The X-Ray Structure of Bis-2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionatolead(II): an Eight-coordinate Dimer with Bridging Fluorine Atoms

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The title complex, a useful precursor for a range of lead oxides, has an unusual structure involving dimeric, eight-coordinate lead units bridged by the fluorine atoms of the ligand; the compound is unusually volatile which may in part be explained by the structure.

There is considerble interest in the use of volatile metal β-diketonate complexes as precursors for the deposition of thin films of oxides by MOCVD. Studies are predominantly concerned with high T_c superconductors,[1-8] but materials for use in nonlinear electrooptic, ferroelectric, insulating, piezoelectric, pyroelectric and dielectric applications[9-12] have also been prepared. In the 1960s bis-2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionatolead(II), $Pb(fod)_2$, was prepared by Sievers and Schweitzer *et al.* during work aimed at developing volatile, thermally stable complexes for gas-chromatographic analysis.[13] More recently the compound has successfully been used by Trundle and Brierley[9,11,12] for the deposition of a number of lead oxides including PbO, $PbTiO_3$, $PbTiO_2$ and $Pb(Sc_{0.5}Ta_{0.5})O_3$. Surprisingly, there have been relatively few studies of such compounds which is in marked contrast to the related group 2 compounds useful for high T_c superconductors. In the present paper we report on the preparation of $Pb(fod)_2$, its full

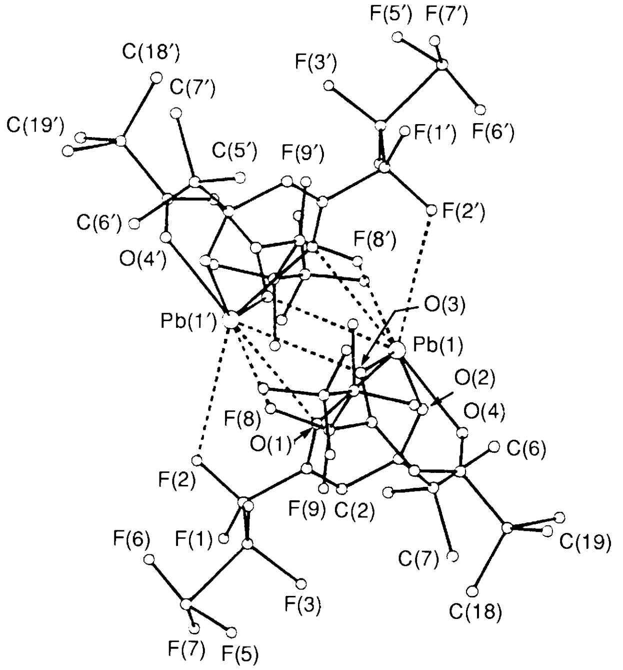

Fig. 1 Structure of [{Pb(fod)$_2$}$_2$]. Important bond lengths (Å) and angles (°): O(1)–Pb(1) 2.26(10), O(2)–Pb(1) 2.41, O(3)–Pb(1) 2.40(10), O(4)–Pb(1) 2.29, F(2)–Pb(1') 3.48(11), F(8)–Pb(1') 3.30(11), O(1)–Pb(1') 3.17(11), O(3)–Pb(1') 3.09(11), O(2)–Pb(1)–O(1) 76.9(4), O(3)–Pb(1)–O(1) 72.9(4), O(3)–Pb(1)–O(2) 138.6(3), O(4)–Pb(1)–O(1) 89.0(4), O(4)–Pb(1)–O(2) 76.3(4), O(4)–Pb(1)–O(3) 75.7(4).

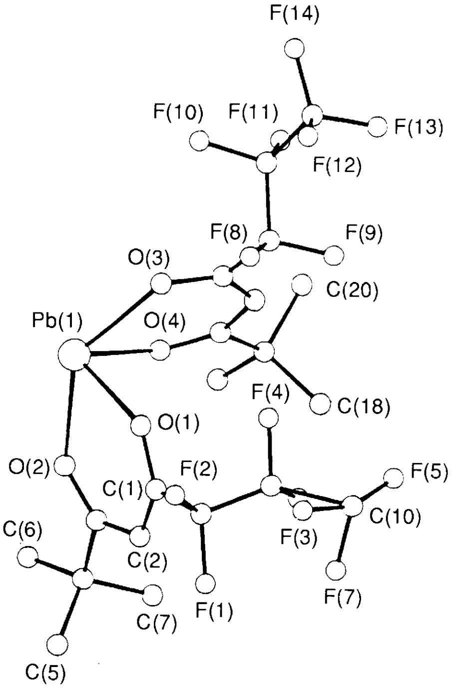

Fig. 2 Structure of the monomer Pb(fod)$_2$

chracterization and a single-crystal X-ray structure determination.

The compound was prepared from the reaction of lead nitrate (2.0 g, 6.4 mmol) in liquid ammonia (30 cm^3) with 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dione (4.0 g, 13.5 mmol) at room temperature. The yellow solid product was recrystallised from toluene to give yellow transparent cubes, m.p. 71 °C (lit.[13b] 72 °C). The compound was characterized by spectroscopic and X-ray crystallographic methods.†‡

The structure of Pb(fod)$_2$ is based on units of {Pb(fod)$_2$}$_2$ (Fig. 1). Each lead atom is chelated by the oxygens of two diketonate ligands (with Pb–O between 2.29 and 2.40 Å). These, principal, lead–oxygen separations are shorter than those in other divalent lead complexes such as lead(II) formate (Pb–O 2.53–2.85 Å).[14] The four oxygen atoms can be viewed as somewhat distorted away from a largely stereochemically inactive lone pair of electrons (Fig. 2). Coordination at lead is completed by two fluorines and two further oxygens to give eight-coordination at each lead atom.

The most interesting feature of the structure is the way that the dimers are formed with a number of unusual bridging atoms. These include the oxygen atoms O(1') and O(3'), 3.17 and 3.09 Å respectively away from Pb(1) [sum of atomic (Pb) and van der Waals radii (O) 3.04 Å]. Relatively short contacts are found for F(2), 3.29 Å, and F(8), 3.48 Å, from Pb(1) [sum of atomic (Pb) and van der Waals radii (F) 3.14 Å].[15]

There are now an increasing number of reports of interactions between organofluorine molecules and main group elements. The present interactions are probably weaker than those reported for Ru–F (2.49 Å) in [Ru{SC$_6$F$_4$(F$_2$)}(SC$_6$F$_5$)$_2$(PMe$_2$Ph)$_2$][16], Ca–F (2.52 Å) in [Ca(hfa)$_2$(OH$_2$)$_2$] or Ba–F (2.92–2.97 Å) in [Ba(hfa)$_2$(OH$_2$)$_2$][4] (Hhfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione). However, the interactions in the present compound are sufficient to support the dimeric structure observed for the compound. Other comparable M–F interactions include: Cs···F (3.21–3.75 Å) in [CsY(hfa)$_4$],[17] Rb···F (2.80–3.35 Å) in [Rb$_2$Na(hfa)$_3$][18] and some lanthanide complexes of trifluoromethyl alkoxy ligands.[19] The weak Pb–O contacts are comparable to some of the contacts in bis(*o*-nitrophenolato)barium(II) (2.71–3.12 Å).[20]

Eight-coordination for lead is in itself relatively unusual[14] but we know of no other examples of a discrete dimeric, rather than polymeric structure, being supported by bridging fluorine atoms. Many fluorinated pentanedionato group 2 complexes form stable hydrates which may impair, or make unpredictable, the behaviour of these complexes as precursors.[2,4] Indeed we have ^{1}H NMR evidence for the formation of a stable hydrate by Ph(hfa)$_2$. In his original work Sievers[13a] noted the exceptional volatility of the present compound. The origin of its volatility may well lie in the ability of the fod ligand to bridge and allow a dimeric rather than a polymeric complex to form.

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† The compound has a satisfactory microanalysis; NMR spectra: ^{1}H (CDCl$_3$, 250.1 MHz) δ 5.90 (18H, s, CMe$_3$) and 0.89 (2H, s, CH), ^{13}C (CDCl$_3$, 62.9 MHz) δ 209 (CF$_3$), 170.53 (β-CF$_2$), 121.02 (α-CF$_2$), 96.19 (CH), 43.41 (*C*Me$_3$) and 28.17 (C*Me*$_3$). No signal was observed for *C*–C$_3$F$_7$ and *C*–CMe$_3$; ^{19}F (C$_7$D$_8$, CFCl$_3$ as external ref. 235 MHz) δ −126 (4F, s, α-CF$_2$), −119.10 (4F, q, CF$_2$) and 80.82 (6F, t, CF$_3$); *m/z* 798 [M$^+$, Pb(fod)$_2$ 1.8%], *m/z* 57 (CMe$_3$, 100%); other major peaks at *m/z* 503 [Pb(fod) 32.8%] and 296 (fod) 5.3%]; IR (Nujol mull), ν/cm^{-1} 474 (Pb–O), 1541 (C–O) and 1068 (C–F).

‡ *Crystal data* for $C_{40}H_{40}O_8F_{28}Pb_2$, M = 1595.108, a = 9.943(4), b = 12.229(2), c = 12.616(4) Å, α = 112.53(2), β = 82.57(4), γ = 91.55(3)°, V = 1404.62(79) Å^3, space group $P\bar{1}$, Z = 1, D_c = 1.886 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ = 61.62 cm^{-1}. Data were recorded with a CAD4 diffractometer in the ω/2θ scan mode; 3912 unique reflections measured, 3029 observed with $F_o > 3\sigma(F_o)$. Structure solved by direct methods, and refined with the inclusion of hydrogen atoms to R = 0.0582, R_w = 0.0685 for 355 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue no. 1.

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