

Radical formation during the reaction of bis(fluorosulfonyl)peroxide, $S_2O_6F_2$, with tetrasulfur tetranitride, S_4N_4 , and elemental sulfur, S_8

F. Mistry, F.G. Herring, A. Haas* and F. Aubke†

Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1 (Canada)

Abstract

The radical intermediates formed initially in the reaction of $S_2O_6F_2$ with S_4N_4 and S_8 have been studied by ESR spectroscopy at X-band level. The transient radical formed in the reaction between $S_2O_6F_2$ and S_4N_4 has the spin Hamiltonian parameters $g_{xx}=2.0014$, $g_{yy}=2.0054$, $g_{zz}=2.0249$, $A_{xx}=22.5$ MHz, $A_{yy}=4.5$ MHz, $A_{zz}=2.0$ MHz and $Q_{zz}=4$ MHz as determined by simulation of ESR lineshapes obtained from polycrystalline samples. The spin Hamiltonian parameters are very similar to those previously reported for $[S_3N_2]^{+\cdot}$, and the spectra are interpreted as being most likely due to the $[S_3N_2]^{+\cdot}$ radical. The reaction between $S_2O_6F_2$ and S_8 under similar conditions produces a radical that has a g -tensor of the form $g_{xx}=2.0026$, $g_{yy}=2.0184$, $g_{zz}=2.0258$, as determined by simulation. The transient species generated is postulated to be a similar $S_5^{+\cdot}$ radical.

Introduction

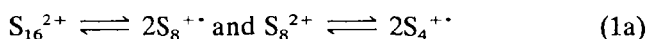
The synthetic aspects of the oxidations of cyclo-octasulfur, S_8 [1, 2], and tetrasulfur tetranitride, S_4N_4 [3], by bis(fluorosulfonyl)peroxide, $S_2O_6F_2$, have been reported previously. While solid S_4N_4 is oxidized quantitatively to give $[S_4N_4][SO_3F]_2$ with a planar $[S_4N_4]^{2+}$ cation [3, 4], solid S_8 is oxidized further under UV irradiation to give SO_2 , $S_2O_5F_2$ and $S_3O_8F_2$ according to Shreeve and Cady [1]. However, various color changes observed during the reactions suggest the existence of transient intermediates.

If the oxidation of S_8 by $S_2O_6F_2$ is carried out in solutions of fluorosulfuric acid or sulfur dioxide [2], spectroscopic evidence is obtained for some of the intermediate polysulfur cations, S_{16}^{2+} , S_8^{2+} and S_4^{2+} , the last in the form of $S_4[SO_3F]_2$. Both S_8^{2+} [5] and S_4^{2+} [6] have also been obtained in the form of their AsF_6^- salts. The isolation and characterization of the unusual and unexpected S_{19}^{2+} cation in $S_{19}[AsF_6]_2$ from solutions supposedly containing S_{16}^{2+} [7] points to a considerable complexity in these systems.

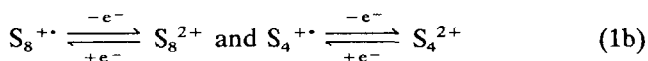
In addition to these cyclic, dipositive cations, a number of unipositive radical cations derived from both S_8 [8] and S_4N_4 [9] have been postulated and some have been identified by ESR spectroscopy. The oxidation of S_8 produces radical cations in addition to the diamagnetic

cyclic cations discussed above. A number of equilibria have been proposed [8], linking all the polysulfur cations together:

Dissociation–association



Oxidation–reduction



The γ -irradiation of S_8 in $CFCl_3$ at 77 K was found to be a convenient method to generate $S_8^{+\cdot}$ [10]. The paramagnetic species produced from ^{33}S -enriched S_8 dissolved in 65% oleum was identified by ESR spectroscopy as being $S_5^{+\cdot}$ [11a], rather than the previously postulated $S_4^{+\cdot}$ [8]. This finding, along with the lack of definitive structural evidence for S_{16}^{2+} , has cast some doubt on these proposals [eqns. (1a) and (1b)], as discussed previously [11b].

A number of agents have been used to oxidize both S_8 [8] and S_4N_4 [9], in particular AsF_5 or SbF_5 in SO_2 solution, and SO_3 in sulfuric acid solution (oleum). The use of AsF_5 and SbF_5 as oxidants has allowed the synthesis of well-crystallized AsF_6^- or SbF_6^- salts [8], but the formation of reduction products such as AsF_3 and SbF_3 may lead to complex reactions.

In contrast to the above oxidants, $S_2O_6F_2$, with two SO_3F^\cdot radicals linked by a weak O–O bond [12], often takes part in oxidative addition as in the case of SF_4 , to give $SF_4[SO_3F]_2$ [1, 12]. The oxidation of S_4N_4 by

*Lehrstuhl für Anorganische Chemie II, Ruhr Universität, D-4630 Bochum, Germany.

†Author to whom correspondence should be addressed.

$S_2O_6F_2$, however, results in the formation of ions, with the $S_2O_6F_2$ acting as a two-electron oxidizer [3], according to:



The initial step in this reaction, and the nature of the previously reported transient black radical [3], is, in part, the subject of this study. One possible interpretation involves the cyclic radical cation $[S_4N_4]^{+\cdot}$. Its isolation as $[S_4N_4][FeCl_4]$ and identification by single-crystal X-ray diffraction [13] has been seriously questioned [14], and the diffraction data were subsequently attributed to $[S_4N_4H][FeCl_4]$ [15]. The structure of the $[S_4N_4H]^+$ cation has been reported previously with BF_4^- as the counteranion [16]. The only other report of $[S_4N_4]^{+\cdot}$ involves its generation by γ -irradiation of S_4N_4 in $CFCl_3$ and its study by ESR spectroscopy [10]. A broad, single resonance without detectable hyperfine splitting was observed.

Another persistent sulfur nitrogen radical cation, the cyclic 1,2,4-trithio-3,5-diazolyl radical $[S_3N_2]^{+\cdot}$, is commonly observed during the oxidation of many S-N compounds and has received extensive attention [17–27]. Most studies have involved ESR spectroscopy with $[S_3N_2]^{+\cdot}$ in solution, in the solid state, or trapped as an impurity in a single crystal, as in the case of $[CH_3CNSNS^+][AsF_6^-]$ [25]. Although a crystal structure of the monomeric cation in $[S_3N_2^+][AsF_6^-]$ has been reported as well [20], re-examination of the data has revealed it to be that of the dimer $[S_6N_4]^{2+}$, with the two S_3N_2 fragments joined by relatively long S-S bonds [27]. However, reaction of $Tc_6[AsF_6]_2$ with S_4N_4 has allowed the synthesis of $[S_3N_2^+][AsF_6^-]$ [27].

The purpose of this study was to detect the presence of any radical species formed initially in the oxidation of S_4N_4 and S_8 by $S_2O_6F_2$. The oxidant used in this study, bis(fluorosulfonyl) peroxide, $S_2O_6F_2$, is a very good source of SO_3F^\cdot radicals. The exothermic reversible dissociation of $S_2O_6F_2$ into SO_3F^\cdot , i.e.



is temperature-dependent and the magnitude of K is such that there is always a small amount of SO_3F^\cdot present in $S_2O_6F_2$. The ESR spectrum of this radical has been extensively studied in the gas [28], liquid [29] and solid phases [30, 31]. It has recently also been studied in HSO_3F solution [32] and thus its presence can be readily determined.

Experimental

Materials and syntheses

Tetrasulfur tetranitride was synthesized from S_2Cl_2 and Cl_2 in NH_3 [33]*. The crude product was purified

*Caution: S_4N_4 is shock-sensitive and potentially explosive, and samples should not be subjected to friction or sudden heating!

by extraction with benzene and recrystallized twice from benzene. The purity was ascertained by microanalysis and melting point determination. $S_2O_6F_2$ was prepared as reported previously [34]. Sulfur (99% purity) was obtained commercially from MCB Inc. and used without further purification. In a typical reaction, 0.08 g (0.43 mmol) of S_4N_4 was taken in a 5 mm o.d. glass tube fitted with a 4 mm Kontes Teflon stopcock and a B10 ground glass joint. Excess $S_2O_6F_2$ (c. 2.0 g, c. 10 mmol) was vacuum-distilled onto the orange crystals. On warming the mixture to room temperature, a black-brown color appeared on the surface of the S_4N_4 crystals. The mixture was cooled to 77 K, and the ESR spectrum was recorded at 103 K. Addition of HSO_3F , as an ionizing solvent, to the reaction mixture resulted in the rapid formation of $[S_4N_4]^{2+}$ (solv.) at room temperature. S_8 (0.059 g, 0.23 mmol) was reacted with excess $S_2O_6F_2$ in a similar manner as above. Upon warming to room temperature, a black-brown coating was formed on the surface of the yellow sulfur. The tube was cooled to 77 K, and the ESR spectrum was recorded at 103 K.

Instrumentation

The samples were held at 103 K using a Varian E-257 temperature controller and the ESR spectra were run on an X-band homodyne spectrometer with a Varian 12-in. magnet equipped with MkII Fieldial control. An Ithaco Dynatrac 391A lock-in amplifier was used to obtain phase-sensitive detection at 100 kHz. Data acquisition was carried out using a Qua-Tech 12-bit data acquisition board (ADM 12-10) together with a Qua-Tech parallel expansion board (PXB-721) incorporated into an IBM XT computer. The relevant data processing software was as described previously [35, 36]. The microwave frequency was measured with an HP5246L frequency counter equipped with an HP5255A plug-in. Field calibration was accomplished using a Varian Gaussmeter, the output of which was also collected by the IBM computer. The absolute field was corrected for the placement of the gaussmeter probe by calibrating against peroxyamine sulfate in aqueous solution and was in error by c. 0.01 G. The precision of the data was typically c. 0.02 G for 2 K points over a 100 G sweep which, together with the c. 10 kHz error in the microwave frequency, corresponds to an error of c. 0.00002 in the g -values quoted.

Simulations

These were performed using FORTRAN programmes written by P.S. Phillips based on the equations of McLung [37] and EPR analysis software (POWD and QPOW) supplied by the Illinois ESR Research Center, NIH Division of Research (Resources Grant No. RR01811). The computations were carried out on an 80386-based personal computer.

Results

The exposure of solid tetrasulfur tetranitride, S_4N_4 , to liquid or gaseous bis(fluorosulfonyl)peroxide, $S_2O_6F_2$, at room temperature, generates within seconds a dense black coating on the surface of S_4N_4 which gives rise to an ESR signal. The ESR spectrum (Fig. 1(d)) displays features typical of a free radical with a non-axial g -tensor with hyperfine splitting ($8.4 \text{ G} \approx (A_N)_\perp$) observed on the manifold due to the g -component with the lowest g -value.

The interesting feature of this spectrum is the asymmetrical distribution of the hyperfine resonances about the cross-over. The most straightforward interpretation for such a spectrum is that of a radical with an orthorhombic g -tensor and a coincident hyperfine coupling tensor of the approximate form $(A_1, 0, 0)$ and $g_1 < g_2 < g_3$, i.e. the lowest g -value manifold exhibits the resolved hyperfine. Such a hyperfine coupling pattern and g -tensor anisotropy is consistent with a π -radical of symmetry C_{2v} or lower. The lowest g -value (g_1) corresponds to the axis perpendicular to the plane of the radical. The hyperfine intensity pattern corresponds to 1:2:3:2:1 and is clearly due to the presence of two equivalent ^{14}N atoms. The hyperfine tensor has the form $(A, 0, 0)$ due to the fact that the odd electron resides in a p -orbital (giving a tensor of the form $2B, -B, -B$) plus an isotropic (Fermi contact) term of opposite sign to B of magnitude $c \cdot B$.

The spectrum obtained here is very similar to that reported by McNeil *et al.* [18] for a species that was later identified as $[S_3N_2]^{+\cdot}$. As mentioned previously, the reaction of S_4N_4 with sulfuric acid in the presence of S_2N_2 [22] leads to the formation of $[S_3N_2]^{+\cdot}$. The identification of this radical has been established by

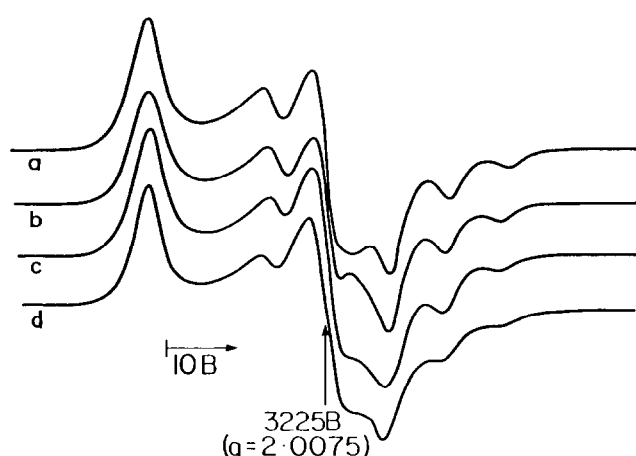


Fig. 1. ESR spectrum (a) simulated using parameters observed by Johnson *et al.* [26], (b) including changes in the g - and A -tensor components and (c) including a ^{14}N quadrupole coupling constant of 4.0 MHz, and g -strain and A -strain parameters. (d) Spectrum of $[S_3N_2]^{+\cdot}$ recorded at 103 K.

studies in both polycrystalline media [26] and single crystals [25]. In most of these studies ^{15}N -enriched samples were employed but in the present study naturally occurring ^{14}N was observed as by McNeil *et al.* [18].

As a starting point for the interpretation of the ESR spectrum of the radical formed by the reaction of $S_2O_6F_2$ with S_4N_4 , the hyperfine and g -tensor parameters for the $[S_3N_2]^{+\cdot}$ radical observed by Johnson *et al.* [26] were employed in a simulation, the ^{14}N hyperfine components being converted from the ^{15}N values quoted by them. A comparison of the result of this simulation with the ESR spectrum observed in this study is shown in Fig. 1(a). Careful inspection of the simulation shows that there are small variations in the g -values and hyperfine constants which suggest that a radical has been formed which was very similar to that observed by Johnson *et al.* [26], the major discrepancy being in the central region of the spectrum. This is not unexpected since the work of Preston *et al.* [25] shows the spin Hamiltonian parameters to be dependent on the method of preparation. Adjustment of the spin Hamiltonian parameters to take into account changes in the g - and A -tensor components produced the simulation shown in Fig. 1(b).

It is clear that the simulation was still not quite correct. In order to optimize the simulation of the spectrum of the radical formed by the reaction of $S_2O_6F_2$ and S_4N_4 , we found it necessary to include a ^{14}N quadrupole coupling constant of 4.0 MHz along with the g -strain and A -strain parameters. The result of the simulation is shown in Fig. 1(c). The presence of the quadrupole has a small, but obvious, effect on the central region of the spectrum because $Q_{zz} > A_{xx}$ or A_{yy} for ^{14}N , leading to forbidden transitions that give the manifold corresponding to g_{xx} and g_{yy} the shape it has. Although the spectrum can be simulated without including g -strain and A -strain values, a quadrupole coupling constant of 13 MHz must be employed. This value is unrealistic however, since the theoretical maximum for Q_{zz} is 6.5 MHz.

In a similar experiment with S_8 and $S_2O_6F_2$, we have generated a radical with similar values for g_1 and g_3 , but g_2 has increased, i.e. the g -tensor is approaching the axial case. The spectrum of the radical formed and its simulation, using the g -values and linewidths given in Table 1, are shown in Fig. 2. A spectral comparison of the two radicals described in this work indicates a general increase in the g -values for the radical generated from S_8 . This is expected due to the increased spin-orbit coupling of sulfur relative to nitrogen. The g -values are clearly different from those observed by Chandra *et al.* [10] for $S_8^{+\cdot}$, but correspond roughly to the g -values quoted by them for the radical formed during the reaction between S_8 and SbF_5 . In addition, the g_{iso} value is similar to that reported for $S_5^{+\cdot}$ by Low and

TABLE 1

Radical	Medium	g-Tensor			A-Tensor (MHz)			Ref.
		g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	
S_5^{++}	65% oleum	2.020	2.020	2.002	–	–	–	10
S_8^{++}	25% oleum	2.042	2.031	2.0024	–	–	–	10
S_8^{++}	$CFCl_3$	2.044	2.034	2.0035	–	–	–	10
S_n	oleum	2.007	2.020	2.020	–	–	–	18
S_5^{++}	$S_2O_6F_2^a$	2.0026	2.0184	2.0258	–	–	–	TW ^c
$S_3^{15}N_2$	D_2SO_4	2.0013	2.0062	2.0250	36.4	2.8	2.8	23
$CH_3CS_2N_2$	$CD_3C_6D_5$	2.0026	2.009	2.0215	40.0	2.2	3.1	24
$C_6H_5CS_2N_2$	$CD_3C_6D_5$	2.0021	2.008	2.0218	39.5	3.1	1.1	24
$S_3^{14}N_2$	D_2SO_4	2.0013	2.0062	2.0250	25.8	2.8	2.8	24
$S_3^{14}N_2$	$CH_3CS_2N_2 + AsF_6^-$	2.0021	2.0072	2.0248	25.4	<2.5	<2.9	25
$S_3^{15}N_2$	D_2SO_4	2.0013	2.0060	2.0252	36.4	<0.5	<0.5	26
$S_3^{14}N_2$	$S_2O_6F_2^b$	2.0014	2.0054	2.0249	22.5	4.5	2.0	TW

^aLorentzian lineshape for simulation with linewidths of 12.5, 8.0 and 9.5 G in the x, y and z directions, respectively.

^bGaussian lineshape for simulation with linewidths of 7.0, 7.0 and 6.0 G, and g-strain parameters of 0.4, 0.5 and 0.5 in the x, y and z directions, respectively, an A-strain parameter of 5.0 in the y direction and $Q_{zz} = 4$ MHz.

^cTW = this work.

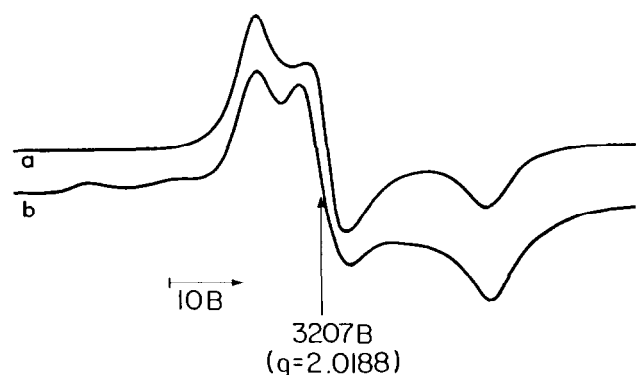


Fig. 2. ESR spectrum of S_5^{++} obtained (a) by simulation using the parameters listed in Table 1, (b) as observed experimentally at 103 K.

Beaudet [11a]. These observations suggest that the radical formed is likely to be S_5^{++} . The similarity in g-tensors also suggests that the radical is similar to that formed by the reaction of S_4N_4 with $S_2O_6F_2$, i.e. S_5^{++} rather than $[S_3N_2]^{++}$.

Thus it would appear that on oxidation with $S_2O_6F_2$, both S_4N_4 and S_8 initially give rise to the structurally similar radicals $[S_3N_2]^{++}$ and S_5^{++} . It should be remembered that both radicals observed here are obtained on the surface of solid S_4N_4 and S_8 , respectively.

Discussion

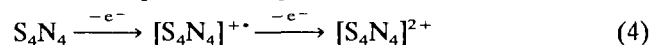
An interpretation of the spectra observed here will concentrate primarily on the radical generated from S_4N_4 , because the observed hyperfine splitting provides additional information and complete oxidation results

in the quantitative formation of $[S_4N_4]^{2+}$ with retention of the cyclic structure.

As stated above, the reaction of $S_2O_6F_2$ with S_4N_4 leads to a radical very similar to that extensively studied by Preston *et al.* [17–25]. Simulations show that the radical formed in this work is indeed $[S_3N_2]^{++}$, although the fact that the reaction of S_4N_4 with $S_2O_6F_2$ proceeds smoothly and quantitatively through to $[S_4N_4]^{2+}$ [3], according to eqn. (2), tends to mitigate against the initial formation of $[S_3N_2]^{++}$ and its subsequent recombination to form $[S_4N_4]^{2+}$, unless the $[S_3N_2]^{++}$ radical is formed in trace quantities which are not representative of the course of the reaction.

The absence of vibrational bands due to the possible fragments NS^+ [38] or NS_2^+ [39] in the final product also argues against any substantial ring-fracture. The further oxidation of NS^+ to NO^+ by $S_2O_6F_2$ [40] does not appear to take place, because bands attributable to NO^+ [41] were not present in the vibrational spectra of the product.

The work of Preston *et al.* shows that the spin Hamiltonian parameters of $[S_3N_2]^{++}$ are dependent on the method of preparation and the environment in which the radical is formed. In the present work, we have formed a radical with two equivalent N atoms by the surface reaction of $S_2O_6F_2$ with S_4N_4 , which ultimately reacts quantitatively to give $[S_4N_4^{2+}][SO_3F^-]_2$ [3]. It may be assumed that the two-electron oxidation of S_4N_4 to $[S_4N_4]^{2+}$ by $S_2O_6F_2$ probably occurs in two distinct steps according to:



The molecular geometries of S_4N_4 and $[S_4N_4]^{2+}$ are depicted in Fig. 3(a) and (b), respectively.

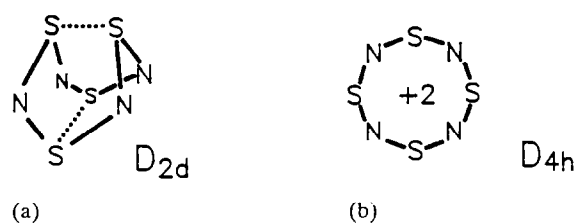


Fig. 3. Molecular geometries of (a) S_4N_4 and (b) $[S_4N_4]^{2+}$.

The reported ESR spectrum of $[S_4N_4]^{+\cdot}$ in $CFCl_3$ is a broad single line [10]. Furthermore, if hyperfine splitting were observable, a nine-line pattern would be expected rather than the five-line pattern observed here. Such a nine-line spectrum is indeed observed for the radical anion $S_4N_4^{\cdot-}$ formed when S_4N_4 undergoes one-electron reduction [42]. Consequently, the radical observed here is not likely to be a planar or nearly planar $[S_4N_4]^{+\cdot}$ radical.

Although the low ionization potential of S_4N_4 (9.5 eV) [43] supports the formation of cationic S_4N_4 along with anionic SO_3F^- , the experimental findings strongly suggest that the radical observed here is indeed $[S_3N_2]^{+\cdot}$ as reported previously. Likewise, the oxidation of S_8 by $S_2O_6F_2$ generates $S_5^{+\cdot}$; again the similarity to the reported spectrum allows no other conclusion.

Conclusions

The motivation for this study has been the search for the two related radical cations $[S_4N_4]^{+\cdot}$ and $S_8^{+\cdot}$, generated by the controlled oxidation of S_4N_4 and S_8 , respectively, with bis(fluorosulfonyl) peroxide and their identification by ESR spectroscopy. The transient radicals that form initially indeed give rise to ESR spectra; however, the spin Hamiltonian parameters strongly suggest that $[S_3N_2]^{+\cdot}$ [26] and $S_5^{+\cdot}$ [10] are responsible for the ESR resonances observed. In the oxidation of sulfur, the final products are fully oxidized molecular species such as SO_2 , $S_2O_5F_2$ and $S_3O_8F_2$, the last formed by the oxidation of SO_2 by an equimolar amount of $S_2O_6F_2$ [12]. This is not in discordance with the presence of an intermediate $S_5^{+\cdot}$ species. In the case of the oxidation of S_4N_4 , which leads quantitatively to $[S_4N_4][SO_3F]_2$ [3], the appearance of $[S_3N_2]^{+\cdot}$ would imply an initial fragmentation of the eight-membered S_4N_4 ring and a subsequent recombination to give $[S_4N_4]^{2+}$. Since no other fragments were detected, this becomes a remote possibility. It appears more likely that the formation of $[S_3N_2]^{+\cdot}$ may be a side-reaction that ultimately does not affect the yield adversely, because the main course of the oxidation reaction does not appear to involve radical intermediates that can be detected by ESR spectroscopy.

Hence, the elusive radical cation $[S_4N_4]^{+\cdot}$ still remains to be discovered. It is interesting to note that the radicals formed in the initial stages of the oxidation of S_8 and S_4N_4 are the five-membered cyclic radicals $S_5^{+\cdot}$ and $[S_3N_2]^{+\cdot}$, respectively.

Acknowledgement

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References

- 1 J.M. Shreeve and G.H. Cady, *J. Am. Chem. Soc.*, **83** (1961) 4521.
- 2 R.J. Gillespie, J. Passmore, P.K. Ummat and O.C. Vaidya, *Inorg. Chem.*, **10** (1971) 1327.
- 3 R.D. Sharma, F. Aubke and N.L. Paddock, *Can. J. Chem.*, **59** (1981) 3157.
- 4 R.J. Gillespie, J.P. Kent, J.F. Sawyer, D.R. Slim and J.D. Tyrer, *Inorg. Chem.*, **20** (1981) 3799.
- 5 C.G. Davies, R.J. Gillespie, J.J. Park and J. Passmore, *Inorg. Chem.*, **10** (1971) 2781.
- 6 J. Passmore, G. Sutherland and P.S. White, *J. Chem. Soc., Chem. Commun.*, (1980) 330.
- 7 R.C. Burns, R.J. Gillespie and J.F. Sawyer, *Inorg. Chem.*, **19** (1980) 1423.
- 8 (a) R.J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, **17** (1975) 49; (b) R.J. Gillespie and J. Passmore, *MTP International Review of Science, Inorganic Chemistry, Series 2*, Butterworths, London, 1975, Vol. 3, p. 121.
- 9 R.T. Oakley, *Prog. Inorg. Chem.*, **36** (1988) 313.
- 10 H. Chandra, D.N. Ramakrishna Rao and M.C.R. Symons, *J. Chem. Soc., Dalton Trans.*, (1987) 729.
- 11 (a) H.S. Low and R.A. Beaudet, *J. Am. Chem. Soc.*, **98** (1976) 3849; (b) J. Passmore, G. Sutherland, P. Taylor, T.K. Whidden and P.S. White, *Inorg. Chem.*, **20** (1981) 2839.
- 12 R.A. DeMarco and J.M. Shreeve, *Adv. Inorg. Chem. Radiochem.*, **16** (1974) 109.
- 13 U. Müller, E. Conradi, U. Demant and K. Dehnicke, *Angew. Chem., Int. Ed. Engl.*, **23** (1984) 237.
- 14 T. Chivers, *Chem. Rev.*, **85** (1985) 341.
- 15 U. Thewalt, K. Holl, U. Demant, U. Müller and K. Dehnicke, *Z. Naturforsch.*, **41b** (1986) 1061.
- 16 A.W. Cordes, C.G. Marcellus, M.C. Noble, R.T. Oakley and W.T. Pennington, *J. Am. Chem. Soc.*, **105** (1983) 6008.
- 17 D. Chapman and A.G. Massey, *Trans. Faraday Soc.*, **58** (1962) 1291.
- 18 D.A.C. McNeil, M. Murray and M.C.R. Symons, *J. Chem. Soc. A*, (1967) 1019.
- 19 S.A. Lipp, J.J. Chang and W.L. Jolly, *Inorg. Chem.*, **9** (1970) 1970.
- 20 R.J. Gillespie, P.R. Ireland and J.E. Vekris, *Can. J. Chem.*, **53** (1975) 3147.
- 21 H.W. Roesky and A. Hamza, *Angew. Chem., Int. Ed. Engl.*, **15** (1976) 226.
- 22 S.A. Fairhurst, K.F. Preston and L.H. Sutcliffe, *Can. J. Chem.*, **62** (1984) 1124.

- 23 S.A. Fairhurst, A. Hulme-Lowe, K.M. Johnson, L.H. Sutcliffe, J. Passmore and M.J. Shriver, *Magn. Reson. Chem.*, **23** (1985) 828.
- 24 S.A. Fairhurst, K.M. Johnson, L.H. Sutcliffe, K.F. Preston, A.J. Bannister, Z.V. Hauptman and J. Passmore, *J. Chem. Soc., Dalton Trans.*, (1986) 1465.
- 25 K.F. Preston, J.P. Charland and L.H. Sutcliffe, *Can. J. Chem.*, **66** (1988) 1299.
- 26 K.M. Johnson, K.F. Preston and L.H. Sutcliffe, *Magn. Res. Chem.*, **26** (1988) 1015.
- 27 R.J. Gillespie, J.P. Kent and J.F. Sawyer, *Inorg. Chem.*, **20** (1981) 3784.
- 28 R.A. Stewart, S. Fujiwara and F. Aubke, *J. Chem. Phys.*, **48** (1968) 5524.
- 29 P.M. Nutkowitz and G. Vincow, *J. Am. Chem. Soc.*, **91** (1969) 5936; *idem*, *J. Phys. Chem.*, **75** (1975) 245.
- 30 R.A. Stewart, *J. Chem. Phys.*, **51** (1969) 3406.
- 31 F. Neumayr and N. Vanderkooi, *Inorg. Chem.*, **4** (1965) 1234.
- 32 W.V. Cicha, F.G. Herring and F. Aubke, *Can. J. Chem.*, **68** (1990) 102.
- 33 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd edn., Academic Press, New York, 1963, p. 406.
- 34 J.M. Shreeve and G.H. Cady, *Inorg. Synth.*, **7** (1963) 124.
- 35 F.G. Herring and P.S. Phillips, *J. Magn. Reson.*, **57** (1984) 43.
- 36 F.G. Herring and P.S. Phillips, *J. Magn. Reson.*, **62** (1985) 19.
- 37 R.E.D. McLung, *Can. J. Phys.*, **46** (1968) 2271.
- 38 O. Glemser and W. Koch, *Angew. Chem., Int. Ed. Engl.*, **10** (1971) 127.
- 39 A.J. Bannister, R.G. Hey, G.K. MacLean and J. Passmore, *Inorg. Chem.*, **21** (1982) 1679.
- 40 A. Haas and F. Aubke, *Abs. 12th Int. Symp. Fluorine Chem.*, Santa Cruz, CA, Aug. 1988, p. 202.
- 41 A.M. Qureshi, H.A. Carter and F. Aubke, *Can. J. Chem.*, **49** (1971) 35.
- 42 R.A. Meinzer, D.W. Pratt and R.J. Myers, *J. Am. Chem. Soc.*, **91** (1969) 6623.
- 43 W.R. Salaneck, J.W-p. Lin, A. Paton, C.B. Duke and G.P. Caesar, *Phys. Rev. B*, **13** (1976) 4517.