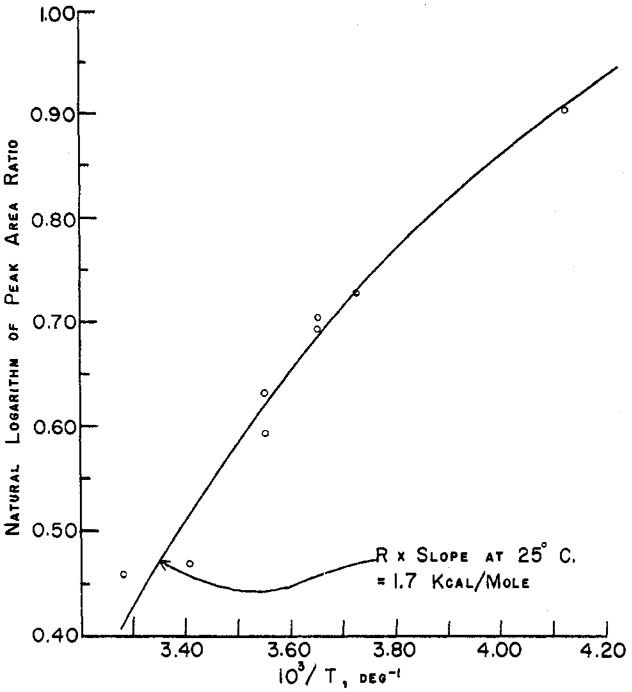
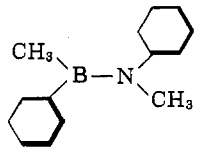
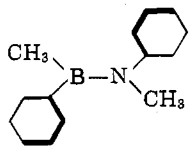


Fig. 1.—Temperature dependence of the equilibrium ratio of isomers of (methylphenylamino)-methylphenylborane.

with the experimental results) if steric effects produce not only nonplanar arrangement of the phenyl groups but also cause a minor tilting about the B–N linkage. This tilting then can lead to different magnetic environments for the corresponding methyl groups in the two forms.



(a)



(b)

This assumption could also provide an explanation for the behavior of the N-methyl resonances, where the merged peak at 75° is observed at 6.90 p.p.m. Normally, merged peaks have a chemical shift which is the concentration-weighted average of separate isomer peaks, as was observed for the B-methyl resonance.

Experimental

(Methylphenylamino)-methylphenylborane was distilled into Raman cuvettes under high vacuum; greased joint connections were avoided. A slight fluorescence of the compound was observed in the blue region but it was possible to record useful spectra. The ratio of line intensities to the background was comparable to those of other Raman spectra of aromatic substituted aminoboranes reported previously.[6d] The Raman spectra were recorded with a Cary Raman spectrophotometer Model 81 of a liquid sample at room temperature and at 125° and of a solidified sample which had crystallized after prolonged standing in the Raman cuvette at room temperature. The spectrum of the crystalline material was less intense due to a generally increased amount of scattered light in the spectra of solid materials. However, all lines of medium or strong intensity which were observed in the spectra of the liquid species were also found in the spectrum of the crystalline material at identical frequencies.

Infrared spectra were obtained of mulls in Kel-F and Nujol and of a carbon tetrachloride solution with a Perkin-Elmer Model 21 double beam spectrophotometer using sodium chloride optics.

Nuclear magnetic resonance data were obtained on a Varian Model V-4300-B spectrometer at 40 and 12.8 Mc. and a Varian 4013-B at 60 Mc. The final p.m.r. spectra were obtained on a Varian V-4300-2 high-resolution spectrometer at 60 Mc., using the Varian variable-temperature probe. Side bands were applied by an audio oscillator, monitored continuously by an electronic counter, and peak separations were taken as an average of measurements on replicate spectra. The sample was dissolved to a concentration of approximately 35% in carbon tetrachloride, and tetramethylsilane was used as an internal standard. In addition, spectra were recorded of the neat liquid.

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Structure of $Se_2Fe_3(CO)_9$ and Evidence for a New Type of Seven-Coordinated Metal[1a]

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Received March 13, 1963

We wish to report the structural determination of $Se_2Fe_3(CO)_9$ by X-ray diffraction which not only provides definite stereochemical information concerning the iron carbonyl chalcogenides, $X_2Fe_3(CO)_9$ (where X = S, Se, and Te),[2] and related derivatives, but also confirms the existence of a new type of seven-coordinated metal. These relatively stable trinuclear metal complexes were first prepared and characterized by Hieber and Gruber[2] as diamagnetic, hydrophobic solids which display similar infrared absorption bands characteristic of only terminal carbonyl groups.

The dark violet crystals of $Se_2Fe_3(CO)_9$ are triclinic with reduced cell parameters: a = 6.83 Å., b = 9.22 Å., c = 13.12 Å., α = 93°50′, β = 94°20′, γ = 110°40′. There are two molecules per unit cell in the general positions of the space group $P\bar{1}$. The molecular parameters have been obtained from a least-squares refinement[3] and error analysis[4] based on 2003 independent reflections. Weights for the least-squares process were based on the precision of the visually-judged photographic data obtained with Mo Kα radiation. The discrepancy index after refinement with individual isotropic temperature factors is $R_1 = 13.5\%$.

The molecular configuration (Fig. 1) consists of an $Se_2Fe_2(CO)_6$ fragment of *idealized* C_{2v}-2mm symmetry bonded to an $Fe(CO)_3$ group *via* two bent Fe–Se bonds and two bent Fe–Fe bonds. The *idealized* configuration

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(1) (a) Presented in part at the National Meeting of the American Crystallographic Association, Cambridge, Mass., March 28–30, 1963. (b) National Science Foundation Predoctoral Fellow.

(2) W. Hieber and J. Gruber, *Z. anorg. allgem. Chem.*, **296**, 91 (1958).

(3) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37 (1959).

(4) W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," Oak Ridge National Laboratory Report 59-12-3 (1959).

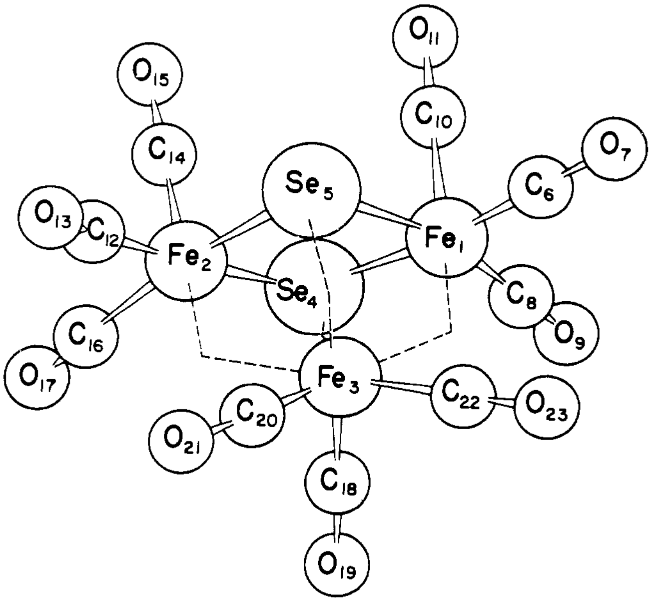

Fig. 1.—Molecular configuration of $Se_2Fe_3(CO)_9$: The iron–iron and iron–selenium bond distances are Fe_1–Fe_3 = 2.64 Å., Fe_2–Fe_3 = 2.66 Å., Fe_1–Se_4 = 2.34 Å., Fe_1–Se_5 = 2.35 Å., Fe_2–Se_4 = 2.35 Å., Fe_2–Se_5 = 2.36 Å., Fe_3–Se_4 = 2.34 Å., Fe_3–Se_5 = 2.37 Å. (all with e.s.d. 0.017 Å.); the nonbonding distances are $Fe_1 \cdots Fe_2$ = 3.51 (e.s.d. 0.017 Å.) and $Se_4 \cdots Se_5$ = 3.10 (e.s.d. 0.016 Å.). For the nine terminal carbonyls the Fe–C and C–O distances are 1.79 Å. (av.) and 1.14 Å. (av.), respectively (the e.s.d.'s for the individual Fe–C and C–O distances are 0.030 and 0.034 Å., respectively).

for the $Se_2Fe_3(CO)_9$ molecule *preserves* only one vertical mirror plane. This configuration and proposed bonding are in complete accord with the observed diamagnetism of the compound. The heavy atom (*i.e.*, Se and Fe) framework of the molecule can be described as a square pyramid with an Fe situated at the apex and alternate Se and Fe atoms located at the corners of the basal plane. The base to apex distance along an Fe–Fe edge is 2.65 Å. (av.).[5] The only significant distortion from a "true" square-pyramidal configuration is achieved by the movement of the two Se atoms along their respective Fe_3–Se edges directly toward the apical Fe_3; the extent of this symmetrical shift of the Se atoms is that required to make each of the six Fe–Se distances equal to 2.35 Å. (av.). The four basal heavy atoms then form a puckered rhombus with two similar Se–Fe–Se angles of 82.4° (av.), two similar Fe–Se–Fe angles of 96.6° (av.), and a dihedral angle along the Se–Se line of 166°. As a result of this symmetrical distortion *each* of the four other faces of the pyramid forms an isosceles triangle of equal Fe–Se sides with two Se–Fe–Fe angles of 56° (av.) and an Fe–Se–Fe angle of 68° (av.).

Each of the two basal irons (Fe_1 and Fe_2), which are related to each other by the *idealized* mirror plane, is surrounded by three carbonyls and the two seleniums at the vertices of a distorted tetragonal pyramid (Fig. 1). This localized environment is essentially identical with that for the two iron atoms found in $[C_2H_5SFe(CO)_3]_2$.[7] It should be noted that a bent Fe–Fe bond arising from the overlap of octahedral-type iron orbitals is presumed to be mainly responsible for the molecular geometry of $[C_2H_5SFe(CO)_3]_2$; for $Se_2Fe_3(CO)_9$ the sixth octahedral-type orbital of each of the two basal irons also is presumed to form a bent Fe–Fe bond with an appropriate orbital of the apical iron (Fig. 1).

For $Se_2Fe_3(CO)_9$ the remarkably acute bridge Fe-(basal)–Se–Fe (apical) angles of 68° (av.) are identical in magnitude with the Fe–S–Fe angles found in $[C_2H_5SFe(CO)_3]_2$. In both types of compounds each of the chalcogen atoms no doubt has an approximately tetrahedral (or trigonal-pyramidal) configuration involving three bonding pairs and one lone pair of electrons; as postulated for $[C_2H_5SFe(CO)_3]_2$ such sharp angles for $Se_2Fe_3(CO)_9$ presumably would require bent Fe_3–Se bonds.

The coordination of the apical iron atoms is of special interest, since the molecular conformation provides *persuasive* evidence of a new type of seven-coordinated metal. This seven-coordination of the apical iron atom can be viewed from the classical valency theory of localized electron-pair bonds on the basis of *quasi*-equivalence of the seven Fe, Se, and CO ligands which occupy regular coordination sites about the metal atom. Relative to an axis through the apical iron and the centroid of the basal plane of the pyramid, the four basal ligands possess approximately fourfold symmetry and the three carbonyls essentially threefold symmetry. The resulting orientation of the apical $Fe(CO)_3$ fragment with respect to the four basal atoms is such that an *idealized* vertical mirror plane (in this case corresponding to the *idealized* mirror plane of $Se_2Fe_3(CO)_9$) passes through the apical iron, one CO, and two of the basal atoms (*i.e.*, Se_3 and Se_4) and relates the other iron-coordinated atoms in pairs (Fig. 2 (a)).

It is possible to consider a similar 4:3 orientation of ligands about a metal in $[(CH_3)_4C_4NiCl]_2C_6H_6$[8] and $(C_6H_5)_4C_4Fe(CO)_3$[9] where in both cases the metal is symmetrically coordinated to a cyclobutadiene group and three other ligands (*i.e.*, three CO and three Cl, respectively). Since the ligands for these compounds are not individual entities, the bonding directions are not clear-cut; however, our results suggest that for these compounds the metal–ring interaction involves a combination of four equivalent metal orbitals. The symmetrical bending of the substituents attached to the cyclobutadiene ring for these compounds conforms to such a four-point metal–ring attachment.[10]

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(5) This distance corresponds to Fe–Fe distances reported for other iron carbonyl compounds with metal–metal bonds.[6]

(6) *Cf.* E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962).

(7) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

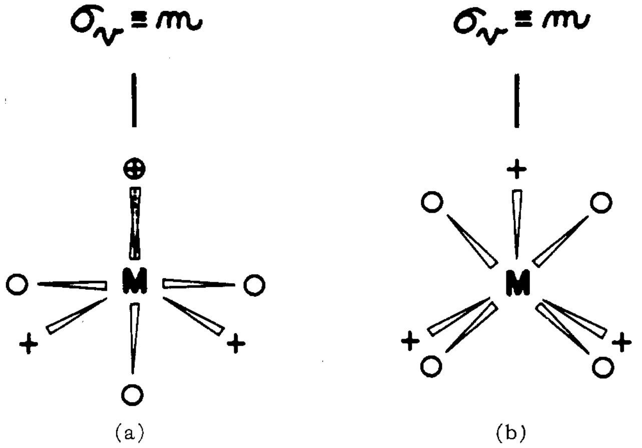
(8) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).

(9) R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1962); R. P. Dodge, private communication, 1963.

(10) A striking example that the detailed molecular geometry of each compound needs to be examined before conclusions on bonding can be reached is shown from the results of an X-ray investigation[11] of π-cyclopentadienyltetrakistrifluoromethylcyclopentadienonecobalt(I), $C_5H_5Co(CF_3)_4C_4CO$, which revealed a cyclopentadienone ring distortion interpreted on the basis of a localized three-point Diels–Alder metal–diene interaction similar to that reported from an X-ray study[12] of 2,4,6-triphenylcycloheptatrienoneiron tricarbonyl.

(11) R. Mason, private communication, 1962.

(12) D. L. Smith and L. F. Dahl, *J. Am. Chem. Soc.*, **84**, 1743 (1962).



(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.

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(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).

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

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

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(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).

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(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.

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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.

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(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).