

The Identification of S_5^+ as a Paramagnetic Species in Sulfur–Oleum Solutions by Electron Spin Resonance

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Abstract: The ESR spectrum of 91.81% ^{33}S enriched sulfur in 65% oleum has been determined. Analysis of this spectrum conclusively determines the radical species to be S_5^+ . The g value is 2.0134 and $A = 8.92$ G.

The nature of the paramagnetic species of sulfur in oleum solutions has been under discussion for numerous years. As early as 1804,¹ it was known that sulfur dissolves in oleum to produce brown, green, and blue colored solutions. Vogel² isolated a bluish green solid from the reaction between sulfur and sulfur trioxide. This solid was later analyzed to be S_2O_3 .³ Later work had also concluded that this species was $(S_2O_3)_x$,⁴ or $(SO_3 + S)_x$.⁵ Though the blue color was principally attributed to S_2O_3 , numerous postulates have been made concerning the nature of the blue species.

The ESR spectrum of sulfur in 30% oleum was first measured by Gardner and Fraenkel.⁶ They concluded that two paramagnetic species existed. Ingram and Symons showed that the paramagnetic species was present in low concentration because no bulk susceptibility was detected by conventional methods.⁷ They measured the ESR spectrum of S in 65% and 20% oleum at 90 K. Symons suggested that one species (R_1) may be S_2O_3 , SO , or HS^+ .⁸ In 1967, McNeil, Murray, and Symons⁹ studied the ESR of solutions of 10% ^{33}S -enriched sulfur in 65% oleum. Also from electrolysis experiments, they showed that the blue species had a positive charge and suggested that the R_1 species was S_2^+ in the form of $[S(HS_2O_7)(HS_2O_6)]_2^+$.

However, Gillespie and Passmore synthesized $S_8(AsF_6)_2$ (blue) and $S_{16}(AsF_6)_2$ (red). From this they inferred that the blue species was S_8^{2+} and that the paramagnetism was due to the slight equilibrium dissociation of S_8^{2+} into S_4^+ .^{10–12} Barr, Gillespie, and Ummat also inferred the presence of S_{16}^{2+} and S_8^{2+} from their ESR and uv absorption studies.¹³ By correlation of S, Se, and Te absorption and MCD spectra, Stephens inferred that S_4^{2+} existed in these oleum solutions.¹⁴ Giggenbach supported the identification of the blue color (R_1) as S_4^+ in equilibrium with a yellow S_8^{2+} ion.¹⁵ R_2 was thought to be an open S_n^+ chain. By studying the ESR of solutions containing sulfur enriched with 10 and 25% ^{33}S in 65% oleum, Stillings et al. concluded from line-shape analysis that R_1 is S_8^+ and excluded S_4^+ as a possibility.¹⁶ In order to differentiate between S_2^+ , S_4^+ , and S_8^+ , Beudet and Stephens studied the ESR of a 92% ^{33}S -enriched sulfur solution in 65% oleum. They concluded that S_4^+ was the only reasonable alternative for R_1 .¹⁷ As pointed out by Symons and Wilkinson,¹⁸ the g value disagreed with prior results. They concluded that the R_1 species must be S_5^+ or S_7^+ .

We wish to report our ESR studies and interpretation of a 91.81% ^{33}S enriched solution of sulfur in 65% oleum. We have carefully considered all structures, S_n^+ with $2 \leq n \leq 10$, and the magnetic equivalence of the nuclei. We also were concerned that the g -value determined¹⁷ differed substantially from values obtained for normal sulfur solutions earlier. We have completed our investigations of 91.81% ^{33}S solutions in 65% oleum and we have independently concluded that the species is S_5^+ . We have seen all 16 lines and

shown that there are no other lines. We have analyzed the experimental results by comparison with simulated spectra, and we can conclude that the species is S_5^+ and not S_7^+ . The g value was determined to be 2.0134 and A is 8.92 G (cf. Table I).

Experimental Section

The 65% oleum was prepared by distilling stabilized liquid sulfur trioxide (Sulfan, Allied Chemical) into reagent grade sulfuric acid. The concentration was approximated by weighing the amount of reagents used.

Sulfur enriched to 25.54% ^{33}S and 91.81% ^{33}S was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tenn. Approximately 0.2 mg of enriched sulfur was placed in a glass tube formed by sealing off a pipette. Approximately 1 ml of oleum was then added, mixed until a homogeneous solution formed, and then was transferred into a stoppered flat quartz cell.

Spectra at room temperature were taken at X-band with a Varian E-12 spectrometer. In some runs, a Varian C-1024 time averaging computer was used to enhance the wings of the spectrum. The g values were obtained by calibrating with solid DPPH ($g = 2.00354$). Because the solutions degraded rapidly, four samples of 91.81% ^{33}S were prepared during the course of our experimental work. Particular attention was paid to the wings to find weak lines. The spectrum of the 91.81% ^{33}S enriched sulfur in 65% oleum solution is given in Figure 1.

Resolution could be increased somewhat by lowering the microwave power, but then the outermost lines could not be detected since the sensitivity was also reduced. The optimum compromise between sensitivity and resolution seemed to occur at a microwave power of 10 mW. Under no circumstances were the strongest lines completely resolved.

Analysis and Interpretation of Results. The spectrum taken without time averaging was first analyzed visually to determine the number of lines. Since ^{33}S has a spin of $I = \frac{3}{2}$, there should be $(3n + 1)$ lines if all the nuclei are identical in S_n^+ . In the course of our original analysis, only S_2^+ , S_4^+ , and S_8^+ had been seriously considered. The disagreement of the g values of the normal and the ^{33}S enriched species was a concern. When this work was repeated with a new sample of ^{33}S , 16 peaks were observed. Now the g values of the ^{33}S and the ^{32}S isotopic species were identical. Along with the symmetry of the spectrum this dictates that the spectrum must have an even number of lines, i.e., an odd number of equivalent sulfur atoms. Since 16 peaks were observed, the formula of S_n^+ must have $n \geq 5$. Because the 16 lines are equally spaced, and the relative intensities obey the expected relationships, we concluded all sulfurs are equivalent. Unfortunately, because the peaks were not totally resolved, simple inspection was not sufficient to deduce the relative intensities of the lines in the spectrum.

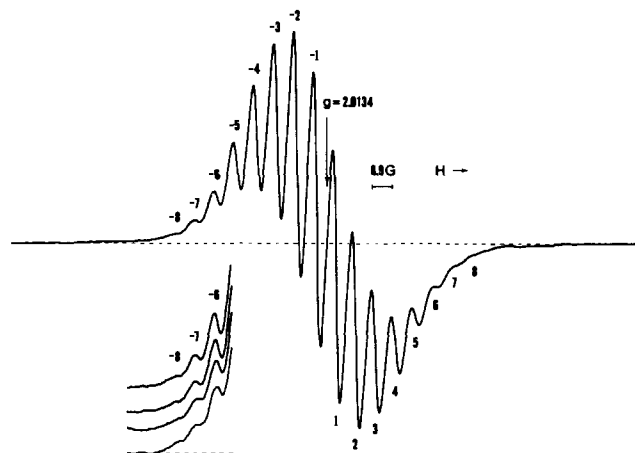
The spectrum obtained by time averaging for 20 h yielded a S/N enhancement of approximately 5 over our best spectrum taken with normal scanning. Averaging longer was not possible because the sample decomposed too rapidly. Our ability to detect further weak peaks on the right wing was hampered by a small signal found in the oleum, probably due to trace impurities. The source of this minute signal was confirmed by scanning a blank oleum sample. Hence a line count was unable to positively rule out S_7^+ or S_9^+ .

A general program was written to (a) calculate the line positions

Table I. The g Values Determined for R_1 and R_2 in Oleum Solutions

R_1	R_2	Ref
$g = 2.016 \pm 0.003$	$g = 2.026 \pm 0.003$	6
$g = 2.018$ (glass, 90 K)	$g = 2.025$ (glass, 90 K)	7
$g = 2.0134 \pm 0.0003$		9
$A = 8.92$		
$g = 2.0131$		15
$g = 2.013$ $A = 7.2 \pm 0.4$		16
$g = 2.0134$ $A = 7.7 \pm 0.5$		
$g = 2.014$	$g = 2.027$	12
$g = 2.0163^a$ $A = 8.87$		17
$g = 2.0134$ $A = 8.87$		18
$g = 2.0134 \pm 0.0003$	$g = 2.0262$	This
$A = 8.92 \pm 0.13$ G	± 0.0003	work

^a This work and ref 18 have shown this value of g to be erroneous. The value of $g = 2.0163$ was obtained by not retaining the same g value when ^{33}S replaced ^{32}S . The spectrum was interpreted as having an even value for n .

**Figure 1.** ESR spectrum of 91.81% ^{33}S enriched sulfur in 65% oleum.

and relative intensities for a variable number of equivalent sets of nuclei. (b) From the line width, the actual spectral shape is calculated by assuming a Lorentzian derivative line shape. (c) The line shapes of each line in the spectrum are summed to obtain the overall spectrum for an isotopic species. (d) The process is repeated for each isotopic species, and the total spectrum is calculated by summing the spectra of the individual species weighted by their relative abundance. (e) The final summed spectrum is plotted on a Calcomp plotter.

The relative abundances of the isotopic species which are present when 91.81% ^{33}S and 25.54% ^{33}S enriched sulfur is used are given in Table II for S_3^+ , S_5^+ , S_7^+ , and S_9^+ . It should be noted that the abundance of the $(^{33}\text{S})_5$ species is still only 65.2% when 91.81% enriched ^{33}S is used. When 25% enriched ^{33}S sulfur is used the most abundant isotopic species in S_5^+ is $(^{33}\text{S}_1\ ^{32}\text{S}_4)^+$ and the abundance of $(^{33}\text{S}_5)^+$ is only 0.1%. This explains the difficulty of Stillings et al. in obtaining the correct empirical formula. We have also remeasured the ESR spectrum of the 25% enriched ^{33}S , and have run the computer simulation for S_3^+ , S_5^+ , S_7^+ , and S_9^+ . Our experimental result agrees with Stillings et al.¹⁶ The computer simulation indicated very little qualitative difference in the overall spectrum of S_n^+ with $3 \leq n \leq 9$ when 25% ^{33}S was used because the predominant species have low ^{33}S concentrations. A high enrichment of ^{33}S is necessary to determine n .

Hence the ESR spectrum of the 91.81% ^{33}S enriched sulfur oleum solution was necessary for an unambiguous analysis. The simulated spectra of S_3^+ , S_5^+ , S_7^+ , and S_9^+ were calculated and are compared to the experimental results in Figure 2. In each case, the line widths and hyperfine constants were adjusted until the observed spectrum was optimally reproduced.

Of course, the spectra of $(^{33}\text{S})_m(^{32}\text{S})_{n-m}^+$ contain an odd num-

Table II. Relative Abundances of Isotopic Species for S_3^+ , S_5^+ , S_7^+ , and S_9^+ Enriched with 91.81% ^{33}S and 25.54% ^{33}S

Compd	Isotopic species	91.81% ^{33}S	25.54% ^{33}S
S_3^+	$^{33}\text{S}_3$	0.7739	0.0167
	$^{33}\text{S}_2\ ^{32}\text{S}$	0.2071	0.1457
	$^{33}\text{S}\ ^{32}\text{S}_2$	0.0185	0.4248
S_5^+	$^{32}\text{S}_3$	0.0005	0.4128
	$^{33}\text{S}_5$	0.6523	0.0011
	$^{33}\text{S}_4\ ^{32}\text{S}$	0.2909	0.0158
	$^{33}\text{S}_3\ ^{32}\text{S}_2$	0.0519	0.0924
	$^{33}\text{S}_2\ ^{32}\text{S}_3$	0.0046	0.2693
S_7^+	$^{33}\text{S}_7$	0.0002	0.3925
	$^{33}\text{S}_6\ ^{32}\text{S}$	0.0000	0.2289
	$^{33}\text{S}_5\ ^{32}\text{S}_2$	0.5498	0.0001
	$^{33}\text{S}_4\ ^{32}\text{S}_3$	0.3433	0.0014
	$^{33}\text{S}_3\ ^{32}\text{S}_4$	0.0919	0.0127
	$^{33}\text{S}_2\ ^{32}\text{S}_5$	0.0137	0.0615
	$^{33}\text{S}\ ^{32}\text{S}_6$	0.0012	0.1792
	$^{32}\text{S}_7$	0.0000	0.3135
	$^{33}\text{S}_9$	0.0000	0.3047
S_9^+	$^{33}\text{S}_9$	0.0000	0.1269
	$^{33}\text{S}_8\ ^{32}\text{S}$	0.4635	0.0000
	$^{33}\text{S}_7\ ^{32}\text{S}_2$	0.3721	0.0001
	$^{33}\text{S}_6\ ^{32}\text{S}_3$	0.1328	0.0014
	$^{33}\text{S}_5\ ^{32}\text{S}_4$	0.0276	0.0096
	$^{33}\text{S}_4\ ^{32}\text{S}_5$	0.0037	0.0421
	$^{33}\text{S}_3\ ^{32}\text{S}_6$	0.0003	0.1227
	$^{33}\text{S}_2\ ^{32}\text{S}_7$	0.0000	0.2385
	$^{33}\text{S}\ ^{32}\text{S}_8$	0.0000	0.2980
	$^{32}\text{S}_9$	0.0000	0.2172
			0.0000

ber of lines when m is even. These lines occur between the lines of those stronger species where m is odd. Shoulders on the slope of the observed lines appear prominently on spectra taken at 1 mW. Also as n becomes large, the relative intensity of the most intense central peaks is nearly identical for $n \geq 5$ while the outer lines are not intense enough to be observed. Visual comparison of the S_5^+ and S_7^+ calculated spectra was close to the observed spectrum, but S_5^+ is definitely preferred.

There is an obvious asymmetry in this spectrum. It has been demonstrated¹⁹ that when the anisotropy in g , $\Delta g = g_{\parallel} - g_{\perp}$, and in the hyperfine coupling constant, $b = A_{\parallel} - A_{\perp}$, are large

$$\Delta\nu \approx \frac{1}{T_2} \approx \tau_c(\Delta g\beta H_0 + bm_1)^2/\hbar^2$$

where τ_c = correlation time of the radical in the solvent. For R_1 ¹⁶

$$\Delta g \approx 2.004 - 2.020 = -0.016$$

$$b \approx \sim 46 - 20 = 26 \text{ G}$$

Hence the asymmetry in the spectrum is probably due to the differences in the linewidths, $\Delta\nu$. Since the lines in this spectrum are not completely resolved, we have not attempted to take this asymmetry into account.

To quantitatively compare the observed and simulated spectral intensities, the spectrum was decomposed into two Lorentzian curves: a single Lorentzian derivative curve representing the varying baseline originating from the partial overlap of the lines and a resolved 16-line spectrum on a flat baseline as shown in Figure 3. After this procedure, the line height defined as the line intensity was measured from the minimum to the maximum of each derivative line for the observed and the simulated spectra. The most intense peak was arbitrarily set to one. Comparison of these results for S_5^+ , S_7^+ , and S_9^+ clearly shows that only S_5^+ fits the observed spectrum.

Also expansion of the wings of the simulated spectrum for S_7^+ beyond the seventh and eighth peaks have clearly different shapes than the observed time averaged spectrum. Therefore, we conclude that the species present in the blue sulfur solution is definitely S_5^+ and not S_7^+ .

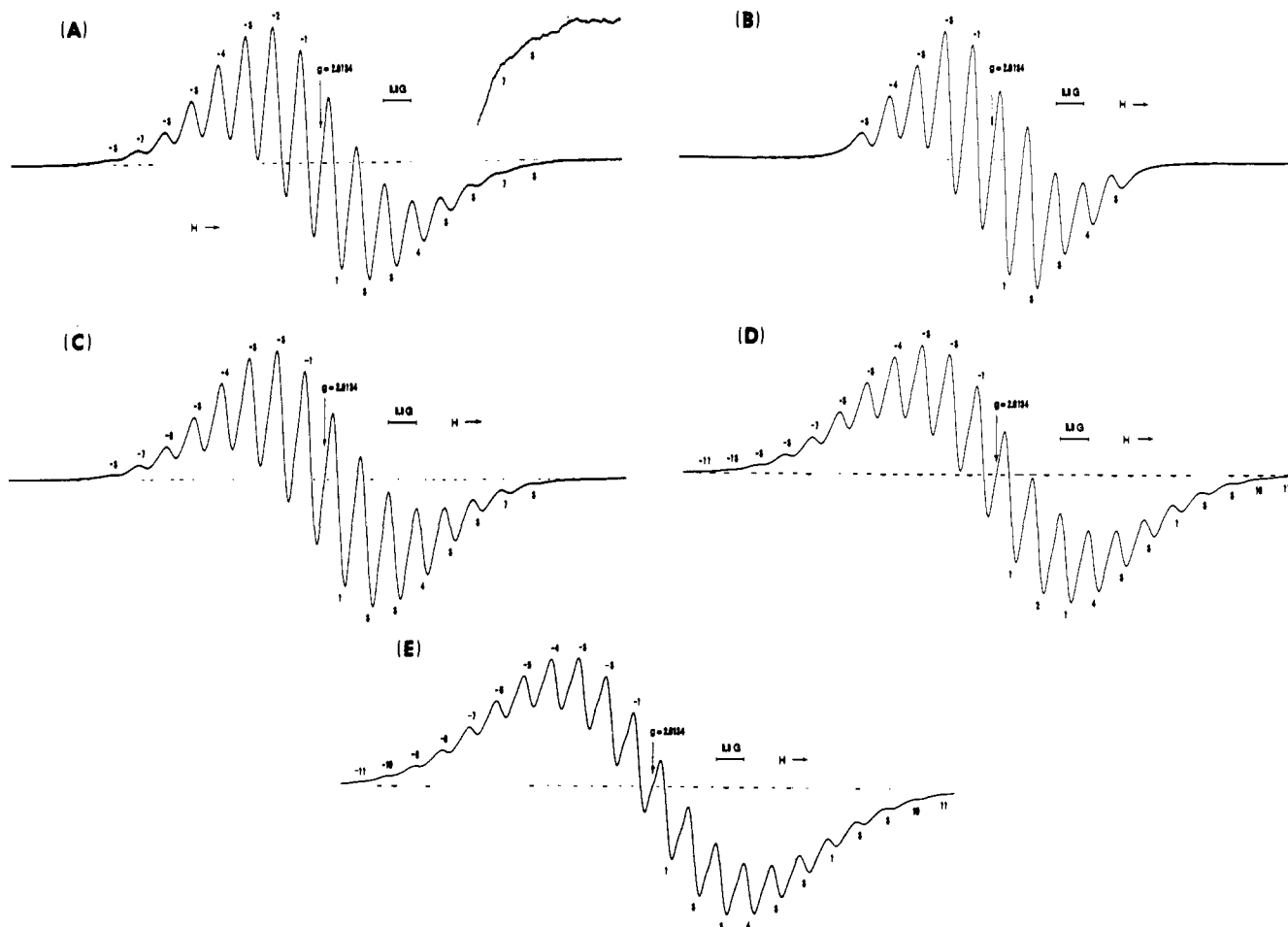


Figure 2. Comparison of experimental ESR spectrum with computer simulations: (A) experimental spectrum, (B) computer simulation of S_3^+ , (C) computer simulation of S_5^+ , (D) computer simulation of S_7^+ , (E) computer simulation of S_9^+ .

Table III. Relative Line Intensities Observed and Simulated for S_n^+

Line no.	Exptl	Relative line intensity ^a			
		S_3^+	S_5^+	S_7^+	S_9^+
-10				0.6	1.4
-9				2.5	3.5
-8	0.7		1.6 (0.9)	4.5 (3.8)	7.8 (7.1)
-7	3.5		4.2 (0.7)	10.9 (7.4)	16.8 (13.3)
-6	9.8		11.3 (1.5)	21.6 (11.8)	29.4 (19.6)
-5	24.2	11.0 (-13.2)	25.7 (1.5)	36.6 (12.4)	46.4 (22.2)
-4	46.0	29.1 (-16.9)	45.4 (-0.6)	56.1 (10.1)	63.0 (17.0)
-3	69.7	49.0 (-20.7)	66.4 (-3.3)	74.3 (4.6)	79.6 (9.9)
-2	92.4	93.0 (0.6)	89.7 (-2.7)	91.6 (-0.8)	93.9 (1.5)
-1	100.0	99.6 (-0.4)	99.8 (-0.2)	100.0 (0)	100.0 (0)
1	91.0	100.0 (9.0)	100.0 (9.0)	100.0 (9.0)	99.8 (8.8)
2	72.6	93.4 (20.8)	89.5 (16.9)	92.9 (20.3)	94.1 (21.5)
3	47.1	49.3 (2.2)	66.5 (19.4)	74.2 (27.1)	80.0 (32.9)
4	26.4	29.3 (2.9)	45.2 (18.8)	55.7 (29.3)	62.6 (36.2)
5	11.8	11.3 (-0.5)	25.3 (13.5)	37.4 (25.6)	46.8 (35.0)
6	4.0		11.5 (7.5)	21.8 (17.8)	30.3 (26.3)
7	1.5		4.1 (2.6)	10.3 (8.8)	17.4 (15.9)
8	0.3		1.6 (1.3)	4.2 (3.9)	7.8 (7.5)
9				2.4	3.1
10				0.6	1.8

^a Numbers in parentheses are deviations from experimental values.

Discussion

The characterization of the radical as S_5^+ is surprising insofar as only even values of n had been expected prior to

this investigation. Of course, small concentrations (<1%) of S_2^+ , S_4^+ , etc., also could be present; their spectra, hidden under that of S_5^+ , could probably not be detected. Since there is strong evidence for the presence of S_4^{2+} , and

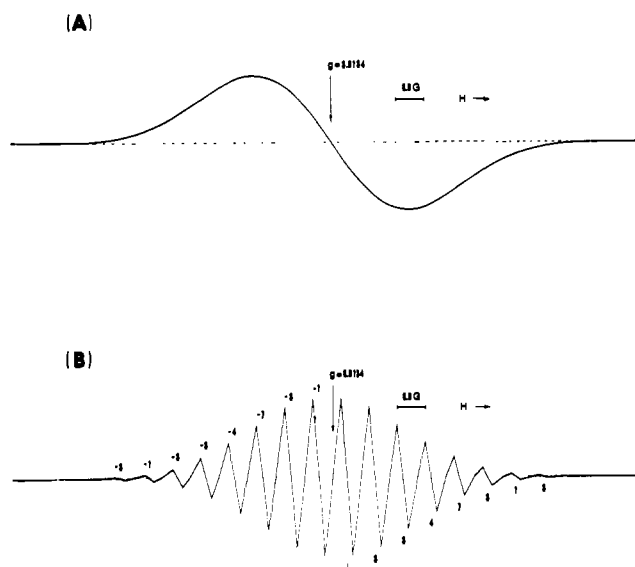


Figure 3. Decomposition of simulated ESR spectrum of S_5^+ into resolved and unresolved portion: (A) Lorentzian shaped background, (B) resolved portion.

S_8^{2+} ,¹⁰⁻¹² the radical is probably in equilibrium with these diamagnetic species. The reaction which produces S_5^+ would then be more complex than previously expected. The disproportionation of $S_8^{2+} \rightleftharpoons S_3^+ + S_5^+$ would also produce an S_3^+ species which is not observed. If the S_3^+ species is somehow rapidly used up, then higher concentrations of S_5^+ should be produced, but no bulk susceptibility was observed.⁷ Possibly the S_8^{2+} could react with neutral sulfur: $S_8^{2+} + S_2 \rightleftharpoons 2S_5^+$.

Comparison of A_{iso} (8.9 G), with that of the free sulfur nucleus (975 G),²⁰ suggests that the free electron is in a π orbital. Since the five sulfurs are equivalent, it seems likely that S_5^+ is planar. Simple molecular orbital theory dictates

that S_5^+ has an E degenerate ground state and probably an E excited state. Also it should exhibit a Jahn-Teller effect which would lower the D_{5h} symmetry by distortion to a less symmetric planar or nonplanar structure. This distortion may only be small, and the tautomerism between various equivalent forms may be so rapid that the sulfurs appear equivalent in the ESR spectrum.

In addition, the identification of the blue species as S_5^+ is not inconsistent with the MCD.¹⁴ Since the ground state is degenerate, the MCD spectrum should exhibit a derivative line shape. A similar line shape is expected for S_4^+ . However, the MCD of S_5^+ should be temperature dependent while that of S_4^+ should be temperature independent.

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An Investigation of the Ring Size of Cyclopolyposphines¹

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Abstract: Several alkyl-, aryl-, and perfluoroalkylcyclopolyposphines have been examined by NMR, ir-Raman, and mass spectroscopy. It is found that three-, four-, and five-membered rings can be distinguished in solution by observing the ^{31}P NMR spectrum while decoupling all other nuclear spins. The decoupled ^{31}P NMR spectrum of a four-membered ring collapses to a sharp singlet, while spectra of the three- and five-membered rings yield second-order AB_2 and $\text{AA}'\text{BB}'\text{C}$ (or ABCDE) spin systems, respectively. The ^{31}P NMR chemical shift is found to be indicative of ring size and linearly dependent upon the average endocyclic P-P-P bond angle. The molecule $(\text{C}_2\text{F}_5\text{P})_n$ has been shown to exist as a stable three-membered ring. The determining factor in the ring size of alkylcyclopolyposphines appears to be steric crowding of the pendant organic groups, with four-membered rings being favored when the organic group is bulky. Attempts to prepare mixed cyclopolyposphines $(\text{RP-PR}')_n$ were unsuccessful. No Lewis basicity was exhibited in solution by either methyl- or ethylcyclopolyposphine rings towards either trichloroborane or trifluoroborane.

The ring size of cyclopolyposphines $(\text{RP})_n$ has been determined with certitude only in a very few cases, usually by x-ray crystallography.²⁻⁶ Even when the solid state structure is known, there is some question as to the integrity of the ring in solution.⁷ Solution molecular weight determinations, for reasons that are not understood, usually yield anomalously low

values. For example, $(\text{C}_6\text{H}_5\text{P})_5$ and $(\text{C}_6\text{H}_5\text{P})_6$, for which the solid state structures are known,^{5,6} both had isopiestic, cryoscopic, and ebullioscopic molecular weights corresponding to $(\text{C}_6\text{H}_5\text{P})_4$.⁸ As with cyclopolyposphines,⁹ the determination of molecular weights of cyclopolyposphines by mass spectrometry is also of questionable utility. The fragmentation is