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## Further Study of the Low-Temperature Magnetic Properties of the Complex Bimetallic Salt $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$

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Magnetic susceptibility measurements (70–2 K) for polycrystalline powder samples of the cubic bimetallic salt  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  indicate weak antiferromagnetic exchange interactions ( $J = -0.19 \text{ cm}^{-1}$ ) and suggest possible three-dimensional magnetic order at even lower temperatures. The latter is confirmed via zero-field Mössbauer spectra that undergo resolved magnetic hyperfine splitting between 0.9 and 0.72 K. The internal hyperfine field at 0.34 K is 507 kG.

### Introduction

To our knowledge the previous low-temperature magnetism study of complex bimetallic salts of cobalt III is that<sup>1</sup> of  $[\text{Co}(\text{pn})_3][\text{FeCl}_6]$  (I) (pn = 1,2-propanediamine) and the present title compound,  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  (II). For both of these materials the complex cation corresponds to diamagnetic low-spin  $d^6$  Co III, and thus the paramagnetism must arise from the anion sublattice in an  $S = 0$ ,  $S = 5/2$  salt. Materials such as these are attractive for detailed study in view of the apparent high symmetry of the paramagnetic lattice. In addition, there can be no directly bonded superexchange pathways (classical bridging ligands) connecting paramagnetic centers. The exchange pathways must involve some combination of closely contacting centers of delocalized metal electron spin density (closely spaced  $\text{FeCl}_6^{3-}$  polyhedra) and perhaps hydrogen bonding. To summarize the previous study,<sup>1</sup> Mössbauer spectroscopy and susceptibility measurements show I to order as an essentially cubic 3D antiferromagnetic at a surprisingly high temperature,  $\sim 9$  K, while Mössbauer spectroscopy showed no evidence of order for II to as low as 1.6 K. The latter may correlate with the fact that there are no nonbonded  $\text{FeCl}_6^{3-}$  interanion, Cl–Cl contacts in II of  $< 4.2 \text{ \AA}$  as determined<sup>1</sup> from its X-ray packing.<sup>2</sup> Unfortunately there is no X-ray structure available for I at present, and thus rational comparison of I and II is precluded for now. In any event, our study of II is now further extended via Mössbauer spectra determinations to lower temperatures than previously available as well as susceptibility measurements, none having been previously reported for II for  $T < \sim 80$  K.

### Experimental Section

**Sample Preparation.** The hexachloroferrate  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  was prepared as described earlier,<sup>3</sup> and elemental analysis, performed by Galbraith Laboratories, Inc., confirmed the identity and purity of the sample. High signal to noise zero-field Mössbauer spectra at ambient temperature and  $\sim 78$  K also confirm essential sample purity. Anal. Calcd for  $\text{Co}_6\text{H}_{18}\text{FeCl}_6$ : N, 19.56; H, 4.22; Cl, 49.51. Found: N, 19.44; H, 4.15; Cl, 49.61.

**Magnetic Susceptibility Determinations.** Magnetic susceptibility and magnetization data were collected with the use of a Foner-type<sup>4</sup> Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM). The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating-coil gaussmeter) were calibrated with use of procedures described earlier.<sup>5</sup> The VSM was calibrated with mercury tetrakis(thiocyanato)cobaltate(II).<sup>6–8</sup> Temperatures were measured with a gallium arsenide diode, which has been standardized against a commercially calibrated diode.<sup>9</sup> The data were corrected for diamagnetism of the constituent atoms by using Pascal's constants.<sup>10–12</sup> Powdered samples (approximately 150 mg) of the calibrant and compound of this study were contained in precision-milled Lucite sample holders. Magnetic susceptibility for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  was measured at 10 kOe in the temperature range 2.0–70 K and at 100 Oe in the temperature range 2.0–10.0 K.

**Mössbauer Spectra Determinations.** Spectra between ambient temperature and  $\sim 1.6$  K were determined by using a Janis "Super-Vari temp" flow cryostat where the sample could be submerged directly in cryogen or alternatively kept in a flowing atmosphere of cryogen vapor. Temperature control and measurement were based on uncalibrated and calibrated silicon diodes, respectively (Lake Shore Co. DTC-500 set point controller and DT-500K silicon diodes). The Mössbauer spectrometer was a conventional constant-acceleration drive system incorporated with any of several standard multichannel analyzers. Spectra in the temperature range from  $\sim 1.6$  K extending to  $\sim 0.3$  K were initially determined by using a circulating gas system-sealed vacuum pump type helium-3 cryostat (as opposed to a closed-cycle carbon-sorption-pumped system) available in the Physics Department at Northeastern University. The sample for these measurements was mounted on a copper block "cold finger" in vacuo with temperatures measured via a calibrated germanium resistor (Cryo-cal Co.). Samples ( $\sim 35$  mg of compound diluted in and bulked with dry boron nitride) were packed tightly in nylon holders and wrapped in standard commercially available household aluminum foil ( $\sim 1$  mil thick) such as "Reynolds Wrap" for "good" thermal interfacing with the copper cold finger. The heater-controller system for the germanium resistance sensor in these preliminary Mössbauer spectra determinations<sup>13</sup> was of local origin.

Subsequent to the foregoing Mössbauer spectra determinations, another series of low-temperature spectra was measured by using a new closed-cycle carbon-sorption-pumped helium-3 cryostat recently set up in the Chemistry Department at Northeastern University and designed in conjunction with the Janis Research Co., Wilmington, MA. The spectra obtained with this unit are of significantly higher quality signal to noise and narrower line width than those (e.g. at 0.82 K, Figure 3) initially determined with the circulating system cryostat. Specifically the cobalt-57 source was intense ( $\sim 75$  mC) and used in conjunction with high count rate electronics. Furthermore, counting geometry was much more favorable with this cryostat than (source to detector distance 2.5 in. vs.  $\sim 6$  in.) that of the initial work. In addition, the cold finger sample mount and drive system used were found much more stable with respect to vibration problems, thus reducing environmental line width broadening effects.

Temperature measurement and control at the copper sample mount were based on a calibrated germanium resistor (driven with a 1- $\mu\text{A}$  current source) and an uncalibrated silicon diode (driven with a 10- $\mu\text{A}$  source in a Lake Shore Model DTC-500 set point controller), respectively, where both sensors were purchased from Lake Shore Cryotronics

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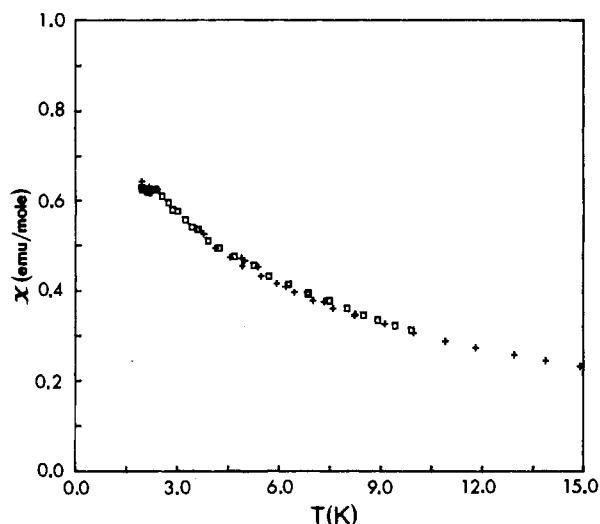


Figure 1. Plots of magnetic susceptibility vs.  $T$ : (□) 100 Oe; (+) 10 kOe.

Co. (Westerville, OH). Interestingly, self-heating effects from the 10- $\mu\text{A}$ -driven silicon diode were not large (0.01 K) at lowest temperatures, 0.3 K. The temperature at the copper sample mount was continuously correlated with that of the carbon-sorption-pumped helium-3 bath where the latter was determined via helium-3 vapor pressure manometry measurements. The difference of these temperature measurements was generally  $\sim 0.02$  K, warmer at the mount. The pressure measurements were made by using Datametrix Co. (Wilmington, MA) Model 5000 absolute pressure capacitance manometer heads having full-scale transducer ranges of 10 and 100 Torr. After several experiments, it was found possible to best control (temperature variation of  $\pm 0.01$  K) the temperature at the sample mount via simultaneously controlling the pumping speed of the carbon-sorb cryo pump and the heat input to the copper cold finger sample mount. The former was done by using a 50- $\Omega$  sorb heater unit that was driven and controlled by another uncalibrated silicon diode in conjunction with a Lake Shore Co. DTC-500 SP set point controller. Sample temperature variation was generally  $< 0.01$  K over the course of a spectral determination ( $\sim 2$ -3 h).

"Good" thermal interfacing of the sample (itself a relative thermal insulator) was ensured as follows. The sample was tightly packed in a wrapping of 99.9995% aluminum foil (1 mil thick) (Alfa Inorganics Co., Danvers, MA) and held in a 12-mm-diameter nylon sample holder, which was itself wrapped in the same high-purity aluminum foil. As mentioned previously, we used ordinary household aluminum wrap for sample holder-cryo mount interfacing in our initial spectral determinations. Unfortunately, subsequent to these determinations, we have found that such foils are typically contaminated with varying and sometimes significant amounts of iron. They exhibit an easily discerned iron-57 resonance absorption near zero velocity even at ambient temperature. Their use for iron-57 Mössbauer spectroscopy studies is clearly not recommended. In addition, for our initial work, the sample holder, not the sample proper, was wrapped in (probably contaminated) aluminum foil. There was a persistent unsplit singlet at the center of the low-temperature spectra initially measured to as low as 0.34 K that is clearly absent in the later spectra. We attribute this to a combination of improper cryogenic interfacing and contamination of the aluminum foil wrapping as discussed. The samples of  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  used were prepared in the same manner, and thus differences owing to defects or particle size variation (an unordered superparamagnetic fraction) are reasonably ruled out.

## Results

Magnetic properties and Mössbauer spectra have been measured for powdered samples of hexamminecobalt(III) hexachloroferrate(III) ( $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ ). The crystal structure of this system has been determined<sup>2</sup> and it was found that the compound crystallizes in the cubic space group  $P\bar{a}3$ .

**Susceptibility Study of  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ .** Magnetic susceptibility data for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  collected at 10 kOe obey the Curie-Weiss law. The material exhibits no sign of magnetic order at or above 1.95 K. As discussed subsequently, zero-field Mössbauer studies reveal that  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  orders at  $\sim 0.9$  K. Plots of temperature-dependent magnetic susceptibilities collected at 100 Oe and 10 kOe are shown in Figure 1. The Curie-Weiss equation  $\chi_m = C/(T - \theta)$  where  $C = Ng^2\beta^2S(S +$

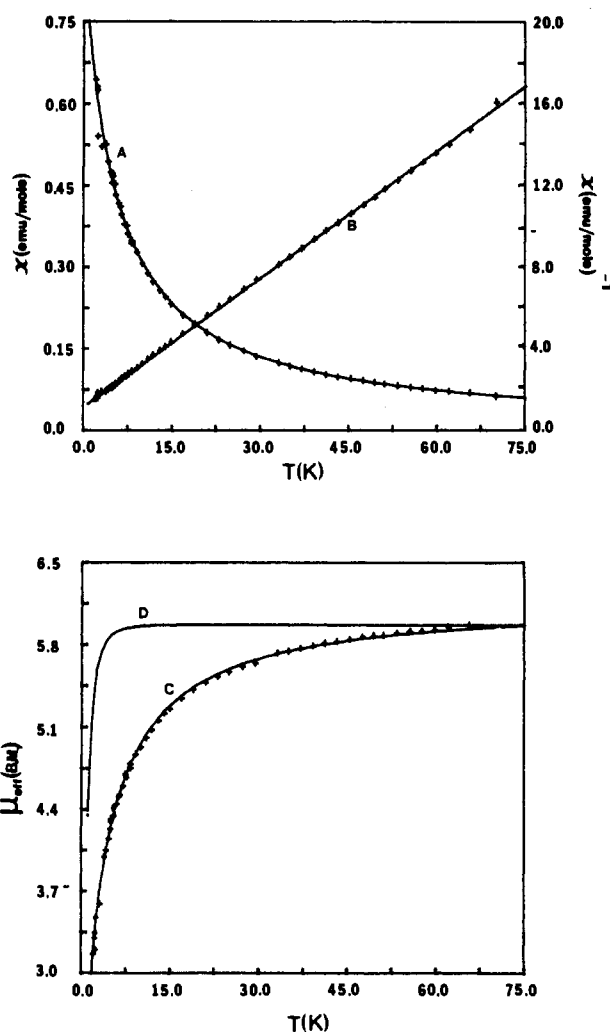


Figure 2. Plots of magnetic susceptibility data for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  taken in an applied field of 10 kOe: (A)  $\chi$  vs.  $T$ ; (B)  $\chi^{-1}$  vs.  $T$ ; (C)  $\mu_{\text{eff}}$  vs.  $T$ ; (D) theoretical line for  $\mu_{\text{eff}}$  and zero-field splitting of  $0.317 \text{ cm}^{-1}$ ,  $g = 2.0112$ .<sup>14</sup> The theoretical lines through experimental curves A, B, and C are those obtained by using the simple cubic lattice model equation of Lines.

$1)/3k$ , was fit to the experimental magnetic susceptibilities over the entire temperature range (2-70 K) with the use of a Simplex least-squares fitting program, yielding the best-fit parameters  $g = 2.089$ ,  $\theta = -5.50$  K and  $C = 4.78$  emu/mol by minimizing the function  $\sum[(\chi_i(\text{obsd}) - \chi_i(\text{calcd}))^2/\chi_i(\text{obsd})^2]$ . This is to be compared to a  $g$  value of 2.0122 determined from EPR measurements<sup>14</sup> of polycrystalline powder samples with  $\text{Fe}^{3+}$  isomorphously diluted in  $[\text{Co}(\text{NH}_3)_6][\text{InCl}_6]$ . The plot of  $\mu_{\text{eff}}$  vs. temperature for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  given in Figure 2 shows a decrease in the effective magnetic moment from the spin-only value ( $35^{1/2}$ ) for an  $S = 5/2$  system as the temperature decreases, reaching a value of  $3.1 \mu_B$  at the low-temperature limit of the experiment. This behavior is characteristic of antiferromagnetic exchange effects as well as zero-field splitting of the  ${}^6A_1$  ground state of iron(III). The temperature variation of the magnetic moment expected for the observed  $D$  value<sup>14</sup> ( $0.317 \text{ cm}^{-1}$ ) is shown in Figure 2. The experimental magnetic moment for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  decreases much more rapidly than expected for zero-field splitting effects alone and leads to the conclusion that antiferromagnetic exchange effects dominate the low-temperature magnetic behavior of  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  as opposed to single-ion zero-field splitting. Thus for example for the case of a large ( $\geq 10 \text{ cm}^{-1}$ ) axial zero-field splitting,  $D$ , such that  $D$  is positive, one has a well-isolated  $m_s = \pm 1/2$  ground Kramers doublet corresponding to  $g_{\parallel} = 2$  and  $g_{\perp} = 6$ . The limiting-low-temperature value of  $\mu_{\text{eff}}$ ,

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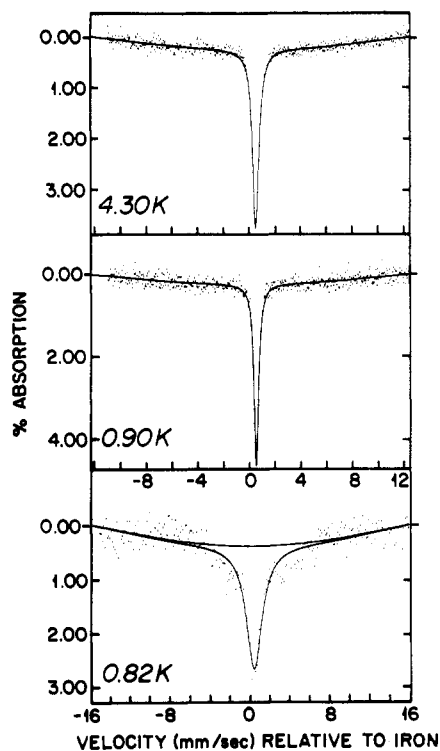


Figure 3. Zero-field iron-57 Mössbauer spectra of  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  at 4.30, 0.90, and 0.82 K.

Table I. Hyperfine Field of  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$

$T$ , K	$H$ , kG	$T$ , K	$H$ , kG
0.336	506.5	0.583	439.9
0.498	488.3	0.643	419.7
0.578	457.4	0.721	361.8

i.e. for a polycrystalline powder in this situation<sup>15,16</sup> is  $19^{1/2}$  ( $\sim 4.36 \mu_B$ ), still some  $\sim 1.2 \mu_B$  larger than the lowest value observed herein.

An approximation of the exchange coupling constant in  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  was obtained by fitting the expansion given by Lines (eq 1) for the simple cubic lattice to the experimental data

$$-\chi_0 J = (1/6\theta)[1 - \sum B_i/\theta_i] \quad (1)$$

in the temperature range 6–70 K.<sup>17</sup> In eq 1,  $\chi_0 = \chi/Ng^2\mu_B^2$ , and  $\theta = kT/JS(S+1)$ , with Heisenberg exchange described by  $H = -2J\sum S_i S_j$  being assumed. The best least-squares fit of eq 1 (curves A–C of Figure 2) to the experimental data yielded  $J = -0.19 \text{ cm}^{-1}$ .

**Mössbauer Spectra.** Some zero-field Mössbauer spectra for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  are shown in Figures 3–5. As reported previously,<sup>1,13</sup> a single, unbroadened Lorentzian is observed to  $\sim 1.4$  K, indicating an absence of quadrupole splitting effects consistent with local ferric ion coordination of cubic symmetry. At 0.90 K incipient hyperfine splitting is evident and at 0.75 K there is nearly full resolution of the nuclear Zeeman transition pattern. The data suggest a critical temperature for three-dimensional ordering of somewhere between  $\sim 0.8$  and 0.9 K as  $H_n$  approaches 0 in this range. The hyperfine field ( $H_n$ ) reaches a limiting value of  $\sim 510$  kG at 0.34 K. This value is typical of high-spin iron(III) where the primary contribution to  $H_n$  is Fermi contact in nature (110 kG/unpaired spin) and for which there is some reduction ( $\sim 40$  kG in the present case) owing to covalency spin delocalization effects. Further reduction of  $H_n$  can also occur through the zero-point spin-reduction effects that are often significant<sup>18</sup> for magnetically low-dimensional (1D or 2D) materials.

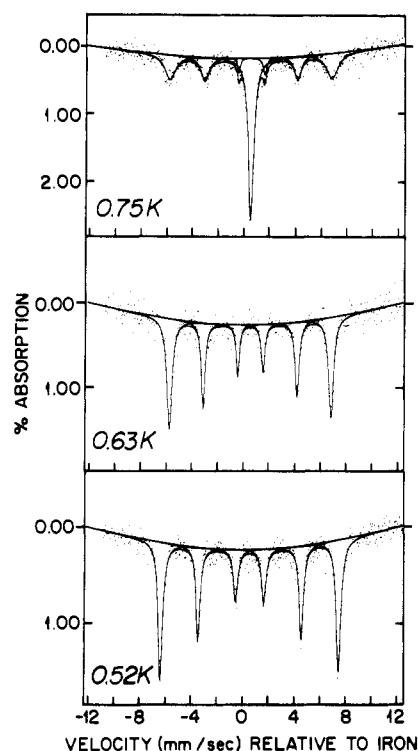


Figure 4. Zero-field iron-57 Mössbauer spectra of  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  at 0.75, 0.63, and 0.52 K.

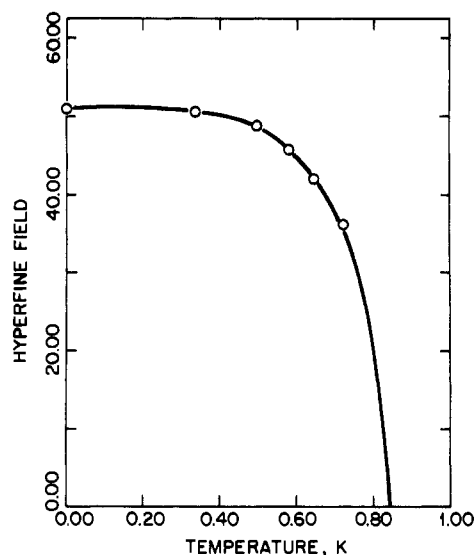


Figure 5. Plot of internal field vs. temperature for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ .

However these effects are certainly not expected to be important for the title compound.

### Conclusions

The results presented herein clearly demonstrate antiferromagnetic exchange and probable three-dimensional antiferromagnetic order for  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ . The Néel temperature for this process is nearly an order of magnitude smaller than that for the related  $[\text{Co}(\text{pn})_3][\text{FeCl}_6]$  and clearly suggests significant differences in anion packing and/or hydrogen bonding between the two. The definitive approach to understanding the magnetism of these interesting "new" systems is of course neutron powder diffraction study wherein one can ideally quantitate patterns of spin delocalization to various ligand atoms as well as determine the direction of spin in the ordered state. Should appropriate

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single crystals become available for principal susceptibilities study at very low temperatures, we speculate that they are likely to demonstrate that  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  is an excellent example of a near perfect easy-axis antiferromagnet as opposed to a metamagnet. The likely small anisotropy field ( $H_A$ ) and implied ( $T_{\text{Nrel}}$  only  $\sim 0.9$  K) low value of exchange field ( $H_E$ ) lead to the prediction of rather easily induced transformations in its  $H$  vs.  $T$  phase diagram. For instance one can study the antiferromagnetic to spin-flop transition ( $H_{\text{SF}} \propto (2H_A H_E)^{1/2}$ ) or at higher values of applied field spin-flop to "paramagnetic" transformation.

We find that these can often<sup>1</sup> be observed in applied-field Mössbauer spectra even for powder samples (e.g.,  $H_{\text{SF}}[\text{Co}(\text{pn})_3][\text{FeCl}_6]$  is  $\sim 10$  kG).

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**Registry No.**  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ , 15928-89-9.

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## Synthesis and $^{119}\text{Sn}$ Mössbauer Spectra of Novel Cationic Tin(II) and Dimethyltin(IV) Compounds

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A systematic synthetic study is undertaken to obtain cationic derivatives of the tin(II) and dimethyltin(IV) cations, stabilized by weakly basic acid and superacid anions. Besides the mixed-valency compound  $\text{Sn}^{\text{II}}[\text{Sn}^{\text{IV}}(\text{SO}_3\text{F})_6]$ , three types of dimethyltin compounds are reported:  $(\text{CH}_3)_2\text{Sn}[\text{M}(\text{SO}_3\text{F})_6]$  and  $[(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2][\text{M}(\text{SO}_3\text{F})_6]$  ( $\text{M} = \text{Sn, Pt}$ ) and salts containing the  $[(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_4]^{2-}$  anion. In addition some of the corresponding  $\text{SO}_3\text{CF}_3$  derivatives are obtained as well. The solution behavior of the principal reactants in the reaction medium  $\text{HSO}_3\text{F}$  provides a rationale for the course of the various synthetic reactions.  $^{119}\text{Sn}$  Mössbauer spectra provide evidence for an undistorted environment for  $\text{Sn}^{2+}$  and linear C-Sn-C groupings for all  $(\text{CH}_3)_2\text{Sn}$ -derivatives. Quadrupole splittings are found in the region 5.5–5.7  $\text{mm s}^{-1}$  and represent the largest values reported for tin so far.

### Introduction

Two dipovalent cations of tin, the tin(II) ion,  $\text{Sn}^{2+}$ , and, representative for all diorganotin(IV) cations, the dimethyltin(IV) cation,  $(\text{CH}_3)_2\text{Sn}^{2+}$ , form the focal point of this study. Both have many common but also many diverging characteristics. The oxidation state of tin differs in the two cations, but the common ionic charge of +2 suggests formation of ionic solids with identical or similar anions. The electronic structures of the cations differ again. For the atomic ion  $\text{Sn}^{2+}$ , a valence electron configuration of  $5s^2$  is expected. The molecular  $(\text{CH}_3)_2\text{Sn}^{2+}$  ion is expected to have a perfectly linear C-Sn-C group, suggesting a  $5sp$  hybridization on tin. As a direct reflection of the electronic structure of tin in the two cations, the  $^{119}\text{Sn}$  Mössbauer spectra should differ markedly. A perfectly spherical  $5s^2$  pair on  $\text{Sn}^{2+}$  should not cause any quadrupole splitting, while the high  $5s$ -electron density suggests a high isomer shift, and a value of  $\delta = +4.84$   $\text{mm s}^{-1}$  relative to  $\text{SnO}_2$  has been calculated.<sup>1,2</sup> For  $(\text{CH}_3)_2\text{Sn}^{2+}$  an intermediate isomer shift of  $\delta \sim 2.0$   $\text{mm s}^{-1}$  relative to  $\text{SnO}_2$  and a very large quadrupole splitting are expected.

Common to both cations is the frequently reported<sup>3,4</sup> observation that neither  $\text{Sn}^{2+}$  nor  $(\text{CH}_3)_2\text{Sn}^{2+}$  exist in solid compounds in their idealized forms. In most tin(II) compounds, a distorted environment for tin is found,<sup>3,5</sup> and their  $^{119}\text{Sn}$  Mössbauer spectra show, with very few exceptions, measurable quadrupole splittings and/or isomer shifts well below 4.84  $\text{mm s}^{-1}$ .<sup>2,6</sup> In dimethyltin(IV) salts a linear C-Sn-C group is not always found.<sup>5</sup> Where this group is linear, as in  $(\text{CH}_3)_2\text{SnF}_2$ ,<sup>7</sup> the structure is 2-dimensional

polymeric rather than ionic. The  $^{119}\text{Sn}$  Mössbauer spectrum with  $\delta = 1.23$   $\text{mm s}^{-1}$  relative to  $\text{SnO}_2$  and a quadrupole splitting  $\Delta E_Q$  of 4.52  $\text{mm s}^{-1}$ <sup>8</sup> provides additional indications for a polymeric structure. A pronounced room-temperature effect and a noticeable asymmetry of the two quadrupole split lines, termed the Goldanskii-Karyagin effect,<sup>9,10</sup> are observed.<sup>8</sup> The relatively small energy separation in the valence shells between  $5s$  and  $5p$  levels, found for post transition elements and ions may be seen as the underlying reason for both the distortion about  $\text{Sn}^{2+}$  and the strong covalent "cation" and "anion" interaction in dimethyltin(IV) salts. For  $\text{Sn}^{2+}(\text{g})$  the separation of the ground state,  $^1\text{S}(5s^2)$ , and the lowest excited state,  $^3\text{P}_0(5s^15p^1)$ , is only 6.64 eV.<sup>11</sup>

In the solid state, the strong polarizable  $\text{Sn}^{2+}$  ion will gain additional stabilization energy by  $5s$ - $5p$  mixing, which in turn requires distortion and a departure from a centrosymmetrical coordination environment.<sup>12</sup> In particular, small, strongly polarizing anions like  $\text{F}^-$  induce strong distortions as evidenced by the various polymorphic forms of  $\text{SnF}_2$ ,<sup>5</sup> and their  $^{119}\text{Sn}$  Mössbauer spectra,<sup>2,3,13</sup> all of which show nonzero quadrupole splittings. On the other hand, weakly basic and weakly polarizing anions composed of highly electronegative constituent atoms should be more capable of producing electronic environments expected for the  $\text{Sn}^{2+}$  and  $(\text{CH}_3)_2\text{Sn}^{2+}$  cations.

Support for this line of reasoning is found in the structural chemistry of divalent tin as probed by  $^{119}\text{Sn}$  Mössbauer spectroscopy. The strongly basic  $\text{F}^-$  ion is converted into the less basic anions  $\text{SbF}_6^-$  and  $\text{SO}_3\text{F}^-$  by reaction with the strong acceptors  $\text{SbF}_5$  and  $\text{SO}_3$ , respectively. As the data collected in Table I show, the

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