Unstable Intermediates. Part CL.[1] Nitrogen Dioxide, Nitrogen Trioxide, and Nitrate (2−) in Irradiated Lead(II) Nitrate: Electron Spin Resonance Evidence for Electron Transfer to and from Lead(II) Ion

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All three of the title radicals have e.s.r. spectra which display satellite lines assignable to ^{207}Pb hyperfine components. The radical NO_3^{2-} interacts strongly with three magnetically equivalent Pb^{2+} ions and weakly with a fourth. The hyperfine coupling is anisotropic, suggesting the acquisition of spin density by the 6*p* manifold. This is supported by the large shift to high field for the NO_3^{2-} features, compared with results for this species in alkali-metal salts. Single-crystal studies show that the principal directions of the ^{207}Pb hyperfine-tensor components are strongly displaced from those of the ^{14}N hyperfine tensor and hence various anomalous features of the powder spectrum are interpreted. A radical, thought to be NO_3, is also formed by ^{60}Co γ rays at 77 K. This also displays a large shift to high field (low *g* values) relative to ' normal ' NO_3, and strong, almost isotropic, hyperfine coupling to three neighbouring Pb^{2+} ions. This species is stationary at 4·2 K, but exhibits in-plane rotation at 77 K and free rotation at *ca.* 200 K. On storage at room temperature it is slowly replaced by a species with normal magnetic properties for NO_3 and no detectable coupling to ^{207}Pb nuclei. At room temperature, features for NO_3^{2-} also decay, being replaced by those characteristic of NO_2 undergoing in-plane rotation. This exhibits isotropic coupling to three equivalent Pb^{2+} ions. On cooling at 77 K, the radicals become stationary on the e.s.r. time scale and exhibit strong, almost isotropic, coupling to a single Pb^{2+} ion and weak coupling to two other ions. These results are discussed in the light of the ability of Pb^{2+} to act both as an electron donor and acceptor.

NITRATE salts have been extensively studied by radiation chemists. Analytical studies showed that the products are primarily,[2-4] but not solely,[5] nitrite ions and oxygen, and e.s.r. spectroscopic studies have revealed the presence of several trapped paramagnetic

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entities.[6-8] There now seems to be general agreement that the identifications of these magnetic centres proposed by Atkins and Symons [9,10] is correct, and we use these identifications herein.

The radical NO_2, originally studied in rare-gas matrices at 4·2 K,[11,12] has e.s.r. parameters which, it was subsequently shown,[9] require that the radical undergoes restricted rotation about its long axis (y). Later, it was shown that, in irradiated potassium nitrate, NO_2 can undergo specific rotation about its x axis, which corresponds to rotation within the plane of the parent nitrate ion.[13] This alternative is understandable since the NO_2 radicals remain trapped in the original nitrate site.

Weak hyperfine coupling to nuclei of alkali-metal gegen-ions is often exhibited by radical anions in solvents of low dielectric constant,[14] and has occasionally been detected for trapped radical anions in irradiated salts.[15,16] This coupling, which is almost isotropic, is caused by slight electron transfer into the outer s orbital of the alkali-metal ions. In 1964, Golding and Henchman [17] reported a detailed e.s.r. study of the effect of high-energy radiation on single crystals of lead(II) nitrate. After exposure at room temperature, the crystals were cooled to 77 K for measurement and two major radical species, identified as NO_3 and NO_2 ,were detected in accord with the assignments of Atkins and Symons.[9] Analysis of the g and hyperfine tensors for NO_2 led to the conclusion that these radicals were rotating in the radical plane at 77 K, and no interaction with neighbouring Pb^{2+} ions was detected. It was concluded that the outer components of the triplet assigned to NO_3 arose, not from ^{14}N hyperfine coupling, but from very weak coupling to three equivalent Pb^{2+} ions.

Recently, Eachus and Symons [18] briefly reported that weak hyperfine interaction with cation nuclei could be detected in various irradiated salts such as cadmium(II) nitrate and silver(I) carbonate. These cations can act as electron acceptors in the same manner as alkali-metal cations, and the extent of interaction seemed to be comparable. In the present work, we have made a detailed study of lead(II) nitrate irradiated at 77 K and have obtained clear evidence for interaction with neighbouring cation nuclei. Similar interactions were also briefly reported for NO_3 in irradiated thallium(I) nitrate and for CO_2^- and $CH_2CO_2^-$ in irradiated thallium(I) formate and acetate.[19]

EXPERIMENTAL

AnalaR lead(II) nitrate was recrystallised from purified water, and single crystals were grown from aqueous solution as triangular plates. Finely powdered material and single crystals were exposed to ^{60}Co γ rays at 77 K in a Vickrad source at a nominal dose rate of 4 Mrad h^{-1} for up to 2 h,* and studied on a Varian E3 e.s.r. spectrometer at 77 K without warming. Annealing experiments comprised warming slowly in an enclosed empty Dewar vessel *in situ*, with rapid recooling to 77 K whenever significant spectral modifications were observed. Alternatively, because physical and chemical modifications were evident, samples were studied over a range of temperatures between 77 K and room temperature using a Varian variable-temperature insert. In order to check the studies of Golding and Henchman,[17] powders were also irradiated at room temperature for periods between 5 min and 2 h, followed either by immediate cooling to 77 K or storage at room temperature for various periods.

Single-crystal spectra were recorded at 77 K after mounting appropriately on a Perspex rod. Spectra were measured every 5° for three orthogonal rotations. Hyperfine and g tensors could be obtained directly from these spectra since comparison with the powder spectra established that one of the selected rotations included the parallel and perpendicular directions for ^{14}N coupling of one of the four radicals in the unit cell. Spectra at 4·2 K were recorded on a Varian V.4502-03 spectrometer fitted with a liquid-helium Dewar insert, using superheterodyne detection.

RESULTS AND SPECTRAL INTERPRETATION

The powder spectrum obtained at 77 K was dominated by signals from two species, (A) and (B) (Figure 1). Species (A) gave a broad asymmetric line with sets of satellites of the same form. This species, thought to be NO_3 interacting with neighbouring Pb^{2+} ions, is discussed further below. Species (B) exhibited a well defined triplet indicating hyperfine interaction with a single ^{14}N nucleus. The values for $A_{\parallel}$ (^{14}N) and $A_{\perp}$ (^{14}N) were close to those previously assigned to NO_3^{2-} (Table 1),[9] and we use this assignment in the following discussion. g Values were, however, shifted to high fields (Table 1) relative to normal NO_3^{2-} radicals (see below). In addition to the major features for NO_3^{2-}, a large number of satellite lines were detected. Those in the region of the $M_I(^{14}N) = -1$ line are shown at high gain in Figure 1(*b*). The most intense sets of satellites are associated with NO_3^{2-} interacting with one $^{207}Pb^{2+}$, the weaker lines with NO_3^{2-} near two equivalent $^{207}Pb^{2+}$ ions, and the third very weak set with NO_3^{2-} interacting with three equivalent $^{207}Pb^{2+}$ ions. (^{207}Pb has a natural abundance of 21·11% and $I = 1/2$.) The most notable feature of these satellite lines is that they were not equally disposed about the main NO_3^{2-} features for radicals associated with non-magnetic lead nuclei. This is indicative of ^{207}Pb coupling having a large anisotropic component and magnetic axes quite different from those for NO_3^{2-}. Since we were therefore precluded from deriving the ^{207}Pb hyperfine coupling parameters with certainty from the powder spectra, we resorted to a single-crystal study.

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* 1 rad $= 10^{-2}$ J kg^{-1}.

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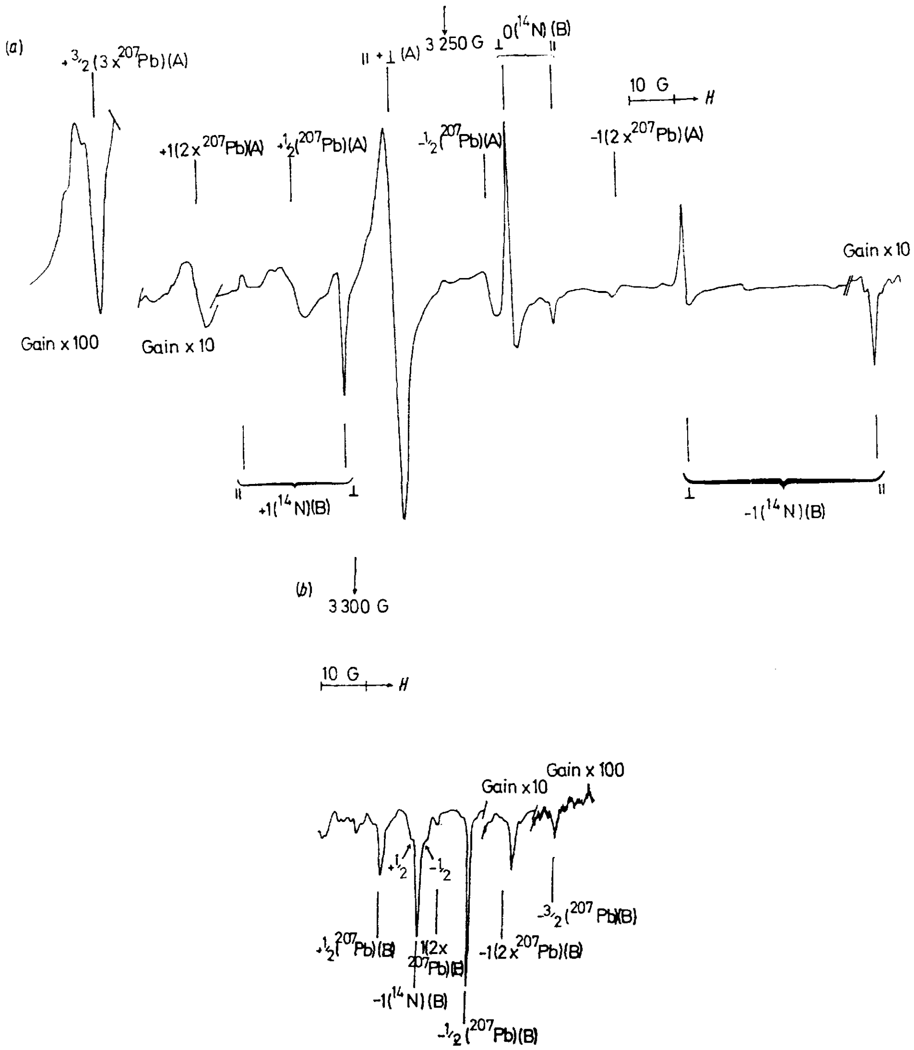

FIGURE 1 First-derivative X-band e.s.r. spectrum for powdered $Pb(NO_3)_2$ after exposure to ^{60}Co γ rays at 77 K, showing (*a*) the overall spectrum containing features assigned to NO_3 (A), including ^{207}Pb satellites, and NO_3^{2-} (B) radicals, and (*b*) the high-field region at high gain, containing features assigned to $^{207}Pb^{2+}$–NO_3^{2-} units

TABLE 1

Magnetic data for NO_3^{2-}, NO_3, and NO_2 radicals in irradiated lead(II) nitrate, and other hosts

Host	T/K	Radical	^{14}N Hyperfine-tensor[a] components/G				^{207}Pb Hyperfine tensor			g-Tensor components		
			A_x	A_y	A_z	A_{iso}	$A_{\parallel}$	$A_{\perp}$	A_{iso}	g_x	g_y	g_z
$Pb(NO_3)_2$	4·2	NO_3^{2-}	38	38	69·5	48·5	36	$\pm3 \pm 1$	*ca.* 12 ± 3	1·991	1·1991	1·985
$CaCO_3$[b]	77	NO_3^{2-}	34·3	34·3	66·8	45·1				2·006	2·006	2·002
$Pb(NO_3)_2$	4·2	NO_3	-2 ± 1	-2 ± 1	-2 ± 1	-2 ± 1			118 (1)		2·0067	
	77								8 (2)			
	200								43 (3)			
	77[c]								32 (3)			
			-3 ± 1	-3 ± 1	-3 ± 1	-3 ± 1				2·029	2·029	2·000
KNO_3[d]	77		−3·46	−3·46	−4·31	−3·74				2·0232	2·0232	2·0031
$Pb(NO_3)_2$	77	NO_2	48·5	46	66·5	53·7				2·0029	1·9910	1·9982
									311 (1)			
									14 (2)			
	300		48·5	56·3	56·3	53·7			85 (3)	2·0029	1·9946	1·9946
	77[e]		57	57	50	54·7				1·995	1·995	2·004
Gas[f]		NO_2	46·13	44·88	66·76	52·59				2·0062	1·9910	2·0020

[a] 1 G = 10^{-4} T. [b] Data of R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 790. [c] After irradiation at room temperature. [d] From ref. 13. [e] From ref. 17. [f] Data of R. M. Lees, R. F. Curl, jun., and J. G. Baker, *J. Chem. Phys.*, 1966, **45**, 2037.

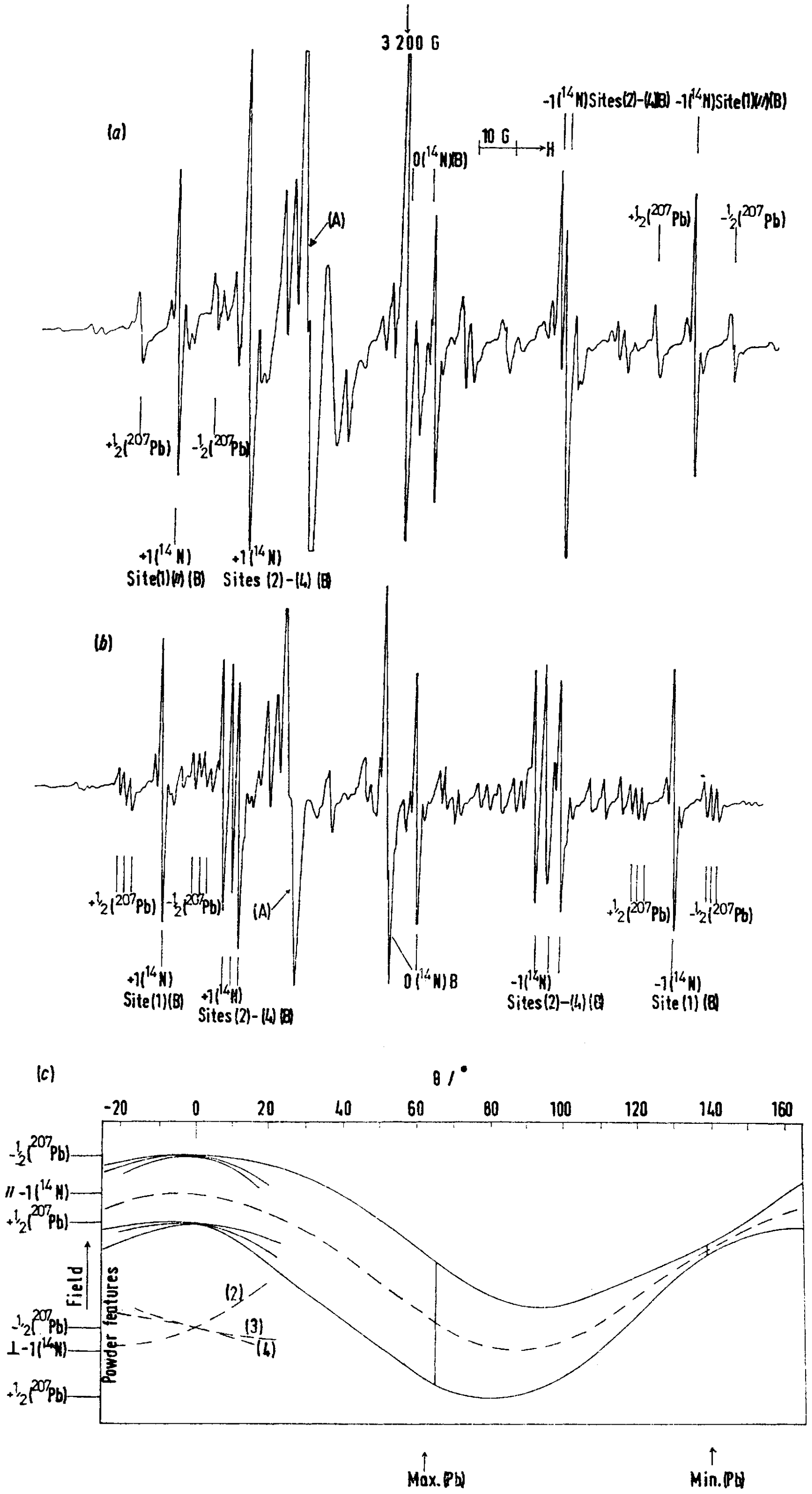

FIGURE 2 First-derivative X-band e.s.r. spectra for a single $Pb(NO_3)_2$ crystal after exposure to ^{60}Co γ rays at 77 K, showing (*a*) the high-field half of a spectrum for which one of the four equivalent NO_3^{2-} radicals is very close to the parallel orientation [features(A)] (^{207}Pb satellite lines for this radical are indicated), (*b*) for a 5° rotation off this direction, showing the splitting of ^{207}Pb satellite lines into three components, and (*c*) an isofrequency plot of the angular dependence of these lines in the parallel region together with the way in which the powder spectral features arise [(——), Units containing one $^{207}Pb^{2+}$ ion; (— — —), units having no magnetic lead nuclei.]

Lead(II) nitrate crystals are cubic, having a distorted fluoride structure with four molecules per unit cell.[17] Four orientationally distinct NO_3^{2-} ions were detected which evidently remained in the sites of the parent nitrate ions. When the static magnetic field is parallel to the C_{3v} axis for NO_3^{2-}, the three other NO_3^{2-} radicals in the unit cell should be magnetically equivalent, as was in fact the case. Furthermore, for this orientation all three of the interacting Pb^{2+} ions should, and did, become equivalent [Figure 2(*a*)]. As the field departed from this direction, three separate Pb^{2+} satellite pairs were detected [Figure 2(*b*)], thus confirming the presence of three strongly coupled Pb^{2+} ions. In addition to these lines, there were two relatively weak lines close to the main ^{14}N line. These lines, which appeared as weak shoulders in the powder spectrum on the parallel ^{14}N components (Figure 1), are assigned to a weakly coupled fourth $^{207}Pb^{2+}$ ion.

On moving between parallel and perpendicular (^{14}N) orientations of the static magnetic field, the coupling to one set of strongly coupled $^{207}Pb^{2+}$ ions increased to a maximum of *ca.* 36 G, at an angle of *ca.* 65° from the parallel direction. At 135° from this direction the coupling reached a minimum of *ca.* 3 G [Figure 2(*c*)]. A complete study of other rotations and of all three ^{14}N hyperfine components confirmed that these values are in fact the principal values for $^{207}Pb^{2+}$. The way in which the powder spectrum results from the crystal data can be visualised from the juxtaposition given in Figure 2(*c*). We call attention to these unusual effects, and the fact that, had $^{207}Pb^{2+}$ been the only isotope of lead, incorrect ^{14}N and g-value data would have been derived from the powder spectrum. However, the differences in relative intensities of the $M_I = \pm 1/2$ components is a significant clue to the off-axis effects. The weaker sets of lines associated with centres containing two $^{207}Pb^{2+}$ ions gave the same results and again the powder spectral features are well accommodated.

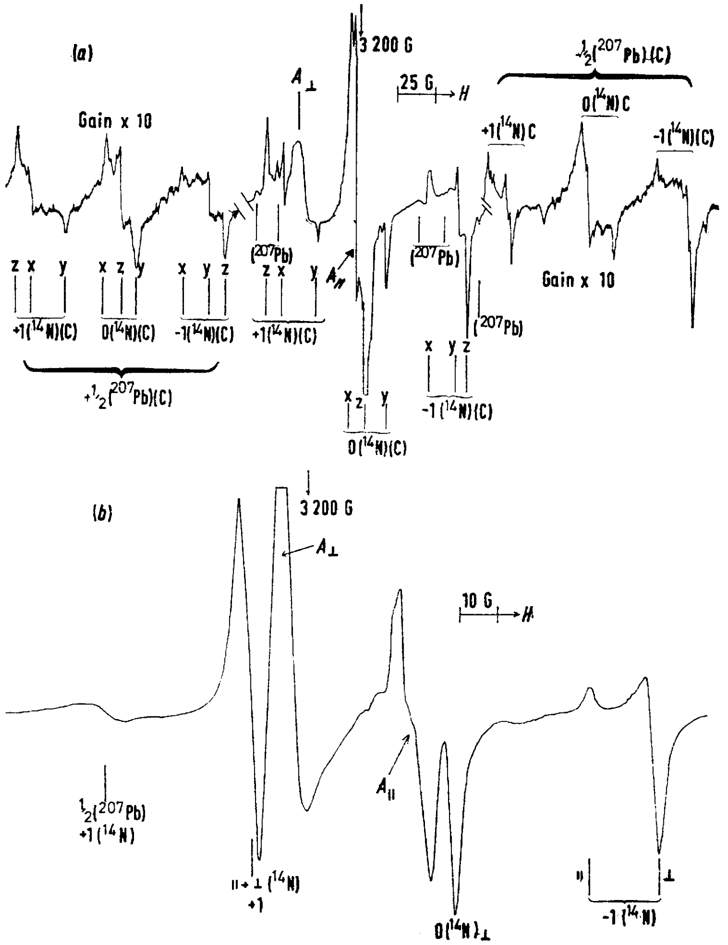

FIGURE 3 First-derivative X-band e.s.r. spectrum for powdered $Pb(NO_3)_2$ after exposure to ^{60}Co γ rays at ambient temperature, showing features assigned to ' normal ' NO_3 radicals (A) and to NO_2 radicals (C) at 77 K (*a*) and room temperature (*b*)

Calculations and experiment suggest that the $M_I = 0$ line for ^{14}N in the powder spectrum is sufficiently isotropic to allow direct determination of the $^{207}Pb^{2+}$ coupling parameters. We were indeed able to see the required features, thus confirming the crystal analysis. [At 77 K the low-field ($+1/2$) shoulders for $^{207}Pb^{2+}$ on the $M_I = 0$ line were concealed by the strong satellite from centre (A) (NO_3). Fortunately, on cooling to 4·2 K these moved away and revealed the expected features for NO_3^{2-}.]

On warming above 77 K, the perpendicular lines for ^{14}N in NO_3^{2-} were almost unchanged, but the parallel features shifted to high field with no appreciable change in $A_\parallel$ (^{14}N). Similarly, on cooling to 4·2 K, they moved slightly to low field. There was no clear change in the $^{207}Pb^{2+}$ satellites, except that they broadened slightly at high temperatures. At room temperature, features for ^{14}N were broad and decayed over a period of several hours, to features (C) assigned to NO_2 radicals. Exposure to low doses of ^{60}Co γ rays at *ca.* 40 °C (ambient in the γ cell) followed by rapid cooling to 77 K gave a mixture of NO_2 and NO_3^{2-}, but after prolonged exposure features (C) for NO_2 completely dominated [Figure 3(*a*)].

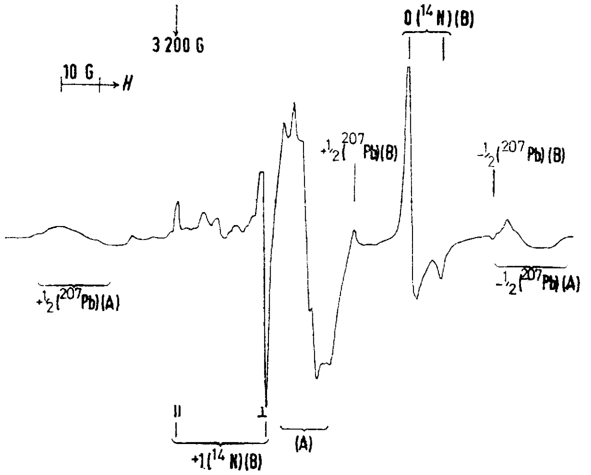

FIGURE 4 First-derivative *X*-band e.s.r. spectrum for powdered $Pb(NO_3)_2$, after exposure to ^{60}Co γ rays at 77 K, measured at 4·2 K, showing modified features for NO_3 and ^{207}Pb–NO_3 satellites

The (A) features are assigned to NO_3 because the ^{14}N hyperfine interaction lies between 2 and 3 G, which is close to results for NO_3 in potassium nitrate.[13] However, as with NO_3^{2-}, the g values were shifted to high field, and there were clear sets of satellite lines (Figure 1). These lines were almost isotropic with respect to the ^{207}Pb interactions, and again correspond to NO_3 interacting with one, two, or three equivalent $^{207}Pb^{2+}$ ions. [The third, $M_I = +3/2$ (^{20}Pb), line on the low-field side of the $M_I = +1$ (^{14}N) component is shown in Figure 1(*a*).] There were marked changes in the features for radical (A) on cooling to 4·2 K (Figure 4). The axial symmetry of the main ^{14}N features was lost, and the ^{207}Pb satellites split into two sets, one closer to and the other much farther from the central lines. There were no extra sets of lines associated with the larger ^{207}Pb coupling, so the radical at 4·2 K only interacts strongly with one Pb^{2+} ion. Unfortunately, the presence of stronger lines from NO_3^{2-} ions prevented detection of extra satellites associated with the weakly coupled $^{207}Pb^{2+}$, but we assume that there are in fact two equivalent Pb^{2+} ions involved. On warming to *ca.* 200 K, these (A) features were modified once more, giving a broad isotropic singlet for the main component and similar broad sets of satellites from $^{207}Pb^{2+}$ ions with reduced hyperfine coupling (Table 1). As at 77 K, at high gain, features containing three equivalent $^{207}Pb^{2+}$ ions were detected. We attempted to detect possible features from four equivalent $^{207}Pb^{2+}$ ions, but the noise level was too high for us to draw any firm conclusions one way or the other. At room temperature, the signals associated with species (A) slowly decayed, but a new feature at low field developed, having a g value close to the perpendicular value for normal NO_3 (*ca.* 2·029). This feature was far better developed after prolonged irradiation at *ca.* 40 °C, together with those for species (C)(NO_2) (Figure 3). No ^{207}Pb satellite lines could be detected that were linked to this centre, which we describe as ' normal NO_3.' The parallel line for this centre displayed a clear triplet from ^{14}N hyperfine interaction.

Species (C) had ^{14}N hyperfine parameters close to those for NO_2 [9,20] and we used this assignment. This is presumably the species studied by Golding and Henchman.[17] They, however, failed to detect the well defined satellite lines for centres trapped close to $^{207}Pb^{2+}$ cations. At 77 K the e.s.r. spectrum of NO_2 was characteristic of the stationary radical and the $^{207}Pb^{2+}$ satellites comprised sets from two equivalent ions with a small interaction and one with a very large interaction [Figure 3(*a*)]. However, as the temperature was raised, the wing lines broadened beyond detection at the same temperature as the central ^{14}N y and x features merged to give perpendicular features [Figure 3(*b*)]. On further warming new wing lines appeared and the spectrum was the same as that obtained at room temperature. Since the x axis is normal to the plane of the radical, a rotation that averages y and z must be the in-plane rotation expected for NO_2 trapped in the parent NO_3^- site. The Pb^{2+} satellite lines remained broad, but two sets were clearly resolved. At high gain, some evidence for a third set was obtained but the noise level was high and the evidence not convincing.

DISCUSSION

The parent nitrate ions are equidistant from three of the four Pb^{2+} ions that define their sites in the crystal, and considerably further away from the fourth, which lies along the symmetry axis of NO_3^- (Figure 5). Formation of NO_3^{2-} by electron attachment results in a small deviation from planarity for NO_3^{2-},[10] but the presence of three equivalent, strongly coupled, Pb^{2+} ions and one weakly coupled ion shows that there has been no major migration within the cavity. This is to be expected since the 2− ion should be strongly held in position by the increased coulombic interaction. The unpaired electron in NO_3^{2-} is in an a_1 orbital having considerable spin density on oxygen. We envisage the main interaction with lead to be *via* weak bonding to the oxygen ligands,

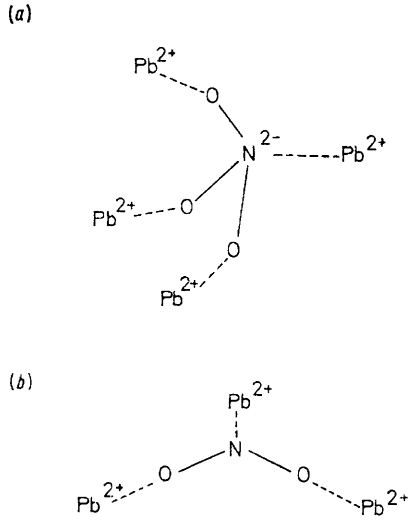

FIGURE 5 Possible modes of interaction between NO_3^{2-} (*a*) and NO_2 radicals (*b*) with neighbouring Pb^{2+} ions

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[20] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3075.

and our results show that the principal directions for the magnetic interaction to each lead ion lie roughly along the lines connecting the lead and oxygen atoms.

The large anisotropic coupling and relatively small isotropic coupling can best be understood in terms of slight electron transfer from NO_3^{2-} to the formally vacant $6p$ manifolds on the lead ions. The degeneracy of these levels must in fact be considerably lifted by the ligand-field effect of the NO_3^{2-} and other adjacent nitrate ions, but nevertheless the g values, which are a property of the whole unit, are considerably shifted by this interaction, in the sense expected for coupling *via* empty p orbitals. The greater shift for $g_{\parallel}$ can be qualitatively understood partly because all three Pb^{2+} ions contribute to the g shift in this direction, and partly because, as judged from the crystal structure, $6p$ orbitals coupled by $H_{\parallel}$ are likely to be closer in energy than those coupled by $H_{\perp}$. The fourth, more distant, lead ion contributes its maximum coupling along the ^{14}N parallel direction, as expected, and the coupling falls to near zero in the perpendicular direction. Thus this also seems to arise primarily as a consequence of electron donation from NO_3^{2-}.

The increase in the shift for $g_{\parallel}$ from the ' normal ' value as the temperature increases is surprising, since one might have expected that thermal motion would increase the average separation between NO_3^{2-} and the three strongly coupled Pb^{2+} ions, thus decreasing the g shift and also the hyperfine interaction. In fact, however, the hyperfine coupling barely decreases and $\Delta g_{\parallel}$ increases. In our view, this shows that the ligand-field splitting of the $6p$ manifold is very dependent on the proximity of the nearest neighbour NO_3^- and Pb^{2+} ions. Crystal expansion increases the mean separation between these ions far more than that between NO_3^{2-} and its nearest neighbours because of the weaker coulombic attraction, and as the p-orbital splitting falls so the g shift increases.

Clearly NO_3^{2-} acts as a powerful electron donor and Pb^{2+} as an acceptor. However, NO_3 must behave as an acceptor and the isotropic character of the contribution from $^{207}Pb^{2+}$ confirms this. In that case the marked negative g shift is more difficult to understand, since the spin on lead will be, in first order, confined to the $6s$ orbital. The unpaired electron in NO_3 is, in the absence of distortion, in an a_2' orbital which comprises the three in-plane $2p$ orbitals on oxygen. The normally large value for $g_{\perp}$ (*ca.* 2·029) comes from the excitation of an electron from the e'' π-orbital to the a_2' orbital, and we therefore require a ligand field from the neighbouring Pb^{2+} ions that will increase the energy gap between these levels. Since in-plane rotation for NO_3 is found to be facile, we suggest that the major bonding interaction between Pb^{2+} and the oxygen ligands is *via* the electrons in the e'' orbital. This would effectively stabilise the e'' electrons and hence decrease $\Delta g'$.

The in-plane rotation is only quenched (on the e.s.r. time scale) at temperatures close to 4·2 K. At these low temperatures the molecule loses its apparent axial symmetry, and interaction with a single Pb^{2+} ion is favoured. The tendency for molecules isoelectronic with NO_3 to distort spontaneously has been a controversial issue for some time. Whiffen and his co-workers have drawn attention to the marked departures from axial symmetry found for the g-tensor components for both NO_3 and CO_3^-.[21] They proposed spontaneous distortion, such as in-plane departure of one of the bond angles from 120°, to explain the observed deviations from axial symmetry. We have stressed, however, that the experimental results can hardly be cited as good evidence in favour of spontaneous distortion in view of the presence of potential asymmetric hydrogen bonding both for CO_3^- in $K[HCO_3]$ and for NO_3 in urea nitrate.[10] This does not, of course, disprove the theory, and unfortunately the results for NO_3 in lead(II) nitrate are again unsuitable for probing this theory, since it could always be argued that the observed distortion is caused by ligand-field forces of the Pb^{2+} ions rather than being spontaneous.

In-plane rotation averages the hyperfine parameters for the three interacting Pb^{2+} ions as expected. However, when ' free ' rotation sets in at higher temperatures, the total average coupling to ^{207}Pb is considerably reduced. Indeed, the value is close to that expected if the fourth, previously non-interacting, Pb^{2+} ion were brought into the sphere of influence of NO_3 by the rotation. Unfortunately, our extensive attempts to verify this possibility failed through lack of sensitivity. We consider it improbable that such apparently high symmetry should result from free rotation in an asymmetric cavity and prefer the postulate that the mean distance between the three coupled Pb^{2+} ions and the NO_3 radical is considerably enhanced by the rotation and that the mean effective overlap is thereby reduced.

The change at room temperature to give ' normal ' NO_3 with no hyperfine coupling to Pb^{2+} ions must mean that NO_3 radicals can migrate out of their parent nitrate sites into sites defined by NO_3^- rather than by Pb^{2+} ions. We suggest that these are lead vacancy sites. There are several drawbacks to this explanation, a major one being that we can find no reason why NO_3 should be able to leave its parent site and yet be deeply trapped and unable to depart from a Pb^{2+} vacancy at room temperature. Also, a similar migratory tendency might be expected for NO_2. The only alternative that we can devise involves formation of NO_4^{2-}, since this radical, which is isostructural with PO_4^{2-}, is the only other reasonable species expected to exhibit a small ^{14}N hyperfine interaction of the type observed. Since, however, NO_3 is expected to be a *primary* product of irradiation, it would be necessary to identify species (A) as NO_3 and the room-temperature product as NO_4^{2-}. In the light of the definitive work of Whiffen and his co-workers,[21] this can surely be rejected.

The identification of species (C) as NO_2 seems to be unambiguous. We suggest that at 77 K a structure such as that in Figure 5(*b*) is favoured, the large ^{207}Pb coupling stemming from the Pb^{2+} ion close to nitrogen. In-plane rotation should give an average A value for $^{207}Pb^{2+}$ ions, but if the smaller (14 G) coupling to the two equivalent

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[21] G. W. Chantry, A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, 1962, **5**, 589.

cations is taken to be positive, the mean value becomes 113 G which is considerably larger than the experimental value of *ca.* 85 G. Taking the smaller coupling to be negative gives the more acceptable average of 94 G. Alternatively, the fourth Pb^{2+} ion could be involved, but we are again unwilling to postulate that its coupling be fortuitously equal to that of the others, and there is no experimental or structural support for strong coupling with an NO_2 radical rotating in the plane.

Our results for NO_2 at 77 K, though close to those obtained by others for non-rotating NO_2 (summarised in ref. 20), are at variance with those of Golding and Henchman[17] (see Table 1). They found that, even at 77 K, NO_2 exhibited rapid in-plane rotation, and the magnitude of their coupling constants (^{14}N) strongly suggest some out-of-plane libration in addition.[20] We are not able to offer an explanation for these differences, unless after prolonged room-temperature irradiation NO_2 can also migrate into cation vacancies. However, we were unable to reproduce their data under any circumstances.

Spin-density Distributions.—Despite the large coupling constants exhibited by ^{207}Pb nuclei, the actual transfer of electrons to or from Pb^{2+} ions is small, because of the very large atomic parameters (A^0 and $2B^0$). The best A^0 value to use in calculating spin-density distributions for the NO_2, NO_3, and NO_3^{2-} radicals is probably the experimental value for ' Pb^{3+} ' of *ca.* 10 000 G,[22] and we used the $2B°$ value of 350 G estimated from recent wavefunctions of Froese.[23] The results are summarised in Table 2. Similarly, the orbital populations for nitrogen were very similar to those previously estimated for all three radicals (Table 2). Both NO_2 and NO_3^{2-} show a fall in $p:s$ ratio implying a slight increase in bending. We previously suggested that this reflects a shift in spin density from oxygen to nitrogen which increases as the effective crystal field of the cations increases.[20,24] These changes make it difficult to monitor overall changes in spin density on these radicals.

TABLE 2

Some estimated spin-density distributions for NO_3^{2-}, NO_3, and NO_2 radicals in irradiated lead(II) nitrate

Radical	Orbital population on *N* [a]		Orbital population on Pb [b]	
	a_{2s}^2	a_{2p}^2	a_{2s}^2	a_{2p}^2
NO_3^{2-}	0·088	0·62	*ca.* 0·0012	*ca.* 0·07
NO_3	*ca.* 0·0036		(1) 0·012	
			(2) 0·0008	
NO_2	0·096	0·42	(1) 0·031	
			(2) *ca.* 0·0014	

[a] Using $A^0 = 550$ G, $2B^0 = 34$ G. [b] Using A^0 *ca.* 10 000 G, $2B^0$ *ca.* 350 G. These are maximum values since no estimate for spin-polarisation effects was attempted.

Aspects of Mechanism.—The initial reaction is the simple electron-transfer process (1), both primary

$$2NO_3^- \longrightarrow NO_3 + NO_3^{2-} \qquad (1)$$

radicals being trapped. We were unable to detect any signal from $^{207}Pb^{3+}$ ions, which can sometimes be formed and stabilised in lead salts,[22] which must mean that process (2) is energetically favourable. We stress that

$$Pb^{3+} + NO_3^- \longrightarrow Pb^{2+} + NO_3 \qquad (2)$$

this process is really less simple than is immediately apparent, since the NO_3 radical is strongly stabilised by slight electron transfer from three Pb^{2+} ions, and this must modify the energy balance of (2) considerably. On annealing to room temperature NO_3^{2-} is lost but NO_2 is formed. We suggest that reaction (3) is facile. This

$$Pb^{2+} + NO_3^{2-} \longrightarrow PbO + NO_2 \qquad (3)$$

may well be a significant step in high-temperature formation of NO_2 from pure lead(II) nitrate. If this is correct, then irradiation at room temperature initially forms NO_3^{2-}, which is concurrently converted into NO_2 by process (3). Previously Golding and Henchman[17] concluded that NO_2 could not be a product of secondary interaction with nitrite ion that accumulates during irradiation. Our mechanism strongly supports this conclusion.

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