Three-co-ordinate Scandium(III) and Europium(III); Crystal and Molecular Structures of their Trishexamethyldisilylamides

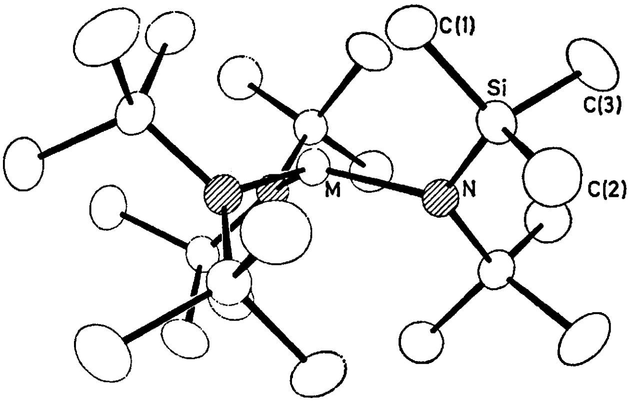
By Joginder S. Ghotra, Michael B. Hursthouse,* and Alan J. Welch
(Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS)

Summary Single-crystal X-ray studies have shown the trishexamethyldisilylamides of scandium(III) and europium(III) to have unusual pyramidal three-co-ordinate structures.

In continuation of our studies of compounds containing the hexamethyldisilylamide ligand, we have collected and refined single-crystal X-ray data for the tris-silylamides of scandium and europium. We report here preliminary details of their structures, which show a significant difference from those of the analogous derivatives of aluminium,[1] iron,[2] and other first-row transition metals.[3]

Crystal data: $[C_{18}H_{54}N_3Si_6M]$, M = Sc, Eu; both compounds crystallise in the same trigonal space group, $P31c$, as $Fe(NSi_2Me_6)_3$ with $a = 16{\cdot}16$, $c = 8{\cdot}53$ Å for M = Sc, $a = 16{\cdot}48$, $c = 8{\cdot}41$ Å for M = Eu, and $Z = 2$ in each case. The molecules must therefore occupy the same D_3 site symmetry as in the Fe compound.

Intensity data were recorded on a G.E. XRD6 manual diffractometer in a manner described previously.[4] Using the atomic parameters found for the iron compound as a starting point, refinement for both compounds gave R values of *ca.* 0·09 and reasonable atomic parameters except for the U_{33} values for the metal atoms, which were of the order 0·35 Å^3, compared with *ca.* 0·04 Å^3 for U_{11} and U_{22}. The refinement was successfully completed (R values of *ca.* 0·06) with "half metal atoms" sited *ca.* 0·04 Å above and below the N_3 plane. Although these results can easily be explained in terms of disorder of a pyramidal molecule, they do imply a rather unusual type of pyramidal structure for the individual molecules. The three silylamide ligands retain the D_3 configuration found in the planar tris-silylamides. The normality of the ligand bond lengths and angles (Si–C distances in both compounds all lie in the narrow range 1·87—1·89 Å) confirming the validity of this ordered model. Similarly, the metal–nitrogen lengths of 2·049 (Sc–N) and 2·259 Å (Eu–N) for the pyramidal structure are chemically more sensible than those derived for a completely planar molecule, 1·963 and 2·168 Å for Sc and Eu, respectively.



Figure

The basic molecular structure is shown in the Figure. The pyramidal N–M–N angles of 115·5 and 116·6° for the Sc and Eu compounds are similar to that of 117·3° in the $Cr(NSi)_3$ group in $ONCr(NSi_2Me_6)$,[5] but in this latter case, the silylamide ligands adopt a truly pyramidal configuration around the metal with the Cr–N bond coincident with the bisector of the Si–N–Si angle.

The adoption of this unusual structure by the Sc and Eu compounds can be tentatively explained in terms of bonding which is predominantly ionic and thus stereochemically less rigid. Dipole moment studies indicate that the molecule is planar in solution since its dipole moment is zero. It is thus suggested that the loss of planarity occurs on formation of the crystalline phase, when the metal ion is squeezed out of the co-ordination plane by a symmetrical contraction arising as a result of intramolecular-interligand van der Waals attractions. Even in the structure as found, the shortest interligand carbon–carbon contact is only *ca.* 3·89 Å. The changes in N–N contacts in the co-ordination sphere, which under this description would be ionic repulsions, when going from a planar structure to that found, are very small (ΔN–N *ca.* 0·07 Å) and involve energy changes (2—3 kcal mol^{-1}, even assuming almost complete ionisation) well within the range usually associated with van der Waals forces. Some degree of support for the idea of ionic bonding is found in the geometry of the silylamide ligand in the Eu compound, where the N–Si bond length of 1·68 Å and Si–N–Si angle of 129·4° are similar to values found for the anion in $[KNSi_2Me_6{\cdot}2Dioxan]$.[6] The ligand geometry in the scandium compound is more normal, however, with Si–N at 1·73 Å and Si–N–Si at 121°.

We thank the S.R.C. for support of this work.

(*Received*, 26*th June* 1973; *Com.* 923.)

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