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New μ-Oxo-heterobinuclear Complex Containing the Fe–O–Si Linkage: Synthesis and Structural Characterization of [FeSALEN]OSi(CH_3)$_3$

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Abstract

The reaction of hexamethyldisilazane with the μ-oxo iron SALEN dimer in toluene under N_2 gives the μ-heterobinuclear title complex, $FeC_{19}H_{23}N_2O_3$-Si. Crystals of the compound are monoclinic, space group $P2_1/c$ with $a = 6.087(2)$, $b = 10.497(3)$, $c = 28.567(7)$ Å, $\beta = 97.78(2)$ and $Z = 4$. Solution of the structure by direct methods led to a final weighted and unweighted R factors of 6.2 and 5.6%, respectively. The coordination geometry of the iron center is square-pyramidal with the iron displaced 0.56 Å from the best least-squares plane of the coordinating oxygens and nitrogens of the SALEN ligand. The Fe–O–Si angle is bent at 142.7°. The Fe–O–Si linkage does not hydrolyze under neutral pH conditions.

Introduction

Titanium and silicon dioxide surfaces may be chemically modified by treatment with hexamethyldisilazane (HMDS) [1]. The HMDS undergoes a condensation reaction with the surface hydroxyl groups, resulting in surface silanization. HMDS also reacts with vanadyl complexes, forming μ-oxo silyl species [2]. The driving force for these reactions seems to be the formation of a silicon–oxygen bond.

In this report, the reaction of HMDS with [FeSALEN]$_2$O, where SALEN is the condensation product of salicylaldehyde and ethylenediamine, is investigated. Formation of an iron–oxygen–silicon linkage from the μ-oxo starting material would involve the cleavage of a thermodynamically stable iron–oxygen bond. The geometry of the bridging linkage in a silanized iron SALEN species is also of interest. Structurally, oxo-bridged iron complexes are unique in that their bridging geometry varies considerably from being linear to bent at 139° with not widely varying ligands. However, most oxo-bridged iron dimers are bent. The reasons for μ-oxo iron complexes preferring a bent geometry are not clearly understood. According to the MO model and SCCC calculations of electronic structure [3], the angular bridge of d^5 systems is more energetically favorable. Replacement of an iron atom with a hetero atom, like silicon, in the bridging linkage could conceivably cause a perturbation in the electronic structure of the remaining iron center. This study undertakes to determine how the bond parameters of the asymmetric M–O–M′ linkage in the μ-heterobinuclear complex differ from the homonuclear analogs.

Experimental

Materials

All chemicals were reagent grade and were used without further purification.

[FeSALEN]$_2$O

The SALEN ligand [4] and the μ-oxo FeSALEN complex [5] were prepared according to the previously reported procedures.

FeSALEN-O-Si(CH_3)$_3$

In a typical preparation, 20 mg of [FeSALEN]$_2$O is suspended in 10 ml of toluene and the system is deaerated with N_2. A large excess (0.5 ml) of HMDS is added via syringe through the serum cap. The reaction mixture is then heated and stirred at 110 °C for several hours until all of the starting materials have gone into solution. At this point, the reaction appears to be complete. Addition of petroleum ether precipitates bright red–orange air-stable needles.

Physical Measurements

Infrared spectra of the solid materials were recorded on a Perkin Elmer 983 spectrometer between 4000 and 500 cm^{-1} as Nujol mulls with NaCl plates. UV–Visible spectra were measured on a Cary 14 spectrophotometer. Magnetic susceptibility measurements were determined by the Evans method on a 200 MHz Bruker/IBM spectrometer.

Growth and Selection of X-ray Data Crystals

X-ray quality single crystals were grown by adding a small amount of petroleum ether to the reaction

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mixture and allowing the solution to stand for several days. The crystals were filtered from the solution and rinsed with a small amount of ethanol and allowed to air-dry. A crystal 0.4 × 0.2 × 0.2 mm was selected for unit cell determination and data collection.

Collection and Reduction of X-ray Diffraction Data

The diffraction data were obtained on an Enraf-Nonius CAD-4 diffractometer controlled by a Digital PDP 11/34 computer with the use of graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$) at room temperature. Unit cell parameters were obtained by the least-squares fitting of 25 centered reflections with the 2θ limits $25° \geqslant 2\theta \geqslant 15°$. The title complex crystallizes in the monoclinic crystal system. The space group was uniquely determined by the systematic absences to be $P2_1/c$. The intensities of three standard reflections were measured every two hours of X-ray exposure and no decay with time was noticed. The data were corrected for Lorentz and polarization effects. The details of data collection are summarized in Table I.

TABLE I. Crystallographic Data and Data Collection Parameters for $C_{19}H_{23}N_2O_3FeSi$

Formula	$C_{19}H_{23}N_2O_3FeSi$
Molecular weight	411
Crystal system	monoclinic
Space group	$P2_1/c$
a (A)	6.807(2)
b (A)	10.497(3)
c (A)	28.567(7)
α (deg)	90.00
β (deg)	97.78(2)
γ (deg)	90.00
V (A^3)	2022.4(1.9)
Z	4
D_{calc} (g cm^{-3})	1.344
Crystal color	red–orange
Radiation	Mo Kα
Diffractometer	Enraf-Nonius CAD-4
Absorption coefficient (cm^{-1})	8.184
Scan speed (deg min^{-1})	variable
Scan technique	θ–2θ
Data collected	2266
2θ Scan range (deg)	1–40
Unique data	1866
Unique data with $I > 2\sigma(I)$	1717
Standard Reflections	3/120
R, %(F_o)	5.6
R_w, %(F_o)	6.2

TABLE II. Positional Parameters for all Non-hydrogen Atoms for $C_{19}H_{23}N_2O_3FeSi$

Atom	x	y	z
Fe	0.9418(2)	0.1867(1)	0.83053(4)
Si	0.8999(4)	0.3660(3)	0.92289(9)
O1	0.7118(9)	0.1126(5)	0.7967(2)
O2	1.0236(9)	0.0310(6)	0.8611(2)
O	0.8489(9)	0.3016(6)	0.8706(2)
N1	0.973(1)	0.2851(7)	0.7668(2)
N2	1.239(1)	0.2397(6)	0.8383(2)
C1	0.664(1)	0.2158(8)	0.7217(3)
C2	0.543(2)	0.2330(10)	0.6783(3)
C3	0.373(2)	0.1661(11)	0.6687(3)
C4	0.312(2)	0.0822(10)	0.7005(4)
C5	0.430(1)	0.0656(9)	0.7434(3)
C6	0.603(1)	0.1320(8)	0.7551(3)
C9	1.277(1)	0.3547(10)	0.8148(4)
C10	1.384(1)	0.1753(10)	0.8620(3)
C11	1.368(1)	0.0617(9)	0.8873(3)
C12	1.537(1)	0.0122(12)	0.9144(3)
C14	1.353(2)	−0.1568(11)	0.9422(4)
C15	1.186(2)	−0.1128(10)	0.9154(3)
C16	1.189(1)	−0.0048(9)	0.8875(3)
C7	0.846(1)	0.2842(9)	0.7297(3)
C8	1.159(2)	0.3545(9)	0.7665(3)
C13	1.532(2)	−0.0940(12)	0.9420(4)
C17	1.062(2)	0.5075(11)	0.9211(4)
C18	1.034(2)	0.2534(12)	0.9651(3)
C19	0.664(2)	0.4157(11)	0.9423(4)

Solution and Refinement of the Structure

The structure was solved by direct methods using MULTAN 78 [6] and refined by successive least-squares and Fourier techniques. Anisotropic thermal parameters were used for all non-hydrogen atoms in the final stages of refinement. Hydrogen atoms were fixed at their calculated positions and were included in structure factor calculations, but were not refined. Table II lists the positions of the non-hydrogen atoms with their standard deviations. The final weighted and unweighted R indices are 6.2 and 5.6%, respectively.

Results and Discussion

Synthesis of the title compound from the reaction of hexamethyldisilazane with the μ-oxo iron SALEN dimer heated in toluene yields a bright red-orange crystalline material, $FeC_{19}H_{23}N_2O_3Si$. These crystals are not sensitive to aerial oxidation or hydrolysis. No decomposition has been observed in our laboratory over a six month period. The compound dissolves readily in dichloromethane and chloroform and is stable to hydrolysis from traces moisture in solution. A ^1H NMR study in D_2O saturated $CDCl_3$ showed no cleavage of the trimethylsilyl group over a two week period. This group gives a paramagnetically broadened resonance around 0.15 ppm. Cleavage should show the growth of a sharp singlet further upfield due to the $(CH_3)_3SiOH$ product which would not be expected to be shifted appreciably by the paramagnetic iron SALEN residue in dilute solution. A reference spectrum of hexamethyldisilazane and its hydrolyzed components were used as comparisons.

Description of the Structure

The crystal structure of the title compound consists of a binuclear μ-oxo bridged complex of trimethyl silane and iron SALEN. The five-coordinate iron center has a square pyramidal geometry as is typical of many planar iron macrocyclic systems. A perspective view of the molecule showing the numbering scheme is given in Fig. 1. Figures 2 and 3 provide stereoscopic views of the molecule and the unit cell packing arrangement, respectively The SALEN moiety adopts the inverted umbrella structure found for both the μ-oxo iron SALEN complex and for the iron(III) SALEN chloride monomer [7, 8]. A tabulation of selected bond distances and angles and the displacement of the iron atom from the coordination plane is given in Table III for the title compound and for some other square pyramidal iron complexes [7–10] A comparison of various MOM′ bond distances and angles, where M′ can be either a metal or silicon atom, is presented in Table IV [11–17].

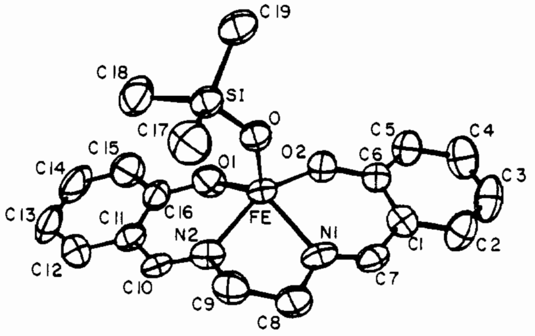

Fig. 1. Numbering scheme for [FeSALEN]OSi(CH_3)$_3$.

As shown in Table III, substitution of the trimethylsilyl group for an iron SALEN moiety produces only slight changes in the coordination geometry of the iron center. Within the iron SALEN moiety, the average Fe–O and Fe–N distances are 1.897 and 2.106 Å respectively. These fall within the range of Fe–O (1.882–1.923 Å) and Fe–N (2.053–3.120 Å) bond distances reported for other

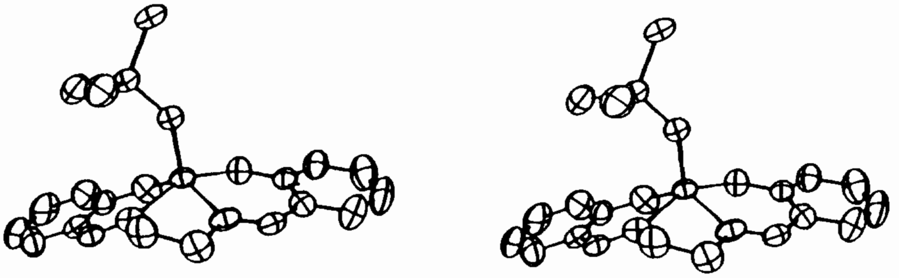

Fig. 2. Stereoview of [FeSALEN]OSi(CH_3)$_3$.

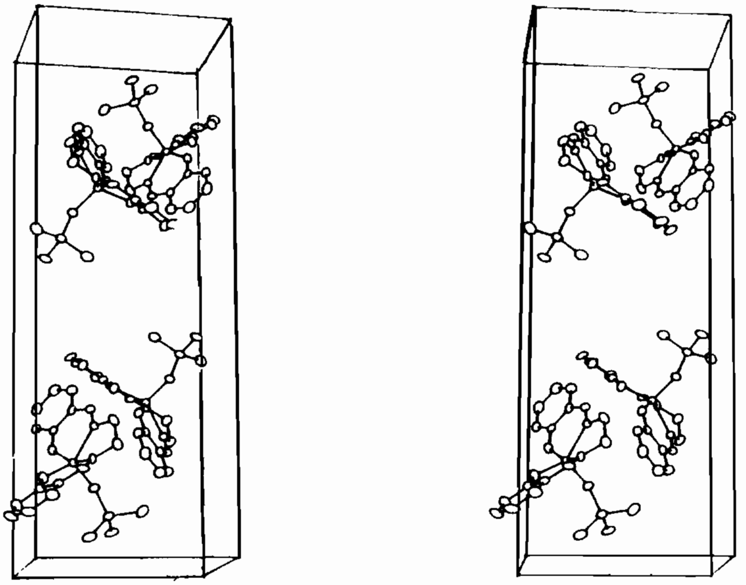

Fig. 3. Unit cell packing of [FeSALEN]OSi(CH_3)$_3$.

TABLE III. Comparison of Coordination Geometry Parameters with those of Related Iron Complexes

Compound	Fe–O–M′	*d*A-average	Fe–O distance	Reference
FeSALEN OSi(CH$_3$)$_3$	142.7(4)	0.56	1.834(6)	This work
[FeSALEN]$_2$O·2py	139.1(9)	0.56	1.80(1)	7
[FeSALEN]$_2$O·CH$_2$Cl$_2$	142.4(5)	0.56	1.794(9)	7
[FeSALEN]$_2$O	144.6(6)	0.58	1.78(1)	7
[FeSALEN]Cl		0.46		8
[FeTPP]$_2$O	174.5(1)	0.50	1.763(1)	9
[FeHEDTA]$_2$O	165.0(8)	0.36	1.79 (avg)	10

TABLE IV. Comparison of M–O–M′ Parameters with other μ-Oxo Homonuclear Bridged Complexes

Compound	M–O–M′	Distance		Reference
		M–O	M′–O	
FeSALEN–OSi(CH$_3$)$_3$	142.7(4)	1.834(6)	1.633(6)	This work
[(CH$_3$)$_3$Si]$_2$O	148(3)	1.631(3)	1.631(3)	11
[Ti(C$_{22}$H$_{22}$N$_4$)](OSi(CH$_3$)$_3$)$_2$	166.7 avg.	1.84(1)	1.60(1)	12
[Ti(C$_{12}$H$_{25}$N$_4$)]$_2$O	152.0(2)	1.838(3)	1.838(3)	13
K$_2$[Ti$_2$O$_5$(C$_7$H$_3$O$_4$N)$_2$]	178.1(8)	1.825(2)	1.825(2)	14
K[Ru$_2$OCl$_{10}$]·H$_2$O	180	1.80	1.80	15
[Mn(pc)]$_2$O·2py	178(2)	1.71(1)	1.71(1)	16
[Al(C$_{10}$H$_8$NO)$_2$]$_2$O	178.0(3)	1.676(4)	1.678(4)	17

iron(III) SALEN complexes [7, 8]. Tables of interatomic distances and bond angles are available as supplementary material. The displacement of the iron atom from the coordination plane is the same, on the average, as that for the solvated μ-oxo iron SALEN species and only 0.015 Å closer than the unsolvated complex. In the [FeSALEN]Cl monomer, the iron is 0.1 Å closer than in the μ-oxo complexes. Thus, the iron does have some freedom to move closer to the coordination plane. If this displacement is a result of purely electronic considerations, the trimethylsilyl group may be said to be electronically equivalent to the iron SALEN moiety.

In all of the μ-oxo iron SALEN complexes, the bridging Fe–O distance is approximately 1.80 Å. This is considerably shorter than the distance between the iron center and the ligating oxygens of the SALEN ligand (1.92 Å). This bond shortening may be attributed to some degree of π bonding along the Fe–O bridge. This is also observed for the title compound, but the effect is not as great. The Fe–O distance of 1.834(6) Å is slightly longer than the 1.80 Å average value for the μ-oxo complexes. This is probably due to the fact that the strength of the silicon oxygen bond destabilizes the iron–oxygen bond, resulting in the longer Fe–O bond length.

The bent oxygen bridging angle of the title compound is comparable to that of the μ-oxo iron SALEN species (see Table III). This contrasts with the more nearly linear Ti(IV)–O–Si angle of the complex [C$_{22}$H$_{22}$N$_4$]Ti[OSi(CH$_3$)$_3$]$_2$ [12], but is as expected for iron–oxygen bridges. The bridging angle in the title compound is more acute than in the μ-oxo trimethylsilyl dimer [11], but the silicon–oxygen bond length is the same for both compounds (see Table IV).

Magnetic Susceptibility

The magnetic susceptibility of the title compound, determined by the Evans method [18] with methylene chloride as the standard was 10656 × 10^{-6} cgs units. This value corresponds to an effective magnetic moment of 5.03 BM, confirming the expected high spin configuration.

Vibrational Spectra

The infrared spectrum of the title compound shows a very strong peak at 958 cm^{-1}, tentatively assigned the Fe–O–Si antisymmetric stretching frequency. This falls between the Fe–O–Fe stretch at 825 cm^{-1} in the μ-oxo iron SALEN complex and the Si–O–Si stretch of a series of open chain polymethyl siloxanes which absorb between 1055 and 1024 cm^{-1} and have a second strong absorption between 1093 and 1076 cm^{-1} [19]. Most other peaks in the spectrum are attributed to previously assigned SALEN ligand absorptions.

Electronic Spectra

The UV–Visible spectrum of the title compound, as well as the μ-oxo FeSALEN species, consists predominantly of a strong charge transfer band with a broad shoulder between 320 and 400 nm, and a smaller shoulder at 280 nm. While the spectra are virtually identical, for equal molar concentrations, the μ-oxo FeSALEN absorbances are more than twice as intense as those of the title complex. Thus, most of the absorbances in this region are due to iron SALEN charge transfer interactions, and therefore are rather independent of the nature of the bridging group. The greater relative intensity per mole of FeSALEN for the μ-oxo complex as compared to the title compound is probably the result of a super exchange mechanism between the iron centers, which makes some transitions more allowed. This is not possible for the title compound.

Conclusion

The reaction of HMDS with $[FeSALEN]_2O$ results in the formation of a Fe–O–Si linkage; a trimethylsilyl group replacing an FeSALEN moiety. This replacement, however, does not significantly alter the geometry of the FeSALEN moiety, and has remarkably little effect on the electronic structure of the iron center. Except for intensity, the electronic spectra of the title complex and the $[FeSALEN]_2O$ species are indistinguishable. Structurally, the title compound is rather similar to the μ-oxo FeSALEN dimeric species. The displacement of the iron from the least-squares plane of the chelating nitrogens and oxygens of the SALEN ligand is identical (0.56 Å). The title compound also exhibits a bridge angle of 142.7° which falls within the range of values observed for the μ-oxo FeSALEN species (see Table III). Thus, the trimethylsilyl group seems to be electronically similar to the FeSALEN moiety.

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atom positions and thermal parameters, bond distances and angles, and observed and calculated structure factors are available as 'Supplementary Material'.

References

1 T. Hayes and J. Evans, *J. Phys. Chem., 88,* 1965 (1984).

2 (a) Von A. F. Shihada, *Z. Anorg. Allg. Chem., 408,* 9 (1974); (b) Von A. Slawisch, *Z. Anorg. Allg. Chem., 374,* 291 (1970); (c) F. Becker, *J. Organomet. Chem., 51,* C9 (1973).

3 B. Jeżowska-Trzebiatowska, *Pure Appl. Chem., 27* (1–2), 89 (1971).

4 N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem., 33,* 3847 (1971).

5 F. Calderazzo, *J. Chem. Soc. A,* 1378 (1969).

6 P. Main, 'MULTAN 78', a system of computer programmes for the automatic solution of crystal structures from X-ray diffraction.

7 K. S. Murray, *Coord. Chem. Rev., 12,* 1 (1974) and refs. therein.

8 M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A,* 1598 (1967).

9 A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava and J. L. Hoard, *J. Am. Chem. Soc., 94,* 3620 (1972).

10 S. J. Lippard, H. Schugar and C. Walling, *Inorg. Chem., 6,* 1825 (1967).

11 B. Csakvari, Zs. Wagner, P. Gomory, F. C. Mijlhoff, B. Rozsandai and I. Hargittai, *J. Organomet. Chem., 107,* 287 (1976).

12 C. H. Yang and V. L. Goedken, in preparation.

13 M. M. Olmstead, P. P. Power and M. Viggiano, *J. Am. Chem. Soc., 105,* 2927 (1983).

14 D. Schwartzenbach, *Inorg. Chem., 9,* 2391 (1970).

15 A. M. Matheson, D. P. Mellor and N. C. Stephenson, *Acta Crystallogr., 5,* 185 (1952).

16 L. H. Vogt, Jr., A. Zalkin and D. H. Templeton, *Inorg. Chem., 6,* 1725 (1967).

17 Y. Kushi and Q. Fernando, *J. Am. Chem. Soc., 92,* 91 (1970).

18 D. F. Evans, *J. Chem. Soc.,* 2005 (1959).

19 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Wiley, New York, 1975, p. 379.