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Synthesis and crystal structure of triphenyltin and lead complexes with organic peroxides

Alexander G. Medvedev,[a] Mikhail Yu. Sharipov,[a] Dmitry A. Grishanov,[a,b] Artur V. Eshtukov,[c] Andrei V. Churakov,[a] Ivan A. Buldashov,[a] Pavel A. Egorov,[a] Ovadia Lev[b] and Petr V. Prikhodchenko*[a]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: prikhman@gmail.com*
[b] *Casali Center of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel*
[c] *State Research Institute for Chemistry and Technology of Organoelement Compounds, 105118 Moscow, Russian Federation*

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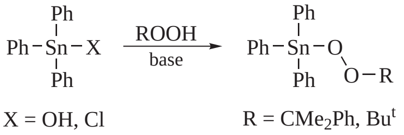
Crystalline triphenyltin cumyl and *tert*-butyl peroxides ($Ph_3SnOOCMe_2Ph$ and $Ph_3SnOOBu^t$, respectively) and triphenyllead cumyl peroxide ($Ph_3PbOOCMe_2Ph$) were synthesized and characterized by single crystal and powder X-ray diffraction, NMR, FTIR and Raman spectroscopies, TG and DSC analysis. The formation of triphenyltin *tert*-butyl peroxide in benzene in the presence of a base was proved by ^{119}Sn, ^{13}C and ^{1}H NMR spectroscopy. To the best of our knowledge, the obtained complexes are the first structurally characterized coordination compounds of tin and lead with organic peroxides.



Keywords: peroxo complexes, organic hydroperoxides, coordination peroxo compounds, lead, tin, hydrogen peroxide.

Organic peroxides (ROOH) are selective and cheap oxidizing agents widely used in the oxidation of various substrates to obtain epoxides, ketones, aldehydes, carboxylic acid esters and nitro or azoxy compounds, as well as in asymmetric Sharpless epoxidation and dihydroxylation of alkenes.[1–4] These compounds are used as precursors for more complex organic peroxides and salts.[5] Most of the organic hydroperoxides produced are used as initiators of radical polymerization.[6] Organic hydroperoxides are often used in oxidation reactions in combination with catalysts such as Lewis acids containing *d*- and *p*-block elements.[1] The synthesis of organoperoxo complexes $R_3M–OO–R'$ of several main group elements, including tin and lead, has been reported.[7,8] Coordination compounds of germanium and tin with organic peroxides have been proposed as precursors in peroxide transfer reactions with alkyl triflates, leading to dialkyl peroxides.[9] According to the Cambridge Structural Database (CSD), the coordination compounds of tin and lead(IV) with organic peroxides have not yet been structurally characterized.

Complexes of antimony,[10] silicon,[11,12] gallium,[13,14] germanium,[15] aluminum[16,17] and boron[18] with organic peroxides have been obtained and structurally characterized. In most cases, *tert*-butyl hydroperoxide (Bu^tOOH) was used as a reagent. To the best of our knowledge, the crystal structure of complexes of main group elements with cumene hydroperoxide has not been reported.

Here, we report for the first time ^{119}Sn NMR studies to develop a synthetic approach to the crystallization of triphenyltin cumyl peroxide, $Ph_3SnOOCMe_2Ph$ **1**, triphenyltin *tert*-butyl peroxide, $Ph_3SnOOBu^t$ **2**, and triphenyllead cumyl peroxide, $Ph_3PbOOCMe_2Ph$ **3**, and the characterization of these compounds by single crystal X-ray diffraction.

It was previously shown by J. Mayer that hydrogen peroxide is a poor ligand to main group elements,[19] and hydroperoxo and peroxo complexes are formed only after deprotonation of hydrogen peroxide in the presence of a base.[20–24] According to ^{119}Sn NMR studies, organic hydroperoxides exhibit coordination properties similar to hydrogen peroxide and, being poor ligands for tin(IV) in an acidic medium, do not interact with triphenyltin chloride (Figure 1). Indeed, the ^{119}Sn NMR spectra of the triphenyltin chloride solution before and after the addition of *tert*-butyl hydroperoxide

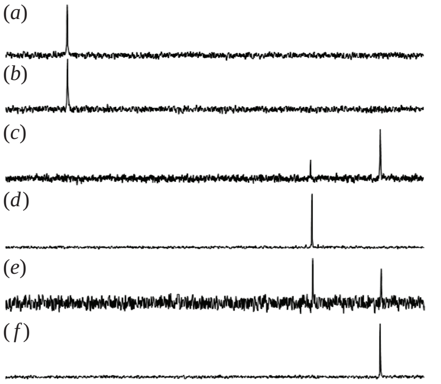
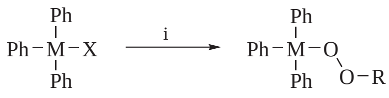


Figure 1 ^{119}Sn NMR spectrum of Ph_3SnCl (0.1 M) in benzene (*a*) before and after the sequential addition of (*b*) *tert*-butyl hydroperoxide (0.4 M) and (*c*) sodium amide (0.4 M). ^{119}Sn NMR spectrum of Ph_3SnOH (0.05 M) in benzene (*d*) before and after the addition of (*e*) 0.075 M and (*f*) 0.2 M *tert*-butyl hydroperoxide.



X = OH, Cl

1 M = Sn, R = CMe_2Ph
2 M = Sn, R = Bu^t
3 M = Pb, R = CMe_2Ph

Scheme 1 *Reagents and conditions*: i, $PhMe_2COOH$, PhH (for X = OH) or Bu^tOOH, Et_2O, NH_3 (gas) (for X = Cl).

are identical and reveal only one sharp signal at –45.5 ppm, corresponding to the initial Ph_3SnCl complex [Figure 1(*a*),(*b*)]. However, the addition of a base, sodium amide, leads to the deprotonation of Bu^tOOH and the formation of the corresponding *tert*-butyl peroxide anion, which is an active ligand and coordinates with triphenyltin to give the organoperoxo complex $Ph_3SnOOBu^t$, which exhibits an intense signal at –92.9 ppm in the ^{119}Sn NMR spectrum [Figure 1(*c*)]. The low-field NMR signal at –82.8 ppm corresponds to triphenyltin hydroxide, which is formed due to the partial hydroperoxide decomposition under basic conditions during NMR measurements [see Figure 1(*c*)]. On the other hand, the use of basic triphenyltin hydroxide as a starting compound provides basic conditions for deprotonation of hydroperoxide and subsequent coordination with tin(IV), confirmed by the ^{119}Sn NMR spectroscopy [Figure 1(*d*)–(*f*)]. The addition of *tert*-butyl hydroperoxide to a Ph_3SnOH solution with corresponding molar ratio of 1.5 results in the appearance of a signal at –92.9 ppm attributed to the triphenyltin organoperoxo complex [Figure 1(*e*)]. An increase in the hydroperoxide/Sn^{IV} molar ratio to 4 leads to the complete disappearance of the ^{119}Sn NMR signal of Ph_3SnOH at –82.8 ppm [Figure 1(*f*)].

Compounds **1** and **3** (Scheme 1) were prepared from triphenyltin and triphenyllead hydroxides, respectively, by direct interaction with cumene hydroperoxide in benzene. At the same time, compound **2** was obtained from triphenyltin chloride by reaction with *tert*-butyl hydroperoxide in diethyl ether while bubbling dry NH_3, providing basicity of the medium.

Compounds **1** and **2** crystallize in the triclinic $P\bar{1}$ and monoclinic *Pn* space groups, respectively.[†] The lead peroxide **3** is isostructural to the tin analog **1**. The crystal structures of peroxo complexes **1**–**3** consist of discrete molecules (Figure 2). The tin and lead atoms are linked to three phenyl groups and one oxygen atom of the peroxo group, leading to a distorted tetrahedral geometry. The Sn(1)–O(1) bond lengths in triphenyltin peroxides **1** and **2** are 2.020(2) and 2.014(2) Å, respectively. According to the CSD, these values are close to the average for Ph_3Sn–O–C fragments (2.067 Å, 186 CSD entries). The Pb(1)–O(1) distance in the lead peroxide **3** is 2.135(2) Å. The absence of interactions between the tin and lead centers and the second oxygen atom O(2) of the peroxo group results in the Sn(1)···O(2) distances of 2.727 and 2.678 Å for compounds **1** and **2**, respectively, and the Pb(1)···O(2) distance of 2.830 Å for the lead peroxide **3**. Selected bond lengths and angles for complexes **1**–**3** are listed in Table S1 (see Online Supplementary Materials). The peroxide O–O distances in complexes **1**–**3** are 1.484(2), 1.493(3) and 1.483(5) Å, respectively. These values are slightly longer than in free organic hydroperoxides (on average 1.460 Å, 327 CSD entries) and close to the values observed in other coordination compounds of *d*-block elements[25,26] and main group elements with organic peroxides,[10–12,18] as well as in cesium hexahydroperoxostannate.[27] The Sn(Pb)–O–O angles are 101.11(10), 98.46(13) and 101.37(15)° for complexes **1**–**3**, respectively, which are in good agreement with the values for the corresponding peroxides of the main group elements. The powder X-ray diffraction patterns of peroxides **1**–**3** fit well to those calculated from the single crystal data (Figure S1, see Online Supplementary Materials).

To the best of our knowledge, complexes **1**–**3** are the first crystal structures of tin and lead with organic peroxides. In addition, compounds **1** and **3** are the first crystal structures of *p*-block elements with cumene hydroperoxide as a ligand, although such complexes of *d*-block elements have been previously reported.[28–32]

The absence of absorbance above 3100 cm^{-1} in the FTIR spectra of complexes **1**–**3** confirms the deprotonation of the corresponding hydroperoxides and the substitution of the OH groups for organoperoxide ligands in the Sn^{IV} and Pb^{IV} coordination environment (Figure S2). In complexes **1**–**3**, the characteristic O–O stretching vibrations of organic peroxides appear as bands at 850, 850 and 835 cm^{-1} in the FTIR spectra (see Figure S2) and lines at 845, 856 and 840 cm^{-1} in the Raman spectra, respectively (Figure S3).

The thermal stability of complexes **1**–**3** was characterized by differential scanning calorimetry and thermogravimetry (Figures S4–S6). The melting points of peroxides **1** and **2** are 114 and 68 °C, respectively. These values are in good agreement with previously published values.[8] Pronounced exothermic peaks starting at 146, 140 and 150 °C and reaching a maximum at 171, 167 and 157 °C for complexes **1**–**3**, respectively, correspond to the decomposition of peroxo complexes with the evolution of oxygen and, probably, to oxidation reactions of organic fragments. According to thermogravimetric data, these exothermic effects are accompanied by significant weight loss. The obtained crystalline compounds **1**–**3** are relatively stable compared to organic hydroperoxides and inorganic peroxo complexes of the main group elements.[27,30]

Thus, crystalline triphenyltin cumyl peroxide, isostructural lead(IV) compound and triphenyltin *tert*-butyl peroxide were

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[†] *Crystal data for* **1**. $C_{27}H_{26}O_2Sn$, *M* = 501.17, triclinic, space group $P\bar{1}$, a = 9.1360(4), b = 11.3620(4) and c = 11.7072(4) Å, α = 85.404(1), β = 84.767(1) and γ = 69.516(1)°, V = 1132.15(7) Å^3, Z = 2, d_{calc} = = 1.470 g cm^{-3}, μ(MoKα) = 1.149 mm^{-1}, F(000 = 508, colorless prism with dimensions *ca.* 0.35×0.30×0.05. Total of 14274 reflections (6527 unique, R_{int} = 0.0262) were measured on a Bruker SMART APEX II diffractometer (graphite monochromatized MoKα radiation, λ = 0.71073 Å) using ω-scan mode at 150 K. The final residuals were: R_1 = 0.0339 for 5866 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0649 for all data and 375 parameters. GOF = 1.057.

Crystal data for **2**. $C_{22}H_{24}O_2Sn$, *M* = 439.10, monoclinic, space group *Pn*, a = 9.6530(4), b = 8.8256(4) and c = 12.0691(5) Å, β = 104.826(1)°, V = 993.98(7) Å^3, Z = 2, d_{calc} = 1.467 g cm^{-3}, μ(MoKα) = 1.296 mm^{-1}, F(000) = 444, colorless prism with dimensions *ca.* 0.10×0.10×0.05. Total of 9795 reflections (4464 unique, R_{int} = 0.0221) were measured on a Bruker D8 Venture diffractometer (graphite monochromatized MoKα radiation, λ = 0.71073 Å) using ω-scan mode at 100 K. The final residuals were: R_1 = 0.0118 for 4401 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0392 for all data and 226 parameters. GOF = 1.102.

Crystal data for **3**. $C_{27}H_{26}O_2Pb$, *M* = 589.67, triclinic, space group $P\bar{1}$, a = 9.1476(4), b = 11.2927(4) and c = 11.7494(4) Å, α = 85.205(1), β = 84.837(1) and γ = 69.334(1)°, V = 1132.15(7) Å^3, Z = 2, d_{calc} = = 1.734 g cm^{-3}, μ(MoKα) = 7.490 mm^{-1}, F(000) = 572, colorless prism with dimensions *ca.* 0.1×0.05×0.05. Total of 8489 reflections (4006 unique, R_{int} = 0.0254) were measured on a Bruker D8 Venture diffractometer (graphite monochromatized MoKα radiation, λ = 0.71073 Å) using ω-scan mode at 100 K. The final residuals were: R_1 = 0.0191 for 3807 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0415 for all data and 273 parameters. GOF = 1.021.

The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[33] Hydrogen atoms in compound **1** were found from difference Fourier synthesis and refined isotropically. All hydrogen atoms in compounds **2** and **3** were placed in calculated positions and refined using a riding model.

CCDC 2082383, 2082386 and 2107630 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

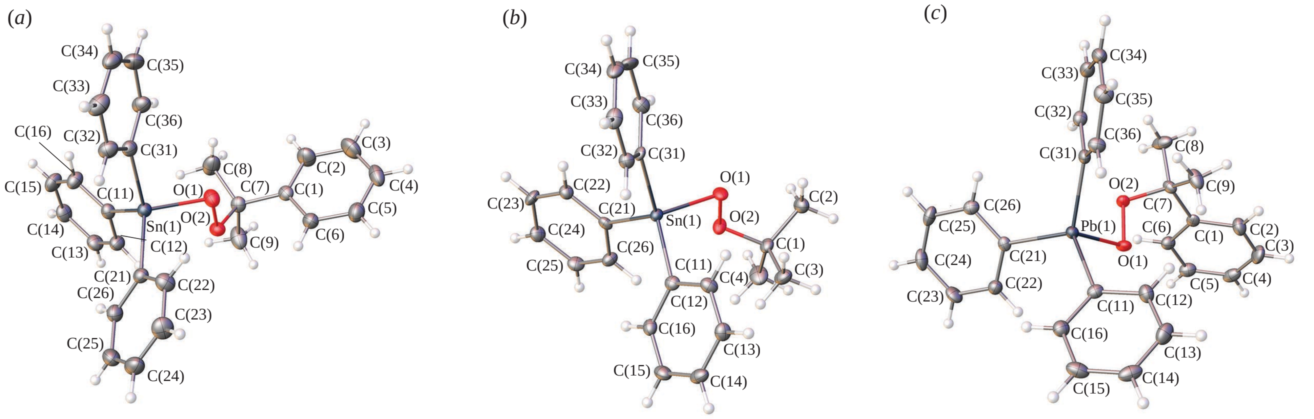

Figure 2 Molecular structures of (*a*) peroxide **1**, (*b*) peroxide **2** and (*c*) peroxide **3**. Displacement ellipsoids are drawn at 50% probability level.

obtained and characterized by single crystal and powder X-ray diffraction, NMR, FTIR and Raman spectroscopies, TG and DSC analysis. The formation of triphenyltin *tert*-butyl peroxide in benzene in the presence of a base was proved by ^{119}Sn, ^{13}C and ^{1}H NMR spectroscopy. We propose that basicity-driven coordination of organoperoxide is typical for triphenyllead and cumene hydroperoxide interaction and is probably common in the coordination chemistry of main group elements and organic peroxides. Thus, Mayer's rule stating that hydrogen peroxide is a poor ligand to main group elements[25] can be extended to organic hydroperoxides as well, and they become active ligands only after deprotonation with a base.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.018.

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