Unstable Intermediates. Part CLII.[1] Radicals in Thallous Nitrate

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Exposure of thallous nitrate to ^{60}Co γ-rays at 77 K gave NO_3 radicals which exhibited strong charge-transfer interaction with two equivalent thallous ions and a weaker interaction with two others. Two well defined species were formed, one being lost preferentially on annealing above 77 K. These results are rationalised in terms of the crystal structure of the nitrate.

Exposure at room temperature gave NO_2 which again exhibited strong hyperfine interaction with four thallous ions, together with a second species, possibly also NO_2, but in a completely different environment, with one very strongly coupled thallous ion. The thallous hyperfine coupling was essentially isotropic, which indicates that the interaction stems from an electron donation from Tl^+ to the radical, which is the reverse of that normally associated with alkali-metal radical-anion systems.

We have recently found that cations having an electron configuration $\cdots d^{10},s^2$ can act either as electron-donors or as electron-acceptors depending upon the demand of their partners.[2] This effect is well demonstrated by e.s.r. spectroscopy when the partner is a radical. Thus, for example, Pb^{2+} acts as an electron-donor with NO_3 or NO_2 radicals, but as an acceptor with NO_3^{2-} radicals.[3] Thallous ions would be expected to be better electron-donors, but poorer acceptors than plumbous ions, and in the present studies its role appears to be invariably that of donor. We stress that the difference between these roles is readily detected by e.s.r. spectroscopy since partial donation gives an incipient $\cdots d^{10},s^1$ configuration leading to a large hyperfine coupling and no anisotropy or g-shift, whilst partial acceptance leads to an incipient $\cdots d^{10},s^2,p^1$ configuration with a consequently small, strongly anisotropic, coupling and appreciable g-shift.

We are not aware of any previous studies of radicals in irradiated thallous salts. However, in addition to our study of lead nitrate,[3] a recent report on irradiated lead(II) salts gave evidence for the species $CO_2^-(Pb^{2+})$, $H_2\dot{C}CO_2^-(Pb^{2+})$, and $ClO_2(Pb^{2+})$.[4]

EXPERIMENTAL

Thallous nitrate (B.D.H.) was used without further purification in most experiments since the salt recrystallised from water showed no spectral differences. The higher temperature forms were prepared by heating in unsealed tubes at 380 K (β) and 440 K (α) for 2 h and immersion directly into 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 between 77 K and room temperature, and at 4·2 K on a Varian E3 X-band spectrometer.

RESULTS AND DISCUSSION

Thallium has two abundant nuclei, $^{205}Tl[I = 1/2, 70{\cdot}48\%]$ and $^{203}Tl[I = 1/2, 29{\cdot}52\%]$ with such similar magnetic moments that the transitions are normally coincident, as in the present work. The hyperfine coupling for Tl^{2+} ions in aqueous solution was found to be *ca.* 43 000 G,[5] so that even weak charge-transfer interactions can lead to large splittings in e.s.r. spectra. This accounts for the fact that the e.s.r. features in irradiated thallous nitrate cover a range of *ca.* 1000 G (Figure 1). In all three studies the powder spectra demonstrate that the e.s.r. spectra are almost isotropic, so that little would be gained by the use of single crystals, and this has not been undertaken.

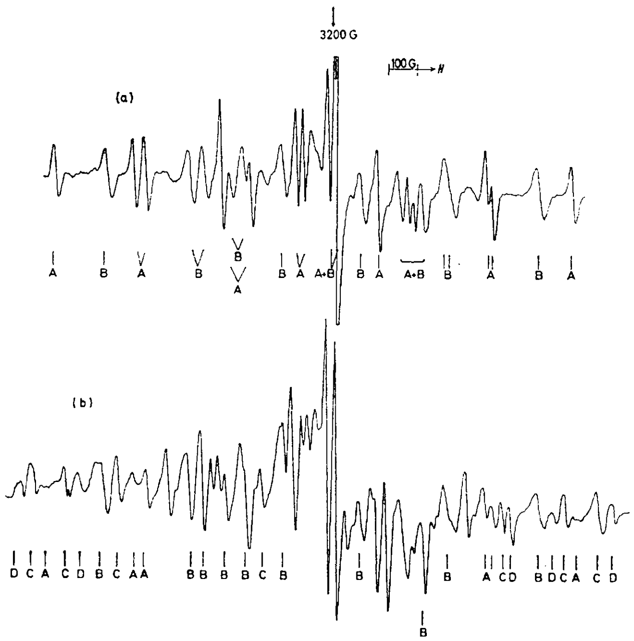

FIGURE 1 First derivative X-band e.s.r. spectra for thallous nitrate after exposure to ^{60}Co γ-rays at 77 K, showing sets of features assigned to NO_3 interacting with four neighbouring thallous ions: (a) the γ-form showing A and B features; (b) the α-form showing the outer features for A, B, C and D features [Note the second order splitting for the inner features for A and B.]

Identification of Radicals.—Since no coupling to ^{14}N was resolved in the initial spectrum obtained from irradiated thallous nitrate, even at 4·2 K, we set $A(^{14}N) \leqslant 5$ G. This means that neither NO_3^{2-} nor NO_2 can be responsible for the observed features, and

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[1] S. P. Mishra, K. V. S. Rao, and M. C. R. Symons, *J. Phys. Chem.*, 1974, **78**, 576, is taken as Part CLI.

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

[3] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, 1974, 2247.

[4] H. C. Starkie and M. C. R. Symons, *J.C.S. Dalton*, 1974, 731.

[5] M. C. R. Symons and J. K. Yandell, *J. Chem. Soc. (A)*, 1971, 760.

leaves NO_3 as being most probable. In our study of lead(II) nitrate[3] the e.s.r. spectrum assigned to NO_3 differed from that normally obtained[6] in that the g-value variation was greatly reduced, all three components being close to the free-spin value. Absence of any detectable anisotropy for the species in thallous nitrate leads us to postulate that a similar effect is occurring in this instance. The hyperfine coupling to ^{14}N of *ca.* 3 G expected for NO_3 would be lost in the line-width even for the narrowest lines detected in this study.

However, one of the species formed in thallous nitrate at room temperature comprises sets of triplets (Figure 2) which closely resemble features for NO_2 in the solid-state,[7,8] although they are less well resolved than usual. We therefore confidently assign the major features in this spectrum to NO_2. The wide doublet of closely spaced lines in Figure 2 is less readily assigned. If the large coupling is assigned to one very strongly coupled thallous ion ($A \doteqdot 1100$ G), the sets of lines separated by *ca.* 20 G must stem from a mixture of interactions with thallium and nitrogen nuclei. This limits $A(^{14}N)$ to *ca.* 20 or *ca.* 40 G, the latter being preferable in terms of predicted intensities. The species cannot be NO_2^{2-} or NO_3^{2-} since these would not act as electron acceptors, and we therefore tentatively conclude that the species is a modified NO_2 radical, strongly interacting with one thallous ion.

The NO_3 *Centre.*—This centre in the normal salt (γ) gives rise to two clearly separate sets of lines, labelled A and B in Figure 1. Both sets can be analysed in terms of two pairs of equivalent Tl^+ ions, four Tl^+ ions for each centre. For A, the strongly coupled pair of Tl^+ ions have $A_{iso}(A_1) = 550$ G and the weakly coupled pair have $A_{iso}(A_2) = 280$ G. For centre B, similarly, $B_1 = 410$ G and $B_2 = 320$ G. These results can be interpreted in terms of the crystal structure.

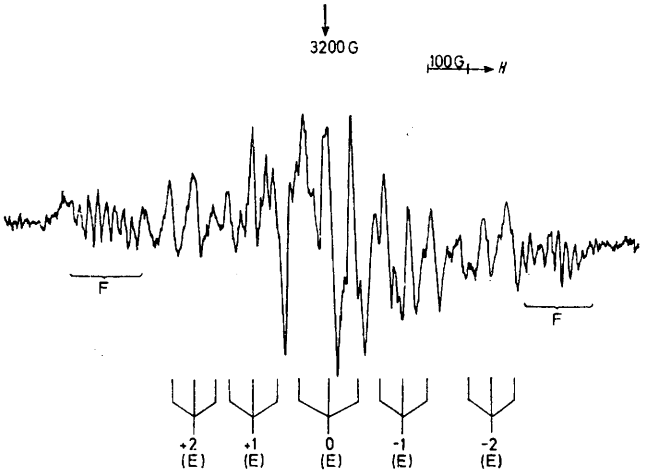

FIGURE 2 First derivative X-band e.s.r. spectra for thallous nitrate after exposure to ^{60}Co γ-rays at room temperature and cooling to 77 K, showing features assigned to NO_2 radicals (E) interacting with four equivalent Tl^+ ions having $A_{iso} \doteqdot 200$ G and (F) outer features assigned to NO_3 interacting with one strongly coupled Tl^+ ($A \doteqdot 1100$ G) and three weakly coupled Tl^+ ions ($A \doteqdot 20$ G)

Thallous nitrate exists in three closely similar crystal forms, the normal variety, designated γ, having a rhombic structure, with eight molecules per unit cell. The β-form, stable above *ca.* 350 K has a trigonal structure, whilst the α-variety, stable above *ca.* 420 K is cubic.[9] However, all forms share a sub-cell comprising an array of eight cations with a body centred nitrate ion. We can discuss the present results in terms of this sub-structure. Since only four of the eight cations interact appreciably in either the A or B species of NO_3, we suggest that after the electron is lost, coulombic forces, which normally force NO_3^- to maintain the body-centred site, are lost, and in order to maximise the charge-transfer interactions, which fall off sharply with increasing separation, the NO_3 radical moves towards one of the six cell faces. The four interacting thallous ions are then differentiated by the fact that one pair will tend to interact *via* two oxygen atoms and the other pair *via* the third (Figure 3).

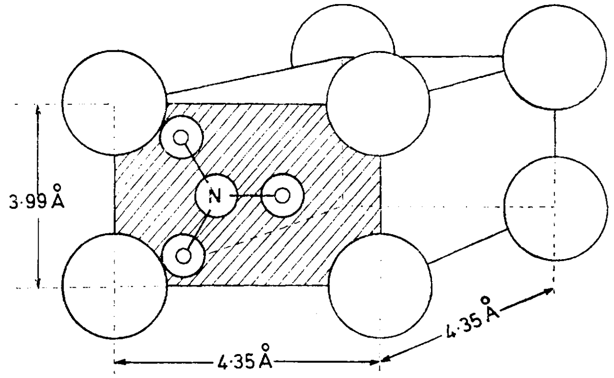

FIGURE 3 Crystal structure for γ-thallous nitrate showing the sub-cell containing eight thallous ions together with a central nitrate ion

There are now two ways in which A and B can be generated, one being through alternative orientation within a given face, and the other being the choice of alternative faces, with one specific orientation of NO_3 dominating for each face.

These alternatives can be differentiated by considering the thermal modifications. Three significant facts emerge: (i) all hyperfine coupling constants are markedly dependent upon temperature (Figure 4), and (ii) the line-widths show selective broadening (especially for A), and (iii) the lines broaden beyond detection for A in the region of 120—130 K. (Unfortunately, A is lost, irreversibly, in the region of 160 K and hence it is impossible to achieve a line-narrowing on increasing the temperature.) The features for B broaden in the 170—180 K region, but narrow lines, presumably assignable to B, reappear in the 200+ K range, although

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

[7] P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 1962, 4794.

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

[9] F. Wallerant, *Bull. Soc. France Mineral*, 1905, **28**, 311.

they are rapidly and irreversibly decaying at those temperatures.

We conclude that A and B are not connected by a simple rotatory motion which would make all four thallous ions equivalent. This eliminates the first alternative set of structures indicated above. The results are, however, quite compatible with the second model, which we adopt. We suggest that species A, having the two most strongly coupled cations, comprises NO_3 in either of the two faces sharing the two longer sides (*ca.* 4·35 Å each), whilst B comprises NO_3 in any of the four faces having two shorter sides (3·99 Å) (as depicted in Figure 3). This is based on the fact that the concentration of B is roughly twice that of A as required statistically. It is not clear why two of the Tl^+ ions are more strongly coupled in A, but this probably is a subtle function of the effective overlap between the 6*s* orbital on thallium and the orbital of NO_3, which is confined to the in-plane oxygen 2*p*-orbitals. The temperature dependence probably reflects the crystal expansion. However, slight movement of NO_3 back towards the face-centred site is also likely as the temperature increases, although this is never enough to introduce a coupling to the more distant set of thallous ions. Such a movement might facilitate jumps between opposite faces at rates sufficient to cause line-broadening, and the distance involved is greater (4·35 Å) for B than for A (3·99 Å) so A should broaden at a lower temperature than B as is observed. Various other migrations could cause line-broadening, and may well also contribute to the overall effect. One probable movement is for NO_3 to pivot about the two most strongly bonded thallous ions so that the more weakly interacting pair are exchanged for those diagonally opposite. This would initially lead to an apparent reversible fall in intensity, which appears to be the case. Eventually, however, the three components for the two more weakly coupled Tl^+ ions would become five, covering the same field range. However, extra lines in the expected regions were never observed.

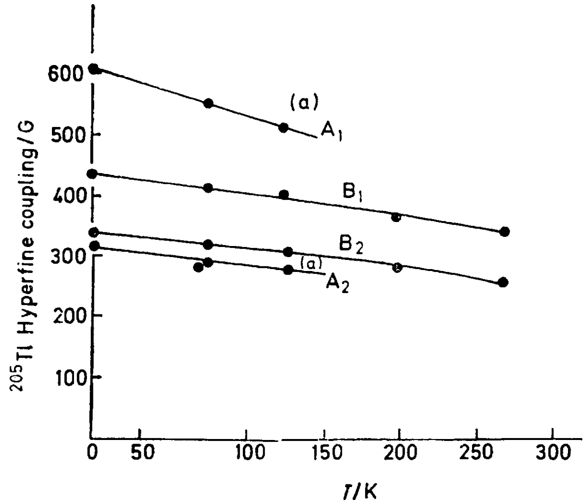

FIGURE 4 Temperature dependence of the hyperfine coupling constants for centres A and B. (a) At about this temperature the A features become undetectable

We have endeavoured to 'freeze in' the α- and β-crystal modifications by quenching heated material in liquid nitrogen, but the results were relatively uninformative. In both cases A and B were again formed, though generally B dominated in these experiments. However extra features, labelled C and D in Figure 1b appeared from new, well defined, centres. Although complete analysis of these new features was not possible because too few lines were defined, nevertheless both are clearly very similar to A and B, and must comprise NO_3 trapped in subtly different sites. We suggest that these are preferentially formed near to ionic vacancies induced by the heat treatment. This would accord with the fact that centres C and D are far less thermally stable than A or B.

The NO_2 *Centres*.—These centres decay at room temperature, and hence it proved to be very difficult to accumulate sufficient for satisfactory e.s.r. analysis. The fact that they appear during the annealing process strongly suggests that NO_3^{2-} centres are initially formed, but not detected:

$$NO_3^- \longrightarrow NO_3 + e^- \qquad (1)$$

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

$$Tl^+ + NO_3^{2-} \longrightarrow TlO^- + NO_2 \qquad (3)$$

We suggest that NO_3^{2-} ions have features that are too severely broadened to be detected in the presence of the intense NO_3 lines because they act as electron donors towards thallous ions and this should lead to strongly anisotropic features, as was observed for NO_3^{2-} coupled to $^{207}Pb^{2+}$ ions.[3]

The major NO_2 centre (central features in Figure 2) exhibits strong coupling to four equivalent thallous ions ($A \doteqdot 200$ G) at 77 K. We suggest that NO_2, like NO_3, moves towards one of the faces of the parent 'cube,' in which case some form of rotation is necessary in order to render the four thallous ions equivalent. This is most likely to be about the long axis, and such a rotation is known to be ready even at 4·2 K.[7] In fact, this rotation is evident in the form of the hyperfine features as shown in Figure 2. Although the lines are broad, the form of the spectrum is caused by averaging the x and z components, leaving y as apparent parallel features. If this is correct, we find '$A_\perp$' = 60 G and '$A_\parallel$' = 55, whereas the predicted values are 56·5 and 45 respectively. The small anisotropy suggests some libration about the other two axes,[8] whilst the increase in A_{iso}, despite the delocalisation onto four Tl^+ ions, suggests an increase in the bond angle, induced by the 'co-ordinated' thallous ions.

As mentioned above, the remaining outer features are more difficult to analyse. We favour a ^{14}N coupling of *ca.* 40 G but this is by no means certain. In this case the NO_2 (if correctly identified) has moved towards one Tl^+ ion and is probably bonded *via* nitrogen. This would now be expected to decrease the bond angle for NO_2, which would account for the fall in the isotropic coupling. It is not clear to us why NO_2 should favour two such different modes of interaction, but in view of the uncertainties in identification further speculation is surely unwarranted. There is also a weak interaction ($\sim$20 G) to three other Tl^+ ions.

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