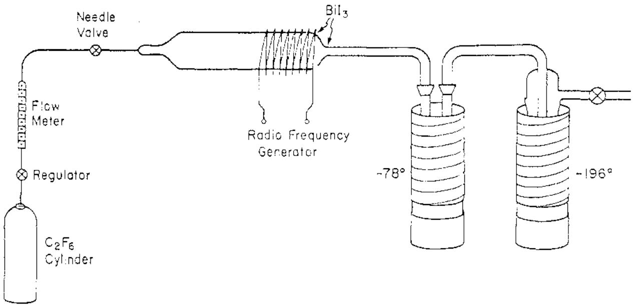

Figure 1. Diagram of the plasma apparatus.

afluoroacetone,[8] the metallic layer was removed but no bismuth-containing species were isolated. The preparation of $Bi(CF_3)_3$ by the plasma route thus appears to provide a critical test of the ability of the plasma system to generate compounds of limited thermal stability.

Experimental Section. In a typical experiment 18 g of BiI_3 was introduced into the reactor in the indicated region (see Figure 1) and the system was evacuated. Hexafluoroethane, after pressure reduction, was then admitted at a rate of 15 cm^3/min. During the course of the reaction the pressure was maintained at ca. 1 Torr. The Lepel radiofrequency generator, operating at 8.6 MHz, was adjusted to provide about 20 W of power to the load coil which was ample to maintain the discharge. The reaction was allowed to proceed for 100 h with periodic removal of the contents of the −196 °C trap. Upon completion of the experiment, the contents of the −78 °C trap were removed and, after fractionation, the appropriate portions of the two samples were combined and further separated by low-temperature distillation. Aliquots for the thermal decomposition studies were vacuum distilled into Pyrex tubes, sealed off with a torch, and placed in a water bath maintained at the appropriate temperature. Infrared (Beckman IR-20A 10-cm gas-phase cells), ^{19}FMR (Perkin-Elmer R20B), and mass (Hitachi RMU-6E) spectra were obtained by standard procedures.

On the plasma vacuum line, tris(trifluoromethyl)bismuth was found in both the −78 °C trap and the −196 °C trap. Under static vacuum, the compound slowly passes through a trap maintained at −45 °C and is held in a −63 °C trap. $Bi(CF_3)_3$, 0.79 g, 6% conversion, 32% yield,[9] was then purified by low-temperature distillation (−55 °C). This compound is a colorless liquid, which fumes when exposed to air. At room temperature, it is hydrolyzed by base with the evolution of 3 equiv of fluoroform. In sealed 3-mm tubes, decomposition to deposit metallic bismuth occurs at 100 °C with a half-life of approximately 15 min. At 180 °C thermal decomposition occurs in seconds. The ^{19}FMR spectrum of the compound sealed in a 4-mm tube consists of a singlet at −45.9 ppm (downfield) from external trifluoroacetic acid.

With the spectrometer cooled to room temperature the positive ion mass spectrum at 70 eV contains the following peaks [*m/e*, assignment, (intensity)]: 416, $Bi(CF_3)_3$, (6.8%); 397, $Bi(CF_3)_2CF_2$, (1.6%); 347, $Bi(CF_3)_2$, (62.0%); 328, $Bi(CF_3)CF_2$, (0.7%); 297, $BiCF_4$, (17.1%); 278, $BiCF_3$, (14.5%); 259, $BiCF_2$, (4.8%); 247, BiF_2, (28.5%); 228, BiF, (11.6%); 209, Bi, (100.0%); 69, CF_3, (32.5%); 50, CF_2, (2.7%). The existance of the molecular ion in the spectrum indicates that ionization occurs by the loss of one of the lone pair electrons from the bismuth atom. The observed metastable ions are ascribed to the following decompositions

$$Bi(CF_3)_3^+ \xrightarrow{m^*=289.5} Bi(CF_3)_2^+ + \cdot CF_3 \quad \text{(calcd 289.4)}$$

$$Bi(CF_3)_2^+ \xrightarrow{m^*=176} BiF_2^+ + C_2F_4 \quad \text{(calcd 175.8)}$$

$$BiCF_3^+ \xrightarrow{m^*=157} Bi^+ + CF_3 \quad \text{(calcd 157.1)}$$

The infrared spectrum contains absorptions at 2135 (vw), 1235 (m), 1180 (vs), 1140 (s), 1120 (s), 1060 (vs), 1032 (w), and 718 (m) cm^{-1}. The appearance of the spectrum between 1000 and 1300 cm^{-1} is very similar to that of the corresponding arsine, $As(CF_3)_3$,[10] but the entire envelope is slightly red-shifted. It should be noted that authentic $Bi(CF_3)_3$ is significantly more volatile than the material obtained in the earlier experiment;[8] furthermore the band shapes, intensities, and energies of the infrared spectrum of our sample are exactly as expected in light of the spectra of the known lighter group 5 trisubstituted analogues.

Results and Discussion. The thermal stability experiments reported above clearly show why the earlier attempts to prepare $Bi(CF_3)_3$ resulted in failure. The desired product is not thermally stable at the temperatures required for its formation by these methods. Thus ligand-exchange reactions of methyl(trifluoromethyl)bismuthines (cf. eq 3) do not proceed[7] to yield the trisubstituted product at temperatures less than 100 °C even with very long reaction times. The reaction of metallic Bi with CF_3I as well as the attempted thermal decarboxylation of $(CF_3COO)_3Bi$ requires temperatures of at least 200 °C before the reactions proceed at a measurable rate, yet the desired product, $Bi(CF_3)_3$, is capable of only fleeting existence under these conditions. In the Paneth reaction,[8] in which CF_3 radicals were generated by the pyrolysis of hexafluoroacetone, the temperature is not reported but appears to be several hundred degrees, again too high to allow the isolation of the compounds. In conclusion, it appears that the plasma method for the preparation of trifluoromethyl-substituted compounds affords the only currently available route to several marginally stable species which lack the thermodynamic stability to survive preparation by more classical methods.

Acknowledgment. This work was generously supported by the National Science Foundation.

Registry No. $Bi(CF_3)_3$, 5863-80-9.

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Received December 13, 1976

Comments on the Observation of Carbon-13 Hyperfine Interaction in the Electron Spin Resonance Spectra of Bis(diethyldithiocarbamato)copper(II)

AIC70083H

Sir:

Recently, the observation of different sets of satellite lines, in the ESR spectra of $^{63}Cu(dtc)_2$ I, diluted in a single crystal

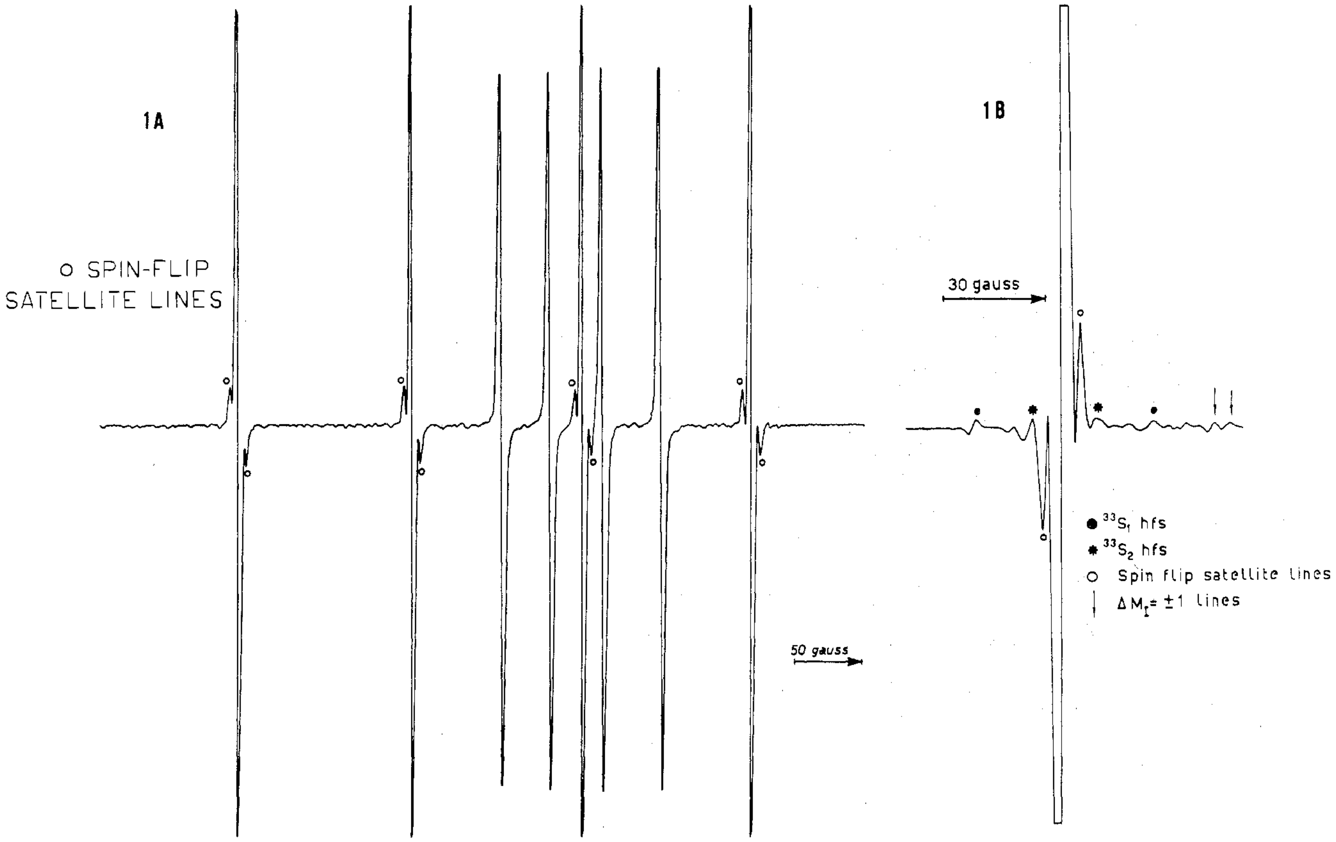


Figure 1. X-Band single-crystal spectrum of ^{63}Cu(dtc)$_2$–Ni(dtc)$_2$ for an arbitrary orientation of the external magnetic field. Part B is a magnification of the low-field line in spectrum A. Different kinds of extra lines are indicated.

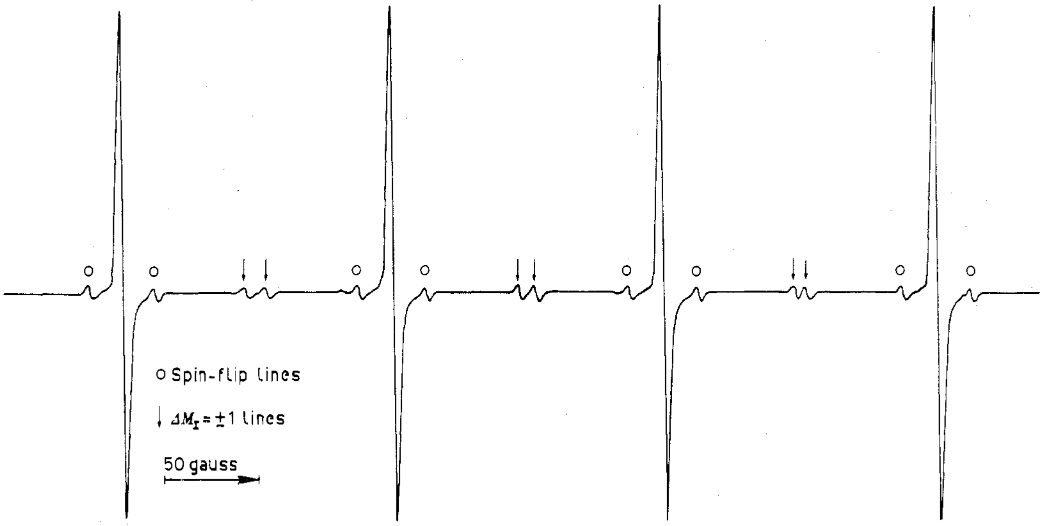
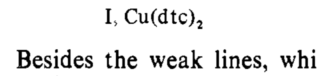
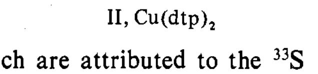


Figure 2. Q-Band single-crystal spectrum of ^{63}Cu(dtc)$_2$–Ni(dtc)$_2$ showing the spin–flip satellite lines. The external magnetic field lies in the *ac* plane.

of the Ni(II) analogue, has been reported by Kirmse and Solovev.[1]



I, Cu(dtc)$_2$



II, Cu(dtp)$_2$

Besides the weak lines, which are attributed to the ^{33}S hyperfine interaction, each copper line appears to be symmetrically flanked by two satellites which, according to Kirmse and Solovev, arise because of the hyperfine coupling of the unpaired electron with one ^{13}C nucleus (^{13}C, 1.1%, $I = {}^1/_2$). An isotropic coupling constant of 9.6×10^{-4} cm^{-1} is reported.

We believe that there is enough evidence to show that misinterpretation of the spectra occurred and that the so-called ^{13}C hyperfine lines have a totally different origin.

In the very similar phosphorodithioate complexes II, phosphorus (^{31}P, 100%, $I = {}^1/_2$) hfs has been measured for both the Cu^{2+} and VO^{2+} ions, the isotropic part of the interaction being, respectively, 9.3 and 42.1×10^{-4} cm^{-1}.[2,3] The large difference between these two values can be accounted for considering that only for the VO^{2+} complex does the ground-state orbital have the correct symmetry ($^2A_1$, in C_{2v}) to interact directly with the 3p and 3s orbitals of the phosphorus atoms, forming appreciable σ bonds.

The coefficients of the P 3s orbital in the molecular orbital containing the unpaired electron can be evaluated by means of the equation

$$A^P_{\text{iso}} = {}^8/_3 g_e g_n \mu_b \mu_n |\psi_{3s}(0)|^2 c_s^2 \qquad (1)$$

using the reported values of $|\psi_{3s}(0)|^2$.[4] In this way c_s^2 has been estimated to be 0.0027 and 0.0135 respectively for the copper and vanadyl compounds.[2,3]

In the case of the dithiocarbamate ligand, ^{13}C hfs has been measured only for the VO^{2+} complex,[5] A^C_{iso} being 6.1 × 10^{-4} cm^{-1}. On the basis of the above argument a value of 9.6 × 10^{-4} cm^{-1} for the ^{13}C splitting in the Cu(dtc)$_2$ complex appears to be far too large. The corresponding value of c_s^2 is 0.0091, pointing to a surprisingly higher covalency of Cu(dtc)$_2$ with respect to Cu(dtp)$_2$, whereas previous results[2,6] show that this difference, if any, is small.

We suggest that the lines detected by Kirmse and Solovev are the so-called hydrogen spin–flip satellites. In the case of the Cu^{2+} complexes of various S-containing ligands, such as phosphorodithioates, 1,2-dithiolates, and the diethyldithiocarbamate ligand itself, some results have already been reported[2] and further study is now in progress. Some spectra illustrating our results are reported in Figures 1 and 2. The behavior of the satellite lines differs from that of "normal" hyperfine lines in that their spacing, as well as their intensity, is field dependent. This has been verified via spectra taken at different frequencies. At X- and Q-band frequencies the observed spacings, referred to the central main line, are respectively 5.0 and 18.2 G, exactly corresponding to the proton resonance frequency calculated using the experimental values of the magnetic field strength. These values are quite similar to those reported by Kirmse and Solovev for the low-frequency experiments. The intensity of the satellites varies as the inverse square of the applied field and is also orientation dependent.

Such properties allow[7,8] the presence of the satellites to be attributed to a weak dipolar interaction between the unpaired electron and the magnetic moment of neighboring protons. The two extra lines correspond to the $\Delta M_I = \pm 1$ hydrogen transitions, while the two $\Delta M_I = 0$ signals are hidden under the width of the main line because of the small value of the dipolar coupling tensor. Figure 3 gives a schematic illustration of the spin–flip mechanism. In the Cu(dtc)$_2$–Ni(dtc)$_2$ system only one hydrogen nucleus is responsible for the observed coupling. It belongs to an alkyl group of the same molecule and is located at 2.64 Å from the metal ion and ~6° out of the z axis in the z–x plane.[9] In the phosphorodithioate complex complete deuteration of the ligand with subsequent disappearance of these satellite lines gives conclusive support to our interpretation.

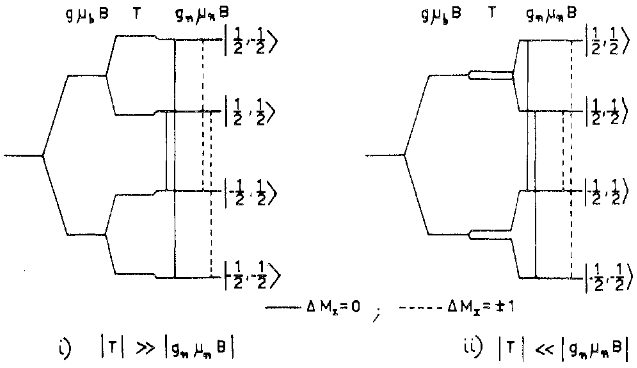


Figure 3. Schematic representation of the spin–flip effect: (i) usual interaction of the electron spin with a nuclear spin $I = {}^1/_2$; (ii) same interaction assuming a very weak dipolar coupling. In this case the two $\Delta M_I = 0$ transitions are unresolved, giving rise to the central main line. The two $\Delta M_I = \pm 1$ transitions flank the main line with a spacing which approximately corresponds to the proton resonance frequency.

Registry No. ^{63}Cu(dtc)$_2$, 62682-82-0; Ni(dtc)$_2$, 14267-17-5.

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Received February 2, 1977