The Structure of a Three-Co-ordinate Iron(II) Compound

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IN papers[1,2] dealing mainly with the chemistry of bis-(trimethylsilyl)amine, Bürger and Wannagat reported the preparation of tris(hexamethyldisilylamine)-iron(III) and -chromium(III). In conjunction with our spectroscopic and magnetic studies on these and related compounds,[3] we have carried out an X-ray diffraction analysis of the iron compound and find it to be truly three-co-ordinate. This is the first reported structure of a monomeric three-co-ordinate transition-metal compound. Hexagonal columns of tris(hexamethyldisilylamine)iron(III) were obtained from the reaction involving lithium bis(trimethylsilyl)amine and iron(III) chloride in benzene. Single crystals used in the analysis were sealed *in vacuo* in Lindemann capillaries.

Crystal Data. $C_{18}H_{54}Si_6N_3Fe$, $M = 537{\cdot}06$, trigonal, $a = 16{\cdot}112$, $c = 8{\cdot}556$ Å, $D_m = 1{\cdot}06$, $Z = 2$, $D_c = 0{\cdot}96$, space group $P31c$ or $P\bar{3}1c$. The latter was chosen after inspection of the three-dimensional Patterson map, and the refinement has vindicated this choice. The intensity data were recorded with Mo-K_α radiation on a Siemens diffractometer, giving a total of 1063 reflections with intensities greater than background. No absorption corrections have been made [μ (Mo $-K_\alpha$) $= 5{\cdot}9$ cm.$^{-1}$]. The presence of only two molecules in the unit cell requires the molecular symmetry D_3, with the iron and nitrogen atoms in special positions. The silicon positions were determined from the Patterson map and the carbon atoms from the first electron-density synthesis phased on iron, nitrogen, and silicon. Full-matrix least-squares refinement, with anisotropic temperature factors gave an R factor of 0·094.

The arrangement of the ligands around the iron atom is seen in the Figure which shows the molecule viewed down the c axis. The (FeN_3) and $(FeNSi_2)$ groups are planar by symmetry, and make an angle of 49° with each other. The Fe–N bond length of **1·918** ± **0·004** Å compares with other reported values[4] which range from 1·95—2·02 Å, for a single bond, to 1·83 Å where significant π-bonding is postulated.

The Si–N bond length of **1·731** ± **0·003** Å is similar to other values where p_π–d_π bonding has been suggested.[5] Examination of non-bonding contacts in the molecule shows that the planarity of the ($\mathrm{FeNSi_2}$) groups (Fe–$\hat{\mathrm{N}}$–Si = 119·38 ± 0·22° and Si–$\hat{\mathrm{N}}$–Si = 121·24°) is not a consequence of steric requirements, and is therefore consistent with π-electron delocalization. Si–C bond-lengths (mean 1·886 ± 0·012 Å) and angles (107·16 ± 0·55°) are normal.[6]

Full details of this analysis and that of the isostructural chromium(III) compound will be published elsewhere.

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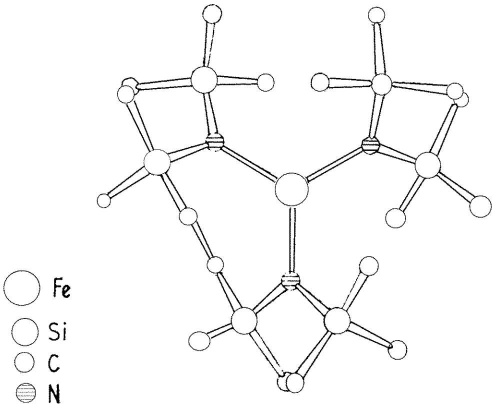

FIGURE

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