Table I. Infrared Absorption Frequencies of $(FSiH_2)_2NSiH_3$

Freq, cm^{-1}	Assignment[a]	Freq, cm^{-1}	Assignment[a]
2264 m	ν(Si-H)	878 m	ν(Si-F)
2182 s		849 m	
1050 m	ν(Si-N)(asym)	738 s	ρ(SiH_3 and/or SiH_2)
992 vs	δ(SiH_3 and/or SiH_2)	560 w	
950 vs		482 w	ν(Si-N)(sym)

[a] Tentative assignments of the major bands were made with the aid of detailed spectra reported for $(SiH_3)_3N$[7] and $(FSiMe_2)_2NH$.[15]

However, under the particular conditions chosen, we still observed the predominant formulation of $SiH_3N(SiH_2F)_2$ in the reaction. This differs from the results obtained in the chlorination of $(SiH_3)_3N$ using $SnCl_4$, where conditions could be chosen to favor the mono-, di-, or trichloro derivative. Variation of the reaction temperature was studied in our work. Temperatures below −50° seemed to prevent the reaction from occurring at all and we found that the optimum temperature range for fluorinating the silicon–hydrogen bond of the amine was between −23 and 0°, with the −23° temperature being recommended for synthetic work. At temperatures above 0°, the cleavage reaction was exclusive. Even at low temperatures, the cleavage reaction is very troublesome and the formation of SiH_2F_2 suggests that the silicon–nitrogen bonds of the fluorosilylamines themselves undergo cleavage.

Owing to its predominant formation in the reaction, the new compound $SiH_3N(SiH_2F)_2$ was the product most completely characterized in our study. The melting point of the material, determined by the Stock magnetic plunger method, is −89.7 ± 0.2°. Infrared absorption frequencies for $SiH_3N(SiH_2F)_2$ taken on a sample in the gas phase are given in Table I, with tentative assignments.

The proton NMR spectra of both $SiH_3N(SiH_2F)_2$ and $(FSiH_2)_3N$ were recorded. The SiH_2 protons of the latter compound appeared as a doublet (J_{H-F} = 60.3 Hz) centered at τ 5.15. The spectrum of $SiH_3N(SiH_2F_2)_2$ consisted of a doublet (J_{H-F} = 60.3 Hz) centered at τ 5.20 for the SiH_2 protons and a closely spaced triplet (J_{H-F} = 1.5 Hz) at τ 5.59 for the SiH_3 protons. The triplet arises from the long-range splitting of the SiH_3 protons by the two fluorines on the $FSiH_2$ groups. The peak areas were in the expected intensity ratios. The positions of the protons of the $FSiH_2$ groups are to the low field of $(SiH_3)_3N$ (τ 5.56)[16] as expected. The 60.3-Hz adjacent H–F coupling constants are consistent with the values for other systems with two electronegative atoms on silicon (e.g., J_{H-F} values for $FSiH_3$ and F_2SiH_2 are 45.8 and 60.5 Hz, respectively;[17] J_{H-F} of $(FSiH_2)_2O$ is 61.2 Hz).

It was somewhat puzzling to find that the silicon–hydrogen bonds of $[HSi(CH_3)_2Si]_2NH$ could not be fluorinated successfully with PF_5 without subsequent cleavage of the silicon–nitrogen bond. The presence of PF_3 and $(CH_3)_2SiF_2$ in the reaction products indicated that fluorination did occur; however, the only silicon products that we could detect were the fluoromethylsilanes $(CH_3)_2SiHF$ and $(CH_3)_2SiF_2$, at least under the conditions we chose to employ. The first step in the general silicon–nitrogen bond cleavage reaction most likely involves the coordination of the nitrogen of silazane to the phosphorus of the PF_5.[18] The increased basicity of the methylated amine would tend to promote this step and hence favor the cleavage. Only when the basicity of the silylamine is low as in the case of $(SiH_3)_3N$ can the hydrogen–fluorine exchange proceed satisfactorily without subsequent cleavage of the silicon–nitrogen bond. We did not pursue the fluorination of $[H(CH_3)_2Si]_2NH$ any further since $[F(CH_3)_2Si]_2NH$ has previously been prepared by the reaction of $[(CH_3)_2SiNH]_4$ with $F_4Si(NH_3)_2$.[15] The lesson to be learned from this result is that in the general fluorination of the silicon–hydrogen bond of hydrosilyl derivatives by PF_5, small differences in molecular composition may cause the undesired cleavage reaction to be favored exclusively.

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Registry No. $(FSiH_2)_2NSiH_3$, 56689-17-9; $(SiH_3)_3N$, 13862-16-3; PF_5, 7647-19-0; $(FSiH_2)_3N$, 56689-18-0.

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Electron Paramagnetic Resonance of Tris(ethyl xanthate)chromium(III)

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The spin-Hamiltonian parameters for d^3 complexes have been thoroughly elaborated within the context of molecular orbital theory[1-3] including charge-transfer effects, ligand spin–orbit effects,[1] and metal spin–orbit reduction.[2] From such theory, the molecular orbital mixing coefficients can, in principle, be determined if environmental effects are small.

Evaluation of lattice effects for a series of ionic complexes[3-5] indicates that spin-Hamiltonian parameters are intramolecular if host charge and site symmetry match those of the guest. Likewise, Kawasaki and Forster[6] have determined that lattice distortions for the ionic tris(oxalato)chromium(III) complex, a trigonal complex, cause a variation that can give a nonzero rhombic E parameter.

The effect of the lattice (environment) upon the spin-Hamiltonian parameters for molecular complexes has not been

Table I. Spin-Hamiltonian Parameters

Compd	*g* values	*D* and *E*, cm^{-1}	Trigonal angles, deg
Cr(acac)$_3$ in Al(acac)$_3$[a]	$g_x = g_y = g_z = 1.9820$ (5)	$D = 0.5920$ (20)	93[b]
		$E = 0.0096$ (5)	
Cr(dtp)$_3$ in Co(dtp)$_3$[c] (*y* and *z* permuted)	$g_x = 1.9903$ (10)	$D = -0.1152$ (10)	78.0[d]
	$g_y = 1.9901$ (10)	$E = 0.0476$ (1)	79.1
	$g_z = 1.9914$ (10)		77.1
Cr(exan)$_3$ in In(exan)$_3$	$g_x = g_y = 1.9987$ (5)	$D = 0.169$ (3)	
	$g_z = 1.9947$ (2)	$E < 10^{-3}$	69.7 (1)

[a] References 7 and 8. [b] Reference 20. [c] Reference 10. [d] Reference 21.

considered although EPR data are available for tris(acetylacetonato)chromium(III) (Cr(acac)$_3$)[7-9] and tris(diethyldithiophosphinato)chromium(III) (Cr(dtp)$_3$).[10]

The data reported for the Cr(dtp)$_3$ are unique since the rhombic zero-field parameter, *E*, reported is quite large and greater than the axial zero-field parameter, *D*. Spectral studies[11-14] of Cr(dtp)$_3$ and the tris(xanthato)chromium(III) complex Cr(exan)$_3$[11,12] indicate comparable optical absorption properties for these four-membered chelate ring systems. Therefore we have determined the single-crystal EPR spectra of Cr(exan)$_3$ and reevaluated the data reported for the Cr(dtp)$_3$ and the Cr(acac)$_3$ systems to determine if the spin-Hamiltonian parameters for these trigonal (C_3 or D_c) symmetry molecular species are influenced by lattice effects.

Experimental Section

Both chromium(III) and indium(III) tris(ethyl xanthate) complexes (Cr(exan)$_3$ and In(exan)$_3$) were prepared after the method of Galsbol and Schaffer[15] with the materials stored at 0°C since some slow decomposition occurred at room temperature. Colorless host In(exan)$_3$ crystals had an index of refraction of 1.7 and density determined by flotation in H_2SO_4 of 1.68, consistent with those of the X-ray analysis[16] therefore indicating two molecules per unit cell. Doped crystals containing up to 4 mol % of Cr(III) could be obtained by growth from acetone in 1 single day. Single-crystal X-ray analysis[16] indicated the crystal structure of the host to be rhombohedral, therefore possessing a threefold symmetry axis.

Electron spin resonance spectra were obtained with JEOLCO Me X- and K-band systems using 100-kHz modulation. Magnetic field strength was determined with a Magnion NMR gaussmeter, Model G-502, with a Hewlett-Packard 5245C electronic counter and 5252A prescaler. Microwave frequencies were determined using solid DPPH ($g = 2.0036$). Angular rotation of the single-crystal samples was accomplished with the JES-UCR-2X angular rotation device with crystals mounted on quartz rods using the *hk*0 face to mount the rotation axis relative to the C_3 crystal axis.

Results

ESR spectra were obtained with the quartz rod along the crystalline (and molecular) C_3 axis (A mounting) and with it normal to this axis (B mounting). For the A mounting rotation of $\vec{H}$ in the plane normal ($\perp$) to the C_3 axis gave only three lines, therefore verifying the magnetic equivalence of the two ions in the unit cell. Further, since the field positions in this mounting are essentially independent of rotation angle, the rhombic distortion must be approximately zero ($E \approx 0$) (see eq 1–10, ref 2). Mounting B exhibits substantial variation in the field and observation of up to six lines for some orientations. Since an inaccuracy in the mounting of 0.5° could produce an error of ±20 G (therefore an error in the spin-Hamiltonian parameter), a third parameter was used to enable simultaneous fitting of *g*, *D*, and *E*, i.e., ϕ, the angular misalignment. Spectra were thereafter measured at intervals of 10° for a total of 180° in the A orientation and 10° for a total of 90° in the B orientation for X band. For K band, data were obtained only for the 90 and 0° orientations of $\vec{H}$ relative to the C_3 axis.

Computer programs PARA and EPR[17,18] obtained from the Quantum Chemistry Program Exchange, Indiana University, were used with PARA adapted to double precision and with the additional angular misorientation parameter, ϕ. The spin-Hamiltonian parameters (eq 1) produced from PARA are listed

$$\mathcal{H} = \beta g_{ii} H \cdot S + D(S_z^2 - 5/4) + E(S_x^2 - S_y^2) \qquad (1)$$

in Table I and, along with experimental angles, were used to compute angular rotation spectra. Hyperfine structure of ^{52}Cr was observed at high-field absorptions at *H* parallel and *H* perpendicular (to *z*) orientations and the *A* value was determined from the outermost hyperfine components of the parallel spectra.

Discussion

Table I lists spin-Hamiltonian parameters obtained from X and K band for the three molecular D_3 chromium complexes, Cr(acac)$_3$, Cr(dtp)$_3$, and Cr(exan)$_3$, along with the trigonal angles[19,20] of isomorphous host lattice materials. Inequality of trigonal angles shows loss of C_3 axial symmetry and would be expected to result in a nonzero rhombic term and perhaps three unequal *g* components.

The spin-Hamiltonian parameters listed in Table I for Cr(dtp)$_3$ in Co(dtp)$_3$ (isomorphous with In(dtp)$_3$) have been here recalculated so that the *z* axis coincides with the molecular C_3 axis as determined by Palmer and coworkers[21] in recent structural results for the isomorphous In(dtp)$_3$ complex. Gregorio, Weber, and Lacroix[10] in their original results chose the *b* axis (approximately normal to the C_3 axis) as the *z* axis. The net result is that a simple permutation of axis occurs.

Both the Cr(acac)$_3$ and Cr(exan)$_3$ complexes possess relatively small *E* terms consistent with the D_3 molecular symmetry expected and the lack of environmental perturbation as determined for the host lattice materials with the inequality of the trigonal axis in the host lattice.

Therefore, the data show that matching an axially symmetric Cr(III) complex with an axially symmetric host lattice produces an axial spin-Hamiltonian while substituting an axial Cr(III) complex into a host lattice having lower than axial symmetry can result in an environmental perturbation producing a nonzero *E* value.

Registry No. Cr(exan)$_3$, 15276-08-1; In(exan)$_3$, 21630-86-4.

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