and other hazardous materials including the solvent benzene. This involves, primarily, working in a well-ventilated hood and special precautions were taken in the disposal of these toxic materials, so that the same may not pollute the environment.

Germanium and tin were estimated as oxide and lead was estimated as lead sulfate. C, H and N analyses were carried out on Elementar Vario EL III Carlo Erba 1108 elemental analyzer. ^{207}Pb{^{1}H} NMR spectra were recorded as $CDCl_3$ solutions on a Bruker DPX-300 NMR spectrometer operating at 62.7 MHz. ^{207}Pb chemical shifts are relative to external Et_3PbCl in $CDCl_3$ (δ 472.6 relative to Me_4Pb). All other experimental conditions and spectroscopic techniques are the same as described earlier.[2]

Preparation of [$Et_3Ge\{ON=C(Me)Py\}$]: To a methanolic solution of the sodium salt of the ligand [prepared by the reaction of sodium (146 mg, 6.35 mmol) with 2-acetylpyridyl oxime (865 mg, 6.35 mmol) in refluxing methanol], a benzene solution of Et_3GeCl (1.24 g, 6.35 mmol) was added and the mixture was refluxed for 5 h. The NaCl formed (367 mg, 6.28 mmol) during the reaction was filtered off and the filtrate was concentrated in vacuum to give a pinkish liquid which was distilled under vacuum (160°C, at 5 mm of Hg, 1.81g, 96 % yield) as a colourless liquid. The other triethylgermanium(IV) complexes were prepared similarly. Pertinent data are summarised in Table 2.

Preparation of [$Et_3Pb\{ON=C(Me)Py\}$]: To a methanolic solution of sodium salt of the ligand [prepared by the reaction of sodium (128 mg, 5.56 m mol) with 2-acetylpyridyl oxime (757 mg, 5.56 mmol) in refluxing methanol], a benzene suspension of Et_3PbCl (1.83 g, 5.56 mmol) was added and refluxed for 5 h. The NaCl formed (317 mg, 5.42 mmol) during the reaction was filtered off and the filtrate was concentrated in vacuum to give a dark yellow liquid (2.37 g, 99 % yield). All other triethyllead(IV) oximates were prepared in a similar manner. Attempted vacuum distillation [~100°C, at 5 mm of Hg] gave Et_4Pb and a black uncharacterised residue.

Conclusion

The above mentioned spectral data and a comparison of these with the corresponding organotin(IV) compounds,[2] privides the following structure (Fig.1) for these triethyl metal (metal = Ge and Pb) derivatives derived from internally functionalised oximes:

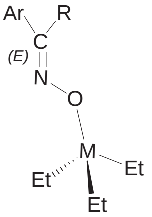

Fig.1 Proposed structure of $Et_3M[ON=C(R)Ar]$, where M = Ge and Pb; R = H or Me and Ar = 2-C_5H_4N, 2-C_4H_3O or 2-C_4H_3S.

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Table 2 Physical and analytical data for triethylgermanium, -tin and -leadoximates

Compound	Colour	B.p. °C/ mm of Hg	% yield (after distillation)	Elemental analysis in % found (Calcd.)			
				C	H	N	M
$Et_3Ge\{ON=C(Me)Py\}$ **(1)**	Colourless	160/5	96	52.8	7.6	9.6	24.5
				(52.9)	(7.5)	(9.5)	(24.6)
$Et_3Ge\{ON=C(Me)C_4H_3O\}$ **(2)**	Colourless	140 /5	92	50.9	7.5	4.8	25.4
				(50.8)	(7.5)	(4.9)	(25.6)
$Et_3Ge\{ON=C(Me)C_4H_3S\}$ **(3)**	Colourless	170/5	95	48.2	7.2	4.8	24.0
				(48.0)	(7.1)	(4.7)	(24.2)
$Et_3Ge\{ON=C(H)Py\}$ **(4)**	Colourless	180/5	93	51.4	7.3	10.2	25.7
				(51.3)	(7.2)	(10.0)	(25.8)
$Et_3Ge\{ON=C(H)C_4H_3S\}$ **(5)**	Colourless	200/5	96	46.1	6.6	4.9	25.3
				(46.2)	(6.7)	(4.9)	(25.4)
$Et_3Sn\{ON=C(Me)Py\}$ **(6)**	Pink	160/0.1	90	45.9	6.4	8.3	34.6
				(45.8)	(6.5)	(8.2)	(34.8)
$Et_3Sn\{ON=C(Me)C_4H_3O\}$ **(7)**	Yellow	130/0.1	96	43.6	6.5	4.1	35.8
				(43.7)	(6.4)	(4.2)	(36.0)
$Et_3Pb\{ON=C(Me)Py\}$ **(8)**	Dark yellow	Decom-	Decom-	36.2	5.3	6.6	47.9
		position	position	(36.3)	(5.2)	(6.5)	(48.2)
$Et_3Pb\{ONC(Me)C_4H_3O\}$ **(9)**	Yellow	"	"	34.5	5.2	3.4	49.4
				(34.4)	(5.1)	(3.3)	(49.5)
$Et_3Pb\{ON=C(Me)C_4H_3S\}$ **(10)**	Yellow	"	"	33.4	4.9	3.3	47.6
				(33.2)	(4.9)	(3.2)	(47.7)
$Et_3Pb\{ON=C(H)Py\}$ **(11)**	Yellow	"	"	34.8	4.8	6.6	49.7
				(34.7)	(4.9)	(6.7)	(49.8)
$Et_3Pb\{ON=C(H)C_4H_3S\}$ **(12)**	Yellow	"	"	31.5	4.8	3.4	49.2
				(31.4)	(4.6)	(3.3)	(49.3)