Electron Spin Resonance Study of Adducts of Gallium Trichloride and Digallium Hexachloride with the Free-radical Base, 2,2,6,6-Tetramethylpiperidine Nitroxide

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Reaction of gallium trichloride with 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO) yields two adducts, (I) ($Ga_2Cl_6 \leftarrow$TEMPO) with A_{iso} (^{14}N) = 19·13 G, A_{iso} (^{71}Ga) = −55·3 G and (II) ($GaCl_3 \leftarrow$TEMPO) with $g_\parallel$ = 2·003, $g_\perp$ = 2·007, A_{iso} (^{14}N) = 19·75 G, $A_\parallel$ (^{14}N) = 39 G, $A_\parallel$ (^{71}Ga) = −50 G, $A_\perp$ (^{71}Ga) = −44 G, A_{iso} (^{71}Ga) = −48·0 G. The principal values of the g-tensor are close to those for TEMPO alone, and the Ga hyperfine tensors show that the isotropic component stems from spin polarisation of the O–Ga σ electrons and the anisotropic component probably stems from polarisation of the O–Ga π-electrons.

LEWIS ACID–LEWIS BASE 1 : 1 complexes of the type $R_3N \rightarrow MX_3$ or $R_2O \rightarrow MX_3$ where M is a Group 3 element and X halide are well known. Lewis bases of the type R_2NO, *viz.* organic nitroxides, behave similarly and have the advantage of being paramagnetic so that the unpaired electron can be monitored and new information gained about the structure and bonding in the complex.[1,2] However, since this work was started, there have been reports of the e.s.r. of 2,2,6,6-tetramethylpiperidone nitroxide (TEMPOO) adducts with various aluminium, gallium, and indium halides.[2-4] Our results with 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO) are in accord with those published using TEMPOO. We report here some unusual observations concerning the formation of adducts between the Ga_2Cl_6 and TEMPO and also an analysis of the anisotropic g- and hyperfine tensors of one of the adducts formed.

EXPERIMENTAL

TEMPO was made by the method of Brière.[5] Toluene was redistilled and kept over molecular sieves and all operations were carried out in a dry box. E.s.r. spectra were recorded at various temperatures on a Varian E-3 spectrometer and also at Q-band frequencies.

RESULTS

The room-temperature e.s.r. spectrum of a solution of TEMPO in toluene to which has been added excess of a freshly prepared solution of gallium trichloride in toluene is shown in Figure 1. The spectrum may be analysed in terms of superimposed signals from two species. Species (I), in major abundance, consists of two sets of a quartet of triplets arising from interaction of the unpaired electron with the nitrogen nucleus (I = 1) and the two isotopes of gallium (^{69}Ga, I = 3/2, 60·2%, μ_N = 2·0108; ^{71}Ga, I = 3/2, 39·8%, μ_N = 2·5549). The outer triplets of lines (M_I = ±3/2) were much broader than the inner triplets (*ca.* 8—9 ×). Species (II), in lower abundance (*ca.* 20—30%) has a larger hyperfine coupling to N but smaller coupling to Ga than species (I) and only slight (*ca.* 20%) broadening of the outer lines was seen. Hyperfine couplings are given in the Table. When the solution was warmed to 320 K the proportion of species (II) relative to species (I) approximately doubled. Furthermore, after the solution had stood in a refrigerator for 24 h, the e.s.r. spectrum changed dramatically and consisted only of that for species (II) (Figure 2). In a separate experiment, when the solution of gallium trichloride in toluene was set aside for *ca.* 1 h before being mixed with the TEMPO solution, then the spectrum at room temperature consisted mainly of species (II) but with *ca.* 10% species (I). A ^{13}C hyperfine coupling of 7 G

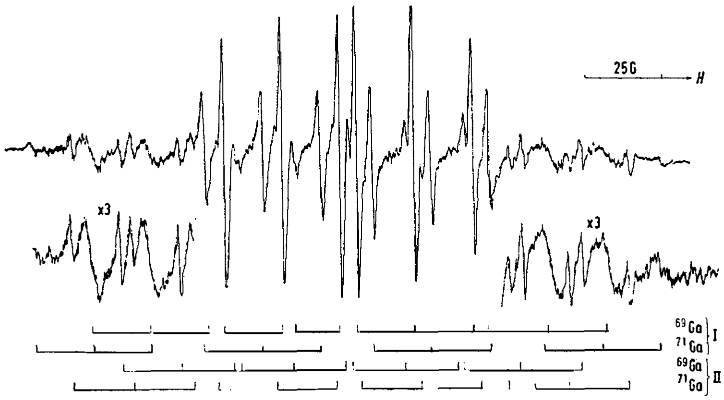

FIGURE 1 E.s.r. spectrum of TEMPO with $GaCl_3$ in toluene showing the reconstruction of the spectra of the two species. Species (I) in major abundance

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[1] T. B. Eames and B. M. Hoffman, *J. Amer. Chem. Soc.*, 1971, **93**, 3141.

[2] G. A. Abakumov, V. D. Tikhonov, and G. A. Razuyaev, *Doklady Akad. Nauk S.S.S.R., Ser Khim.*, 1969, **187**, 571.

[3] G. A. Abakumov and V. D. Tikhonov, *Zhur. strukt. Khim.*, 1972, **13**, 150.

[4] G. A. Razuyaev, V. D. Tikhonov, and G. A. Abakumov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1970, 1732.

[5] R. Brière, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.

was detected on some lines and unambiguously measured on the outermost lines of both species. The gallium hyperfine couplings were very temperature dependent, that for ^{71}Ga in species (II) ranged from 51 to 48 G over the temperature range 250—300 K. A similar effect occurred with species (I). In both cases there was no detectable variation in the nitrogen coupling constants.

At 77 K, the X-band spectrum could not be readily interpreted because of considerable overlap of the lines. However, the Q-band spectrum differed significantly in that more lines were observed and these were mostly narrower than at X-band. The key observation was that the overall width of the spectra were identical, thus showing that the outer features were associated with the same g-value. The separation (*ca.* 228 G) was thus equal to $A(3^{71}\text{Ga} + 2\text{N})$ and, by a process of elimination and consideration of the shape of the peaks, they could only be assigned to parallel features. The spectrum was interpreted in terms of an apparently axially symmetric g-tensor with hyperfine coupling to one ^{71}Ga and ^{14}N nucleus. Coupling to the ^{69}Ga nucleus, is also seen, but does not influence the gross features of the spectrum. The analysis was subsequently checked by computer simulation with the following values $g_{\parallel} = 2{\cdot}003 \pm 0{\cdot}001$, $g_{\perp} = 2{\cdot}007 \pm 0{\cdot}001$, $A_{\parallel}(^{71}\text{Ga}) = 50$ G, $A_{\perp}(^{71}\text{Ga}) = 44$ G, and $A_{\parallel}(^{14}\text{N}) = 39$ G. The perpendicular nitrogen features were not resolved and were presumably less than the linewidth of the perpendicular Ga lines. The high-field perpendicular feature had a linewidth of 20 G and this suggests that the maximum value of $A_{\perp}$ is *ca.* 10 G. As we shall see from analysis of the results (*vide infra*) the spectrum arises from species (II). Whatever the conditions of preparation, the spectra were identical. Presumably at these temperatures the spectra of species (I) were either so broadened or weak as not to be seen, or the anisotropic parameters were essentially the same as species (I).

FIGURE 2 E.s.r. spectrum of TEMPO with $GaCl_3$ under conditions where only species (II) is present

Experimental hyperfine couplings (gauss)

	Species (I)	Species (II)
$A(^{14}\text{N})$	$19{\cdot}13 \pm 0{\cdot}02$	$19{\cdot}75 \pm 0{\cdot}02$
$A(^{69}\text{Ga})$	$43{\cdot}5 \pm 0{\cdot}1$	$37{\cdot}8 \pm 0{\cdot}1$
$A(^{71}\text{Ga})$	$55{\cdot}3 \pm 0{\cdot}1$	$48{\cdot}0 \pm 0{\cdot}1$
$A_{\parallel}(^{14}\text{N})$		39 ± 1
$A_{\parallel}(^{71}\text{Ga})$		50 ± 1
$A_{\perp}(^{71}\text{Ga})$		44 ± 1

DISCUSSION

Comparison with the Free Radical TEMPO.—The unpaired electron in TEMPO is in a π^* molecular orbital on the NO group. Upon complexing, there is strong evidence[1] that the site of complexing is the oxygen atom and the variation in hyperfine splittings is readily interpreted in terms of a simple molecular orbital scheme (Figure 3). The oxygen atom will be lowered in energy upon adduct formation. The effect will be to make the unpaired electron more nitrogen like and thus increase the hyperfine coupling to it.[6] There is, then, a direct relationship between Lewis acid acceptor strength and nitrogen hyperfine splitting. Likewise, there is an associated increase in ^{13}C coupling from α and β carbon atoms.[7] Hyperfine coupling to the acceptor atom will be observed, but there is no direct mechanism whereby spin density can be transferred to an s-orbital on gallium. We suggest the probable mechanism is *via* polarisation of the σ-bonded Ga–O electron pair. The magnitude of the hyperfine coupling to gallium is dependent upon the strength of the gallium–oxygen bond. Strong interactions will cause the unpaired electron to be less on oxygen thus permitting less polarisation of bonding electrons and yielding a small isotropic hyperfine coupling on gallium. As the acid–base interaction becomes weaker, so polarisation will be weaker and there will be a reduction in hyperfine coupling. Our results show that species (I), with the smaller coupling to nitrogen, is a weaker complex than species (II), at the temperature studied.

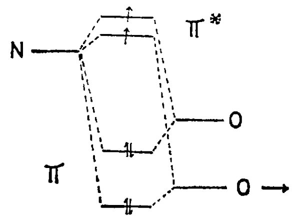

FIGURE 3 The relative energies of the π and π* molecular orbitals in R_2NO and $R_2NO \rightarrow GaCl_3$

The Dissociation of Gallium Trichloride in Solution.—Gallium trichloride is a molecular solid and consists of Ga_2Cl_6 dimers with two bridging chlorine atoms.[8] It dissolves with dissociation in polar solvents forming 1 : 1 solvates of the type $S \rightarrow GaCl_3$ but in non-polar solvents it remains as a dimer. In very weakly basic solvents there appears to be an equilibrium between the monomeric and the dimeric form in solution; for example in chloromethane,[9] vapour pressure studies have shown that discontinuities occur at 1 : 1 and at 1 : 2 mol ratio MeCl : $GaCl_3$ indicating the possible existence of solvates $MeCl \rightarrow GaCl_3$ and $MeCl \rightarrow Ga_2Cl_6$.

Species (I) *and* (II).—The observation of e.s.r. signals from two species each with hyperfine coupling to gallium shows two subtly different adducts present in solution. Our results suggest that in toluene the dimeric form Ga_2Cl_6 dissociates slowly and that with weak Lewis bases (*e.g.* TEMPO) adducts can be formed with both

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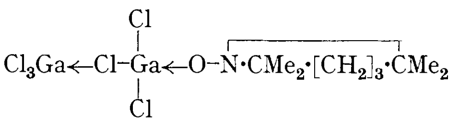
[6] H. Hayat and B. L. Silver, *J. Phys. Chem.*, 1973, **77**, 72.

[7] R. Brière, H. Lemaire, and A. Rassat, *J. Chem. Phys.*, 1968, **48**, 1429.

[8] S. C. Wallwork and I. J. Worrall, *J. Chem. Soc.*, 1965, 1816.

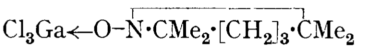
[9] H. C. Brown, L. P. Eddy, and R. Wong, *J. Amer. Chem. Soc.*, 1953, **75**, 6275.

species in solution, the relative concentrations being temperature and time dependent. Both must be bonded to TEMPO *via* the oxygen since the nitrogen h.f.s. are similar. We propose that two different compounds are formed with the structures given below.



$$Cl_3Ga\leftarrow Cl\text{-}\overset{Cl}{\underset{Cl}{Ga}}\leftarrow O\text{-}\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot CMe_2}$$

(I)



$$Cl_3Ga\leftarrow O\text{-}\overline{N\cdot CMe_2\cdot[CH_2]_3\cdot CMe_2}$$

(II)

Bonding to two $GaCl_3$ units *via* the two oxygen lone-pairs is not a possibility since coupling to only one gallium nucleus is observed. Species (I) is formed when one bridging chlorine bond in Ga_2Cl_6 is broken leaving a vacant site for the oxygen lone-pair to co-ordinate weakly. In (II), the Ga_2Cl_6 is fully dissociated and its behaviour is now typical of Group III Lewis acids.

The considerable (and symmetrical) broadening of the outer triplets of lines of (I) arises from a time-dependent hyperfine splitting caused by rapid interconversion of two radicals, one with large gallium h.f.s. and another with a small or zero h.f.s.[10] We propose that the following equilibrium exists:

$$\text{TEMPO}\rightarrow Ga_2Cl_6 \rightleftharpoons \text{TEMPO} + Ga_2Cl_6 \qquad (1)$$

If there was slow interconversion, the spectrum would consist of two separate signals superimposed. Since we do not see the spectrum of TEMPO alone, then there must be a rapid interconversion so that the observed signal is the weighted average. Figure 4 shows in the limits (a) slow and (b) fast association of Ga_2Cl_6 with TEMPO. That rapid association and dissociation can occur implies that the O→Ga bond strength is weak and approximately equal to the strength of the chlorine bridging bond (*ca.* 10 kcal [11]). If the O→Ga bond were weaker, no association with Ga_2Cl_6 would take place, whilst if it were stronger, there would be no time-dependent phenomena. Species (II) exhibited a slight broadening of the outer lines showing that in this case too there is rapid exchange between the adduct and the free base. However, the proportion of free base present must be very small.

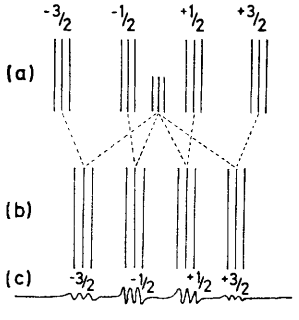


FIGURE 4 Stick diagram representation of a spectrum on the limits of (a) slow and (b) fast exchange for two forms of a radical with $I = 3/2$ and $I = 1$; (c) resultant e.s.r. spectrum

We can now explain why the proportion of species (I) and (II) observed varies with experimental conditions. We propose that the dissociation of Ga_2Cl_6 is slow and addition of TEMPO to a freshly made up solution of gallium trichloride in toluene results in adduct formation with the more abundant Ga_2Cl_6. Upon warming the solution, more gallium trichloride dissolves and dissociates, so that the proportion of the adduct with $GaCl_3$ increases. After 24 h, dissociation was complete and only species (II) was observed. With a 1 h old solution of gallium trichloride, the intermediate stage was observed where species (II) predominated, but there was still some species (I).

The possibility of residual anisotropy causing the linewidth effects is less likely since this mechanism would almost certainly lead to an unsymmetrical line broadening with the components of the $M_I = -3/2$ triplet having a different linewidth from the $M_I = +3/2$ triplet.

Unfortunately it was not possible to calculate equilibrium constants and enthalpy data since our solutions never reached a state of equilibrium because of the slow dissociation of the Ga_2Cl_6. We believe that, in fact, dissociation is eventually complete since when the adduct solution was left for 24 h only signals from species (II) were observed. The temperature dependence of the Ga h.f.s. is explained as follows. At low temperature, the equilibrium (1) lies to the left as shown by the higher value of the coupling constant. The line broadening of the outer Ga lines varied from a ratio of 1·27 to 1·16 as the temperature increased from 250 to 300 K. This also confirms that the relative proportions of the associated and dissociated species is in favour of the associated complex at low temperatures. These results are entirely in accord with the analysis by Hiroto [10] for the case of sodium naphthalenide, the only difference being an inversion of the temperature dependence of the hyperfine coupling.

The Anisotropic Parameters.—The analysis of the *X*- and *Q*-band spectra at 77 K, and a comparison with the published results for TEMPO alone, allows us to be quite precise about the nature of the bonding in the adduct molecule. No anisotropic data have been given for the several other adducts between Group 3 halides and nitroxides which have been reported.

The g-Tensor.—Our experimental *g*-tensor is very close to that found by earlier workers for uncomplexed di-t-butyl nitroxide,[12] indicating that the orbital of the

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[10] G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139; H. Hirota, *ibid.*, p. 127; M. C. R. Symons, *ibid.*, p. 172.

[11] A. W. Laubengayer and F. B. Schirmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1578.

[12] L. J. Libertini and O. H. Griffith, *J. Chem. Phys.*, 1970, **53**, 1359.

unpaired electron is not greatly perturbed from that in the free nitroxide.

The Hyperfine Tensors.—Since the sign of the isotropic coupling to ^{14}N is positive and that to $^{69,71}Ga$ is negative (since spin density can only reach the Ga *via* a polarisation mechanism), then the only combination of signs which fit the experimental tensors are as follows. For ^{71}Ga, $A_{\parallel}$ and $A_{\perp}$ are both negative and yield an A_{av} of -46 G which is close to A_{iso} for species (II) (-48 G). The principal value of the experimental anisotropic tensor is then *ca.* -2 G. For ^{14}N, $A_{\parallel}$ must be positive and since $A_{\perp}$ is <10 G (from linewidths), then a value of $A_{\perp} = +9$ G may be calculated using the isotropic value of $+19$ G. It follows that the principal value of the N tensor is *ca.* $+20$ G, from which the spin population[13] in the N p_z orbital is *ca.* 59%, compared with 49% for free di-t-butyl nitroxide.[6] This is further support for the proposal[1] that, upon complexing, the unpaired electron becomes more nitrogen like.

Because there is no mechanism whereby spin density on the oxygen can interact directly with the gallium, then the observed hyperfine coupling must arise by polarisation. The isotropic hyperfine coupling on gallium almost certainly arises from polarisation of the O–Ga σ-bond. Support for this comes from calculation of the spin-polarisation constant U^{Ga}_{O-Ga} from the equation[14]

$$\frac{100a(\text{Ga})}{A(\text{Ga})} = U^{Ga}_{O-Ga} \times \rho_0 \qquad (2)$$

where a(Ga) = isotropic hyperfine coupling to ^{71}Ga, A(Ga) = calculated value for h.f.s. to ^{71}Ga for electron entirely in 4*s* orbital[13] (3389 G), and ρ_0 = spin density on oxygen (0·4). U^{Ga}_{O-Ga} is found to be 4·1 from which it follows[14] that the *s*-character of the O–Ga bond is *ca.* 0·87. By using the Coulson equation[15] (assuming C_{3v} symmetry), the Cl–Ga–Cl bond angles are *ca.* 90—91°. This value is in good agreement with that found from crystal structures of bridged molecules of the type M_2Cl_6 (M = Fe, Al, Ga, In) and from n.q.r. data[16] on GaI_3 ($94\frac{1}{2}$°) and is strong support for equation (2) and the σ-polarisation mechanism. The constancy in the N h.f.s. is further confirmation of the spin-polarisation mechanism for spin density on gallium.

σ-Polarisation alone is not strong enough to account for the anisotropic hyperfine coupling to Ga (*ca.* 2 G). There is a dipolar coupling of *ca.* +2—3 G and the rest *ca.* -5 G must arise from polarisation of the O–Ga $p\pi$–$d\pi$ bond. It is not possible to be quantitative about this effect since the detailed nature of the π-bonding is not straightforward.

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[13] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[14] T. F. Hunter and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1967, 1770.

[15] C. A. Coulson, 'Contributions à l'Etude de la Structure Moleculaire, Volume Commemoratif Victor Henri,' 1948, p. 15.

[16] R. G. Barnes and S. L. Segel, *J. Chem. Phys.*, 1956, **25**, 180.