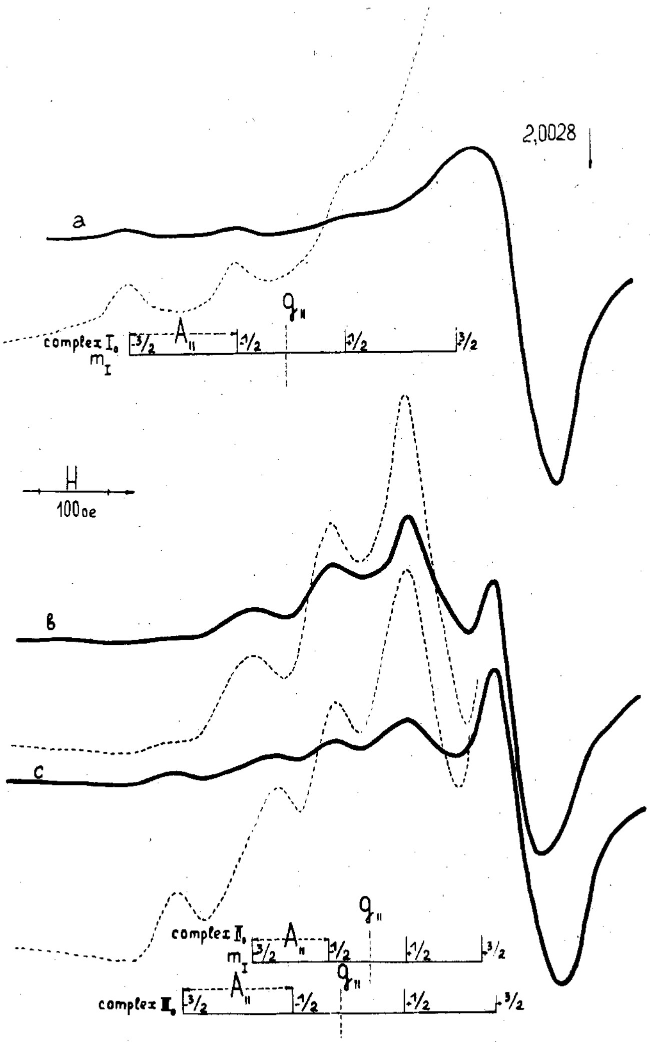

Figure 2. ESR spectra of copper(II) bipyridyl complexes in 60% water–40% ethanol mixtures with $C_{Cu} = 5 \times 10^{-4}$ M, pH 2.2: (a) $C_{bpy} = 1 \times 10^{-3}$ M; (b) $C_{bpy} = 4 \times 10^{-3}$ M; (c) $C_{bpy} = 11 \times 10^{-3}$ M.

the spectrum of the cis isomer of bis(bipyridyl)copper(II) reported by Noack and Gordon.

We also propose that complex II_1, with $A_{\parallel} = 129 \times 10^{-4}$ cm^{-1} observed in solutions containing Cu(II), bpy, H_2Q, H_2O_2, and borate buffer, is the mixed-ligand complex containing bipridyl, H_2O_2, and H_2Q. Replacement of H_2O_2 and H_2Q into the first coordination sphere of Cu(II) appears to increase the $A_{\parallel}$ value which can be seen by comparison with that of [$Cu(bpy)_2(H_2O)_2^{2+}$]. The perpendicular region of the spectra of complexes II_1 and II_2 is different as well. For example, an additional absorption overlapping with the perpendicular region lines is readily detected in the spectrum of complexes II_1 as is noted in Figure 1a and 1b.

In connection with the attempt to determine the composition and structure of bipyridylcopper(II) complexes produced under catalytic reaction conditions, an experiment using D_2O instead of ordinary water was carried out with all other experimental conditions identical. The copper(II) ESR spectrum in D_2O has the same parameters as observed in H_2O as can be seen in Figure 1b. Since the lines are sharper in D_2O, superhyperfine structure (SHFS) arising from interactions with the ^{14}N nuclei is observed in the parallel region of the Cu(II) ESR spectrum.

It is difficult to determine the exact number of SHFS lines arising from the ^{14}N splitting of both the ^{63}Cu and ^{65}Cu isotopes. From an analysis of the spectrum, however, it is apparent that the number of SHFS lines is greater than five. Hence, it is obvious that the spectrum in question can not be that of the mono(bipyridyl)copper(II) species. Moreover, $g_{\parallel}$ and $A_{\parallel}$ for this spectrum differ markedly from $g_{\parallel}$ and $A_{\parallel}$ observed for the tris(bipyridyl)copper(II) complex. Thus, these data give additional indirect evidence for the assignment of the spectrum in question to the *cis*-$Cu(bpy)_2(H_2O)_2^{2+}$ species.[3,9]

The difficulties associated with detection of the complex with $g_{\parallel} = 2.222$ and $A_{\parallel} = 118 \times 10^{-4}$ cm^{-1} suggest the necessity to use precooled copper(II) and bpy solutions. As noted above, Noack and Gordon[1] considered the complex with $g_{\parallel} = 2.227$ and $A_{\parallel} = 128.9 \times 10^{-4}$ cm^{-1} to be the cis isomer of $Cu(bpy)_2(H_2O)_2^{2+}$. From our point of view there are good reasons for this assignment.

Registry No. I_0, 22941-48-6; II_0, 21087-94-5; II_1, 65930-65-6; III_0, 17168-72-8.

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Free Radicals Produced by the γ Irradiation of Thiazyl Fluoride in Sulfur Hexafluoride

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The γ irradiation of solid solutions of inorganic molecules in sulfur hexafluoride has proved to be a fruitful source of free radicals for study by EPR spectroscopy. In addition to being a tumbling matrix at temperatures as low as 100 K, SF_6 is also a source of fluorine atoms upon irradiation.[2] Thus, isotropic EPR spectra of paramagnetic fluorides can be readily generated provided the acceptor molecule is soluble in sulfur hexafluoride. FSO_2 from SO_2, PF_4 from PF_3, ClF_4 from ClF_3, and ClF_6 from ClF_5 are but a few examples of the successful application of this technique.[2,3] In this paper we report the spectra of radicals generated by the γ irradiation of thiazyl fluoride (NSF) in SF_6.

An examination of the EPR spectrum at 110 K of a γ-irradiated solid solution of NSF in SF_6 reveals the presence of a number of lines not detectable in the irradiated pure host. Closer inspection shows that the extra resonances are associated with two distinct centers, both of which show isotropic hyperfine interactions with a single ^{14}N ($I = 1$) nucleus and further interactions with two ^{19}F ($I = 1/2$) nuclei (Table I). The species with two equivalent fluorine nuclei was produced alone by the γ irradiation of solid solutions of $ClNSF_2$ or $BrNSF_2$ in SF_6 and by the codeposition of Na, $ClNSF_2$, and SF_6 on a rotating cryostat.[4] We identify the latter species with the radical NSF_2, having a terminal nitrogen atom and two equivalent fluorines, since it is an expected primary product

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Table I. Isotropic EPR Parameters for NSF_2, FNSF, and Related Radicals[a]

Radical	g	Hyperfine interaction, MHz $a(^{14}N)$	Hyperfine interaction, MHz $a(^{19}F)$	Ref
NSF_2	2.002 21 (1)[b]	14.69 (3)	246.95[c] (3)	This work
FSO_2	2.002 6		401	*d*
FPO_2^-	2.001 1		472	*e*
FNSF	2.004 40 (1)	66.53 (6)	354.1 (1) 267.9 (1)	This work
NF_2	2.005 2	48	168	*f*

[a] Data for NSF_2, FNSF obtained at 110 K in SF_6. [b] Numbers in parentheses are standard errors in the last significant figure as determined from a least-squares fit of all lines in the spectrum. [c] Hyperfine interaction for two equivalent ^{19}F nuclei. [d] J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973). [e] R. W. Fessenden, *J. Magn. Reson.*, 1, 277 (1969). [f] C. A. McDowell, H. Nakajima, and P. Raghunathan, *Can. J. Chem.*, 48, 805 (1970).

of the irradiation[5] of *N*-halogenosulfur difluoride imides or of their reaction with Na. We strongly suspect that the other center observed in irradiated SF_6/NSF mixtures is the isomeric radical FNSF which arises from fluorine atom attack on the nitrogen atom in NSF.

NSF_2 is isoelectronic with the prototypal 25-electron AB_3 radical SO_3^-, and would, therefore, be expected to have a pyramidal structure with the unpaired electron largely located in a sulfur sp^3 hybrid orbital.[6,7] Measurement of the ^{33}S ($I = 3/2$) hyperfine interaction, the most critical test of such a structure, was not possible for NSF_2 (or FNSF) unfortunately, since the estimated intensities of the ^{33}S satellite spectra in natural abundance (0.74%) were well below the limit of detectability. However, comparison of the isotropic ^{19}F hyperfine interaction and g value with those of the isoelectronic species FSO_2 and FPO_2^- (Table I) shows that the assignment to a pyramidal NSF_2 is not unreasonable. An alternative possibility, that the carrier is a nitrogen-centered radical, i.e., $\dot{N}{=}SF_2$, in a valence-bond description, seems much less plausible to us since the ^{14}N hyperfine interaction is appreciably smaller than in $\dot{N}CH_2$ (29 MHz)[8] or $\dot{N}SF_4$ (24 MHz).[9] On the other hand, the N 2s unpaired spin density indicated by the isotropic hyperfine interaction is compatible with a sulfur-centered pyramidal structure, i.e., $N{\equiv}\dot{S}F_2$.

Somewhat surprisingly, INDO I calculations[10] which we have carried out suggest that the radical NSF_2 is planar with a ground-state electronic wave function of the representation A_1 in C_{2v} symmetry. An analogous ground-state wave function has been proposed[11] for the radical SF_3. The present experimental results, unfortunately, do not permit a distinction to be made between planar and pyramidal σ radicals.

The spectral parameters (Table I) for the species which we have labeled FNSF are suggestive of a derivative of the nitrogen-centered π radical NF_2.[12] A large hyperfine interaction of the unpaired electron with the ^{19}F nucleus which is more remote from the nitrogen nucleus in FNSF can be accommodated by assuming a nonplanar structure for the radical, a structure which is predicted by INDO I calculations. The magnitude of the ^{14}N and ^{19}F hyperfine interactions dictates against the alternative formulation as a sulfur-centered radical $F{-}N{=}\dot{S}{-}F$.

Experimental Section

NSF, $ClNSF_2$, and $BrNSF_2$ were all prepared from the mercury compound $Hg(NSF_2)_2$ which was obtained by the reaction of HgF_2 with $FCONSF_2$.[5,13] NSF was also generated via the reactions of SF_4 with urea and with ammonia.[5] Cylinder SF_6 (Matheson) was used as received.

Degassed mixtures of substrate (~5%) in SF_6 were sealed off in quartz EPR tubes and γ irradiated at 77 K for 2 h in a 9000 Ci ^{60}Co source. EPR spectra we recorded and measured with a Varian E-12 spectrometer and ancillary equipment.[11] ^{19}F NMR analysis carried out on the samples prior to γ irradiation confirmed the identity and purity of the reactants.

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Registry No. NSF, 13537-38-7; $ClNSF_2$, 13816-65-4; $BrNSF_2$, 25005-08-7; SF_6, 2551-62-4; NSF_2, 39466-65-4; FNSF, 66142-12-9.

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Structure of Thiotrithiazyl Nitrate ($S_4N_3^+NO_3^-$): Evidence for a Triangular Arrangement with Short Contacts between an Oxygen Atom and the Disulfide Group

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Crystals of a number of compounds containing the disulfide group show unusually short intermolecular contacts of an external atom with both sulfur atoms of the disulfide group.[1-7] Examples summarized by Hordvik[8] include several 1,2-dithiolium and thiuret salts.

The external atom X which most commonly is a chlorine, bromine, or iodine atom generally lies in or close to the plane of the π-bonded system of which the disulfide group is a part. The arrangement has been described as a weak three-center two-electron bond established through partial transfer of charge from a filled orbital on X into empty orbitals on the sulfur atoms.[8] This interpretation is in agreement with the conclusion by Rosenfield, Parthasarathy, and Dunitz,[9] based on the analysis of intermolecular contacts with sulfur, that nucleophiles tend to approach the divalent sulfur atom in the plane of the adjacent bonds.

In the halides described by Hordvik the S···X distance is between 0.25 and 0.51 Å shorter than the sum of the corresponding van der Waals radii. An even larger shortening has been described to occur, however, in the salt thiotrithiazyl nitrate $S_4N_3NO_3$ by Cordes, Kruh, and Gordon,[10] who, from a partial three-dimensional x-ray analysis, report an S—S···O distance of 2.66 and S···O distance of 2.48 Å, compared with a sum of the van der Waals radii of 3.25 Å. As strong intermolecular interactions with sulfur atoms are of considerable importance for the properties of pseudo-one-dimensional molecular metals[11,12] we have redetermined the crystal structure of the title compound.

Experimental Section

The title compound was prepared by treating thiotrithiazyl chloride (S_4N_3Cl) with hot fuming nitric acid. The crystals of $S_4N_3NO_3$ are