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Synthetic routes to lead(II) derivatives of aromatic 1,2-diols and orthoquinones

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Abstract

Complexes of lead(II) of the type $Pb(O_2R)$ where R is a substituted aromatic group, can be prepared by the direct electrochemical oxidation of a lead anode in a non-aqueous solution of the appropriate substituted catechol, $R(OH)_2$. The products, which are colourless, air-stable, insoluble materials, and presumably cross-linked in the solid state, can be oxidised to the corresponding lead(IV) derivatives by iodine or tetrahalogeno-*o*-quinones. The direct reaction of elemental lead with an *o*-quinone in refluxing hexane or toluene yielded identifiable products in only two cases; with 2,5-*tert*-butyl-1,2-benzoquinone, the corresponding lead(II) catecholate was obtained, while with phenanthrenequinone the semiquinonate $Pb(PSQ^\bullet)_2$ was isolated. These latter reactions are shown by electron spin resonance spectroscopy to proceed via free radical intermediates, and the spectra are analysed to give information on the species present in the reaction media.

Keywords: Lead complexes; Diol complexes; Orthoquinone complexes

1. Introduction

The chemistry of the complexes of lead has attracted interest of late, in part because of the potential toxicity of the compounds of this element, but also because this is a relatively unexplored area of coordination chemistry. The latter topic has been reviewed by Parr [1], and more recently the crystal structures of a number of lead(II) complexes have been discussed by Foreman et al. [2]. We now report some studies of preparative routes to compounds in which lead(II) is coordinated by catecholate or orthosemiquinone ligands.

The reactivity of the heavier Group 14 elements with substituted orthoquinones demonstrates an interesting range of behaviour. Germanium reacts with 3,5-di-*tert*-butyl-1,2-benzoquinone (TBQ) to give GeQ_2, GeQ_3 or GeQ_4 depending on the initial mole ratio of reactants (Q represents TBQ or one of its reduced forms) [3]. The reaction is extremely slow, even in refluxing toluene, requiring about 12 days to go to completion. When tetrachloro- or tetrabromo-1,2-benzoquinone is substituted for TBQ, the reaction product is the completely dehalogenated product $Ge(O_2C_6H_4)_3$; this unusual reaction will be discussed elsewhere [4]. Tin reacts rapidly with TBQ, with the reaction going to completion in approximately 12 h, but it was not possible to isolate the presumed product $Sn(TBSQ^\bullet)_2$ ($TBSQ^{\bullet -}$ = 3,5-di-*tert*-butyl-1,2-benzo semiquinonate radical anion) in pure form, although electron spin resonance (ESR) spectroscopy established the presence of a diradical species in the reaction mixture [5]. Russian workers [6–8] studied the reaction of tin amalgam with 3,6-di-*tert*-butyl-1,2-benzoquinone; here again, no solid products were isolated, but ESR spectroscopy identified diradical species in solution. Tin reacts smoothly over a period of 24 h with $Cl_4C_6O_2$-*o* in refluxing toluene to give tin(IV)-bis-catecholate derivatives which have been isolated and characterised [9].

The present work describes studies of the reaction of elemental lead with various substituted orthoquinones.

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There are marked differences between the behaviour of germanium and tin, both in the reactivities and the native of the derivatives. No identifiable product was obtained in the $Pb+X_4C_6O_2$-*o* systems (X = Cl, Br), but we were able to obtain the corresponding lead—tetrahalogenocatecholate species by the method of direct electrochemical synthesis, which had been used earlier to prepare $Sn(O_2R)$ compounds [10,11].

A useful comparison can also be made between the present work and an earlier study in which thallium was found to react with TBQ to give $Tl(TBSQ^{\bullet})$, which slowly decomposes to the corresponding bis-thallium catecholate [12].

2. Experimental

2.1. General

Lead shot was 99.99% pure (Alfa). Solvents were distilled and dried before use; all other reagents were used as supplied.

Metal analysis was by atomic absorption spectrophotometry, using an IL-250 instrument. Iodine analysis was by the Volhard method, involving back-titration with potassium thiocyanate and silver nitrate. Microanalysis was by Canadian Microanalytical Services Ltd. Infrared spectra were run on a Nicolet 5DX instrument, with samples pressed as KBr discs. Electron spin resonance (ESR) spectra were recorded on a Bruker ESP-300E instrument, using the calibration and other methods described earlier [13].

In this work, as elsewhere, we use the abbreviations $Q \rightleftharpoons SQ^{\bullet -} \rightleftharpoons CAT^{2-}$, with suitable prefixes, to identify the triad of oxidised/reduced forms of the ligand.

2.2. Preparative

2.2.1. Pb + TBQ

Lead (0.21 g, 1 mmol) was refluxed with TBQ (0.22 g, 0.44 g, 0.66 g; 1,2 or 3 mmol) in *n*-hexane (50 ml) for 12 h. In each case, the reaction product was a white powder, which was collected by filtration, washed with toluene and dried in vacuo. This diamagnetic solid, which is insoluble in all common organic solvents, was identified as Pb(TBCAT) ($TBCAT^{2-}$ = 3,5-di-*tert*-butylcatecholate) (see Table 1 for analytical results). The yields of Pb(TBCAT) were 65, 61 and 69% (based on initial quantity of lead) for Pb:TBQ ratios of 1, 2 or 3, respectively, so that the stoichiometry has no effect on the nature of the product. The infrared spectra of these solids confirmed the absence of ν(C=O), found at 1665 cm^{-1} in TBQ; ν(C–O) was identified at 1459 and 1434 cm^{-1}. Substitution of toluene as the reaction medium did not significantly change any of these findings.

The volume of the residual green filtrate was reduced by evaporation, and on cooling gave a green solid, in which both ν(C=O) and ν(C–O) vibrations were detected. No satisfactory chemical analysis could be obtained for this material; the ESR spectrum of the solution phase is discussed below. Addition of picoline to the filtrate from a Pb:2TBQ reaction produced a brown solution which yielded a colourless solid analysing as Pb(TBCAT)·0.5 picoline. This is ESR-silent, and showed only ν(C–O) vibrations in the infrared spectrum.

2.2.2. Pb + phenanthrenequinone (PQ)

The procedure here was essentially identical to that described for TBQ, except that a reaction time of 18 h was required for complete consumption of the lead. A dark green solution, essentially free of solid, was obtained over the range Pb:PQ = 1:2, 1:3 and 1:4. This solution is ESR active (see below), and on cooling deposited a green solid which was identified as the bis-semi-quinonate derivative $Pb(PSQ^{\bullet})_2$.

On exposure to air, this solid became grey, and the ESR spectrum lost its diradical character. The chemical analysis is essentially unchanged (C, 52.4; H, 2.66%; c.f. Table 1, line 3), and it appears that Pb(PC) is being formed, presumably with elimination of PQ, by processes analogous to the decomposition of the thallium(I) derivative of $TBSQ^{\bullet -}$ [10].

2.2.3. Pb + 1,2-naphthoquinone (NQ)

Refluxing a 1:2 Pb:Q mixture in tetrahydrofuran over 48 h resulted in only approximately 50% of the metal being consumed. Addition of hexane to the cooled solution gave a dark brown–black solid, for which no satisfactory analytical results could be obtained.

2.2.4. $Pb+X_4C_6O_2$-*o* (X = Cl, Br)

In the case of $Cl_4C_6O_2$-*o*, only 25% of the metal was consumed under similar conditions. The resultant red solution showed a weak ESR activity, but it proved impossible to obtain crystalline material, and the addition of picoline gave a only red syrup. Analysis was unsatisfactory, and attempts to obtain pure products by fractional crystallisation, or chromatography (TLC), failed. Similar results were obtained with $Br_4C_6O_2$-*o*, except that approximately 15% of the metal was consumed over 48 h.

2.3. Electrochemical synthesis

The method followed the techniques developed in this laboratory, with a cell consisting of a 100-ml tall-form beaker containing a solution of the appropriate ligand in freshly distilled MeCN [11,12]. In each case, the anode was a lead billet previously cleaned in conc. HNO_3, suspended from a platinum metal wire, and the cathode

Table 1
Analytical results for lead derivatives of substituted *o*-benzoquinones

Compound	Colour	Found (%)			Calcd. (%)		
		Pb	C	H	Pb	C	H
$Pb(C_{14}H_{20}O_2)$	colourless		40.0	4.78		39.3	4.68
$Pb(C_{14}H_{20}O_2)\cdot 0.5C_6H_7N$	colourless		44.0	5.02		43.1	4.96
$Pb(C_{14}H_8O_2)_2$	green		53.3	2.52		53.9	2.56
$Pb(C_6H_4O_2)$	colourless	66.1	21.7	1.33	65.7	22.9	1.33
$Pb(C_6H_4O_2)I_2$ [a]	green	36.0	12.0	0.94	36.4	12.7	0.71
$Pb(C_6H_4O_2)$phen [b]	gold–yellow	41.7			41.8		
$Pb(C_6H_4O_2)(Cl_4C_6O_2)$	blue	37.2			36.9		
$Pb(C_6H_4O_2)(Br_4C_6O_2)$	dark blue	27.8			28.0		
$Pb(C_{10}H_6O_2)$	colourless	56.7			56.7		
$Pb(C_{10}H_6O_2)$phen	yellow	38.5			38.0		
$Pb(C_{10}H_6O_2)$bpy	yellow	40.3			39.7		
$Pb(Br_4C_6O_2)$	yellow	32.9			32.8		
$Pb(Br_4C_6O_2)$bpy	gold–yellow	26.0			26.3		

[a] I analysis; found 44.9, calcd. 44.6.
[b] phen = 1,10-phenanthroline; bpy = 2,2′-bipyridyl.

was a platinum wire, 0.5 mm diameter. The cell solution was deoxygenated with a stream of dry nitrogen prior to electrolysis, and was blanketed with dry nitrogen to exclude oxygen and moisture during the electrochemical synthesis. The electrolyte added to the solution in order to give a reasonable current was generally tetraethylammonium perchlorate, but tetra *n*-butylammonium trifluoromethanesulfonate was also used satisfactorily. In all cases, subsequent analysis of the prepared compounds confirmed that there had been no incorporation of the electrolyte into the products.

Details of solution composition and other experimental details are given in Table 2. The applied voltage was that required to give a steady current of 40 mA. Hydrogen gas evolved at the cathode, and the product deposited around the anode; this material was collected by filtration at the end of the experiment, washed with MeCN and then Et_2O, and dried in vacuo.

In the cases of catechol, tetrabromocatechol and 2,3-dihydroxynaphthalene ($= R(OH)_2$), the product was the lead(II) derivative $Pb(O_2R)$, (see Table 1 for analytical results); when 2,2-bipyridine or 1,10-phenanthroline (= L) was also present, the 1:1 adducts $Pb(O_2R)L$ were obtained.

2.4. Oxidation of $Pb(O_2R)$ compounds

2.4.1. $Pb(O_2C_6H_4)$ and I_2

A suspension of freshly prepared $Pb(O_2C_6H_4)$ (0.47 g, 1.50 mmol) in 10 ml MeCN was prepared under N_2. When a solution of iodine (0.38 g, 1.50 mmol) in the same solvent (10 ml) was added, the mixture became green, and a finely divided olive-green solid was detected after 1 h. After 6 h, the product was collected by filtration under vacuum, and washed with MeCN (3 × 25 ml) and then Et_2O (3 × 25 ml). The solid was finally

Table 2
Experimental conditions for the direct electrochemical synthesis of $Pb(O_2R)$ compounds and adducts

Diol [a]	Solution composition [b]		Time of electrolysis [c] (h)	Metal dissolved [c] (mg)	Mass of product (g)	Yield [d] (%)	E_F (mol F^{-1})
	Diol (g)	Ligand (g)					
$C_6H_4(OH)_2$	0.25		3.0	492	0.749	98	0.49
$C_6H_4(OH)_2$	0.20	phen, 0.33	2.25	348	0.832	89	0.50
$C_{10}H_6(OH)_2$	0.25		2.25	355	0.551	88	0.50
$C_{10}H_6(OH)_2$	0.25	phen, 0.28	2.5	387	0.967	95	0.50
$C_{10}H_6(OH)_2$	0.25	bpy, 0.24	2.0	305	0.702	92	0.51
$C_6Br_4(OH)_2$	0.55		3.0	455	1.30	94	0.51
$C_6Br_4(OH)_2$	0.55	bpy, 0.20	2.0	315	1.09	91	0.51

[a] $C_6H_4(OH)_2$ = 1,2-dihydroxybenzene; $C_6Br_4(OH)_2$ = 1,2-dihydroxytetrabromobenzene; $C_{10}H_6(OH)_2$ = 2,3-dihydroxynaphthalene.
[b] In 50 ml acetonitrile containing 100 mg electrolyte (see text).
[c] At 40 mA, with applied voltages in the range 20–40 V.
[d] Based on mass of metal dissolved.

dried overnight under vacuum, and identified as $Pb(O_2C_6H_4)I_2$ (yield; 0.69 g, 81%), olive-green in colour.

2.4.2. $Pb(O_2C_6H_4)$ and $Br_4C_6O_2$-*o*

A grey/black suspension of freshly prepared $Pb(O_2C_6H_4)$ (0.47 g, 1.50 mmol) in MeCN (10 ml) under nitrogen was treated with a solution of *o*-O_2C_6Br (0.64 g, 1.50 mmol) in the same solvent (10 ml). The mixture was stirred for 6 h under an inert atmosphere, during which time it became dark blue, with a finely divided deep blue solid product being visible after some hours. The product was filtered under vacuum and washed with MeCN (3 × 25 ml) and then Et_2O (3 × 25 ml). The product was dried overnight under vacuum, and identified as $Pb(O_2C_6H_4)(O_2C_6Br_4)$ (yield: 0.95 g, 86%), dark blue in colour. A similar reaction using $Cl_4C_6O_2$-*o* gave the oxidative addition product $Pb(O_2C_6H_4)(O_2C_6Cl_4)$.

3. Results and discussion

3.1. Electrochemical synthesis

The electrochemical oxidation of lead in the presence of aromatic 1,2-diols is a direct route to $Pb(O_2R)$ compounds. The yields are high, the apparatus is simple, and it is relatively easy to scale up the experiment to produce larger quantities of product than in the present work. Equally, the same procedure can be used to prepare adducts with neutral bidentate donor ligands, and it is reasonable to assume that other diols, and other neutral donors, could be utilized in the same way.

The electrochemical efficiency, E_F, defined as quantity of lead dissolved from the anode per Faraday of charge passed through the cell, is found to be 0.50 Å 0.01 mol F^{-1} for all the systems studied in this work. The simplest interpretation of this result is in terms of the reactions

$$\text{cathode} \quad R(OH)_2 + 2e \rightarrow H_2(g) + RO_2^{2-} \tag{1}$$

$$\text{anode} \quad RO_2^{2-} + Pb \rightarrow Pb(O_2R) + 2e \tag{2}$$

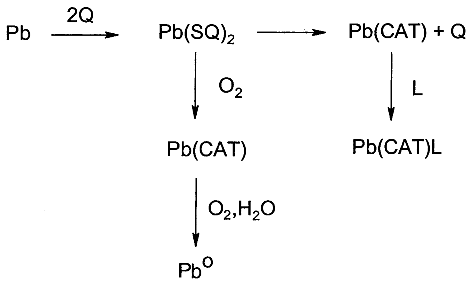
in which the RO_2^{2-} dianion is the current carrier. Other explanations are also possible (see Ref. [10]), but there is no experimental evidence on which to resolve this matter at present. The same E_F value applies to the synthesis of both $Pb(O_2R)$ and $Pb(O_2R)L$, so that the formation of the adduct occurs, not surprisingly, subsequent to the oxidation of Pb to $Pb(O_2R)$. The mechanism in Eqs. (1) and (2) supports the formulation of these products as lead(II) species.

3.2. Reaction of lead with orthoquinones

The preparative results (Sections 2.2.1, 2.2.2, 2.2.3 and 2.2.4) show that there are surprising differences in reactivity between the five substituted *o*-quinones used. With TBQ, the product obtained under all the conditions investigated is the highly insoluble lead(II) compound Pb(TBCAT). Similarly, each residual reaction mixture apparently contains species in which $TBSQ^{\bullet -}$ is interacting with a lead centre (see below). The addition of picoline to this solution produces a diamagnetic 2:1 adduct of Pb(TBCAT) (see Table 1).

When phenanthrenequinone (PQ) was used, the product obtained on cooling the green reaction mixture was $Pb(PSQ^{\bullet})_2$. A solution prepared by dissolving this compound in toluene showed the characteristic ESR spectra of a diradical (see below). Attempted reactions of lead with naphthoquinone or tetrahalogeno-*o*-quinones showed that only a small fraction of the metal was consumed, even over long reaction times, and in the case of $X_4C_6O_2$-*o*, there is a strong similarity to the behaviour of germanium [3,4], with both elements differing markedly from tin [5,9] in this respect.

A schematic summary of these preparative results is shown in Scheme 1. As noted earlier, the decomposition of $Pb(SQ^{\bullet -})_2$ to Pb(CAT) is reminiscent of the inherent instability of $Tl(TBSQ^{\bullet})$, which decomposes spontaneously to $Tl_2(TBCAT)$ [12].



Scheme 1.

3.3. ESR results

As noted above, the reaction of lead with 3,5-di-*tert*-butyl-1,2-quinone was carried with initial mole ratios (Pb:TBQ) of 1:1, 1:2 and 1:3. In each, the reaction product is the insoluble Pb(TBCAT). The residual green solutions were all ESR active, and the spectrum for TBQ:Pb = 3 is shown in Fig. 1; for starting ratios of 2:1 and 4:1, the central portion of the spectrum remains the same but the ^{207}Pb hyperfine peaks are changed. In the central portion of the spectrum there are two doublets, the more intense of which has $g = 1.9995$ and $A(H) = 3.20$ G. This must be $TBSQ^{\bullet}$ coordinated to Pb^{2+}, since the ^{207}Pb hyperfine peaks are centered about this peak. The smaller doublet has $g = 2.0039$ and $A(H) = 3.30$ G

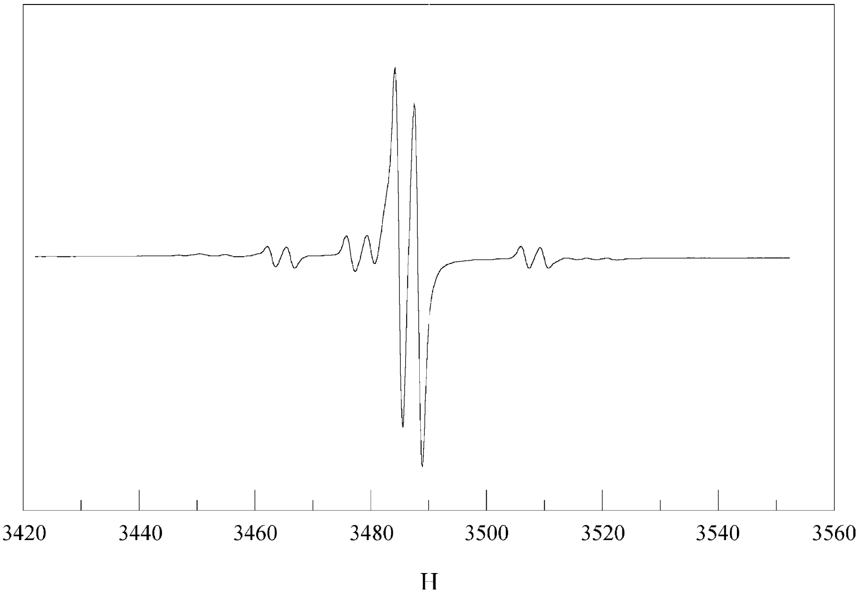


Fig. 1. ESR spectrum, at room temperature, of the residual solution from the reaction of Pb with 3,5-di-*tert*-butyl-1,2-quinone (initial Pb: quinone mole ratio = 1:3).

and is identified as uncoordinated $TBSQ^{\bullet}$. The existence of multiple ^{207}Pb hyperfine peaks indicates the presence of several conformers of $Pb(TBSQ^{\bullet})$ species in the solution. When the solutions are frozen to 100 K, the spectra of both $S = 1/2$ and $S = 1$ species appear, suggesting the presence of $Pb(TBSQ^{\bullet})_2$; the $S = 1$ state is confirmed by the presence of a half-field transition. In previous work on other metal-TBQ systems, addition of a nitrogen base produced an ESR spectrum of a single species, but in the present case addition of picoline produced a precipitate of Pb(TBCAT)·0.5 picoline and the residual filtrate showed only weak ESR activity.

Those results suggest that in the presence of excess TBQ, Pb(TBCAT) reacts by

$$Pb(CAT) + TBQ \rightleftharpoons [Pb(TBSQ^{\bullet})]^{+} + TBSQ^{\bullet -} \qquad (3)$$

and that on cooling the diradical complex $Pb(TBSQ^{\bullet})_2$ is formed. Eq. (3) is a modified form of the well-known equilibrium

$$CAT^{2-} + Q \rightleftharpoons 2SQ^{\bullet -} \qquad (4)$$

and of the analogous intramolecular electron transfer which has been shown to occur in a number of Main Group complexes of these ligands.

Similar results were obtained from the residual filtrate resulting from the reaction of Pb with phenanthrenequinone. The ESR spectrum indicates the presence of a mixture of conformers of $Pb(PSQ^{\bullet -})$, but in this case addition of a nitrogen base produced a clean spectrum (Fig. 2) of a single species, well simulated with the parameters $g = 1.9998$, $A(6H) = 1.66$, $A(2H) = 0.6$, $A(^{207}Pb) = 53.45$ G. The ESR spectra of the frozen solution at 100 K showed the presence of both $S = 1/2$ and $S = 1$ species, as was the case for TBQ and Pb (see above). The major difference between the two systems lies in the relative solubilities of the $Pb(SQ^{\bullet})_2$ species, but the overall mechanism is presumably the same in each system.

The presence of multiple conformers of these lead(II) complexes in solution may be related to the known tendency of such species to form multiply bridged structures in the solid state (see below), and the formation of oligomers of $Pb(SQ^{\bullet -})_2$ or related $Pb(O_2R)$ species in solution would then account for the multiple ESR spectra observed.

3.4. Properties of $Pb(O_2R)$ compounds

The $Pb(O_2R)$ compounds prepared are air-stable powders of high melting point; long exposure to moisture appears to cause decomposition, since the solids blacken, probably due to the formation of metallic lead. The solids are insoluble in non-donor solvents, and in acetonitrile and diethyl ether. Lead(II) catecholate is insoluble in cold dimethylsulphoxide but slightly soluble in the hot. These properties suggest a homo-polymeric solid state structure for $Pb(O_2R)$ compounds, involving cross-linking through Pb–O–Pb bonding. A recent paper [2] has reviewed the earlier literature on the solid state structures of complexes of lead(II) with mono- and polybasic carboxylates, and has shown that O–Pb–O cross-linking frequently leads to polymeric or oligomeric structures in which the metal can display a variety of coordination numbers. We were unable to obtain crystals of any of the $Pb(O_2R)$ compounds prepared, but the properties support the proposed cross-linked solid state structures.

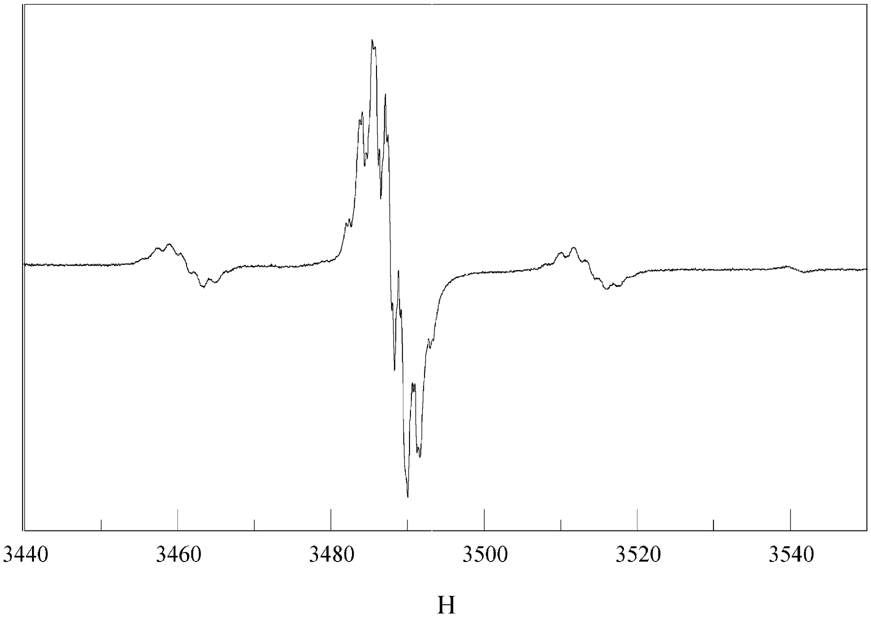


Fig. 2. ESR spectrum, at room temperature, of the residual solution from the reaction of Pb with phenanthrenequinone.

The formation of adducts of $Pb(O_2R)$ with the bidentate donors 2,2-bipyridine and 1,10-phenanthroline is an interesting feature of the coordination chemistry of the compounds. In view of the homopolymerization discussed above, it is not surprising that the lead atom of $Pb(O_2R)$ should also expand its coordination shell by ligation.

3.5. *Oxidation of $Pb(O_2R)$*

Oxidative addition reactions of low oxidation state Main Group compounds have been the subject of many investigations, but few of these have included lead(II) species, in part because for most systems involving common inorganic ligands, lead(II) compounds are more stable than the lead(IV) analogues. We have now shown that $Pb(O_2C_6H_4)$ prepared in this work is readily oxidized by iodine to give the corresponding lead(IV) species $Pb(O_2R)I_2$, which is air-stable, showing no sign of loss of iodine in vacuo. This reaction parallels the behaviour of $Sn(O_2R)$ and $In[O(HO)R]$ compounds [10,14]. The correspondence is further extended by the oxidative reaction with the tetrahalogeno-*o*-quinones, *o*-$O_2C_6X_4$ ($X = Cl$, Br), which have been shown to oxidize indium(I) [15] and tin(II) [16] halides, as well as $In[O(HO)R]$ [14], $In[S(HS)R]$ [17] and $Sn(O_2R)$ [10] complexes, in each case yielding a tetrahalogenocatecholate derivative of indium(III) or tin(IV). In the present work, the reaction of *o*-O_2C_6–X_4 with $Pb(O_2R)$ causes discharge of the characteristic red–brown colour of the tetrahalogenoquinone, and analysis of the products identified the formation of $Pb(O_2R)(O_2C_6X_4)$. The infrared spectra of these substances confirmed that the characteristic $\nu(C{=}O)$ of the *o*-quinones at 1445 and 1270 cm^{-1} was absent, and the $\nu(C{-}O)$ modes of both RO_2^{2-} ligands appear as a complex set of bands in the 1450 cm^{-1} region. The intense colour of these products (see Table 2) suggests inter-ligand charge-transfer processes.

3.6. *Synthetic routes to $Pb(O_2R)$*

The direct electrochemical synthesis of lead(II) catecholate, and two typical substituted catecholates (Table 2) leads to stable insoluble compounds whose stability and insolubility is presumably related to the cross-linking discussed above. This pattern of preparative behaviour is very different from that seen in the reaction, or attempted reaction, of lead with *o*-quinones. Only with 3,5-di-*tert*-butyl-1,2-benzoquinone is the corresponding lead(II) catecholate obtained, and there is evidence that the residual solution contains Pb–TBSQ$^{\bullet}$ derivatives which are presumably intermediates in the formation of the catecholate (see Scheme 1). The bis-semiquinonate $Pb(PSQ^{\bullet -})_2$ has been identified with phenanthrenequinone, but none of the other Pb+Q reactions showed signs of significant consumption of lead. The contrast between this result for $Br_4C_6O_2$-*o*, and the simple electrochemical synthesis of $Pb(O_2C_6Br_4)$ from $C_6Br_4(OH)_2$-1,2, is very marked, and shows that the lack of a facile reaction between Pb and the tetrabromoquinone is not the result of the absence of a stable product. Rather, it indicates that here, as in the case of germanium [4], the strongly oxidising tetrahalogenoquinones do not react with lead in the expected fashion to give Pb/SQ$^{\bullet -}$ or Pb/CAT^{2-} products. We did not identify the products of whatever slow reactions do occur in the $Pb/X_4C_6O_2$-*o* system, but if the germanium case offers any parallel, it may be that reactions between the metal and the C–X sites of the quinone occur instead of the expected metal–quinone electron transfer processes.

4. Supplementary material

The material is available from the authors on request.

Acknowledgements

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