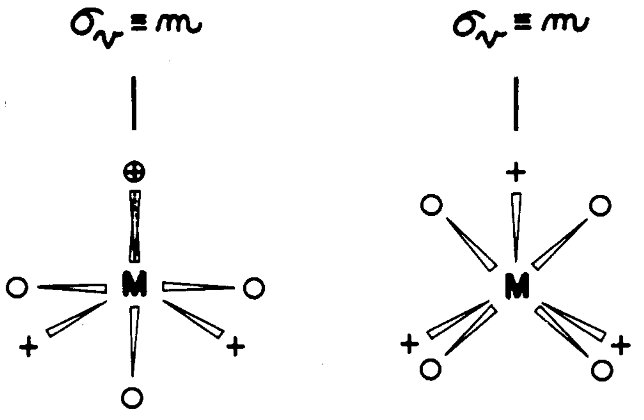

(a) (b)

Fig. 2.—Representation of two general types of the 4:3 orientation of seven ligands about a central metal atom M. The symbol + represents each of the three ligands related by a threefold axis and the symbol O each of the four ligands related by a fourfold axis. These localized principal rotation axes, which are coincident, are both perpendidular to the plane of the paper. Note that the two conformations are related to each other by a 45° rotation of the four ligands about the fourfold axis. (a) corresponds to the seven-coordination found in $Se_2Fe_3(CO)_9$; (b) corresponds to the NbF_7^{2-} type structure.

Previously reported seven-coordinated configurations[13] consist of a pentagonal bipyramid[14,15] (including a symmetrically distorted version)[16,17] related to the dodecahedral type of eight-coordination,[17] a NbF_7^{2-} (or TaF_7^{2-}) type structure,[18] and a ZrF_6^{3-} type structure.[19,20]

The NbF_7^{2-} structure of *idealized* C_{2v} symmetry is described as obtained by the insertion of a seventh atom along the normal to one of the square faces of a trigonal prism.[18] Alternatively, we feel that this configuration can be envisioned as a 4:3 distribution of ligands with a resulting *idealized* fourfold axis (relating four ligands with one another) approximately coincident with an *idealized* threefold axis (relating the other three ligands with one another).[21] In this case, however, the three ligands are so oriented with respect to the other four that the vertical mirror plane which encompasses the central metal and one threefold ligand intersects the mid-points of the opposite edges of the basal square plane formed by the four ligands related by the fourfold axis (Fig. 2 (b)). This configuration is related to the fundamental one described for $Se_2Fe_3(CO)_9$ (Fig. 2 (a)) by a 45° rotation of the four symmetry-related ligands about the fourfold axis relative to the other three ligands.

The seven-coordinated structure involving the introduction of the seventh ligand along a threefold axis of an octahedron[22] (*i.e.*, corresponding to its addition along the normal to an octahedral face) has been formulated for ZrF_7^{3-}[19] (and $NbOF_6^{3-}$)[20] but more recent X-ray results[15] strongly indicate that ZrF_7^{3-} (and consequently $NbOF_6^{3-}$) instead have a pentagonal bipyramidal configuration. A *considerable symmetrical distortion* of the octahedral type model *can lead* to the *idealized* configuration found for $Se_2Fe_3(CO)_9$.

An unemphasized seven-coordinated configuration results from the junction of two octahedra at a common edge, where in addition a direct metal–metal interaction (presumably involving the overlap of d_{xy} orbitals) is necessary to satisfy the susceptibility requirements. Examples are NbI_4,[24] $[Mo(OC_6H_5)_3Cl_2]_2$,[25] and $[C_5H_5Fe(CO)_2]_2$[26] (the $C_5H_5^-$ group can be shown to occupy three octahedral coordination sites).

Another diamagnetic isomer of $S_2Fe_3(CO)_9$ has been synthesized and characterized recently by King.[27] As a result, crystals of the Hieber–Gruber sulfur isomer[2] were prepared and consequently shown by single crystal examination[28] to be isomorphous with those of $Se_2Fe_3(CO)_9$. The structural relationship between King's sulfur isomer and the Hieber–Gruber isomer as yet is unclear.

Acknowledgment.—The authors wish to express their appreciation to Professor W. Hieber and Dr. W. Beck for furnishing a sample of $Se_2Fe_3(CO)_9$ and for their interest in this problem. We also wish to acknowledge the financial assistance obtained from the National Science Foundation (Grant No. 86-3474) and the use of the CDC 1604 computer of the Numerical Analysis Laboratory of the University of Wisconsin.

[13] *Cf.* L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp. 179–180.

[14] W. H. Zachariasen, *Acta Cryst.*, **7**, 783 (1954).

[15] W. H. Zachariasen, *ibid.*, **7**, 792 (1954).

[16] J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

[17] R. D. Burbank, *Acta Cryst.*, **15**, 1207 (1962).

[18] J. L. Hoard, *ibid.*, **61**, 1252 (1939).

[19] G. C. Hampson and L. Pauling, *J. Am. Chem. Soc.*, **60**, 2702 (1938).

[20] M. B. Williams and J. L. Hoard, *ibid.*, **64**, 1139 (1942).

[21] Two independent, equivalent choices of such a 4:3 distribution can be made for NbF_7^{2-} which approximately satisfy the above imposed symmetry relationships.

[22] Each Fe in the molecule $Fe_2(CO)_9$, which was shown[23] to consist of two octahedra joined at a common face, would possess this type of seven-coordination provided of course that the observed diamagnetism of the compound is explained by the assumption of a direct Fe–Fe bond.

[23] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

[24] L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962).

[25] *Cf.* P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).

[26] O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

[27] R. B. King, *Inorg. Chem.*, **2**, 326 (1963).

[28] We are indebted to Dr. C. H. Wei of this laboratory for carrying out this work.

CONTRIBUTION FROM THE MIDWEST
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N-Trimethylsilylhexamethylcyclotrisilazane[1]

BY L. W. BREED AND R. L. ELLIOTT

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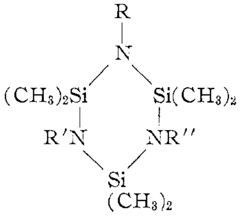
Although two of the N-substituted trimethylsilyl derivatives of hexamethylcyclotrisilazane (I) have been reported in the literature,[2] N-trimethylsilylhexamethylcyclotrisilazane (II) has eluded preparation.

[1] This research was supported by the United States Army under Contract DA-23-072-ORD-1687 and monitored by Rock Island Arsenal, Rock Island, Illinois.

[2] W. Fink *Helv. Chim. Acta*, **45**, 1081 (1962).

Table I

Properties of Hexamethylcyclotrisilazane and its N-Substituted Trimethylsilyl Derivatives



I, R = R′ = R″ = H
II, R = R′ = H; R″ = $Si(CH_3)_3$
III, R = H; R′ = R″ = $Si(CH_3)_3$
IV, R = R′ = R″ = $Si(CH_3)_3$

	Boiling point, °C. (mm.)	n^t_D	d^t	MR_D Calcd.[d]	Exptl.
Hexamethylcyclotrisilazane[a] (I)	111–112 (85); 188 (756)	1.4448^{20}	0.9196^{20}	63.53	63.51
N-Trimethylsilylhexamethylcyclotrisilazane (II)	112–113 (10); 255 (760[c])	1.4596^{26}	$.931^{27}$	86.57	85.75
N,N′-Bis-(trimethylsilyl)-hexamethylcyclotrisilazane[b] (III)	81.0–81.7 (2); 260 (760[c])	1.4420^{20}	$.973^{20}$	109.62	98.95
N,N′,N″-Tris-(trimethylsilyl)-hexamethylcyclotrisilazane[b] (IV)	143–145 (0.09); 333 (723)	1.4823^{20}	$.940^{20}$	132.66	132.31

[a] Reference 6. [b] Reference 1. [c] Extrapolated. [d] A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58,** 174 (1954).

This compound has been found to be accessible *via* the monosubstituted sodium derivative of I, thus completing the series I, II, N,N′-bis-(trimethylsilyl)-hexamethylcyclotrisilazane (III), and N,N′,N″-tris-(trimethylsilyl)-hexamethylcyclotrisilazane (IV).

Fink[2] reported the preparation of III and IV from the di- and trisubstituted lithium derivatives of I and chlorotrimethylsilane at 130–160°. The lithium derivatives were prepared by treating I with the stoichiometric quantity of butyllithium. However, attempts to condense the monosubstituted lithium derivative of I with chlorotrimethylsilane led to disproportionation; approximately equimolar quantities of I and III were isolated.

Tris-(trimethylsilyl)-amine may be prepared through either the lithium or the sodium derivative of hexamethyldisilazane.[3,4] It appeared possible, therefore, to prepare II from a sodium intermediate since both compounds contain three organosilyl groups substituted about a central nitrogen atom. The procedure, which followed a method originally described by Goubeau,[3] gave II in good yields.

II was characterized by elemental analysis, infrared spectrum, and proton magnetic resonance spectrum. The infrared spectrum of II was consistent with the proposed structure. In comparing the spectra of I, II, and III, a band at about 1030 cm.$^{-1}$, which Fink had observed in organosilyl-substituted cyclosilazanes, was absent in I, weak in II, and strong in III. The band is also reported to be strong in IV.

Three peaks attributable to methyl protons were observed in the proton magnetic resonance spectrum of II, but the nitrogen proton peak was too broad to be clearly defined. The methyl proton ratio of the peaks observed at −1.32, −1.38, and −1.45 p.p.m. (cyclohexane reference)[5] was 4.0 : 2.9 : 2.0, corresponding to the calculated ratio, 4.0 : 3.0 : 2.0.

It is of interest to note in Table I the similar vapor pressures of II and III and the random variation in refractive index and density in the series. Molar refractivities were calculated for each member of the series, the data for I, III, and IV being taken from the literature, and the values obtained for III indicate that the reported refractive index and density for this compound are not in line with those that would be expected for the proposed structure. The proton magnetic resonance spectrum of a sample of III, prepared by the method described in the literature and having the reported boiling point and refractive index, consisted of four bands at −1.26, −1.46, −1.48, and −1.51 p.p.m. (cyclohexane reference) with relative intensities of about 3.0 : 3.4 : 0.9 : 2.3, respectively. III requires three peaks with relative intensities of 3.0 : 2.0 : 1.0. These data suggest that the identity of compound III reported by Fink should be reconsidered.

When II was heated at 160 ± 5° for 5 hr. under nitrogen, no significant change in the refractive index of the product ($n^{26}D$ 1.4593) was observed. Since these conditions parallel those employed in condensing the lithium intermediate, II must be considerably more stable than originally suggested. Furthermore, the accessibility of II through the sodium salt suggests that the use of lithium was primarily responsible for the observed disproportionation.

Experimental

Hexamethylcyclotrisilazane was prepared according to the method of Osthoff and Kantor.[6] Styrene was redistilled immediately prior to use. The reactons were carried out in an atmosphere of dry nitrogen.

N-Trimethylsilylhexamethylcyclotrisilazane.—A rapidly stirred suspension of 10.4 g. (0.45 g.-atom) of sodium in 200 ml. of refluxing 1,4-dioxane was treated by dropwise addition with a mixture of 86.6 g. (0.4 mole) of hexamethylcyclotrisilazane and 50 ml. of styrene. After the addition was complete, the mixture was refluxed 5 hr., then cooled at 30° while 54.3 g. (0.5 mole) of chlorotrimethylsilane was added over a period of 1 hr. The product was refluxed 3 hr., cooled, filtered to remove sodium chloride, and devolatilized under reduced pressure. In several experiments yields of 55–69% were obtained when the residue

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(3) V. J. Goubeau and J. Jimenez-Barbera, *Z. anorg. allgem. Chem.*, **303,** 217 (1960).

(4) U. Wannagat and H. Niederprum, *ibid.*, **308,** 337 (1961).

(5) Determined with a Varian Associates Model A-60 n.m.r. spectrometer with cyclohexane as an internal standard. The proton ratio was calculated from the areas of the integrated peaks. Chemical shifts are reported as Δ (cyclohexane) × 10^6/oscillator frequency (c.p.s.).

(6) R. C. Osthoff and S. W. Kantor, *Inorg. Syn.*, **5,** 61 (1957).

was fractionally distilled through an 11 × 350 mm. column packed with glass beads. The properties of the product are given in Table I.

Anal.[7] Calcd. for $C_9H_{29}N_3Si_4$: C, 37.06; H, 10.02; N, 14.40; Si, 38.52. Found: C, 36.68; H, 9.72; N, 14.10; Si, 38.32.

Acknowledgment.—The authors wish to express their appreciation to Dr. J. J. Downs for the preparation and interpretation of the n.m.r. spectra.

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[7] Analyses by Spang Microanalytical Laboratory, Box 1111, Ann Arbor, Michigan.

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Magnetic Studies of Mixed Ligand Complexes of Iron(II)

BY W. A. BAKER, JR., AND H. M. BOBONICH

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Mixed ligand complexes of Fe(II) having the general formula $[Fe(phen)_2X_2]$ (hereafter referred to as the bis complexes; phen = 1,10-phenanthroline) have been reported by a number of investigators.[1-3] Basolo and Dwyer[1] prepared the chloride and reported it to be high spin with μ = 5.3 B.M. at room temperature. Previously, Klemm[2] had reported the bromide and iodide to be diamagnetic. In view of the well accepted order of ligand field strengths for halide ions, these results seem unlikely unless there are important structural differences between the chloride on the one hand and the bromide[4] and iodide on the other.

Schilt[3] has also prepared the analogous cyanide complex and finds it to be low spin but exhibiting paramagnetism corresponding to a room temperature moment of 0.68 B.M. The moment he suggests is due to temperature-independent paramagnetism which is known to be appreciable for low spin Co(III) complexes and is expected for other d^6 systems.[5]

It is the purpose of this note to report results which resolve the apparent anomaly found for the halide complexes, a new method for their preparation, a thiocyanate complex not previously reported,[4] as well as data on the low spin cyanide complex.

Experimental

Preparation of $[Fe(phen)_2X_2]$.—$[Fe(phen)_2(CN)_2]\cdot 2H_2O$ was prepared by the method of Schilt.[3] *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})(CN)_2(H_2O)_2$: C, 61.92; H, 4.00; N, 16.67. Found: C, 62.13; H, 3.86; N, 16.86.

For the preparation of the bis-halides, the pyrolysis techniques of Klemm[2] and Basolo and Dwyer,[1] *i.e.*, the heating of the appropriate $[Fe(phen)_3]X_2$ (hereafter referred to as the tris complexes) under vacuum was attempted. Although this method seemed to give some of the desired product, the analyses on different portions of the same sample were slightly variable and the products were not homogeneous in appearance. Therefore, this method was used only in the case of the iodide, for which other methods of preparation were unsuccessful.

The method used for the other halides as well as the thiocyanate was to suspend the appropriate tris complex in a moderate boiling inert solvent under reflux conditions. The suspended material gradually changed from the characteristic red color of the tris complex to a homogeneous blue. Periodic checks of the magnetic susceptibility indicated a change from low spin to high spin. The suspended material was filtered, washed with pure refluxing solvent, and dried under vacuum previous to analysis and magnetic measurements.

$[Fe(phen)_2I_2]$ was prepared by heating $[Fe(phen)_3]I_2$ under vacuum at 186° for about 7 days. *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})I_2]$: C, 43.01; H, 2.41; N, 8.35. Found: C, 43.44; H, 2.44; N, 8.36.

$[Fe(phen)_2Cl_2]$ was prepared by suspending $[Fe(phen)_3Cl_2]$ in CCl_4 and refluxing for 36 hr. *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})Cl_2]$: C, 59.16; H, 3.28. Found: C, 59.64; H, 3.39.

$[Fe(phen)_2Br_2]$ was prepared by suspending $[Fe(phen)_3]Br_2$ in methylcyclohexane and refluxing for 100 hr. *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})Br_2]$: C, 50.04; H, 2.80; N, 9.72. Found: C, 49.88; H, 2.78; N, 9.34.

$[Fe(phen)_2(SCN)_2]$ was prepared by refluxing $[Fe(phen)_3]\cdot(SCN)_2$ in CCl_4 for 48 hr. *Anal.* Calcd. for $[Fe(C_{12}N_4H_{16})(SCN)_2]$: C, 58.65; H, 3.03. Found: C, 58.33; H, 2.92.

Magnetic Measurements.—Susceptibilities were obtained using a Gouy balance equipped for measurements over the range 77–300°K. $Hg[Co(SCN)_4]$ was used as a calibrant. Diamagnetic corrections were made using values given by Figgis and Lewis.[6] All compounds were measured at three field strengths and showed no field dependence. The moments are accurate to at least ±0.05 B. M. at the high values and ±0.10 at the low values.

Microanalyses.—C, H, and N analyses were performed by the Schwaazkopf Microanalytical Laboratories, Woodside, N. Y.

Discussion

As can be seen from Tab'e I, the paramagnetism of the bis-cyanide is in fact temperature independent. The values of χ_{corr}^M are reasonably constant over a 200° range. Although there is some deviation in the observed susceptibilities (see Table I), these are readily understood when it is realized that the forces involved in the measurements on the bis-cyanide are of the order of 1 mg. The results given represent a typical set of values obtained for a given sample. Values for other samples show the same general results; that is, susceptibilities in the range 200 ± 50 × 10^6.

TABLE I
MAGNETIC DATA FOR $[Fe(phen)_2(CN)_2]\cdot 2H_2O$

T, °K.	χ_{corr}^M (× 10^6)	μ_{eff}, B.M.
297	235	0.74
257	235	.70
193	159	.50
156	185	.48
112	243	.46

The data for the bis-halides are given in Table II.

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[1] F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, **76**, 1454 (1954).

[2] V. W. Klemm, *et al.*, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

[3] A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

[4] K. Maděja and E. Konig, *J. Inorg. Nucl. Chem.*, **25**, 377 (1963), have recently reported the preparation of the bis-bromide and thiocyanate and find both to be high spin, in agreement with our results.

[5] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

[6] B. N. Figgis and J. Lewis, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.