Unstable Intermediates. Part CXLI.[1] Electron Spin Resonance Spectra of various Tin and Lead Centres in their Irradiated Salts

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In addition to Sn^{3+} and Pb^{3+} centres previously reported, the following have been detected in a range of tin(II) and lead(II) salts after exposure to ^{60}Co γ rays at 77 K: Sn^+ [in $Sn(OAc)_2$]; Pb^+ [in $Pb(OAc)_2$]; SnH^{2+} (in $SnSO_4$); PbH^{2+} [in $Pb(ClO_4)_2$]; $CO_2^-(Pb^{2+})$ [in $Pb(HCO_2)_2$]; $H_2\dot{C}CO_2^-(Pb^{2+})$ [in $Pb(MeCO_2)_2$]; and $ClO_2(Pb^{2+})$ [in $Pb(ClO_4)_2$]. After attempting to justify these identifications, the electronic structure of these centres is discussed in the light of the e.s.r. parameters.

In the course of our studies of Sn^{3+} and Pb^{3+} centres in various irradiated tin and lead salts,[2] a range of other centres were detected, some of which also displayed satellite features indicative of hyperfine coupling to low-abundant magnetic tin and lead nuclei [^{117}Sn ($I = \frac{1}{2}$) 7·67%, ^{119}Sn ($I = \frac{1}{2}$) 8·68%, ^{207}Pb ($I = \frac{1}{2}$) 21·1%]. We have already given details of our results for a centre in irradiated lead(II) acetate, described as $PbMe^{2+}$,[3] and, whilst our studies were in progress, Roberts and Eachus reported results for centres described as Pb^+ and PbH^{2+} formed in irradiated $Pb(OAc)_2,3H_2O$.[4]

The centres detected are of three main types: univalent cations having formal configuration $\ldots s^2p^1$; covalent molecular ions similar to $PbMe^{2+}$;[3] and species which resemble ion-pairs or charge-transfer (c.t.) complexes, comprising a radical or radical anion weakly interacting with one or more neighbouring cations. The only $\ldots s^2p^1$ cation previously reported and studied by e.s.r. spectroscopy is Pb^+,[4] but the parameters that we derive for Pb^+ differ markedly from those previously reported. These metallic cations are of unique interest in having an incomplete p shell.

Covalent tin and lead radicals have also been neglected in e.s.r. studies. Bennett *et al.* have recently reported results for $\dot{S}nMe_3$ and $\dot{P}bMe_3$,[5] and we have also detected these species together with other alkyl derivatives and, less firmly, radical anions thought to be R_4Sn^-.[6] We have also prepared the ions Ph_3PbCl^- and Ph_3PhBr^- from the parent molecules by high-energy irradiation.[7]

Although ion-pairs comprising organic radical anions and alkali-metal cations are well known, and a few solid-state centres exhibiting hyperfine coupling to such cations have been described,[8,9] the only work describing weak interactions involving cations having a $d^{10}s^2$ configuration, of which we are aware, is for Pb^{2+} in irradiated lead nitrate and Tl^+ in various thallium(I) salts.[10] In the former, NO_3^{2-} radical anions were found to act as electron donors, the acceptor orbital on lead being therefore $6p$. However, both NO_3 and NO_2 gave weak complexes in which Pb^{2+} ions acted as electron donors rather than acceptors, and Tl^+ generally acted as an electron donor. Single-crystal studies of these centres have revealed details of the number of interacting metal ions, and the way in which the radicals can migrate within their crystal cavities.[10]

EXPERIMENTAL

Experimental details are as described in our previous report on tin and lead salts.[2] The salts were irradiated as fine powders at 77 K, and solutions were degassed prior to freezing as small glassy beads in liquid nitrogen. Samples were irradiated in a Vickrad ^{60}Co source, at a nominal dose rate of 4 MCi h^{-1} for up to 2 h. E.s.r. spectra were measured at 77 K on a Varian E3 X-band spectrometer. Attempts to study the Sn^+ and Pb^+ centres on S- or Q-band spectrometers were unsuccessful because the sensitivities of our instruments were too low.

RESULTS AND DISCUSSION

Results for the most interesting centres detected in this study are summarised in the Table, together with our identifications. Typical e.s.r. spectra for some of these centres are illustrated in Figures 1—5.

Identification.—We consider first the centres described as Sn^+ and Pb^+ (Figures 1 and 2 respectively). The tin centre comprised a high-field group of lines (Figure 1), which had no corresponding set to low field of the intense central features (not shown), and which therefore cannot be assigned to $-\frac{1}{2}$ lines associated with ^{117}Sn and ^{119}Sn. We therefore suggest that the most intense cross-over and downward features are g_x and g_y features for a centre having g_z hidden beneath the intense free-spin lines. The associated features of low intensity are then assigned to very weakly interacting Sn^{2+} ions containing ^{117}Sn or ^{119}Sn, whilst a replica of these features found at much higher fields (not shown) is assigned to the x and y features of the $-\frac{1}{2}$ lines from $^{117}Sn^+$ and $^{119}Sn^+$ centres. Corresponding low-field lines were detected in the expected field region (just on the low-field side of the

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[1] Part CXXXVIII, A. R. Lyons, G. W. Neilson, S. P. Mishra, and M. C. R. Symons, *J.C.S. Perkin II*, submitted for publication; T. A. Claxton, R. E. Overill, and M. C. R. Symons, *Mol. Phys.*, 1973, **26**, 75; E. A. Shaede and M. C. R. Symons, *Canad. J. Chem.*, 1973, **51**, 2492 (taken as Parts CXXXIX and CXL respectively).

[2] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2233.

[3] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J.C.S. Farday II*, 1972, **68**, 638.

[4] H. C. Roberts and R. S. Eachus, *J. Chem. Phys.*, 1972, **57**, 3022; 1973, **59**, 5251.

[5] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

[6] S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Chem. Phys. Letters*, in the press.

[7] O. P. Anderson, S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Mol. Phys.*, in the press.

[8] P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2873.

[9] J. E. Bennett, B. Mile, and A. Thomas, *Trans. Faraday Soc.*, 1965, **61**, 2357.

[10] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Chem. Comm.*, 1974, 108.

central features), giving $A_x \approx A_y$ (^{119}Sn) $\approx$ 730 G. Unfortunately, we were unable to estimate g_z or A_z, but we can confidently state that g_z is *ca.* 2·0, whilst $A_z \gg$ 730 G. The available data can only be satisfactorily accommodated in terms of a centre having the unpaired electron largely in the 5*p* manifold, but with a fairly large 'crystal field' which lifts the degeneracy of the three orbitals in an appropriate manner. The structure of this centre is considered further below.

Hyperfine coupling parameters for various radicals in irradiated tin(II) and lead(II) salts

		Hyperfine coupling (G) [a]			
		^{119}Sn [b] or ^{207}Pb			
Salt	Radical	$A_{\parallel}$	$A_{\perp}$	A_{iso}	Other nuclei
$Sn(AcO)_2$	Sn^+		730		g_x 1·84, g_y 1·82, $g_z \sim$ f.s.
		Sn_1	*ca.* 22		
		Sn_2	*ca.* 70		
$Pb(AcO)_2$	Pb^+				g_x 1·42, g_y 1·37, g_z 1·83
$SnSO_4$	SnH^{2+}			4 300	(^{1}H) *ca.* 260, *g ca.* f.s.
$Pb(ClO_4)_2$	PbH^{2+}			4 950	(^{1}H) *ca.* 160, *g ca.* f.s.
$Pb(ClO_4)_2$	ClO_2 (Pb^{2+})	Pb_1	*ca.* 200		$A_{\perp}$ *ca.* 21 [c] *g ca.* 2·009
		Pb_2	*ca.* 90		
$Pb(HCO_2)_2$	CO_2^- (Pb^{2+})	$2Pb_1$	*ca.* 120		g_x 2·0015, g_y 1·997, g_z 2·006
		$2Pb_2$	*ca.* 30		
$Pb(AcO)_2$	$\dot{C}H_2CO_2^-$ (Pb^{2+})	(*i*) Pb_1	*ca.* 530		2(^{1}H),[d] A_{av} 20·5, g_{av} *ca.* 2·000
		Pb_2	*ca.* 120 [e]		
		(*ii*) Pb_1	*ca.* 712 [f]		
$Pb(AcO)_2$ [g]	$PbMe^{2+}$	1 962	1 689		$g_{\parallel}$ 1·994, $g_{\perp}$ 1·968

[a] Corrected, when necessary, using the full Breit–Rabi equation; 1 G = 10^{-4} T; f.s. = free-spin value. [b] ^{117}Sn Features were often detected and gave appropriately reduced hyperfine coupling constants. [c] The ClO_2 radicals were clearly undergoing restricted rotations, but only the perpendicular features were well resolved. [d] 1 : 2 : 1 Triplet only resolved on the high-field ^{207}Pb line. The lines were not well enough resolved to yield anisotropic coupling. Reduced to a narrow singlet for $Pb(CD_3CO_2)_2,3H_2O$ and $Pb(CD_3CO_2)_2,3D_2O$ salts. [e] Only resolved for the perdeuteriate. [f] Formed at the expense of the 530 G species on dehydration. [g] Data from refs. 2 and 3.

The corresponding Pb$^+$ centre exhibited, as expected because of its greater spin–orbital coupling constant, a far larger *g*-value variation, with g_z shifted into a field region free of intense absorption lines. The centre is of very low intensity, which was not enhanced on further exposure to γ rays, so we were unable to observed ^{207}Pb satellites. Also we were unable to check our assignment by the use of *Q*- or *S*-band spectrometers because of their reduced sensitivity.

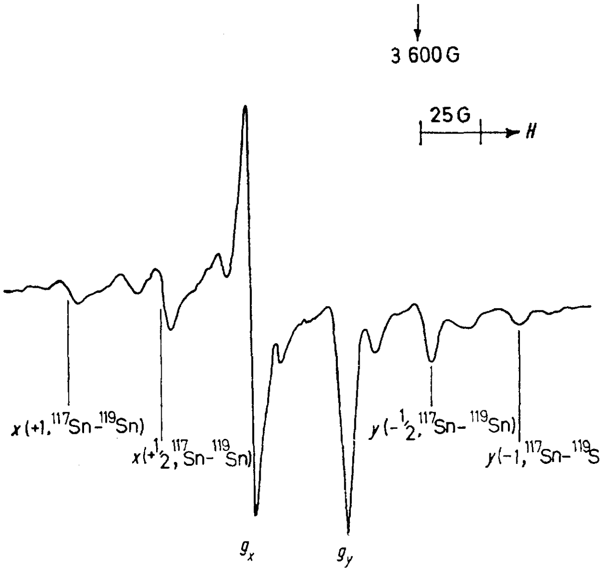

FIGURE 1 First-derivative *X*-band e.s.r. spectrum in the *g* 1·8 region showing g_x and g_y features assigned to Sn$^+$ in tin(II) acetate after exposure to ^{60}Co γ rays at 77 K. The satellite features are assigned to hyperfine coupling to ^{117}Sn^{2+} and ^{119}Sn^{2+} neighbours [A comparable set of lines to higher fields (not shown) are assigned to ^{117}Sn$^+$ and ^{119}Sn$^+$ centres.]

Although our identification of this centre is the same as that of Roberts and Eachus,[4] these authors preferred to assign these features to the ($-\frac{1}{2}$) line for ^{207}Pb$^+$ centres. A more intense almost isotropic free-spin line was then assigned to Pb$^+$ containing non-magnetic isotopes. Although both postulates are feasible, we favour our interpretation because it accords better with our expectation and with results for the Sn$^+$ centre, which is far better

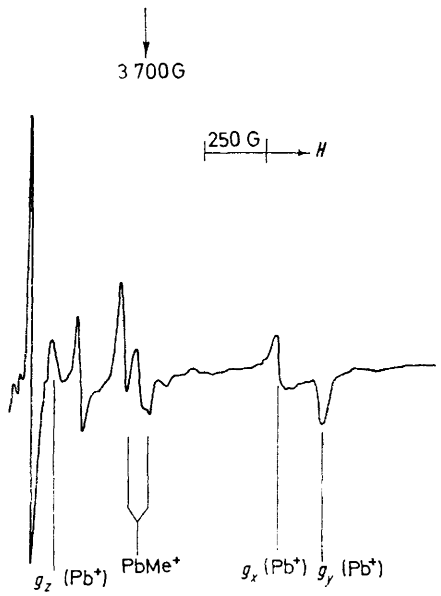

FIGURE 2 First-derivative *X*-band e.s.r. spectrum for lead(II) acetate after exposure to ^{60}Co γ rays at 77 K, showing high-field features ($g_{x,y,z}$) assigned to Pb$^+$ ions [together with the '$I = -\frac{1}{2}$' lines for $H_2\dot{C}CO_2^-$ (Pb^{2+}) and $PbMe^{2+}$ radicals]

defined. In our view, a centre having an almost isotropic g tensor in the free-spin region cannot be properly described as having an electron configuration remotely resembling $6s^26p^1$. We recall that even the covalent radical $Me_3\dot{P}b$ has $g_{\parallel} \simeq 1\cdot9$ and $g_{\perp} \simeq 2\cdot1$.[5,6] Since the parent cations are only weakly bound to the co-ordinated acetate ligands, we would certainly anticipate large high-field g shifts for at least one component. Another factor which is difficult to accommodate is the form of the derived ^{207}Pb hyperfine components[4] (A_{xx} 1 985, A_{yy} 3 581, and A_{zz} 3 454 G).* It is difficult to see how a p^1 system can have $A_{\perp} > A_{\parallel}$, which must hold if the reasonable assignment of positive signs is made. It is also highly significant that no low-field component of the proposed ^{207}Pb coupling could be detected, even though single-crystal spectra were specifically analysed for such features.

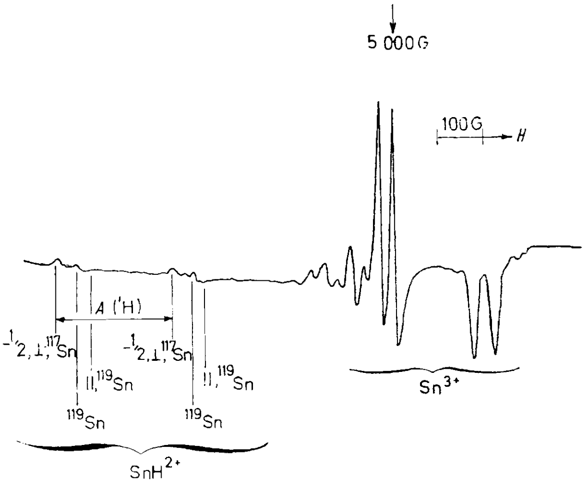

FIGURE 3 First-derivative X-band e.s.r. spectrum for tin(II) sulphate after exposure to ^{60}Co γ rays at 77 K, showing high-field components assigned to ^{117}SnH^{2+} and ^{119}SnH^{2+}. Only the perpendicular features are clear; the parallel features were never well defined in any of the spectra

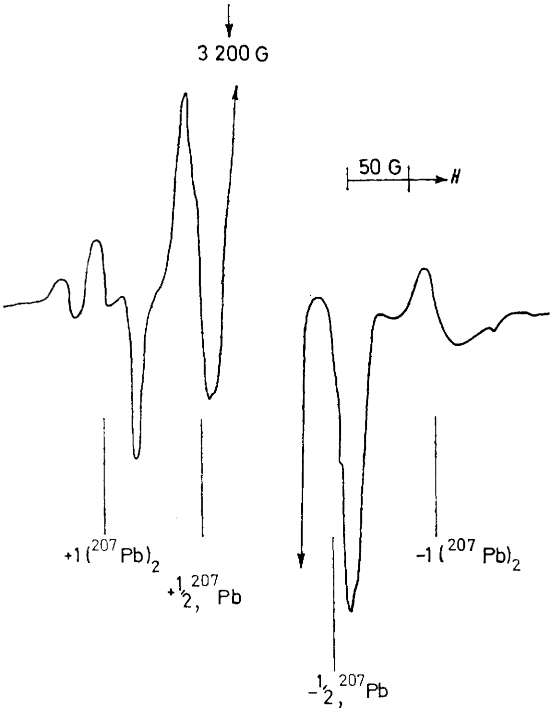

FIGURE 4 First-derivative X-band e.s.r. spectrum for lead(II) formate after exposure to ^{60}Co γ rays at 77 K, showing satellite lines assigned to CO$_2^-$ weakly coupled to two equivalent ^{207}Pb^{2+} ions. The more intense inner doublet is assigned to species containing one magnetic isotope and the weak outer doublet to species in which both lead ions are ^{207}Pb^{2+}

Identification of the ions SnH^{2+} and PbH^{2+} is based on the detection of high-field lines associated with ^{117}Sn and ^{119}Sn for SnH^{2+} (Figure 3) and for ^{207}Pb for PbH^{2+}, together with central lines for the non-magnetic metal isotopes, all of which were divided into doublets by coupling to a single proton. The results (Table) are in good accord with expectation for these species (see below). These centres are clearly covalent molecular cations, having little in common with the hydrogen-atom type centres described as NaH$^+$ or KH$^+$,[11] or indeed with the hydrogen-atom centre described by Roberts and Eachus.[4]

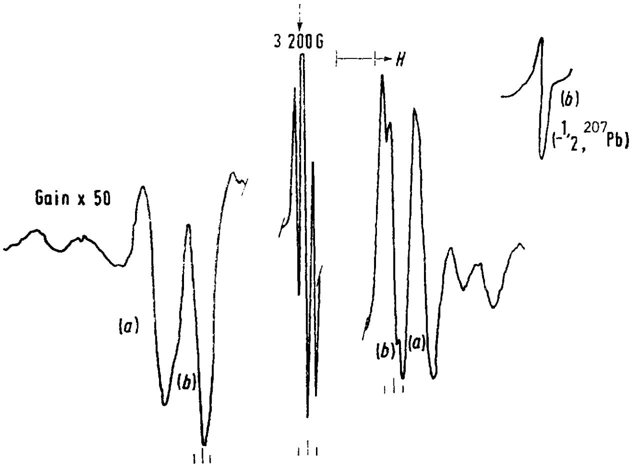

FIGURE 5 First-derivative X-band e.s.r. spectrum for lead(II) acetate hydrate after partial dehydration and exposure to ^{60}Co γ rays at 77 K, showing central features assigned to H$_2\dot{C}$CO$_2^-$ ions adjacent to non-magnetic lead isotopes, and pairs of lines (a) separated by 712 G, favoured on dehydration, and (b) separated by 530 G, favoured in the hydrate. The '$-\frac{1}{2}$' line for (b) obtained from the perdeuteriate is shown in the inset

The radical centres exhibiting weak coupling to Sn^{2+} or Pb^{2+} which were well defined are listed in the Table. Several others were observed in some of the salts discussed in ref. 2, but we will not describe these since we are unable to offer firm identifications. Probably the best defined centre, formed in lead perchlorate, was ClO$_2$ undergoing hindered rotation of a type previously described.[12] Two sets of satellite lines flanked the central quartet indicating weak coupling to two inequivalent Pb^{2+} ions. Unfortunately, we were unable to choose conclusively between one or two equivalent Pb^{2+} ions for these features since the signal intensity was too low

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* Revised data were kindly communicated by Dr. R. S. Eachus.

[11] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 143.

[12] M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 698.

for the detection of centres containing two ^{207}Pb nuclei, were they present, nor could we judge from the relative intensities of the lines since the ^{207}Pb satellites exhibited a small extra anisotropy which contributed to the overall width of the satellites.

The CO_2^- centre, in lead formate, identified by the similarity of its g-tensor components to those for authentic CO_2^- anions,[13] also exhibited poorly defined coupling, this time to two equivalent Pb^{2+} ions (Figure 4), together, probably, with two other very weakly coupled Pb^{2+} ions whose components were largely concealed beneath the central lines. Studies at high instrument gain showed conclusively that no more than two equivalent Pb^{2+} ions were present. E.s.r. spectra for the centres described as $H_2\dot{C}O_2^-$, formed in irradiated lead(II) acetate, are depicted in Figure 5. Since the ^{207}Pb hyperfine coupling for one of these centres (*ca.* 525 G) is close to that assigned to Pb^{2+}–H radicals (*ca.* 540 G),[4] we must justify the present identification with care. We note that (*i*) the satellite lines had intensities that varied directly with those for the $\dot{C}H_2CO_2^-$ central lines, whose form and g value differ enough from those normally obtained to suggest the presence of a weak secondary interaction, and (*ii*) the high-field $(-\frac{1}{2})$ line, which was always considerably narrower than the $(+\frac{1}{2})$ component, showed clear resolution into 1 : 2 : 1 components with the same hyperfine coupling. When $Pb(CD_3CO_2)_2,3H_2O$ or $Pb(CD_3CO_2)_2,3D_2O$ was studied, the central features, together with the high-field satellite, became singlets, as expected for $\dot{C}D_2CO_2^-$ radicals with unresolved lines. Thus, our present identification seems to be reasonable. It is probable that a pair of features separated by *ca.* 120 G, but only clearly defined in the case of the perdeuteriated salt, are due also to $^{207}Pb^{2+}$ hyperfine coupling.

Structural Aspects.—In order to explain the form of the g-tensor components assigned to Sn^+ and Pb^+, we need to postulate a crystal field from co-ordinated acetate ligands that constrains the unpaired electron into one p orbital (say p_z), by destabilising p_x and p_y to almost equal extents. One such situation which seems reasonable in the present cases would be a slightly flattened tetrahedral co-ordination.

Unfortunately, we are unable to comment on the $^{117}Sn^+$–$^{119}Sn^+$ hyperfine coupling except to say that the value for $A_\perp$ of *ca.* 730 G is quite reasonable. In view of the very low intensity of these signals, we suggest that electrons are only permanently trapped at Sn^{2+} or Pb^{2+} ions which differ from those of the perfect crystals, probably because of an adjacent anion vacancy.

The hydrides SnH^{2+} and PbH^{2+} are of interest compared with HgH^{2+} and AgH^+ previously prepared by similar procedures,[14,15] in that they have a $\ldots \sigma_1^2\sigma_2^1(^2\Sigma)$ structure rather than the $\ldots \sigma_1^1(^2\Sigma)$ structure of the silver and mercury compounds. This is reflected in the trend in spin-density distribution that can be derived from the e.s.r. data. Thus on going from the ion SnH^{2+} to PbH^{2+} there is a decrease in spin density on the hydrogen atom, which follows for an antibonding orbital from the decrease in electron affinity of the metal atom. Also the very large change going from BaH, which exhibits very low proton hyperfine coupling of *ca.* 17 G,[16] to the present hydrides is understandable in terms of electronegativity. Indeed, barium hydride clearly tends towards the limiting ionic structure, Ba^+H^-. The metal hyperfine coupling constants also reflect these changes, but the anisotropy was not sufficiently well defined to warrant a detailed estimate of spin density or orbital hybridisation.

Although our results for the weakly interacting complexes are not so clear cut as those for $Pb(NO_3)_2$,[10] they conform to the same general pattern. We stress that isotropic coupling of, say, 100 G for $^{207}Pb^{2+}$ corresponds to net transfer of spin from lead of only *ca.* 1% and is thus quite comparable with the extent of interaction normally observed for single alkali-metal ion-pairs. The number of cations involved is a function of the size and symmetry of the cavity in which the paramagnetic fragment is trapped, whilst the magnitude of the coupling is a function of the mean separation, the donicity of the cation (for isotropic coupling), and the electron-accepting power of the radical. Of the radicals presently under consideration, ClO_2 and CO_2^- have low-lying acceptor orbitals which have minimum energies at bond angles not greatly reduced from those for the radicals. Hence they act as electron acceptors. For the radical anion $H_2\dot{C}CO_2^-$ co-ordination probably occurs *via* the oxygen atoms, which only carry low spin density. It is this factor that differentiates these weakly interacting ion-pairs from the more covalent methyl radical adduct, $PbMe^{2+}$, previously described,[3] and the completely covalent hydrides.

On progressive removal of water from hydrated lead(II) acetate the 530 G spectrum for the ion-pair was reduced and a broader 712 G doublet, also assigned to the ion-pair, appeared. (Both are shown in about equal amounts for the partially dehydrated salt in Figure 5.) This demonstrates that the other co-ordinated ligands also play some part in governing the extent of electron transfer. The basic acetate ions are more strongly co-ordinated to Pb^{2+} than are water molecules, so that the strength of co-ordination of the radical anion $H_2\dot{C}CO_2^-$ is probably increased when other acetate groups are replaced by water molecules, with a consequent increase in coupling.

Other Centres.—Both normal hydrogen atoms and ClO_3 radicals were detected in irradiated lead(II) perchlorate, in addition to the species already discussed. Neither showed any sign of interaction with neighbouring lead cations, as judged by the absence of any ^{207}Pb satellite lines. The $PbMe^{2+}$ centre previously reported was formed in the anhydrous salt. A very similar species

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[13] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[14] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 3198.

[15] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1336.

[16] L. B. Knight and W. Weltner, *J. Chem. Phys.*, 1971, **54**, 3875.

was formed in the hydrate, and in partially dehydrated salts both centres were detected, the one favoured by hydration having slightly increased coupling to ^{207}Pb. No high-field features assignable to Pb^{3+} were detected in the fully hydrated salt.

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