of the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ could not be made since nitromethane absorbs in the region of the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition. Although this transition could be observed in the spectrum obtained in the Nujol mull, it has been demonstrated by Schaffer[18] that this band deviates from the predicted position, possibly due to charge-transfer interactions, and therefore no calculation was made.

TABLE III

LIGAND FIELD PARAMETERS OF THE N,N,N′,N′-TETRAMETHYLMALONAMIDE COMPLEXES

Compound	Dq, cm^{-1}	$E(P) - E(F)$, cm^{-1}	β,[a] %
$[Cr(C_7H_{14}N_2O_2)_3](ClO_4)_3$	1690	9,020	34.3
$[Co(C_7H_{14}N_2O_2)_3](ClO_4)_2$	890	12,300	15.5
$[Ni(C_7H_{14}N_2O_2)_3](ClO_4)_2$	860	13,600	13.6

[a] The per cent lowering of the $E(P) - E(F)$ from that of the free-ion value.

For cobalt the values of the Dq and β were calculated on the basis of O_h symmetry. The $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition could not be resolved but showed up as a broad shoulder on the 18,600 cm^{-1} peak. This transition, which involves two electrons, would be expected to be of very weak intensity.[19]

For nickel(II) the Dq value of 860 cm^{-1} would place N,N,N′,N′-tetramethylmalonamide in the spectrochemical series near water (860 cm^{-1}). For chromium, N,N,N′,N′-tetramethylmalonamide has a Dq value (1690 cm^{-1}) less than that of water (1740 cm^{-1}).

The fact that N,N,N′,N′-tetramethylmalonamide gives larger Dq values than other amides is probably due to a chelate effect as it is a bidentate ligand. The chelate effect is illustrated by comparing the Dq values for nickel(II) of various monodentate ligands and similar bidentate ligands: pyridine (1010 cm^{-1})[20] *vs.* bipyridyl (1150 cm^{-1}),[21] pyridine N-oxide (840 cm^{-1})[22] *vs.* 2,2′-bipyridine-1,1′-dioxide (857 cm^{-1}),[23] methylamine (993 cm^{-1})[24] *vs.* ethylenediamine (1150 cm^{-1}).[25] N,N,N′,N′-Tetramethylmalonamide (860 cm^{-1}) may thus be compared with N,N-dimethylacetamide (769 cm^{-1}).[5] On this basis it is seen that there is a chelate effect. For chromium we also see a pronounced chelate effect when N,N,N′,N′-tetramethylmalonamide (1690 cm^{-1}) is compared with N,N-dimethylacetamide (1517 cm^{-1}).[5]

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The Preparation of Pentafluorosulfanylamine, SF_5NH_2

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Although several α-fluoro secondary amines R_fNHR_f' have been prepared, where R_f and R_f' have been either perfluoroalkyl[1-3] or pentafluorosulfanyl groupings, no α-fluoro primary amines have been reported to date. These secondary amines have generally been prepared by the addition of HF across the carbon–nitrogen bond of a perfluoroimino precursor, *e.g.*, $SF_5N{=}CF_2 + HF \rightarrow SF_5NHCF_3$. We have found that the primary amine SF_5NH_2 can be prepared by the addition of two molecules of HF across the sulfur–nitrogen triple bond[4] in thiazyl trifluoride,[5] NSF_3.

$$NSF_3 + 2HF \longrightarrow SF_5NH_2$$

Pentafluorosulfanylamine is a volatile white solid ($P_{0°} = 29$ mm). It dissociates to NSF_3 and HF slowly at room temperature and rapidly around 45° in the presence of small amounts of moisture. The amine can, however, be handled in a dry glass vacuum system if transfers are made rapidly, and it is stable when stored at −78°. It was found to be soluble in dry diethyl ether even at −78°.

Experimental Section

Reagents.—Thiazyl trifluoride, NSF_3, was obtained[6] as a product of the reaction of N-fluoroformyliminosulfur difluoride,[7] $F_2S{=}NCOF$, with silver difluoride (Harshaw Chemical Co.) and was purified by fractional condensation. The purity of the NSF_3 was confirmed by comparing its infrared spectrum with the published spectrum[5] and by vapor density molecular weight determination. Ultrapure hydrogen fluoride (furnished by the Blockson Chemical Division of Olin Mathieson Corp.) was used directly from the cylinder.

Reaction.—In a typical reaction 9.7 mmoles of NSF_3 and excess HF (143 mmoles) were held in a Kel-F tube reactor (2-cm diameter) for 18 hr at room temperature. (This length of time was arbitrary. Later experiments have indicated that the time required for the reaction to reach completion may actually be very much less.) The contents of this vessel were then distilled under vacuum to another Kel-F vessel packed with 25 g of NaF pellets and were allowed to sit over this NaF at room temperature for several hours to remove the unreacted HF from the sample. The volatiles after this treatment, 3.1 mmoles of SF_5NH_2 and 6.1 mmoles of NSF_3, were separated by passing the gases through two traps cooled to −63 and −196°, respectively. This represents a 34% yield of the amine.

General Methods.—Infrared spectra were studied using a Perkin-Elmer Model 137 Infracord spectrometer. The gaseous

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samples were contained in a 10-cm glass cell with sodium chloride windows. Mass spectra were recorded using a Hitachi Perkin-Elmer RMU-6A mass spectrometer. Vapor pressures were obtained using a static method.

Properties of Pentafluorosulfanylamine.—Experimental measurements gave a molecular weight of 141.5 ± 1.6 (average of seven determinations) compared to a molecular weight of 143.2 calculated for SF_5NH_2. Vapor pressures (given in Table I) in the range -23 to $+10°$ indicate a heat of sublimation of 9.59 ± 0.03 kcal/mole and an extrapolated normal sublimation point of 61°. The high heat of sublimation and also the high "boiling point" imply considerable hydrogen bonding in the condensed phases. The experimental data fit the expression $\log P_{\mathrm{mm}} = -2096/T + 9.145$. The melting point appears to be about 43°. The important infrared absorption peaks observed in the spectrum of gaseous SF_5NH_2 are as follows (cm^{-1}): 3550 (w) and 3440 (w) N–H stretch (*cf.* organic primary amines doublet in the 3500–3300 cm^{-1} region[8]), 1590 (m) N–H bend,[8] 1208 (w) S–N?, 930 (vs) and 885 (vvs) S–F stretch (doublet),[9] 776 (s) N–H bend,[8] and 694 (vw) S–F stretch.[9] Replicate spectra were taken at 2, 4.8, and 12.1 mm.

TABLE I

VAPOR PRESSURE OF SF_5NH_2

T, °C	*p*, mm	*T*, °C	*p*, mm
−22.9	5.7	−6.0	20.4
−18.0	9.6	−5.0	21.6
−16.9	9.2	−4.3	20.4
−16.0	9.6	0.0	29.3
−13.0	11.1	0.0	30.6
−12.3	13.4	0.0	30.7
−10.0	15.0	0.0	33.0
−9.8	15.5	3.5	35.6
−8.0	18.8	10.7	58.0

The mass spectrum of a sample of pure pentafluorosulfanylamine (as judged from the absence of NSF_3 peaks from the infrared spectrum) showed the major peaks above mass number 28 given in Table II. The intensities shown are relative to NSF_3^+.

TABLE II

MASS SPECTRUM OF SF_5NH_2 (70 v)

m/e	Assigned species	Intensity relative to NSF_3^+	*m/e*	Assigned species	Intensity relative to NSF_3^+
145	$S^{34}F_5NH_2^+$	0.002	89	SF_3^+	0.625
143	$SF_5NH_2^+$	0.069	86	$SF_2NH_2^+$	0.037
127	SF_5^+	0.102	85	SF_2NH^+	0.282
124	$SF_4NH_2^+$	0.065	84	SF_2N^+	0.417
105	$SF_3NH_2^+$	0.046	70	SF_2^+	0.361
104	SF_3NH^+	0.236	65	NSF^+	0.282
103	SF_3N^+	1.000	51	SF^+	0.153
91	$S^{34}F_3N^+$	0.028	46	SN^+	0.231

Pentafluorosulfanylamine hydrolyzes rapidly over aqueous base according to the equation

$$SF_5NH_2 + 6OH^- \longrightarrow SO_3NH_2^- + 5F^- + 3H_2O$$

The neutralization equivalent was determined by hydrolyzing the SF_5NH_2 and titrating the excess base with standardized hydrochloric acid to a phenolphthalein end point. Sulfamate ion was identified by its infrared absorption spectrum among the hydrolysis products after evaporation of the titrated solution. The titration equivalent for a 0.1476-g sample was 23.7 mg for the above reaction (calcd 23.85 mg). Fluoride was determined by standard methods on the same solutions. *Anal.* Calcd: F, 66.3. Found: F, 66. Pentafluorosulfanylamine is a white solid at room temperature. It can be stored indefinitely in glass at Dry Ice temperature and appears to be stable at room temperature in the complete absence of water. Traces of water, however, especially in the presence of glass, result in decomposition to NSF_3.

Chemical reactions of pentafluorosulfanylamine are currently under investigation.

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Elucidation of Boron (^{11}B) Nuclear Magnetic Resonance Spectra by Heteronuclear Spin Decoupling

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^{11}Boron spectra are more difficult to evaluate than the spectra of the more popular nuclei. This difficulty arises because the spectra produced by commercially available spectrometers display the $^{11}B-^{1}H$ coupling constants in the same order of magnitude as the ^{11}B chemical shifts. Consequently, only the more simple boranes give completely interpretable spectra. For the higher boranes, one must be content to make symmetry comparisons between the spectrum and the molecule. To illustrate, the spectral assignments[1,2] for two of the dicarbaclovododecaborane(12) isomers have not yet been made.

Obviously, a spectrometer operating at higher field strength would improve the quality of ^{11}B spectra since the chemical shift is proportionate to field strength. Such a spectrometer was built by Nelson and Weaver.[3] Examples of the spectra it produced have been shown.[2] Unfortunately, it has been dismantled and such spectra are presently unobtainable.

We have sought to find if, and to what degree, heteronuclear spin decoupling[4,5] enhances the evaluation of ^{11}B spectra.

Experimental Section

The 19.3-Mc/sec spectra were obtained with a Varian[6] HR-60 spectrometer, modified with an NMR Specialties[7] HD-60 heteronuclear decoupler operating at 60 Mc/sec. Spectral integrals were measured with both the Varian V-3521 integrator and with

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