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Electron Spin Resonance Spectra of Dinitrosyltriorganoantimony-ironbromides in Solution

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ESR data of the complexes $Fe(NO)_2SbR_3Br$ ($R = C_2H_5$, C_6H_5, and $4-(H_3C)_2NC_6H_4$) in solution are presented. The observed hyperfine coupling due to bromine and antimony is interpreted including second order contributions. Nuclear quadrupole effects are discussed and found to be detectable in the antimony hyperfine pattern.

Introduction

Analyzing electron spin resonance spectra including second order hyperfine interactions is a well established procedure.[1,2,3,4] Recently, the importance of nuclear quadrupole coupling to the ESR spectra of polycrystalline samples was demonstrated.[5] In a previous communication[6] we reported the solution ESR spectra of several complexes of the type $Fe(NO)_2LX$ ($L = PR_3$, AsR_3; $X = Br$, J). These spectra, especially those of the arsine compounds, show remarkably clear second order hyperfine effects. In the present paper we have extended our ESR studies to the compounds $Fe(NO)_2SbR_3Br$ ($R = Ph$, Et, $4-Me_2NC_6H_4$ ($=$ Ar)) in which we expected even higher second order effects. We intended to investigate the influence of nuclear quadrupole interactions on ESR spectra of solutions of these complexes.

Experimental Section

All substances, solvents, and solutions were handled under nitrogen atmosphere. Solvents were distilled from sodium and stored over molecular sieves (Merck 4A). The complexes $Fe(NO)_2SbR_3Br$ were prepared according to Hieber and Kramolowsky[7,8] by addition of equivalent amounts of SbR_3 ($R = Ph$, Et, Ar) to solutions of $[Fe(NO)_2Br]_2$ in tetrahydrofurane. These solutions were cooled below 0°C and rapidly evaporated, leaving the desired compounds as dark green crystalline powders ($R = Ph$, Ar) or viscous oil ($R = Et$).

Recrystallization of the compounds $Fe(NO)_2SbR_3Br$ turned out to be difficult, for as was shown before[8] in the case of $Fe(NO)_2SbPh_3J$, the complexes dissociate in solution according to

$$2Fe(NO)_2SbR_3Br \rightleftharpoons [Fe(NO)_2Br]_2 + 2SbR_3$$

into components with different solubilities. ESR spectra are not seriously affected by this dissociation, since $[Fe(NO)_2Br]_2$ is diamagnetic. ESR spectra of $[Fe(NO)_2Br]_2$ in toluene exhibit merely an extremely weak quartet, presumably due to slight dissociation into the monomer $Fe(NO)_2Br$. The compounds had to be measured immediately after preparation, since they tended to decomposition during storage. 10^{-2}m toluene solutions of the complexes were used for measurements. ESR data were obtained on a Varian V4500 X-band spectrometer equipped with 100 Kc field modulation and with a Varian V4540 variable temperature controller. Magnetic fields were measured using an AEG nuclear magnetic resonance gaussmeter, the microwave frequencies with a Hewlett-Packard 5245L frequency counter. The reproducibility was checked with DPPH.

Results

The ESR spectra of $Fe(NO)_2SbPh_3Br$ and $Fe(NO)_2SbEt_3Br$ obtained in toluene solution are represented as examples in Figures 1a and 2a. The spectrum of $Fe(NO)_2SbAr_3Br$ is very similar to that of $Fe(NO)_2SbPh_3Br$. All spectra consist of one set of six quartets and another of eight quartets with lower intensities. These two sets partially obscure each other. The spectra can easily be assigned assuming a monomeric complex ($S = 1/2$) with hyperfine coupling (hfc) due to one bromine nucleus ($I = 3/2$) and one antimony nucleus occuring in two isotopes (^{121}Sb, $I = 5/2$, natural abundance 57.25%; ^{123}Sb, $I = 7/2$, 42.75%).[9] Since the nuclear moments of ^{79}Br and ^{81}Br are very similar ($\bar{m}_{79}$: $m_{81} = 0.93$; $I_{79} = I_{81} = 3/2$),[9] individual couplings to the two bromine isotopes are not resolved under the observed line widths

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(*) Publication delayed for technical reasons.

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[7] W. Hieber and R. Kramolowsky, *Z. Naturforsch.*, *16b*, 555 (1961); *Z. anorg. allg. Chem.*, *321*, 94 (1963).

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of about 10 G. We stress that ^{14}N hfc of the nitrosyl groups is not observed.[6]

The spacings within the antimony sextets and octets differ markedly, while the asymmetry within the bromine quartets is very small. Thus, with negligible error, it is justifiable to consider the geometrical center of the inner lines (m_I = +1/2 and −1/2) of the bromine quartets as an approximation for the actual centers of the quartets, and hence for the virtual positions of the antimony hyperfine lines. Most of the positions of the allowed antimony hyperfine transitions (Δm_I = 0) defined in the above sense by geometrical centers could be determined from the observed spectra and are presented in Table I-IV. The transitions are assigned assuming a positive anti-

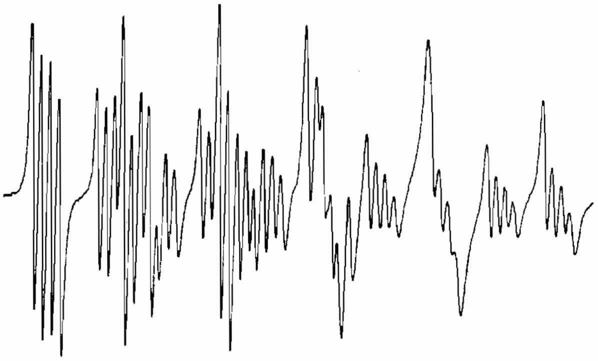

Figure 1a. X-band ESR spectrum of $Fe(NO)_2SbPh_3Br$ in toluene at —10°C.

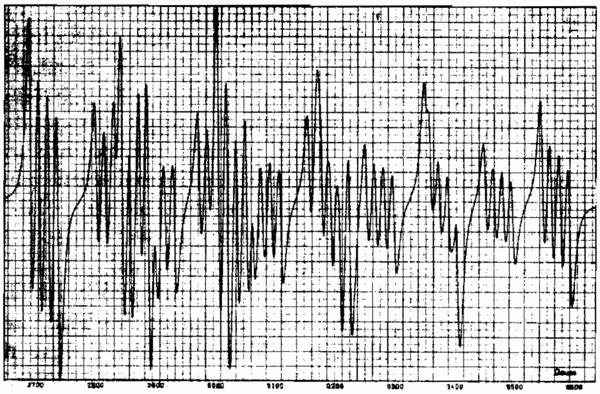

Figure 1b. Calculated X-band ESR spectrum of $Fe(NO)_2$-$SbPh_3Br$.

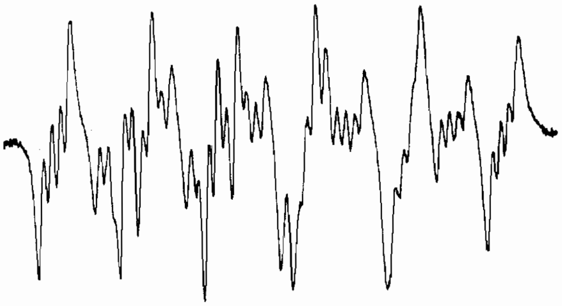

Figure 2a. X-band ESR spectrum of $Fe(NO)_2SbEt_3Br$ in toluene at 22°C.

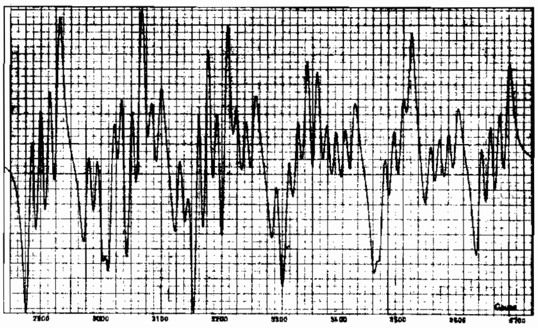

Figure 2b. Calculated X-band ESR spectrum of $Fe(NO)_2$-$SbEt_3Br$.

Table I. Observed and calculated positions of antimony hyperfine transitions of $Fe(NO)_2SbPh_3Br$ (in toluene at 22°C, frequency ν_o = 9.48388 Gc).

Assignment	m_I	Observed line positions [G]	Weight	Line positions calculated with:					
				H_o =	3290.6	3290.6	3290.5	3290.4	3290.4
				a_{121} =	170.44	170.30	170.16	170.04	169.82
				a_{123} =	92.76	92.57	92.39	92.20	91.93
				Q'_{121} =	0	1.4	2.0	2.5	3.0
				Q'_{123} =	0	0.8	1.2	1.5	1.8
				a_{Br} =	15.23	15.23	15.23	15.23	15.23
^{121}Sb	—5/2	3706.7±0.3	1		3706.8	3706.8	3706.8	3706.8	3706.7
	—3/2	3518.3±1	0		3519.5	3519.1	3519.4	3518.9	3518.7
	—1/2	3338.3±1	0		3339.1	3339.0	3339.1	3338.8	3338.8
	+1/2	3166.5±0.3	1		3166.7	3167.0	3166.9	3167.0	3167.2
	+3/2	3003.5±0.6	0.5		3003.7	3004.1	3003.9	3004.2	3004.6
	+5/2	2851.6±0.3	1		2851.7	2851.6	2851.7	2851.5	2851.6
^{123}Sb	—7/2	3611.3±0.4	0.7		3611.0	3610.9	3611.0	3610.9	3610.9
	—5/2	—	—		3510.8	3510.2	3510.5	3509.8	3509.4
	—3/2	3412.1±0.3	1		3412.7	3412.1	3412.4	3411.8	3411.4
	—1/2	—	—		3316.9	3316.7	3316.8	3316.5	3316.5
	+1/2	3223.8±0.3	1		3223.5	3223.9	3223.8	3224.0	3224.3
	+3/2	3133.8±0.6	0.5		3132.9	3133.6	3133.3	3133.9	3134.4
	+5/2	3046.1±0.6	0.5		3045.2	3045.8	3045.6	3046.1	3046.6
	+7/2	2961.1±0.3	1		2960.7	2960.7	2960.8	2960.6	2960.6
		Σ_c = 0.13		Σ_c =	0.14	0.08	0.08	0.11	0.26

Table II. Observed and calculated positions of antimony hyperfine transitions of $Fe(NO)_2SbPh_3Br$ (in toluene at −10°C, frequency ν_o = 9.12791 Gc).

Assignment	m_I	Observed line positions [G]	Weight	Line positions calculated with: $H_o = 3166.7$ $a_{121} = 170.45$ $a_{123} = 92.76$ $Q'_{121} = 0$ $Q'_{123} = 0$ $a_{Br} = 15.23$	 3166.7 170.17 92.39 2.0 1.2 15.23
^{121}Sb	−5/2	3582.6±0.3	1	3582.6	3582.6
	−3/2	3393 ±2	0	3394.7	3394.4
	−1/2	3213 ±2	0	3213.8	3213.8
	+1/2	3041.5±0.6	0.5	3041.3	3041.6
	+3/2	2880.0±0.9	0.3	2878.5	2879.0
	+5/2	2727.3±0.3	1	2727.2	2727.2
^{123}Sb	−7/2	3486.7±0.3	1	3486.9	3487.0
	−5/2	—	—	3386.5	3385.9
	−3/2	3287.9±0.3	1	3288.2	3287.7
	−1/2	—	—	3192.2	3192.1
	+1/2	3099.1±0.3	1	3098.8	3099.2
	+3/2	3008.9±0.3	1	3008.3	3009.0
	+5/2	2921.5±0.6	0.5	2920.7	2921.5
	+7/2	2836.4±0.3	1	2836.6	2836.7
		$\Sigma_c = 0.12$		$\Sigma_c = 0.14$	0.05

Table III. Observed and calculated positions of antimony hyperfine transitions of $Fe(NO)_2SbEt_3Br$ (in toluene at 22°C, frequency ν_o = 9.51198 Gc).

	Assignment m_I	Observed line positions [G]	Weight	Line positions calculated with: $H_o = 3302.7$ $a_{121} = 150.90$ $a_{123} = 82.01$ $Q'_{121} = 0$ $Q'_{123} = 0$ $a_{Br} = 15.27$
^{121}Sb	−5/2	3672.2±0.3	1	3672.1
	−3/2	3508.0±0.3	1	3508.0
	−1/2	3349.4±0.3	1	3349.4
	+1/2	3197.3±0.6	0.5	3197.1
	+3/2	3053.1±0.9	0.3	3052.2
	+5/2	2915.7±0.3	1	2915.6
^{123}Sb	−7/2	3586.3±0.3	1	3586.4
	−5/2	—	—	3498.5
	−3/2	3412.2±0.3	1	3412.4
	−1/2	—	—	3328.0
	+1/2	3245.8±0.3	1	3245.6
	+3/2	3165.4±0.6	0.5	3165.3
	+5/2	3087.1±0.6	0.5	3087.2
	+7/2	3011.6±0.3	1	3011.6
		$\Sigma_c = 0.13$		$\Sigma_c = 0.03$

mony hyperfine coupling constant. Due to line overlap and phase uncertainties, the experimental accuracy of about 0.3 G did not reach the instrumental limit of <0.1 G. During longer periods, the spectra of dilute solutions of the compounds show increasing changes in the region of $m_I(Sb) = +1/2$ transitions. These are certainly caused by decomposition, but, provided compounds and solutions are freshly prepared, are so insignificant that they do not seriously affect the measurements.

Discussion

Theoretical Considerations. Complexes of the type $Fe(NO)_2LX$ can be treated as d^9 systems with one unpaired electron. Thus, we shall base our discussion on a simplified spin Hamiltonian

$$H = \beta_e \mathbf{H}_o \mathbf{g} \mathbf{S} + \Sigma \mathbf{I}_i \mathbf{A}_i \mathbf{S} + \Sigma \mathbf{I}_i \mathbf{Q}_i \mathbf{I}_i \quad (1)$$

neglecting nuclear Zeeman terms, which would give rise to minor contributions in the order of $g_N\beta_N H_o/g_e\beta_e$ only. The last two terms in eq. (1) denote nuclear hyperfine and nuclear quadrupole interactions, respectively. Summations are taken over all relevant nuclei.

Bleaney[2] has shown that calculations of the resonance fields H can be carried out to second order within two limitations:

(a) axial symmetry of the Hamiltonian has to be assumed and

Table IV. Observed and calculated positions of antimony hyperfine transitions of $Fe(NO)_2SbAr_3Br$ (in toluene at 22°C, frequency ν_o = 9.53312 Gc).

Assignment	m_I	Observed line positions [G]	Weight	Line positions calculated with:		
				H_o = 3310.0	3310.0	3309.9
				a_{121} = 162.94	162.83	162.69
				a_{123} = 88.66	88.48	88.31
				Q'_{121} = 0	1.4	2.0
				Q'_{123} = 0	0.8	1.2
				a_{Br} = 14.77	14.77	14.77
^{121}Sb	—5/2	3708.4±0.3	1	3708.3	3708.4	3708.4
	—3/2	3529.4±0.3	1	3530.0	3529.9	3529.7
	—1/2	3357.6±0.6	0.5	3358.1	3358.0	3357.9
	+1/2	3193.6±0.3	1	3193.5	3193.6	3193.7
	+3/2	3038.4±0.6	0.5	3037.3	3037.5	3037.6
	+5/2	2891.0±0.3	1	2891.1	2891.0	2890.9
^{123}Sb	—7/2	3616.5±0.3	1	3616.4	3616.4	3616.5
	—5/2	3520.7±0.6	0.5	3521.0	3520.7	3520.4
	—3/2	3426.9±0.3	1	3427.5	3427.2	3426.9
	—1/2	—	—	3336.1	3336.0	3335.9
	+1/2	3247.1±0.3	1	3246.9	3247.1	3247.2
	+3/2	3160.5±0.3	1	3160.2	3160.6	3160.8
	+5/2	3076.5±0.3	1	3076.1	3076.5	3076.7
	+7/2	2995.1±0.3	1	2995.0	2995.0	2994.8
		Σ_e = 0.12		Σ_c = 0.14	0.07	0.06

(b) quadrupole interactions must be small compared with the nuclear hyperfine interactions.

In solution, the first order and second order terms in Bleaney's results for $\Delta m_i = 0$ transitions reduce by rapid tumbling[10] to

$$H = H_o - am_I - \frac{a^2}{2H}[I(I+1) - m_I^2] \qquad (2)$$

with $H_o = h\nu_o/g\beta$, $g = (1/3)(g_\parallel + 2g_\perp)$, and $a = (1/3)(A_\parallel + 2A_\perp)$. In this case, it seems to be a valid assumption to replace $A_\parallel$ and $A_\perp$ by a, $g_\parallel$ and $g_\perp$ by g, respectively, in the quadrupole terms as well. The spatial average then leads to a simple form of the additional quadrupole term:

$$+\frac{4}{15a}Q'^2 m_I[2I(I+1) - 10m_I^2 + 1] \qquad (2a)$$

$Q' = 3eQ(\partial^2V/\partial z^2)/4I(2I-1)$ represents the nuclear quadrupole coupling constant. We note that the denominator of the second order hyperfine term, which is H_o in Bleaney's original paper,[2] should be replaced by the actual resonance field H.[5] The resulting quadratic equation can be avoided, however, by substituting H by $(H_o - am_I)$ in the second order term. Errors caused by this simplification are negligible in the actual problem.

Though the Hamiltonian is probably not axially symmetric in the complexes $Fe(NO)_2SbR_3Br$, we apply the above result, assuming that formula (2) is at least a good approximation for solution ESR spectra in case of unrestricted spin Hamiltonians. Bleaney[2] further discussed transitions with $\Delta m_I = \pm1, \pm2$. While these transitions may become very important in single crystal ESR studies, they do not contribute to the positions of the resonance fields in solution spectra, because the corresponding energy terms are averaged to zero by rapid tumbling. Moreover, provided $Q' \ll a$, the additional intensity arising from these transitions is extremely small. Consequently, we have ignored all $\Delta m_I \neq 0$ transitions.

Thus, from the last two terms of the Hamiltonian (1), we expect the following effects in the solution spectra similar to single crystal spectra:

(a) Second order nuclear hyperfine terms provide a down field shift of the lines depending on m_I, which is slightly higher on the low field side.

(b) Quadrupole terms produce line shifts of values depending on m_I but not on the field position, and of directions determined by the signs of m_I and a. These line shifts are proportional to the squared quadrupole coupling constant.

Evaluation of hfc Constants and g Factors. To determine the coupling constants and g values from the observed spectra, the following procedure was applied. The bromine hfc constants, causing second order deviations below experimental errors, were approximated by the averages of line distances within the outmost quartets (transitions with $m(^{121}Sb) = \pm5/2$). The results are compiled in Table V. For calculation of the antimony coupling constants, the centers H_+ and H_- of the outmost bromine quartets corresponding to the transitions assigned +I and –I (i.e. ±5/2 for ^{121}Sb and ±7/2 for ^{123}Sb) serve as first approximations in an iteration procedure. Defining

$$a_o = (H_- - H_+)/2I \qquad (3)$$

and

$$H_\infty = (H_- + H_+)/2 \qquad (4),$$

and remembering that the second order shifts appear to be

$$-\frac{a_o^2 \cdot I}{(H_\infty - a_o I)} \qquad (5)$$

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(10) H.M. McConnell, *J. Chem. Phys.*, *25*, 709 (1956).

Table V. ESR parameter of the complexes $Fe(NO)_2SbR_3Br$ in toluene.

		$Fe(NO)_2SbEt_3Br$ (22°C)	$Fe(NO)_2SbPh_3Br$ (22°C)	$Fe(NO)_2SbPh_3Br$ (−10°C)	$Fe(NO)_2SbAr_3Br$ (22°C)
g		2.0578 ± 0.0001	2.0593 ± 0.0001	2.0595 ± 0.0001	2.0570 ± 0.0001
a(Br)	[G]	15.27 ± 0.05	15.23 ± 0.05	15.23 ± 0.06	14.77 ± 0.05
a(^{121}Sb)	[G]	150.9 ± 0.1	170.2 ± 0.1	170.2 ± 0.1	162.7 ± 0.1
a(^{123}Sb)	[G]	82.0 ± 0.1	92.45 ± 0.1	92.45 ± 0.1	88.3 ± 0.1
$\|Q'(^{121}Sb\|$	[G]	0.0 + 0.8	1.7 ± 0.8	1.7 ± 0.8	1.7 ± 0.8
$\|Q'(^{123}Sb)\|$	[G]	0.0 + 0.5	1.0 ± 0.5	1.0 ± 0.5	1.0 ± 0.5

(including the simplifications referred to above), the iterations

$$a_{n+1}=[\underbrace{\frac{H_{-}-H_{+}}{2I}}_{a_o}-\frac{a_n^3 \cdot I}{H^2_{on}-a_n^2 \cdot I^2}] \tag{6}$$

and

$$H_{on+1}=[\underbrace{\frac{H_{-}+H_{+}}{2}}_{H_{oo}}+\frac{H_{on} \cdot a^2_{n+1} \cdot I}{H^2_{on}-a^2_{n+1} \cdot I^2}] \tag{7}$$

(n=0,1,2,...)

are obtained, which rapidly converge below experimental errors. Hence, a close approximation of antimony hfc constants can be achieved, with quadrupole effects still ignored. The final results are listed in Table I - IV. The final values of H_o derived from the ^{121}Sb and ^{123}Sb lines of the same complex are not always identical. The deviations, however, are within experimental error. There is no reason not to assume identical g values.

Quadrupole Influence. The positions of the complete set of allowed transitions can be calculated straight-forward from equation (2) and the approximated hfc constants and H_o. For reasons of better comparability, the positions of the antimony hyperfine transitions were determined as from the experimental spectra by calculation of the geometrical centers of the computed bromine quartets (see Tables I - IV). A quantization of comparison was obtained by considering as correlation factor the normalized sum of weighted, squared deviations, i.e. differences of experimental and computed values for Σ_c or estimated experimental errors for Σ_e, respectively. Weights and experimental errors were estimated.

In the case of $Fe(NO)_2SbEt_3Br$ the calculated values agree well with the experimental measurements ($\Sigma_e > \Sigma_c$). Thus, there is no need to take into account other than second order hyperfine corrections. For $Fe(NO)_2SbPh_3Br$ and $Fe(NO)_2SbAr_3Br$, however, there is a significant deviation ($\Sigma_e < \Sigma_c$). We have tentatively assumed that quadrupole interaction with the antimony nucleus is responsible for this disagreement. Figure 3 contains two examples (two independent measurements of $Fe(NO)_2SbPh_3Br$ at different temperatures) of deviations of the observed values of the ^{123}Sb line centers (circles) from those calculated with zero quadrupole coupling constants Q′ (zero line) plotted against the transition quantum number m_I. The cross signs represent the corresponding deviations of the lines computed with Q′ = 1.2 G. Hyperfine coupling constants were properly adjusted to cover the outmost lines almost exactly.

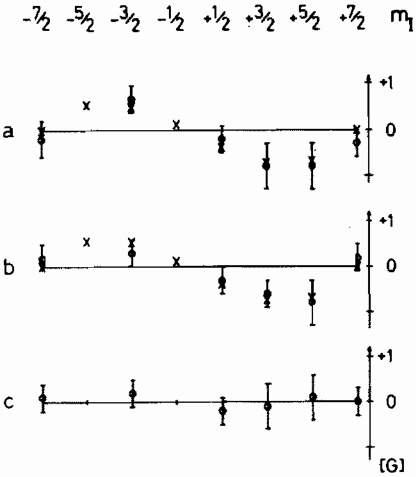

Figure 3. Deviation of line positions of ^{123}Sb hyperfine transitions from calculated second order positions (O experimental, × calculated with Q′ = 1.2 G; horizontal line calculated with Q′ = 0.0 G). a, b: $Fe(NO)_2SbPh_3Br$, two independent measurements; c: $Fe(NO)_2SbEt_3Br$.

The diagrams lend strong support to our contention that the deviations can be interpreted in terms of antimony quadrupole coupling. Tables I - IV list line positions calculated with various quadrupole coupling constants implying the following premises:

(a) The nuclear quadrupole moment of ^{121}Sb is 0.8 that of ^{123}Sb ($Q_{121} = 0.8 \cdot Q_{123}$).[9]

(b) The field gradients are not dependent on the particular antimony isotope and thus, with $Q' = 3eQ(\partial^2V/\partial z^2)/4I(2I-1)$ the relation $Q'_{121} : Q'_{123} = 1.7$ holds.

The values of the correlation factors show that antimony quadrupole coupling constants in the order of $|Q'_{121}| \sim$ 1-2 G (corresponding to $|Q'_{123}| \sim$ 0.6 - 1.2 G) accomodate the observed line positions for $Fe(NO)_2SbPh_3Br$ and $Fe(NO)_2SbAr_3Br$. The quadrupole coupling constant in $Fe(NO)_2SbEt_3Br$ should not exceed $|Q'_{121}|$ = 1 G, presumably reflecting considerably lower field gradients in $SbEt_3$.

The final ESR data of the complexes are listed in Table V. Figures 1b and 2b show two representative spectra simulated with these data. g values of the stibine complexes are somewhat higher than those of the corresponding phosphine or arsine complexes,[6] revealing comparable or even higher donor-acceptor properties of the stibines in this type of complexes.

Conclusions

Based on the above results, it is concluded that it is in principle possible to estimate absolute values of nuclear quadrupole coupling constants from the positions of hyperfine transitions in the ESR spectra of radicals in solution. There is evidence of antimony quadrupole coupling constants of about 1-2 G in the complexes $Fe(NO)_2SbR_3Br$ (R = Ph, Ar) in solution. The observed ratio $a_{121}:a_{123}$ of the hfc constants of antimony is very near to 1.846 in all cases, which is the ratio of the nuclear g factors of the two isotopes.[9]

Calculations

A program based on equation (2) was written in Fortran IV for a Telefunken TR 4 computer. Calculations of line positions were carried out with the simplifications given in the discussion. A second program was generating theoretical spectra with finite line widths. Lorentzian functions were found to be a fairly good approximation to experimental line shape. The spectra of each isotope with different abundances and nuclear spins were summed to give a resultant derivative spectrum. Field dependent line widths and intensities were taken into account by linear approximations of the type $\Delta H = \Delta H_o [1+\beta(H-H_o)]$. Theoretical spectra were plotted on a Calcomp plotter.

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