62. ESR. Study of the Pentacoordinated Arsenic Radical Anion $[(OH)_3(O)AsCH_2As(O)(OH)_2]^{\mp}$

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Summary

The anion $[(OH)_3(O)AsCH_2As(O)(OH)_2]^{\mp}$ has been trapped in an X-irradiated single crystal of methylene diarsonic acid. The $\tilde{g}$-tensor and the hyperfine coupling tensors of the two ^{75}As-nuclei have been obtained and the spin densities in the arsenic 4s- and 4p-orbitals determined.

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1. Introduction. – Arsenic containing compounds are very sensitive to ionizing radiation. In a previous work [1] we have shown that X-irradiation of methylene diarsonic acid gives rise to four main types of radicals: 1) radicals centered on a tetracoordinated As-atom; 2) radicals centered on a tricoordinated As-atom; 3) C-centered radicals, and 4) a species characterized by a very large ^{75}As-coupling (species D in [1]).

In the present work we analyse the ESR. spectra of species D and identify it as a radical anion for which the unpaired electron is mainly localized on a pentacoordinated As-atom.

2. Experimental. – The preparation and X-irradiation of single crystals of methylene diarsonic acid have been previously described [1]. The ESR. spectra were recorded on a *Varian E-9* spectrometer. The magnetic field was calibrated with an NMR. marker and the klystron frequency was measured for each spectrum. The crystal structure is unknown (but probably monoclinic) and an axis system was chosen which coincided with the coalescence of magnetically distinct sites [1].

3. Results and discussion. – The presently discussed spectra are due to a secondary radical which slowly appears at room temperature in an X-irradiated crystal of $(HO)_2(O)AsCH_2As(O)(OH)_2$ (see [1], *Fig. 3*). These spectra exhibit hyperfine interactions with two arsenic nuclei (^{75}As: $I = 3/2$, natural abundance 100%), whose hyperfine tensors together with the $\tilde{g}$-tensor are given in *Table 1*.

Due to the existence of four crystallographic sites, an overlap of the signals frequently occurs. This is of little importance for the large ^{75}As-hyperfine-tensor

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[1]) NRCC No. 20942.

Table 1. *ESR. tensors for* $[(OH)_3As(O)CH_2As(O)(OH)_2]^{\dot{-}}$

Tensor	Eigenvalues	Eigenvectors (in XYZ axes)[1]		
$\bar{g}$	1.996	0.965	0.261	0
	1.988			
	1.988			
$^{75}As_1$-$\bar{T}$ (MHz)	4516	0.939	0.342	0
	4144			
	4138			
$^{75}As_2$-$\bar{T}$ (MHz)	129	0.05	0.97	0.22
	98			
	92			

[1] See [1] for definition of axes.

but leads to imprecise values for the eigenvectors of the small ^{75}As-coupling. The isotropic and anisotropic coupling constants for the two nuclei are given in *Table 2.*

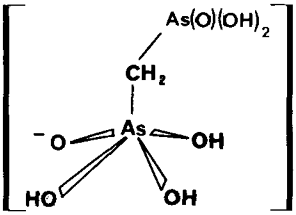
The large isotropic constant (4266 MHz) given in *Table 2* indicates that the trapped radical D is either an arsoranyl radical or a pentacoordinated arsenic anion, *i.e.* either $R_3\dot{A}sCH_2As(O)(OH)_2$ or $[R_4AsCH_2As(O)(OH)_2]^{\dot{-}}$. The first species having been previously observed with a freshly irradiated sample [1], we can unambigously identify the present radical as being of the second type. The increase in the isotropic hyperfine coupling-constant when passing from the arsoranyl radical (2503 MHz [1]) to the radical anion (4266 MHz) agrees with previous observations for $\dot{A}sF_4$ (4412 MHz) and $AsF_5^{\dot{-}}$ (5118 MHz [2]).

Only three pentacoordinated arsenic radical anions have been studied by ESR.: $Ph_3AsF_2^{\dot{-}}$ [3], $AsF_5^{\dot{-}}$ [4], and $AsF_4O^{\dot{=}}$ [4]. These three species exhibit ligand hyperfine interactions which are consistent with a pyramidal structure. In the present case the absence of any magnetic nuclei directly bound to the As-atom prevents us from obtaining any direct information about the conformation of the anion. However, as the formation of $[(OH)_3As(O)CH_2As(O)(OH)_2]^{\dot{-}}$ coincides with the disappearance of the arsoranyl radical $[(OH)_2\dot{A}s(O)CH_2As(O)(OH)_2]^{-}$ we suggest that the trapping of the anion is due to the addition of an hydroxyl ion to the arsoranyl radical. In this mechanism the trigonal bipyramidal structure of the arsoranyl radical is probably replaced by the square based pyramid **I**.

Table 2. *^{75}As-coupling constants and spin densities for some pentacoordinated arsenic radical anions*

Radical	A_{iso} (MHz)	τ_{aniso} (MHz)	c_s^2	c_p^2	Ref.
$[(OH)_3As(O)CH_2As(O)(OH)_2]^{\dot{-}}$					
As_1	4266	250	0.29	0.45	[a])
As_2	106	23	0.007	0.04	[a])
$AsF_5^{\dot{-}}$	5118		0.34		[4]
$AsF_4O_{ap}^{\dot{=}}$	5193		0.35		[4]
$AsF_4O_{bs}^{\dot{=}}$	4621		0.31		[4]
$Ph_3AsF_2^{\dot{-}}$	2613	370	0.18	0.67	[3]

[a]) This work.



I

It is however impossible to know whether the methylene ligand occupies the axial or a basal position. Moreover, the value of the angle (113°) formed by the eigenvectors ^{75}As-$T_{\parallel}$ (arsoranyl) and ^{75}As-$T_{\parallel}$ (anion) is between 90° and 120° and indicates either that the final pyramid is appreciably distorded or that some reorientation occurs. Another possibility is that the radical anion is produced by a reaction between the arsoranyl and a nearby methylene diarsonic acid molecule, and that the radical is located on this neighbouring molecule.

Following the usual procedure, the isotropic and anisotropic coupling constants given in *Table 2* can be compared with the atomic constants associated with a ^{75}As (4s) and a ^{75}As (4p) electron. To facilitate comparison, we have used the same atomic parameters as in [1]. The resulting spin densities are shown in *Table 2*. The s-character is quite similar to that found for $AsF_4O^{\overline{\cdot}}_{basal}$ [4] and to the INDO prediction [5] for $\dot{S}F_5$, but, as for $Ph_3AsF_2^{\overline{\cdot}}$, the spin density in the p-orbital on the central atom is much higher than the INDO prediction (9%).

For $R_2\dot{C}CH_2As(O)(OH)_2$ the high coupling value with the arsenic in the β-position (A_{iso} = 655 MHz) has been attributed to a preferred conformation such as to maximize the overlap with the C,As-bond [6]. Although 45% of the spin is localized in a p-orbital in a β-position with respect to the $As(O)(OH)_2$ group, the A_{iso}-value given in *Table 2* is only 106 MHz. This low value indicates a structure for which hyperconjugation is not efficient and tends to suggest that the $CH_2As(O)(OH)_2$ moiety occupies the apical position.

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