Crystal and Molecular Structure of Tris(hexamethyldisilylamido)iron(III)

By **M. B. Hursthouse** * and **P. F. Rodesiler**, Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction methods from diffractometer data by Patterson and Fourier methods and refined by least squares to *R* 0·094 for 1051 independent observed intensities. The crystals are trigonal, space group $P\bar{3}1c$ with a = 16·112 and c = 8·556 Å, Z = 2. The molecule has D_3 symmetry, with an angle of 49·2° between the FeN_3 and NSi_2 planes. The Fe–N bond, at 1·917(4) Å is somewhat shorter than values found in other compounds. Bond lengths and angles involving the other atoms are normal.

TRIS(HEXAMETHYLDISILYLAMIDO)IRON(III) was first prepared by Bürger and Wannagat.[1] Later studies [2,3] on its spectroscopic and magnetic properties gave results consistent with its formulation as a monomeric, three-co-ordinate molecule. In order to confirm this, we have carried out a single-crystal *X*-ray diffraction analysis, and present here the final results. A preliminary report has appeared elsewhere.[4]

EXPERIMENTAL

Crystals were prepared as described previously [1] as hexagonal columns from benzene. Single crystals used in the analysis were sealed *in vacuo* in Lindemann capillaries.

Crystal Data.—$C_{18}H_{54}FeN_3Si_6$, M = 537·06, Trigonal, a = 16·112(8),† c = 8·556(8) Å, U = 1922(5) Å^3, D_m = 1·06, Z = 2, D_c = 0·96, $F(000)$ = 586. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 5·9 cm^{-1}. Oscillation and Weissenberg photographs recorded with the crystal set about c showed the Laue symmetry to be $\bar{3}m$. Reflections of the type $hh\bar{2}hl$ for l odd were systematically absent and thus the space group is either $P\bar{3}1c$ or P31c.

Intensities were measured, by use of Mo-K_α radiation, for a crystal of dimensions *ca*. 0·1 × 0·1 × 0·6 mm, mounted about the needle axis (c), on a Siemens automatic four-circle diffractometer (A.E.D.), by the θ—2θ scan technique, incorporating a five-point measuring routine. Within a preset maximum time limit of 1·2 s per step (0·01°), measuring times were automatically chosen to give reasonably constant total counts for all reflections. The 060 reflection was used as a reference and measured every 20 reflections. During the course of the data collection, its intensity did not vary by $> \pm 2\%$. Of 1138 reflections measured out to a θ limit of 25°, 1051 had intensities significantly above background with $I > 2{\cdot}4\sigma(I)$.

These data were used to compute a three-dimensional Patterson synthesis, from which the co-ordinates for the iron, nitrogen, and silicon atoms were easily derived. The interpretation was consistent with a D_3 molecular symmetry, suggesting that the space group was the centrosymmetric $P\bar{3}1c$. Most of the following calculations were made on this assumption. All carbon atoms were located on an electron-density map computed with signs calculated from the co-ordinates of the other atoms. Refinement in $P\bar{3}1c$, using a full-matrix least-squares program with individual weights from counting statistics for each reflection was quite straightforward. Neutral atom scattering factors taken from ref. 5 were used, and no corrections were made for extinction or absorption. The final *R*, for fully anisotropic refinement was 0·094.

We considered that this *R* value was rather high, in view of the assumed good quality of the crystal and the intensity measurements. It was felt to be unlikely that the neglect of an absorption correction would account for this, in view of the low value of μ. In addition there appeared to be no indication of any significant extinction effects. Refinement in the non-centrosymmetric space group $P31c$ did not lower the *R* significantly and we feel that the assignment of the space group as $P\bar{3}1c$ is correct. A final difference-Fourier map showed a number of residual peaks, with densities up to 2·7 eÅ^{-3} in cavities in the structure, but these did not appear to form any recognisable shape, such as a benzene molecule (the solvent used for crystallisation). Some degree of solvation is, however, compatible with the measured value for the density of the crystals. Although this could not be recorded very accurately, owing to the reactive nature of the compound, the value found is greater than that calculated assuming no solvation. It is probable, therefore, that there are some disordered solvent molecules remaining in the structure and the high *R* factor results mainly from the failure to take these into account. It is unlikely, however, that this will seriously affect the positions found for the atoms of the silylamide molecule, and no further attempts were made to improve the overall model.

TABLE 1

Atomic co-ordinates and thermal parameters

(*a*) Co-ordinates (fractional × 10^4)

Fe			
N	7354(3)	2646(3)	
Si	7046(2)	1730(2)	1165(3)
C(1)	6243(7)	1761(7)	403(12)
C(2)	6433(8)	508(6)	2126(13)
C(3)	8128(8)	1845(9)	110(15)

(*b*) Anisotropic thermal parameters *

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	41(1)	41(2)	114(3)	20(1)	1(2)	1(2)
N	54(6)	54(6)	121(12)	34(6)	−3(9)	−3(9)
Si	64(2)	52(2)	167(4)	31(1)	1(2)	−13(2)
C(1)	95(8)	78(7)	201(18)	44(6)	−49(10)	−43(9)
C(2)	102(8)	48(5)	268(22)	26(6)	−8(12)	0(9)
C(3)	86(8)	103(9)	300(23)	53(7)	28(11)	−50(12)

* β_{ij} in the expression: $f = f_0 \exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta hk + 2\beta_{13}hl + 2\beta_{23}kl] \times 10^{-4}$.

---

† Estimated standard deviations are given in parentheses throughout this paper.

[1] H. Bürger and U. Wannagat, *Monatsh.*, 1963, **94**, 1007.

[2] E. C. Alyea, Ph.D. Thesis, University of London, 1968; E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J.C.S. Dalton*, 1972, 1580.

[3] E. C. Alyea, D. C. Bradley, R. G. Copperthwaite, K. D. Sales, B. W. Fitzsimmons, and C. G. Johnson, *Chem. Comm.*, 1970, 1715.

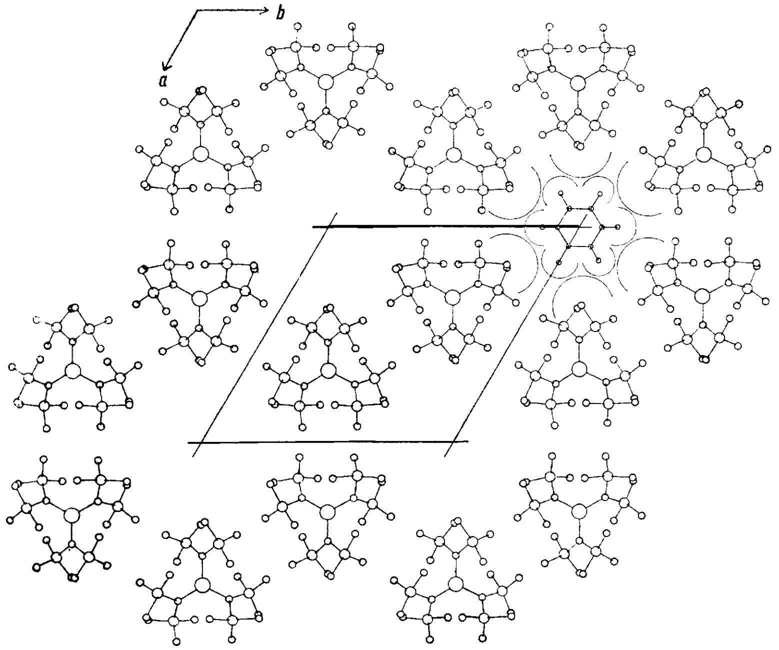
[4] D. C. Bradley, M. B. Hursthouse, and P. F. Rodesiler, *Chem. Comm.*, 1969, 14.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

The final atomic parameters are given in Table 1 and observed and calculated structure factors in Supplementary Publication SUP 20461, 4 pp., 1 microfiche.*

RESULTS AND DISCUSSION

This analysis confirms that the molecule (see Figure) is monomeric and three-co-ordinate. The molecular symmetry is precisely D_3, this being a space group requirement. Thus the FeN_3 and $FeNSi_2$ groups are required to be planar. The dihedral angle between each of the three symmetry-related $FeNSi_2$ planes and FeN_3 plane is 49·2°. This is very similar to the value of 50° reported for the aluminium compound.[6]



View of crystal structure down the *c* axis. The molecule of benzene, which is not part of the structure, has been included to show the size of the axial channel compared with that of a benzene molecule

Bond lengths and angles are given in Table 2. The Si–C bond lengths compare well with the value accepted[7] for a single bond, and angles at the Si atom do not differ appreciably from tetrahedral values.

Table 2

Bond lengths and angles

(*a*) Bond lengths (Å)

Fe–N	1·917(4)	Si–C(2)	1·892(10)
N–Si	1·731(3)	Si–C(3)	1·888(15)
Si–C(1)	1·881(12)		

(*b*) Bond angles (°)

Fe–N–Si	119·4(2)	Si–N–Si	121·2 (by symmetry)
C(1)–Si–C(2)	109·2(5)	C(1)–Si–N	110·7(4)
C(1)–Si–C(3)	105·6(6)	C(2)–Si–N	112·2(4)
C(2)–Si–C(3)	106·6(6)	C(3)–Si–N	112·1(4)

The Si–N bond length, which is less than the sum of the relevant covalent radii, is similar to values found in other compounds,[6] in which N–Si p_π–d_π bonding is assumed. The planarity of the nitrogen atom is also consistent with the presence of π-bonding of this type.

The stabilisation of co-ordinatively unsaturated molecules can usually be attributed to one or other of two factors. The first is steric crowding by ligands already present. The second is the possibility of the central atom gaining extra electrons intramolecularly by ligand–metal π bonding. The silylamide ligand is very bulky and could also act as a π donor (by use of the nitrogen lone-pair), so both these effects may be in use in the tris silylamides.

Steric crowding is likely to result in the presence of a large number of interligand contacts with values close to those of the relevant van der Waals[4] distances. Although the failure to locate the hydrogen atoms makes a precise analysis difficult, one can arrive at a reasonable assessment by using a value of *ca.* 2·0 Å for the effective van der Waals radius of a methyl group. Surprisingly there are only two contacts <4 Å, N(1)–C(1′) (3·64 Å) and C(1)–C(1)′ (3·85 Å), where a prime denotes an atom generated from the corresponding atom in Table 1 by one component of the C_3 operation. Thus, although the Fe atom is fairly well shielded by the hydrocarbon umbrellas of the $SiMe_3$ groups, from further attack by any other sizeable ligand, the molecule is not particularly overcrowded. Indeed, construction of a 'catalin' space-filling model shows that there is a considerable degree of freedom of orientation of the silylamide group

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 2279.

[7] *Chem. Soc. Spec. Publ.*, No. 18, 1965.

in the direction of increasing dihedral angle up to a value of *ca.* 90°.

A structure with this limiting geometry is not likely to occur, however, since this would give rise to maximum repulsions between the lone pairs in the neighbouring nitrogen atoms. A lower dihedral angle is thus favoured, and it is possible that reducing the lone-pair–lone-pair interactions is the deciding factor in the adoption of the geometry found.

A rather qualitative assessment of the bonding situation suggests that π interaction could occur with the geometry found. In D_3 symmetry, the nitrogen p orbitals span representations $E + A_2$ whilst the metal $3d_{x^2-y^2}$, d_{xy}, d_{yz}, d_{xz}, and $3p_x,p_y$ belong to E, and $3p_z$ to A_2. The iron $3p_x,p_y$ are assumed to be used in σ bonding, leaving the rest available for π-bonding if required. Such a simple Group Theoretical approach does not, however, indicate the geometry most favourable for π-bonding. Consequently, it is necessary to seek other evidence of any extra Fe–N interaction.

It is difficult to assess the significance of the value found for the Fe–N bond length, due to the lack of data on structures with three-co-ordinate geometry. Any comparisons which are made are inevitably indirect and rely on a variety of assumptions. One such assumption is that the metal orbitals used in the formation of the bonds in a trigonal planar molecule are basically the same as those used in the formation of the equatorial bonds in a trigonal bipyramidal structure and therefore the 'covalent radii' are the same. Thus we might compare the Fe–N bond lengths in the silylamide with the equatorial bonds in the ion $[Fe(N_3)_5{}^{2-}]$,[8] which have the values of 1·963 and 1·971 Å (the ion has C_2 symmetry). The Fe–N bond lengths in the silylamide are significantly shorter than these, but it is not certain which represents a single bond, *i.e.* whether the bond in the silylamide is shortened, by N–Fe π interaction, or the bond in the azide is lengthened by the presence of the two extra electrons. Sheldrick and Sheldrick[6] considered the possibility of the participation of the aluminium atom in π bonding in the aluminium silylamide, which might be expected to show the effect more distinctly, but decided that the dihedral angle between the N_2Si and AlN_3 planes made it improbable that there would be any appreciable interaction. Nevertheless, a survey of those structures of aluminium compounds which fall into the trigonal bipyramidal class, suggests that the trigonal covalent radius for Al^{III} is *ca.* 1·14 Å. Thus a single Al–N bond would be expected to have a length of *ca.* 1·84 Å. The value in $Al(NSi_2Me_6)_3$ is 1·78 Å. Clearly, more data is needed on this type of system before any real conclusions may be drawn on this aspect of the bonding but, on the basis of the results obtained so far, it is possible that some metal–ligand π interaction is present in addition to the σ bond.

Molecular Packing.—The arrangement of molecules in the unit cell is shown in the Figure. One of the most noticeable features is the channel which runs parallel to and is centered on the *c* axis. The Figure also shows the size of a benzene molecule in relation to this channel. Values of 1·2 and 2·0 Å for the van der Waals radii of a hydrogen atom and a methyl group respectively were used for this construction, which shows that any solvent occluded in this cavity will be very loosely held. It is possible that occlusion of solvent occurs when the crystals are forming, but that much of this tends to drain out when the crystals are removed from the solution. The electron density found in the channel on the final difference-Fourier map could then arise from the remaining haphazardly oriented, benzene molecules. Failure to account for these in the final model could be the cause of the high R factor. This was borne out to some extent when some of the reflections showing poor agreement were left out of the refinement; the heights of most of the residual peaks were reduced to *ca.* $\frac{1}{3}$ of their original value. It was comforting to note that when this was done, the co-ordinates of the atoms in the silylamide did not change by $>1\sigma$. We therefore felt that it was not worthwhile to attempt to improve the model further.

We thank the TAM Division of the National Lead Company for financial support (to P. F. R.) and Professor D. Rogers for use of the A.E.D.

[2/708 *Received, 27th March,* 1972]

---

[8] B. J. Drummond and J. S. Wood, *Chem. Comm.*, 1969, 1373.