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Coordination Chemistry

A Dinuclear Molecular Iron(II) Silicate with Two High-Spin Square-Planar FeO_4 Units**

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Dedicated to Prof. Klaus Rademann on the occasion of his 60th birthday

For a given d^x metal ion surrounded by a given number of ligand donor atoms, various situations are conceivable for the relative energetic positioning of the d frontier orbitals. These depend on the nature of the ligands and their geometric arrangement. Filling the x electrons into the different orbital schemes, considering both high-spin and low-spin configurations, results in ligand-field stabilization energies, and their comparison provides a rationale as to why a certain structure and electron configuration is stable and others are not.

For the coordination number four in a transition-metal complex, two structural motifs usually have to be distinguished: tetrahedral and square-planar ligand geometries. The latter brings about a large separation of the $d_{x^2-y^2}$ orbital from the residual d orbitals, which is beneficial if only those are filled, in particular if the ligand field is strong. Consequently, for d electron counts higher than four, square-planar structures are usually accompanied by low-spin configurations; corresponding compounds with high-spin configuration are extremely rare. Until 2011, only four high-spin d^6 Fe^{II} complexes with planar N_4[1–3] and O_4[4] coordination spheres, provided by macrocyclic or chelating ligands, had been known. These are complemented by a few examples from solid-state science,[5–12] which interestingly includes the rare mineral gillespite ($BaFe^{II}Si_4O_{10}$).[11] This mineral contains an isolated square-planar high-spin $Fe^{II}O_4$ chromophore where the oxygen atoms represent O-functions of extended cyclotetrasilicate anions (see Figure 1). Ceramics,[6,8] such as $SrFe^{II}O_2$, contain such FeO_4 units linked by vertices. Precedent cases with edge-sharing FeO_4 structural motifs have yet not been reported.

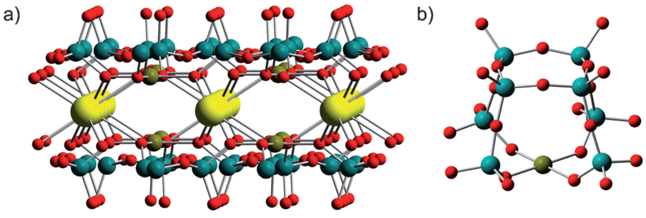
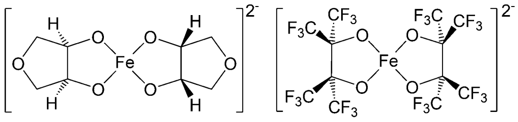


Figure 1. Two different segments of gillespite (Ba bright yellow, Si cyan, Fe green-yellow, O red). a) View along the layers composed of FeO_4 entities; b) the silicate ligand surroundings of one Fe^{II} ion.

Very recently, the first two molecular compounds[13,14] containing high-spin, square-planar FeO_4 arrangements which are not enforced by a macrocyclic ligand were reported by Klüfers et al. and Doerrer et al. (see Scheme 1). These very unusual structures have been rationalized by a Jahn–Teller flattening due to steric repulsion of the d_{z^2} β-spin electron with the lone pairs of the O atoms on the one hand,[13] and by ligand constraints that generate five nondegenerate d orbitals through π donation, on the other.[14] A weak-field character of the ligand donor atoms (ensuring the high-spin case) and short contacts to the iron ions were suggested as prerequisites; a high charge and π basicity were found to be beneficial.



I

II

Scheme 1. Two examples of molecular high-spin square-planar $Fe^{II}O_4$ complexes.

The present work extends these achievements by three further novel aspects: 1) The first dinuclear molecular compound of this type is reported; 2) the FeO_4 units share edges; and 3) the ligand spheres are composed of silanolate functions, thus approaching the situation in gillespite.

We set out by employing the known tripodal organotrisilanol, LH_3,[15] as the ligand precursor, which was reacted with sodium methanolate to deprotonate the SiOH groups and afterwards with iron(II) triflate (Scheme 2); immediately the color changed to intense blue. Slow evaporation of the volatiles from a concentrated solution of the worked-up product in diethyl ether led in good yields to blue single crystals that were investigated by X-ray diffraction analysis. The result is shown in Figure 2.[18]

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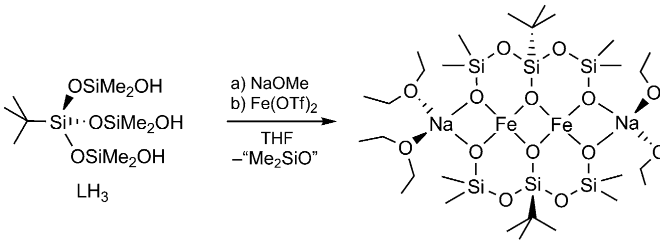


1

Scheme 2. Synthesis of the dinuclear Fe^{II} complex **1**. OTf$^-$ = triflate.

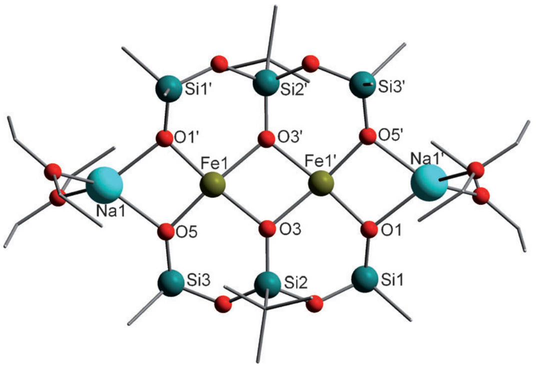


Figure 2. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–O1′ 1.959(2), Fe1–O5 1.9596(18), Fe1–O3 2.025(2), Fe1–O3′ 2.0275(19); O1′-Fe1-O3′ 95.59(8), O5-Fe1-O3 96.44(8), O5-Fe1-O1′ 91.96(8), O1′-Fe1-O3 164.29(8), O5-Fe1-O3′ 165.56(9).

The product contains two trisiloxane ligands, which, however, do not correspond to L^{3-}: They are derived from L^{3-} by elimination of one "Me$_2$SiO" equivalent (→L′$^{3-}$), which was obviously induced by contact with the iron ions. They span two Fe^{II} centers in square-planar coordination spheres. The remaining two negative charges are compensated by two sodium ions (additionally binding Et$_2$O coligands).

The Fe–O bond lengths are 2.0275(19) Å and 2.025(2) Å for the bridging O atoms and 1.9596(18) Å and 1.959(2) Å for the terminal O atoms, respectively. The distances of the Fe atoms to the terminal O atoms thus lie in a range with those of the Fe complexes **I** (1.997(21) Å) and **II** (1.969(21) Å). The O-Fe-O chelate angles (95.59(8)° and 96.44(8)°) are larger than the corresponding angles of the Fe complexes **I** (84.41(5)°) and **II** (83.34(5)°), which is not surprising as, in contrast to these compounds, **1** features six-membered chelating rings. For the same reasons, in **1** the *trans* O-Fe-O angles deviate with 165.56(9)° and 164.29(8)° somewhat from 180°: The six-membered chelates formed by L′$^{3-}$ have to be puckered to some extent, which does not permit perfectly linear O-Fe-O arrangements as in **I** and **II**. Therefore, the square-planar coordination of the Fe^{II} ions in **1** is slightly distorted with a distortion angle (measured as the dihedral angle δ of two FeO$_2$ triangles) of $\delta = 20.2°$. A distortion towards a tetrahedron has also been found in water-rich salts of **I** ($\delta = 19.1°$),[13] in the ceramic CaFeO$_2$ ($\delta = 25.8°$),[8] as well as in the blue high-pressure form of gillespite ($\delta = 33.6°$),[16] and a correlation between δ and the color has been revealed.[13] Of course this does not hold for **1**, the blue color of which is reflected by an absorption maximum at 624 nm (see the Supporting Information), as the electronic structure will be distinct, which is due to the coupling of the two iron centers.

To gain further insight into the electronic structure of the Fe$_2$O$_6$ unit in **1**, SQUID and Mössbauer measurements were performed. The μ_{eff} value at room temperature of 8.28 μ_B (Figure 3, top) is somewhat higher than the spin-only value expected for two $S = 2$ centers (6.93 μ_B) and clearly reveals the high-spin state of the iron(II) ions in **1** with some orbital contribution. The increase of the μ_{eff} curve below 100 K indicates ferromagnetic exchange. At very low temperatures, μ_{eff} drops rapidly, which might be due to the effect of zero-field splitting and/or intermolecular antiferromagnetic interactions. Indeed, analysis of the magnetic data using the isotropic Heisenberg–Dirac–van Vleck (HDvV) exchange Hamiltonian that includes additional terms for zero-field and Zeeman splitting [Eq. (1)] leads to a good fit with values $g = 2.24$, $J = +3.5$ cm^{-1}, $|D| = 12.2$ cm^{-1} (see the Supporting Information for details).

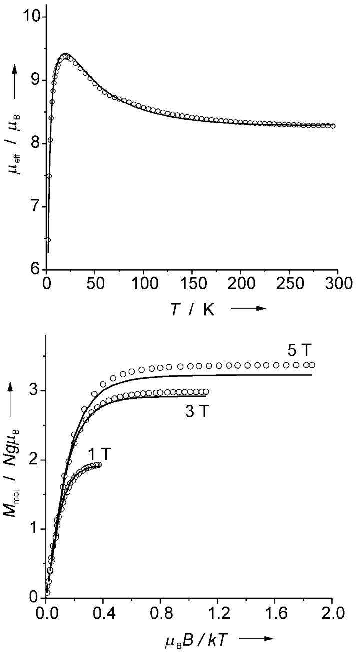


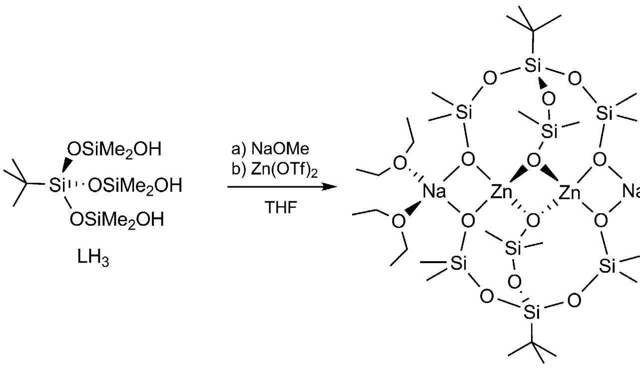
Figure 3. μ_{eff} versus T plot (top) and variable-temperature–variable-field (VTVH) magnetization measurements as M_{mol} versus B/T (bottom) for **1**. Solid lines represent the calculated curve fits (see text).

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + \sum_{i=1}^{2}\left(D(\hat{S}_{zi}^2 - 1/3S_i(S_i+1)) + g\mu_B\vec{B}\cdot\vec{S}_i\right) \qquad (1)$$

To determine the sign of the D value (used here as a phenomenological single ion anisotropy parameter), magnetization measurements at variable temperature and variable field (VTVH; Figure 3, bottom) were performed. The values $g = 2.24$, $J = +3.3$ cm^{-1} and $D = +11.6$ cm^{-1} are in excellent agreement with those derived from susceptibility data and provide evidence of the positive sign of the substantial zero field splitting.

The Mössbauer spectrum of **1** at 80 K (see the Supporting Information) shows a doublet with isomer shift $\delta = 0.91\,\mathrm{mm\,s^{-1}}$ and quadrupole splitting $\Delta E_Q = 0.37\,\mathrm{mm\,s^{-1}}$, again confirming that the iron(II) ions are in their high-spin d^6 configuration. It should be noted that the isomer shift for molecular complex **1** is distinctly higher than those observed in solid-state chemistry for ladder-like or layered structures $MFeO_2$ (M = Ca, Sr; $\delta \approx 0.6\,\mathrm{mm\,s^{-1}}$), while the quadrupole splitting for **1** is comparatively small ($\Delta E_Q > 1.0\,\mathrm{mm\,s^{-1}}$ for $MFeO_2$).[6–8] Detailed electronic structure calculations will be required to rationalize these differences.

An interesting question regarding the formation of **1** concerns the evolution of the ligand L'^{3-}. As the coordination chemistry of its congener LH_3 is basically unexplored, doubts arose as to whether this compound might be intrinsically unstable in the presence of Lewis acidic metal ions. To see in how far "Me_2SiO" elimination is a typical behavior of such trisilanols, LH_3 was also reacted with $Zn(OTf)_2$ under analogous conditions to the case of $Fe(OTf)_2$ (Scheme 3).



2

Scheme 3. Synthesis of the dinuclear Zn^{II} complex **2**.

This, however, almost quantitatively led to a dinuclear zinc complex $[L_2Zn_2][Na(OEt_2)_2]_2$, **2**, containing intact L^{3-} ligands and thus tetrahedrally coordinated zinc ions (Figure 4). The O-Zn-O angles vary between 87 and 122°, as should be expected for distorted tetrahedra.

Although rearrangement reactions of siloxanes/silanols in contact with metal ions are not unusual,[17] formation of **2** shows that LH_3 is not particularly sensitive in this respect. It thus appears that considering the donor functions available, there is even a thermodynamic driving force within the system for the formation of square planar FeO_4 units: Assuming that initially a complex similar to **2** also forms in the Fe^{II} case, elimination of "Me_2SiO", the fate of which remains unclear, is obviously exothermic. However, owing to the complexity of the proceedings, any mechanistic discussions would be highly speculative.

Formation of **1** confirms the previous suggestion that charged π-basic, weak-field ligands promote the formation of high-spin square-planar Fe^{II} complexes, as this leads to a Jahn–Teller flattening. It extends the sparse knowledge in this field with regard to molecular chemistry to silanolate ligands, to dinuclear compounds, and also to six-membered chelate rings. Overall, edge-sharing of FeO_4 units has been observed for the first time. Perhaps in future such units will also be found in ceramics: The work presented herein certainly simulates research in this direction. Currently we are investigating the chemical behavior of these highly reactive compounds.

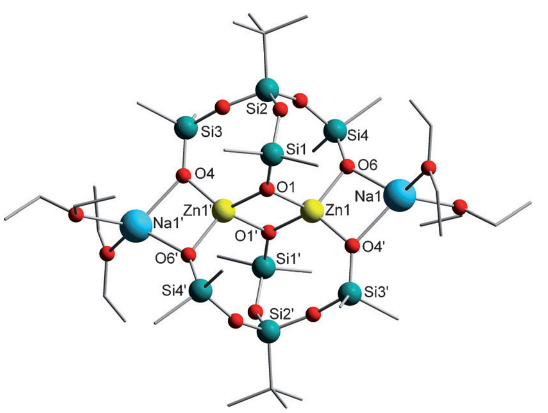


Figure 4. Molecular structure of **2**. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–O1 2.0044(11), Zn1–O1′ 1.9704(11), Zn1–O4′ 1.9152(12), Zn1–O6 1.9279(11); O4′-Zn1-O6 99.37(5), O1′-Zn1-O1 86.71(5), O4′-Zn1-O1′ 122.21(5), O6-Zn1-O1′ 121.29(5).

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[18] CCDC 910101 (**1**) and CCDC 910102 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.