Synthesis and Structure of the First Fe^{II} Heterometallic Alkoxide $[(THF)NaFe(O\textit{t}Bu)_3]_2$ − a Possible Precursor for New Materials

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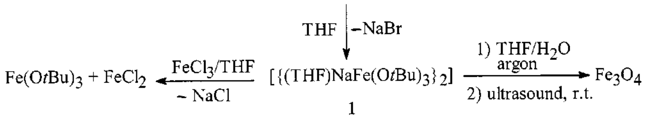
The reaction of $FeBr_2$ with three equivalents of NaO*t*Bu in THF affords the first heterometallic Fe^{II} alkoxide, $[(THF)NaFe(O\textit{t}Bu)_3]_2$ (**1**), to be structurally characterised. The central core of the structure is an $M_2O_6M'_2$ fragment with C_2 symmetry. The compound is shown to be promising as a new precursor for magnetic iron oxide Fe_3O_4.

Introduction

Iron(III) alkoxides have been studied quite extensively. They show a quite unusual structural diversity and possess many interesting physical properties.[1] In contrast, the chemistry of Fe^{II} alkoxides is very poorly developed,[2,3] even though Fe^{II} complexes might be very promising precursors for the preparation (by MOCVD or sol-gel technology) of important iron-based compounds and materials. Here we report the synthesis, structure, and some selected reactions of the first Fe^{II} heterometallic alkoxide $[(THF)NaFe(O\textit{t}Bu)_3]_2$.

Results and Discussion

The reaction of $FeBr_2$ with three equivalents of NaO*t*Bu in THF at ambient temperature proceeds with the precipitation of NaBr to afford the heterometallic Fe^{II} alkoxide $[(THF)NaFe(O\textit{t}Bu)_3]_2$ (**1**). The preparation of **1** and further reactions are summarised in Scheme 1. Compound **1** gave a satisfactory C, H, N analysis and was characterised by IR and ^1H NMR spectroscopy. The structure of **1** was also studied by X-ray single crystal diffraction.



Scheme 1. Synthesis and selected reactions of $[\{(THF)NaFe(O\textit{t}Bu)_3\}_2]$ (**1**)

The IR spectrum of **1** in nujol shows the characteristic C−O stretching bands for metal alkoxides at 1286, 1227 and 1195 cm^{-1} and M−O stretching bands at 618, 574 and 538 cm^{-1}. The ^1H NMR spectrum of **1** in C_6D_6 displays broad, paramagnetically shifted signals for the bridging O*t*Bu groups ($\delta = 11.71$ and -4.08) and THF ($\delta = 12.90$ and 6.27).

X-ray quality crystals of **1** were crystallised from a concentrated solution in THF at ambient temperature. The central fragment of the molecule **1** (Figure 1) is an $Na_2O_6Fe_2$ cage-like unit with C_2 symmetry. A similar fragment (Figure 2) is found in several heterometallic alkoxides, for example in $[LiNbO(OEt)_4(EtOH)]_2$,[4] $[NaWO(OEt)_5(EtOH)_2]_2$,[5] $[MSn(O\textit{t}Bu)_3]_2$ (M = Li, Na),[6] $[LiTi(O\textit{i}Pr)_5]_2$,[7] $[KTi(O\textit{t}Bu)_5]_2$,[8] and $[LiHf(O\textit{i}Pr)_5]_2$.[9] In **1** the M positions in the central metal-oxygen core, which are occupied by alkali metals in the majority of above-mentioned complexes (Figure 2), are occupied by Fe atoms, and the M′ positions, which are occupied by Sn or multivalent transition metals (e.g. Ti, Hf, Zr, Mo, W) in the previously reported compounds, are occupied by alkali metal (Na) atoms. Such an uncommon arrangement of metal atoms has earlier been observed in the structures of, for example, $[LiNbO(OEt)_4(EtOH)]_2$,[4] $[NaMoO_2(OC_2H_4OMe)_3]_2$,[10] and $[NaWO_2(OC_2H_4OMe)_3]_2$.[11] In **1** each of the Fe atoms is coordinated by two μ_2- and two μ_3-O*t*Bu bridging groups with O−Fe−O angles that vary between 78.0(7)° and 150.7(9)°. Because of this the coordination polyhedron around the Fe atom could be described as either a very distorted tetrahedron or, alternatively, as an octahedron in which *cis* apices are missing. A similar geometry around the Fe^{II} atom has been observed before in $[Fe(OCPh_3)_2(THF)_2]$.[2] As expected, the Fe−O(μ_3) bond lengths [2.074(16) and 2.061(14) Å] are longer than the Fe−O(μ_2) ones [1.923(14) and 1.829(19) Å]. There is an asymmetry in the Fe−O bond lengths, which is particularly significant for the Fe−O(μ_2) bonds [Δ(Fe−O) = 0.094 Å].

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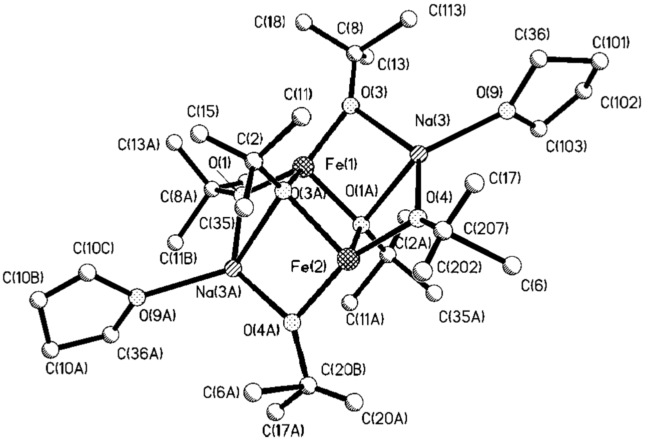

Figure 1. X-ray crystal structure of $[\{(THF)NaFe(OtBu)_3\}_2]$ (**1**); selected bond lengths (Å) and angles (°): Fe(1)−O(3) 1.923(14), Fe(1)−O(3A) 1.923(14), Fe(1)−O(1A) 2.074(16), Fe(1)−O(1) 2.074(16), Fe(1)−Na(3) 2.988(7), Fe(1)−Na(3A) 2.988(7), Fe(2)−O(4) 1.829(19), Fe(2)−O(4A) 1.829(19), Fe(2)−O(1A) 2.061(14), Fe(2)−O(1) 2.061(14), Fe(2)−Na(3A) 3.114(8), Fe(2)−Na(3) 3.114(8), Na(3)−O(3) 2.138(18), Na(3)−O(10) 2.370(11), Na(3)−O(4) 2.425(19), Na(3)−O(1A) 2.468(8); O(3)−Fe(1)−O(3A) 150.7(9), O(3)−Fe(1)−O(1A) 195.2(5), O(3A)−Fe(1)−O(1A) 1107.6(4), O(3)−Fe(1)−O(1) 107.6(4), O(3A)−Fe(1)−O(1) 95.2(5), O(1A)−Fe(1)−O(1) 78.0(7), O(4)−Fe(2)−O(4A) 150.0(10), O(4)−Fe(2)−O(1A) 99.1(5), O(4A)−Fe(2)−O(1A) 104.1(6), O(4)−Fe(2)−O(1) 104.1(6), O(4A)−Fe(2)−O(1) 99.1(5), O(1A)−Fe(2)−O(1) 78.5(8), O(3)−Na(3)−O(10) 112.4(10), O(3)−Na(3)−O(4) 132.2(5), O(10)−Na(3)−O(4) 114.6(11), O(3)−Na(3)−O(1A) 79.4(6), O(10)−Na(3)−O(1A)134.3(4), O(4)−Na(3)−O(1A) 74.5(6); Fe(1)−O(1)−Fe(2) 101.8(3)

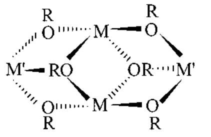

Figure 2. Schematic presentation of the $M'_2O_6M_2$ unit in heterometallic alkoxides (R = *t*Bu or *i*Pr)

In general the Fe−O(*t*Bu) bond lengths in **1** are similar to the corresponding ones in other Fe^{II} alkoxy derivatives: $[Fe(OCPh_3)_2(THF)_2]$ [1.883(1) Å],[2] $[Fe_4(DBCat)_4(py)_6]$ [from 1.974(6) to 2.236(5) Å] and $[Fe_2(DBCat)_2(py)_n]$ [from 1.936(4) to 2.326(4) Å] (DBCat = 3,5-di-*tert*-butylcatechol, *n* = 4, 6).[3] The Fe···Fe distance of 3.208 Å is also quite close to those in the tetranuclear Fe^{II} complex $[Fe_4(DBCat)_4(py)_6]$ [from 3.079(2) to 3.481(2) Å] and in the binuclear complex $[Fe_2(DBCat)_2(py)_n]$ [3.223(3) and 3.195(3) Å].[3] The sodium atom in **1** is coordinated by the oxygen atoms of two μ_2- and one μ_3-O*t*Bu groups and one THF molecule, in a distorted tetrahedral arrangement. The O−Na−O angles vary between 74.5(6)° and 132.2(5)° and the Na−O(*t*Bu) bond lengths between 2.138(18) Å (μ_2-O) and 2.468(8) Å (μ_3-O). Surprisingly, one of the Na−O(μ_2) bonds is substantially longer, at 2.425(19) Å, than the other one, and is in fact very close to an Na−O(μ_3) bond length; this causes a significant asymmetry in the molecule. The observed structure can also be considered as a dimer of $[(THF)Na(OtBu)_2Fe(OtBu)_2Na(THF)]$ held together by additional metal/O*t*Bu bonds.

It was of great interest to us to investigate the chemical properties of **1** as a potential precursor for other iron-containing compounds and materials. The reaction of **1** with two equivalents of $FeCl_3$ in THF at ambient temperature (24 h) gave $FeCl_2$ and $Fe(OtBu)_3$, which were separated by fractional crystallisation and clearly identified by elemental analysis (Scheme 1). This reaction demonstrates the labile nature of **1**.

Fe^{II} compounds have recently been reported to be very good precursors for the preparation of Fe_3O_4 nanoparticles by sol-gel and sonochemical methods.[12−14] For this reason a solution of **1** in THF was hydrolysed with doubly distilled water under argon, followed by ultrasonic treatment (Scheme 1). The black product was characterised by X-ray powder diffraction (XRD). The reflections of the XRD patterns (2*θ* from 5 to 70°) for the sample show *d* spacing values and relative intensities of the peaks that coincide exactly with the JCPDS data of magnetite (Fe_3O_4). The product was also characterised by Mössbauer spectroscopy at room temperature. The Mössbauer spectrum of the Fe_3O_4 sample shows combined magnetic and quadrupole splittings. A least-squares fit to the experimental data indicates that the lines are characteristic of nonstoichiometric magnetite, with a small line-broadening due to a distribution of hyperfine magnetic fields caused by the different iron environments in the structure, and a small contribution from paramagnetic Fe^{3+}. The most plausible mechanism of the magnetite formation in this reaction involves an oxidation of Fe^{II} into Fe^{III} by oxygen from the water during the hydrolysis and subsequent ultrasonic treatment. Ultrasonically generated radical and peroxide species from water might also contribute to the oxidation of Fe^{II}, as has been reported recently.[13,14]

The above reactions demonstrate that the new iron(II) alkoxide **1** can be used as a promising precursor for the facile preparation of magnetite. Work on the further development of this research is currently in progress.

Experimental Section

General: All manipulations were carried out under vacuum or dry argon by Schlenk techniques. Solvents were purified and degassed by standard procedures. $FeBr_2$ and NaO*t*Bu were obtained from Aldrich. Microanalyses were carried out by Medac Ltd. The ^1H NMR spectra were recorded using a Varian-400 (^1H, 400 MHz) instrument. Deuteriated benzene was dried with a K metal mirror and distilled prior to use. IR spectra (500−4000 cm^{-1}) were recorded in Nujol, using KBr discs and a Perkin Elmer instrument.

$[(THF)NaFe(OtBu)_3]_2$ (1): NaO*t*Bu (5.27 g, 54.9 mmol) was added to $FeBr_2$ (3.95 g, 18.3 mmol) in THF (300 mL) at ca. 0 °C. The mixture was stirred for 24 h at ambient temperature and was then filtered. The filtrate was concentrated in vacuo to give grey crystals of **1**. Yield: 4.27 g (64%). $C_{32}H_{70}Fe_2Na_2O_8$ (740.6): calcd. C 51.8, H 9.45; found C 51.7, H 9.39. ^1H NMR (400 MHz, C_6D_6, 22 °C): $\delta = -4.08$ (v. br., 18 H, μ_3-O*t*Bu), 6.27 (br, 8 H, THF), 11.71 (v.

br., 36 H, μ_2-O*t*Bu), 12.90 (br, 8 H, THF). IR (Nujol): $\tilde{\nu}$ = 2709 (s), 1657 (w), 1570 (w), 1356 (w), 1286 (w), 1227 (s), 1195 (w), 1055 (s), 968 (w), 775 (w), 618 (w), 574 (w) 538 (w) cm^{-1}.

Fe_3O_4: A solution of **1** (2.3 g, 3.1 mmol) in THF (100 cm^3) was carefully hydrolysed with doubly distilled water (40 cm^3) under argon. The resultant mixture was then ultrasonically (Ultrasonic bath Grant XB6, 30 kHz, 130 W) irradiated at ambient temperature for one hour under argon. The dark precipitate was filtered and washed five times with distilled water. The product was then dried in vacuum for five hours at room temperature giving a black powder of Fe_3O_4 (0.44 g, 92%) characterised by X-ray powder diffraction (XRD) and Mössbauer spectroscopy.

X-ray Crystallography

A single crystal of **1** was placed in a glass capillary and sealed under vacuum. Data were measured on a SMART CCD 1 K diffractometer using monochromated Mo-K_α radiation. Corrections for absorption were made using the Bruker SADABS program.[15] The crystal was found to be a merohedral twin, with the centre of symmetry as an external symmetry element not belonging to the true symmetry group. Structure solutions were made using the SHELXTL program package Version 5.3. The structure was solved by direct methods and was refined first in an isotropic and then an anisotropic (all non-hydrogen atoms) approximation. The positions of the hydrogen atoms were calculated geometrically and included in the final cycles of the refinement in an isotropic approximation.

Crystal Data for 1: $C_{32}H_{70}Fe_2Na_2O_8$, M = 740.56, monoclinic, a = 18.822(7), b = 12.516(5), c = 9.262(3) Å, β = 91.179 (6)°, U = 2181.4(14) $Å^3$, T = 295(2) K, space group $C2$, Z = 2, ρ = 1.127 Mg/m^3, μ(Mo-K_α) = 0.723 mm^{-1}, 3446 reflections collected, 1675 independent reflections [R(int) = 0.0870], R_1 = 0.0815 for reflections with $I > 2\sigma(I)$, wR_2 = 0.2191 (all data). CCDC 170603 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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