Spectroscopic, Magnetic, and Mössbauer Studies on Tris(hexamethyldisilylaminato)iron(III), $Fe[N(SiMe_3)_2]_3$

By E. C. ALYEA, D. C. BRADLEY,* R. G. COPPERTHWAITE, and K. D. SALES
(*Chemistry Department, Queen Mary College, Mile End Road, London, E.1*)
B. W. FITZSIMMONS
(*Chemistry Department, Birkbeck College, Malet Street, London, W.C.1*)
and C. E. JOHNSON
(*Physics Department, University of Liverpool, Liverpool*)

Summary Magnetic susceptibilities, e.s.r. spectra, and Mössbauer spectra have been measured for $Fe[N(SiMe_3)_2]_3$ over a temperature range, and the data, together with electronic absorption spectra, interpreted in terms of crystal-field calculations for a high-spin d^5 system in D_{3h} symmetry.

THE *X*-ray structural determination on $Fe[N(SiMe_3)_2]_3$[1] showed that the iron atom was trigonally co-ordinated by nitrogen atoms. As part of a programme[2] exploring the ligand field aspects of this comparatively rare stereochemistry for transition elements we have carried out measurements of the magnetic susceptibility, e.s.r. spectra, Mössbauer spectra, and electronic absorption spectra on this highly reactive compound.

Electronic spectra. In various solvents (cyclohexane, pentane, methylcyclohexane, and Nujol mull) the spectrum in the range 4000—35,000 cm^{-1} showed four bands: ν_1 16,100 cm^{-1} (ϵ_M *ca.* 400), ν_2 20,000sh (*ca.* 450), ν_3 25,300 (> 1500), and ν_4 29,700 (> 1500).

Magnetic susceptibility. The compound conformed to the Curie–Weiss law with $\theta = -10°$ and $\mu = 5{\cdot}91$ B.M., independent of temperature or field strength over the range 98—298 K. Preliminary results were low due to the ready thermal decomposition caused by local heating in grinding a sample. Satisfactory and reproducible results were obtained by a special sampling procedure.

E.s.r. spectra. At room temperature a polycrystalline sample gave a large signal at 1·100 kG ($g = 6$) and a small signal at 3·300 ($g = 2$) using *X*-band at 9270·242 MHz. Oriented single crystal studies gave more accurate g values of $g_\perp = 6{\cdot}021$ and $g_\parallel = 2{\cdot}007$, the needle-axis ($\bar{c}$) of the crystal coinciding with $g_\parallel$. Using *X*-band up to 20 kG, and

Q-band, Cotton and Gibson[3] have detected additional transitions corresponding to a zero-field splitting with *D ca.* 1 cm^{-1}.

Mössbauer spectra. At 77K, a two-line spectrum was obtained with $\Delta E = 5{\cdot}12$ mm s^{-1} and $\delta = 0{\cdot}43$ mm s^{-1} (relative to $Na_2[Fe(CN)_5NO],2H_2O$). Some weak peaks, due to decomposition, were often observed at the centre of this absorption. As with many ^6S iron compounds, one peak of the quadrupolar pair was broadened by slow spin relaxation. At 4·2K a five-line hyperfine pattern was observed and application of a weak magnetic field revealed a six-line pattern with *H* 150 kG. This field increased to 170 kG when the temperature was lowered to 1·4K. The low value of *H* doubtless arises from a contribution from a dipolar term consistent with the appreciable quadrupole splitting, whilst its increase with decreasing temperature is characteristic of a slowly relaxing paramagnet. *H* is parallel to *Z* and the principal component of the electric field gradient tensor is positive.

Crystal-field calculations. Although the local symmetry of the $Fe(NSi_2)_3$ framework is D_3 we consider that the electronic spectrum may be interpreted on the basis of D_{3h} (FeN_3). Applying crystal-field calculations to the lower states of the d^5 system in D_{3h} symmetry and using the parameters *Ds* and *Dt* defined with the same convention as Wood[4] for a five-co-ordination system in D_{3h}, we obtained (assuming $B = 1030$ cm^{-1} for Fe^{3+}, *cf.* Cr^{3+}) $Ds = -5800$, $Dt = 770$ cm^{-1}. The *d*-orbital energy levels are: e' +12,370; a_1' −6980, e'' −8800 cm^{-1}; implying strong ligand-field interaction in the *xy* plane. The electronic spectrum is interpreted as follows. Although all of the observed bands are rather strong compared to the expected spin-forbidden transitions, we assign the two weaker bands (ν_1 and ν_2) at 16,100 and 20,000 cm^{-1} as *d–d* bands and the more intense bands as charge-transfer. The two transitions ($^4A_1''$, $^4A''$) ← $^6A_1$ and $^4E'$ ← $^6A_1'$ are symmetry-allowed and are assigned to ν_1 and ν_2, respectively. All other energy transitions are symmetry-forbidden and hence cannot be assigned to the strong bands (ν_3 and ν_4). An interesting feature of the energy level diagram as a function of increasing ligand field strength is the change from $^6A_1'$ to $^2A_1'$ ground state without the intervention of a quartet ground state.

The absence of temperature dependence by μ, the e.s.r. spectra, and the Mössbauer spectra are all consistent with a $^6A_1'$ ground state and a zero-field splitting of *ca.* 1 cm^{-1}. Full details of this and similar work on the titanium, vanadium, and chromium analogues will be published shortly.

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