Electron Paramagnetic Resonance of some Irradiated Ammonium Compounds

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Dedicated to Professor Werner Müller-Warmuth on the occasion of his 65th birthday

Gamma irradiation damage centres in $(NH_4)_2SiF_6$, $(NH_4)_2SnCl_6$, $(NH_4)_2PtCl_6$, $[(CH_3)_2NH_2]_2SnCl_6$, $(NH_4)_2PdCl_6$ and ultraviolet irradiation damage centres in $(CH_3)_4NCH_3COO$ and $(CH_3)_4NBr$ have been investigated by electron paramagnetic resonance spectroscopy. It has been found that the radicals produced in $(NH_4)_2SiF_6$ and $(NH_4)_2SnCl_6$ is $N_2H_4^+$, and those in $(NH_4)_2PtCl_6$ are NH_3^+ and $(PtCl_6)^{3-}$. In $[(CH_3)_2NH_2]_2SnCl_6$ the species is $(CH_3)_2NH^+$, and in $(NH_4)_2PdCl_6$ the species is $(PdCl_6)^{3-}$. Furthermore, it has been shown that the ultraviolet irradiation produces $\dot{C}H_3$ and CO_2^- radicals in $(CH_3)_4NCH_3COO$ and $\dot{C}H_3$ radical in $(CH_3)_4NBr$. The EPR parameters of the observed radicals have been determined.

Key words: EPR, Gamma irradiation, Utraviolet, Ammonium compounds, Free radicals.

Introduction

It is well known that free radicals can be produced in organic and inorganic compounds by X-, γ- and ultraviolet irradiation. In many electron paramagnetic resonance (EPR) studies the irradiation products have been identified [1–8]. In continuation of this kind of research we have studied a series of γ- and ultraviolet irradiated ammonium compounds: $(NH_4)_2SiF_6$, $(NH_4)_2SnCl_6$, $(NH_4)_2PtCl_6$, $[(CH_3)_2NH_2]_2SnCl_6$, $(NH_4)_2PdCl_6$, $(CH_3)_4NCH_3COO$, $(CH_3)_4NBr$, $(NH_4)_2RhCl_6$, $(NH_4)_2RuCl_6$ and $(NH_4)_2IrCl_6$.

Experimental

Most of the compounds used in this study were obtained from commercial sources. Some of the properties of the samples are given in below. Both single crystals and powder samples were irradiated with γ-rays from a ^{60}Co source of 0.1 M Rad/h at room temperature for 24 hours. The ultraviolet irradiations were made directly in the EPR cavity by a Conrad Hannovia 1 kW Xenon lamp. The EPR spectra were recorded with a Varian E-109-C model EPR spectrometer with 100 kHz modulation. The microwave power used was around 2 mW. The low temperature experiments were performed using a Varian temperature controller. The g values were found by comparison with a DPPH sample of $g = 2.0036$.

Results and Discussion

I. $(NH_4)_2SiF_6$ and $(NH_4)_2SnCl_6$

$(NH_4)_2SiF_6$ and $(NH_4)_2SnCl_6$ crystallize in the cubic F_{m3m} structure and their unit cells contain 4 molecules [9]. The single crystals were obtained by slow evaporation of their saturated aqueous solutions.

The EPR spectrum of the $(NH_4)_2SiF_6$ at room temperature is shown in Figure 1 a. The single crystal spectrum, and the powder spectrum as well, consists of 9 lines and is isotropic. The relative intensities of the lines are 1 : 6 : 17 : 29 : 36 : 29 : 17 : 6 : 1, and $g = 2.0045$ indicates the presence of $N_2H_4^+$ radical.

If we consider the two nitrogen nuclei as magnetically equivalent, and so the four hydrogens, the EPR simulation program by McKelvey [10] gives the spectrum in Figure 1 b, which is in good agreement with the experimental one. As a result, the hyperfine coupling constant of the unpaired electron with the nitrogen nucleus is found to be $a_N = 1.15$ mT, and with hydrogen $a_H = 1.025$ mT. These are in good agreement with the previous results for this radical [11, 12]. $(NH_4)_2SnCl_6$ gives similar results, and we attributed

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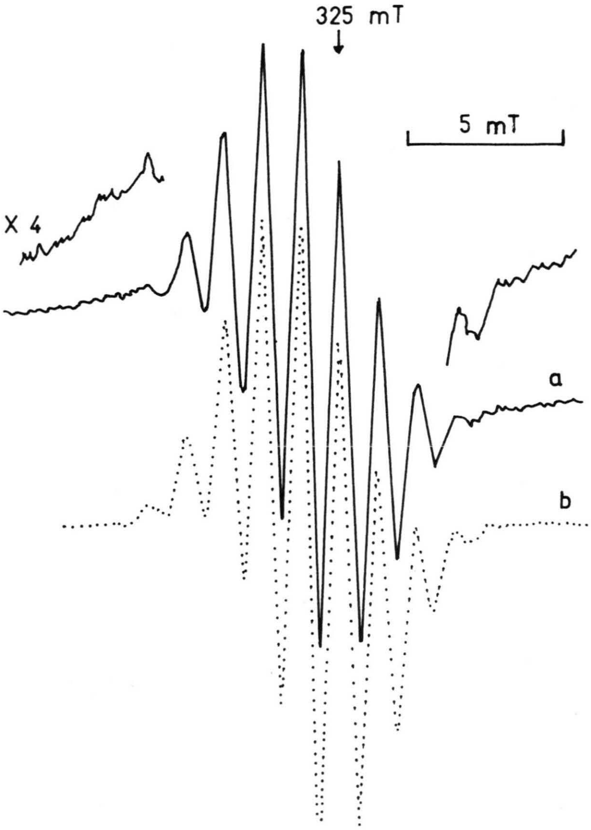

Fig. 1. a) The EPR spectrum of the $N_2H_4^+$ radical in γ-irradiated $(NH_4)_2SiF_6$ single crystal; b) simulation of the spectrum.

the spectrum to $N_2H_4^+$ radical with $g = 2.0040$, $a_N = 1.15$ mT and $a_H = 1.025$ mT. These results indicate that the $N_2H_4^+$ radical is rather mobile in these compounds.

II. $(NH_4)_2PtCl_6$

$(NH_4)_2PtCl_6$ crystallizes in the cubic F_{m3m} structure, its unit cell containing four molecules [9]. The single crystals have been grown as above. The room temperature EPR spectrum of this compound consists of 6 lines and is isotropic, Figure 2. Since the single crystal and the powder spectra do not differ, we performed our experiments with powder samples. The g factor is $g = 2.0051 \pm 0.0005$, and the spectrum can be interpreted as due to a NH_3^+ free radical. The EPR simulation programme [10] gives the spectrum in Figure 2b. This spectrum is in good agreement with the experimental one, and gives the isotropic hyperfine constants of the nitrogen nucleus as $a_N = 2.25$ mT, and that of the hydrogens as $a_H = 1.875$ mT. These are in agreement with previous results [13, 14]. Furthermore, for powder samples, when the temperature is decreased to 130 K, the spectrum which is attributed to NH_3^+ does not change, but new lines appear at the down field side as shown in Figure 3. Since the nuclear spin of ^{195}Pt, having 33.8 per cent natural abundancy, is 1/2, the inner and the outer two lines seem to be the result of the $g_\parallel$ and $g_\perp$ components, respectively, of a kind of platinium complex radical. We suppose that the signal from ^{194}Pt ($I = 0$), having 33.2 per cent natural abundancy, lie buried beneath the central two lines in Figure 2b. The measured values of the principal components of the g tensor are $g_\parallel = 2.438 \pm 0.008$ and $g_\perp = 2.428 \pm 0.008$. The principal values of the hyperfine interaction tensor of the unpaired electron with ^{195}Pt are $A_\parallel = 4.7 \pm 0.5$ mT and $A_\perp = 48.8 \pm 0.5$ mT. We tentatively attribute this radical to $(PtCl_6)^{3-}$. The superhyperfine structure from Cl nuclei is not resolved. It can be around 0.5 mT when the previous studies on platinium based complex radicals are considered [15].

III. $[(CH_3)_2NH_2]_2SnCl_6$

This compound has been produced in our laboratory from $(CH_3)_2NH$, HCl and $SnCl_4$. First $(CH_3)_2NH$ and HCl are mixed in stoichiometric proportion and $(CH_3)_2NH_2Cl$ is obtained. Then, $(CH_3)_2NH_2Cl$ and $SnCl_4$ are mixed in 2 : 1 stoichiometric proportion in a container cooled by icy water and $[(CH_3)_2NH_2]_2SnCl_6$ is obtained. The single crystals of $[(CH_3)_2NH_2]_2SnCl_6$ have been grown from its concentrated aqueous solutions by slow evaporation. The crystal structure of $[(CH_3)_2NH_2]_2SnCl_6$ is unknown. However, for the EPR measurements we have chosen the x, y, and z axes as indicated in Figure 4. Two characteristic room temperature spectra of a gamma irradiated $[(CH_3)_2NH_2]_2SnCl_6$ single crystal are given in Figure 5b. The spectrum with 8 triplets of intensity ratios 1 : 7 : 21 : 35 : 35 : 21 : 7 : 1 clearly displays the hyperfine interaction of an unpaired electron with seven equivalent protons and a ^{14}N nucleus ($I = 1$). At this orientation of the magnetic field the hyperfine coupling constant of the protons is 3.4 mT and that of the ^{14}N is 0.87 mT. Furthermore, Figure 5b displays 9 doublets. This can happen if the protons

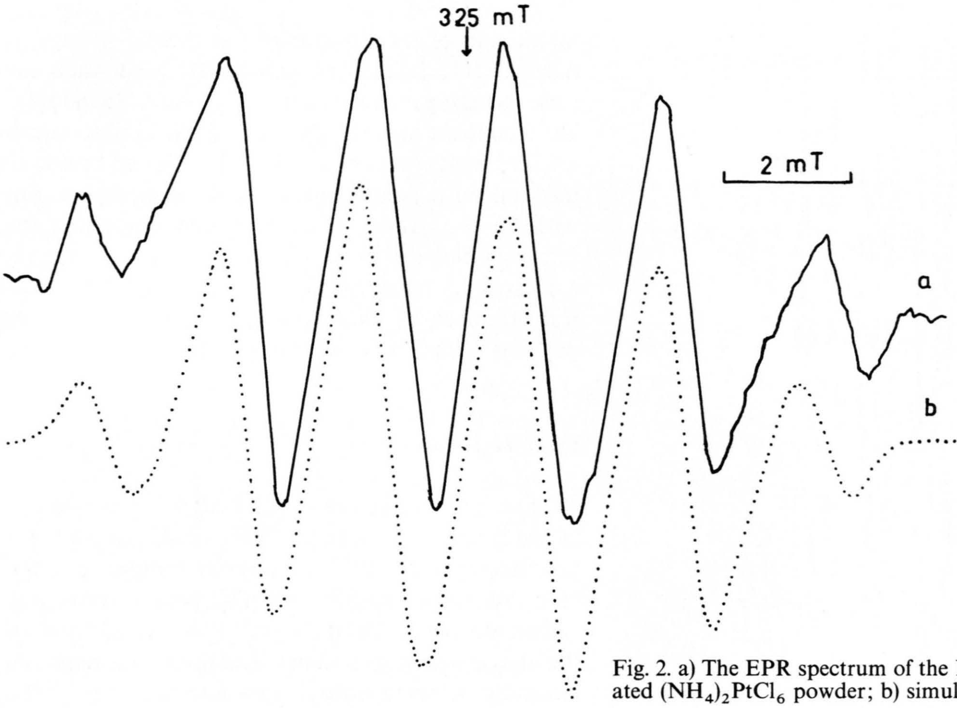

Fig. 2. a) The EPR spectrum of the NH_3^+ radical in γ-irradiated $(NH_4)_2PtCl_6$ powder; b) simulation of the spectrum.

of two methyl groups and a nitrogen nucleus interact with an unpaired electron with equal hyperfine constants, and if another magnetically unequivalent proton splits this spectrum into doublets. At this orientation the hyperfine constant of the six protons and the nitrogen nucleus is 3.4 mT, and that of the unequivalent single proton is 2.5 mT. These findings indicate that the radical is $(CH_3)_2NH^+$, and the unpaired electron is localized on the ^{14}N nucleus. The hyperfine constant of the methyl protons is isotropic, $a_H = 3.4$ mT, and those of the nitrogen and the α proton are anisotropic. The g factor of the $(CH_3)_2NH^+$ radical is also anisotropic. The principal values of the g, A^N and the proton hyperfine splitting A^N tensors have been found by rotating the magnetic field in the $x\,y$, $x\,z$, and $y\,z$ planes in 5° steps and recording the EPR spectrum at those orientations. In this way the principal values and their direction cosines with the chosen axes have

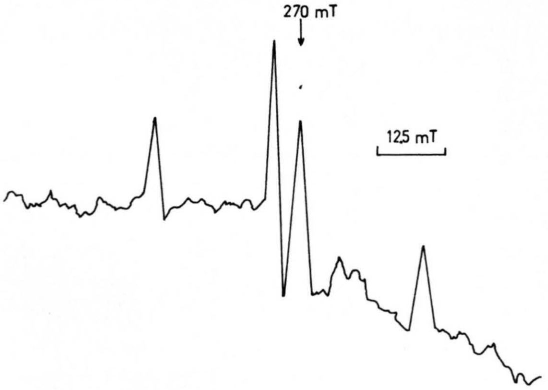

Fig. 3. The EPR spectrum of the $(PtCl_6)^{3-}$ radical in γ-irradiated $(NH_4)_2PtCl_6$ powder.

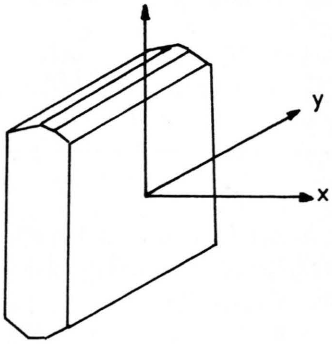

Fig. 4. Chosen x, y, and z axes of the $[(CH_3)_2NH_2]_2SnCl_6$ single crystal.

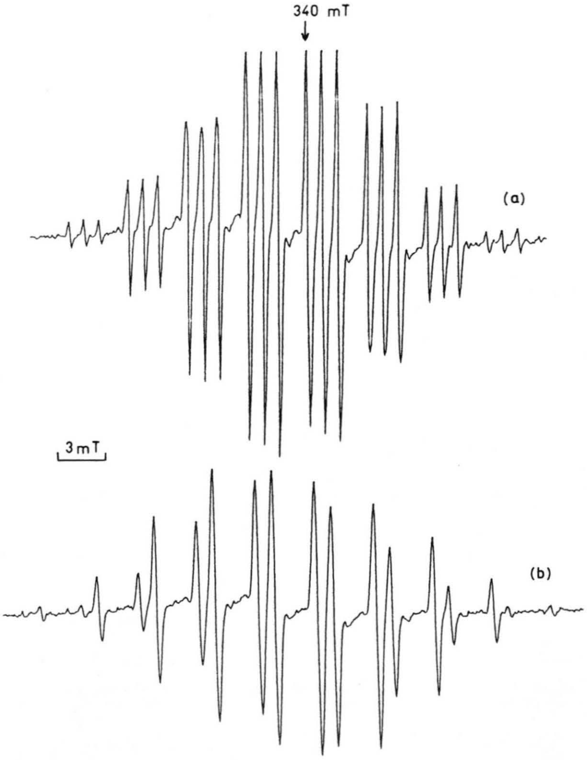

Fig. 5. a) The EPR spectra of the $(CH_3)_2NH^+$ radical in γ-irradiated $[(CH_3)_2NH_2]_2SnCl_6$ single crystal, at $H//y$ orientation; b) H is in the yz plane and 60° to the y axis.

Table 1. The principal values and direction cosines of the g, A^N, A^H tensors of the $(CH_3)_2NH^+$ radical. The A values are in mT.

g_{xx}	= 2.0054	(0.9998	0.0117	−0.0087)
g_{yy}	= 2.0050	(−0.0103	0.9889	0.1417)
g_{zz}	= 2.0028	(0.0103	−0.1476	0.9889)
g_{av}	= 2.0044			
A^N_{xx}	= 1.14	(−0.9041	0.3990	0.1525)
A^N_{yy}	= 0.7	(−0.4063	−0.9135	−0.0187)
A^N_{zz}	= 3.95	(0.1318	−0.0789	0.9881)
a_N	= 1.93			
A^H_{xx}	= 3.39	(0.8206	0.5695	−0.0474)
A^H_{yy}	= 3.41	(0.5633	−0.8201	−0.1006)
A^H_{zz}	= 1.93	(0.0962	−0.0559	0.9938)
a_H	= 2.91			

been obtained (Table 1). As can be seen from Table 1, the g, A^N and the α proton hyperfine tensors have axial symmetry within the limits of experimental error. The direction cosines of the largest principal value of the A^N tensor give the direction of the unpaired electron 2p orbital axis of the radical, and that seems nearly along the z axis chosen in Figure 4. The isotropic interaction of the protons of the methyl groups in $(CH_3)_2NH^+$, 3.4 mT, is significantly larger than the corresponding interaction in $(CH_3)_2\dot{N}$ (2.736 mT) [16] and also those in $(CH_3)_3N^+$ (2.5–2.9 mT) observed in nine different compounds [17–19]. This can be due to more effective hyperconjugation of the methyl groups with the 2p orbital of the nitrogen possessing the unpaired electron in $(CH_3)_2NH^+$. However, our results are in good agreement with the $(CH_3)_2NH^+$ radical produced by photolysis of N-chloramines in 90 per cent sulfuric acid solutions [16].

IV. $(NH_4)_2PdCl_6$

At room temperature no EPR signal could be obtained from the γ-irradiated $(NH_4)_2PdCl_6$ single crystals. However, at 130 K the powder samples give the spectrum shown in Figure 6. The peak-to-peak line widths of each of the two signals is 6 mT, and each of the lines covers about 12 mT. Palladium has only one naturally occuring isotope with nuclear spin (^{105}Pd, $I = 5/2$, 22.3 per cent relative abundance). Therefore a palladium-containing radical should show a strong central line due to the even isotopes ($I = 0$) flanked on both sides by three lines, each of having a relative intensity 4.8 per cent of the central line. In the light of the above statements, we attribute the spectrum in Fig. 6 to $(PdCl_6)^{3-}$ radical. Only the central line corresponding to the even-isotopes of palladium is de-

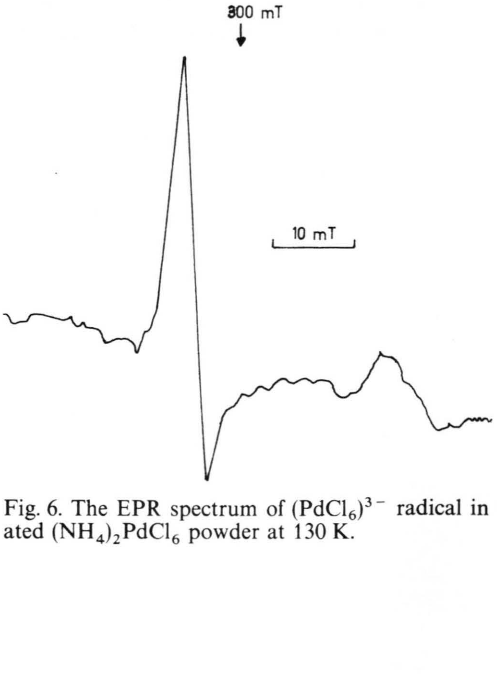

Fig. 6. The EPR spectrum of $(PdCl_6)^{3-}$ radical in γ-irradiated $(NH_4)_2PdCl_6$ powder at 130 K.

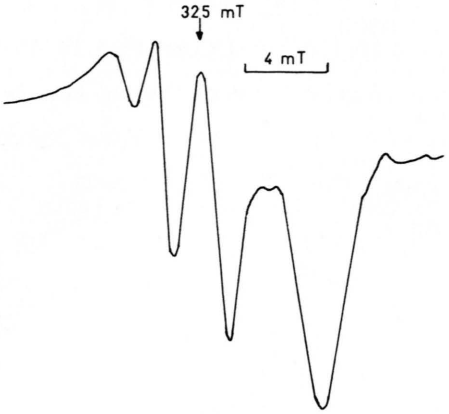

Fig. 7. The EPR spectrum of the $\dot{C}H_3$ and the CO_2^- radicals in ultraviolet irradiated $(CH_3)_4NCH_3COO$ powder at 130 K.

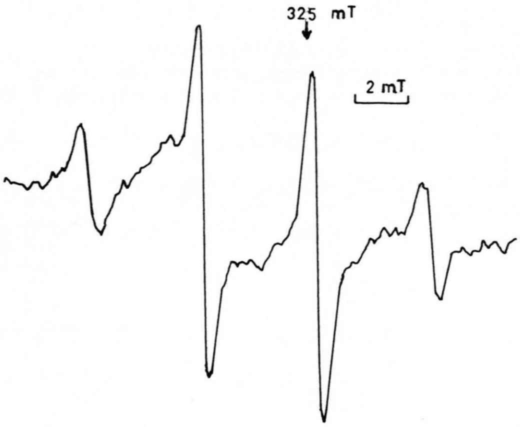

Fig. 8. The EPR spectrum of the $\dot{C}H_3$ radical in ultraviolet irradiated $(CH_3)_4NBr$ powder at 130 K.

tectable, and due to the anisotropic behaviour of the g factor two lines are observed in the powder spectrum. The low field line corresponds to $g_\perp = 2.20 \pm 0.04$ and the high field line to $g_\parallel = 2.04 \pm 0.04$. These, principal values of the g tensor are similar to other palladium-containing radicals [20].

V. $(CH_3)_4NCH_3COO$ and $(CH_3)_4NBr$

Gamma irradiation and in-situ ultraviolet irradiation of $(CH_3)_4NCH_3CO$ powder at room temperature do not produce any detectable EPR signal. However, in-situ ultraviolet irradiation at 130 K for 15 minutes produces the spectrum given in Figure 7. When the ultraviolet irradiation is stopped and the temperature is increased, first the left four lines, and then the right line disappear before room temperature is attained. The separation between the left four lines is 2.3 mT and $g = 2.0039$. Therefore we can state that these four lines correspond to a $\dot{C}H_3$ radical. The EPR parameters are in good agreement with the literature values [21, 22]. The rightest line in Fig. 7 does not show any hyperfine structure, and therefore the unpaired electron must be localized on a nucleus with $I = 0$. The g value is found as $g = 1.9779$, and therefore we attribute this line to CO_2^- radical. The g value is in agreement with the existing literature values [23, 24].

Gamma irradiation of $(CH_3)_4NBr$ single crystals and powder samples, give an unresolved single line with peak-to-peak linewidth of 3.5 mT. We could not interpret this. However, in-situ ultraviolet-irradiation at 130 K gives the spectrum in Figure 8. For single crystal and powder samples the spectrum is the same, and the separations between the lines are 2.3 mT. The g factor is found as $g = 2.0038$. Therefore this species must be the $\dot{C}H_3$ radical [21, 22]. These results indicate that one of the methyl groups in $(CH_3)_4NCH_3COO$ and $(CH_3)_4NBr$ is weakly bound to the nitrogen.

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