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A Series of Homo- and Heteroleptic Iron(III) Alkoxides as Precursors for Fe₂O₃

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Abstract. A series of bulky iron(III) alkoxides was synthesized by a ligand exchange reaction using $[Fe(OtBu)_3]_2$ and 2,4-dimethylpentan-3-ol (H*Odp*). The resulting complexes are dimers, structural details are compared based on single crystal structure analyses. Investigation of

the thermal properties shows a decrease of the melting point upon exchange of the *tert*-butoxy by Odp^- ligands. Thermolysis leads to volatile products and the formation of phase pure hematite.

Introduction

Iron(III) alkoxides came into focus of research as precursors for thin film deposition by CVD and ALD processes and for application in catalysis.^[1–3] E.g., iron(III) alkoxides are promising catalysts for the polymerization of lactides.^[4] Furthermore, iron(III) alkoxides are used as precursors for synthesis of nano- and micro-particles of defined size and shape.^[5,6] Recently an iron(III) alkoxide was used in an ALD process to generate hematite and magnetite nanotubes.^[3]

Iron(III) alkoxides are known for a long time but their synthesis is still challenging due to their structural complexity resulting from the presence of oxo, alkoxide and alcohol ligands. In 1958 Bradley et al. described a reliable synthesis of various alkoxides starting from ferric chloride and the respective primary or secondary alcohol. Treatment with ammonia results in the formation of ammonium chloride and iron(III) alkoxide.^[7,8] This method is applicable for primary and secondary alcohols, but not for tertiary alcohols such as tert-butyl alcohol. An approach to ferric tert-butoxide was provided by Mathur et al. and Spandl et al., who suggested a salt metathesis reaction between ferric chloride and sodium tert-butoxide.[1,9] Adopting this to the reaction of ferric chloride with sodium methoxide or sodium ethoxide does not lead to the desired ferric alkoxides $Fe(OR)_3$, but to the more complex oxo-alkoxides [Na₂Fe₆O(OMe)₁₈(HOMe)₆] and [Fe₉O₃(OEt)₂₁(EtOH)], respectively.^[10,11] Due to the steric demand of the tert-butyl group, iron tert-butoxide could be isolated as [Fe(OtBu)₃]₂. Spandl et al. used this dimer as starting material in a ligand exchange reaction with iron(III) chloride and were able to isolate the heteroleptic compounds [Fe(OtBu)Cl₂]₂ and [Fe(OtBu)₂Cl]₂ with dimeric structures as well.^[9]

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Bradley et al. investigated homoleptic complexes of various iron(III) alkoxides and the influence of the ligand on physical properties. It was found that volatility increases with increasing steric demand of the ligands.^[8] A high vapor pressure is substantial for the use as precursors for CVD and ALD processes. Thus, we describe a series of new homoleptic and heteroleptic iron(III) alkoxides, containing the sterically demanding 2,4-dimethylpentan-3-olate ligand and investigate their thermolysis behavior as well as structural properties.

Results and Discussion

To synthesize homo- and heteroleptic iron(III) alkoxides ferric tert-butoxide was applied as suitable starting material. This alkoxide was synthesized according to literature by reacting FeCl₃ with KOtBu in THF. Due to the +I effect of the tBu group the tert-butoxy ligand is more basic than primary or secondary alkoxides and was used to introduce 2,4-dimethylpentan-3-ol (HOdp) alkoxide ligands by an acid base reaction with the secondary alcohol as shown in Scheme 1. Its steric demand is expected to prevent the formation of polynuclear clusters, in contrast for methoxide or ethoxide; the large alkyl groups provide solubility in non-polar solvents.

$$[Fe(OtBu)_{3}]_{2} (1) \xrightarrow[OH]{} Hodp \qquad for the second s$$

Scheme 1. Preparation of the complexes 2–4.

The synthesis of 2 is based on a ligand exchange reaction by a stoichiometric treatment of 1 with 2,4-dimethylpentan-3ol. The product is obtained as green crystalline material in 65% yield. The same procedure was first applied for the synthesis of 3, but the reaction of a stoichiometric amount of 2,4dimethylpentan-3-ol with 1 in a 2:1 ratio only results in a mixture of 2 and 3, as confirmed by PXRD. This behavior might

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be due to the increased steric demand of the 2,4-dimethylpentan-3-olate ligand. To shift the chemical equilibrium to the desired product, an excess of 2,4-dimethylpentan-3-ol was used. Product **3** could be isolated as green-brown crystalline material in 64% yield despite the steric issues. With respect to these results, exchanging all *tert*-butoxy ligands by 2,4-dimethylpentan-3-ol seems to be unfeasible. However, a complete exchange of all *tert*-butoxy ligands by 2,4-dimethylpentan-3-ol was successful by shifting the chemical equilibrium by removing the *t*BuOH which is released during the reaction. This was accomplished by heating the reaction to reflux while distilling off the produced *t*BuOH together with toluene. With this method **4** could be isolated as brown crystalline material with 50% yield.

Crystal Structure Analyses

From products 2–4 single crystals suitable for crystal structure analysis could be obtained. The basic crystallographic data are summarized in Table 1. All three compounds consist of a dinuclear structure, where the Fe³⁺ atoms are coordinated by four ligands each in a distorted tetrahedral coordination mode. The dimers contain four terminal and two bridging alkoxide ligands to form neutral complexes. These structures are similar to that of ferric *tert*-butoxide 1. Compounds 2 and 4 crystallize in the triclinic space group $P\overline{1}$ (Z = 1) with an inversion center between the two iron atoms. In contrast, compound 3 crystallizes in the monoclinic space group $P2_1/c$ with two formula units per unit cell (Figures S1–S3, Supporting Information). The 2₁ screw axis along *b* and the glide plane create two orientations of the centrosymmetric molecule in the unit cell of 3 as shown in Figure 1. The crystal structure of **2** is shown in Figure 2. Due to its steric demand, the 2,4-dimethylpentan-3-olate (Odp^{-}) ligand acts as a terminal and not as a bridging ligand. The same is observed for **3**, where all four Odp^{-} ligands are in terminal positions (Figure 3) while the less sterically demanding *tert*-butoxy ligands act as μ_2 bridges between the two iron atoms.

Regarding the structure of the homoleptic complex 4, the high steric demand of terminal and bridging Odp- ligands correlates with the challenging synthesis of $[Fe(Odp)_3]_2$. Its crystal structure is shown in Figure 4. The organic residues of the μ_2 -2,4-dimethylpentan-3-olate bridging ligands are orientated almost perpendicular to the FemFe axis. This enables the terminal 2,4-dimethylpentan-3-olate ligands to orientate around the iron center. In Table 2 selected bond lengths and angles of 1-4 are listed. Only small differences in Fe-O bond lengths and O-Fe-O angles could be observed comparing the structures of 1-4. In contrast to compounds 2 and 3 a slightly longer FemFe distance is found in 4 due to the higher steric demand of the bridging Odp- ligand. This also effects the O1-Fe1-O1a angle and results in a smaller angle than in 2 and 3. The bond lengths of Fe-O bonds seem to be not effected significantly by the organic substituent and are in the range of a typical Fe-O bond.^[1] The angle O2-Fe1-O3 between the terminal ligands varies slightly between 114° for 3 and 118° for 2. This angle might be mainly caused by the orientation of the ligands and not only by the type of ligand. The O1-Fe1-O1a angles are in the range of 80-82° and are significantly smaller than the ideal angle of 109.5° for tetrahedral coordination. This is caused by the four-membered ring formed by Fe1-O1-Fe1a-O1a, which enforces a reduced angle. Both, the steric demand of the ligands as well as the formation of the four-membered ring lead to a distorted tetrahedral coordination mode.

Table 1. Crystallographic data of $[Fe(OtBu)_2(Odp)]_2$ (2), $[Fe(OtBu)(Odp)_2]_2$ (3), and $[Fe(Odp)_3]_2$ (4).

	2	3	4
Formula	Fe ₂ O ₆ C ₃₀ H ₆₆	Fe ₂ O ₆ C ₃₆ H ₇₈	$Fe_2O_6C_{42}H_{90}$
Formula mass $M / \text{g·mol}^{-1}$	634.52	718.68	802.83
Temperature T /K	180(2)	180(2)	213(2)
Crystal color and shape	yellow block	brown block	brown block
Crystal size /mm	$0.3 \times 0.3 \times 0.2$	$0.4 \times 0.3 \times 0.1$	$0.3 \times 0.2 \times 0.1$
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a /pm	957.68(4)	961.45(5)	1055.93(6)
<i>b</i> /pm	1002.54(5)	1358.59(5)	1108.43(7)
c /pm	1068.11(5)	1679.44(8)	1136.55(7)
a / °	80.549(4)	90	75.152(5)
β / °	85.040(4)	101.967(4)	82.991(5)
γ/°	67.497(4)	90	67.095(5)
Cell volume $V / 10^6 \text{ pm}^3$	934.25(8)	2146.0(2)	1184.1(1)
Z	1	2	1
Density (calcd.), ρ /g·cm ⁻³	1.128	1.112	1.126
Absorption coefficient μ /mm ⁻¹	0.809	0.712	0.651
heta range / °	2.5-29.0	2.2-26.5	2.1-25.5
Measured reflections	15525	13732	13255
Independent reflections (R_{int})	4954 (0.0614)	4433 (0.0751)	4121 (0.0683)
Observed reflections $[I > 2\sigma(I))$	3976	3344	2943
Parameters	182	211	238
R_1 (observed reflections)	0.0521	0.0356	0.0446
wR_2 (all data)	0.1465	0.0894	0.1086
Max./min. residual e^- density / 10^{-6} pm ⁻³	0.5 and -0.6	0.5 and -0.5	0.6 and -0.2





Figure 1. Simplified packing diagrams of 2 (top), 3 (middle), and 4 (bottom) with view along [100], only Fe and O atoms are shown.

Thermal Properties

The thermal behavior of 2–4 as well as $[Fe(OtBu)_3]_2$ (1) as a reference compound were investigated by simultaneous thermal analysis (TG-DTA-MS). Based on this analysis the melting point, the temperature range of thermolysis, and the weight loss were determined. The expected weight loss was calculated, based on the assumption that the thermal decomposition results in the formation of Fe₂O₃ as reported by *Mathur* et al. for the thermal decomposition of 1.^[1] The thermal analysis data are summarized in Table 3. Noticeably, the melting point, determined as the peak temperature of the endothermic peak in the DTA graph (Figure 5 and Figures S4–S6, Supporting Information) decreases in the series with the number of OtBu⁻



Figure 2. Molecular structure of 2; hydrogen and disordered atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.



Figure 3. Molecular structure of 3; hydrogen atoms are omitted; 50 % ellipsoids.



Figure 4. Molecular structure of 4; hydrogen atoms are omitted; 50 % ellipsoids.

ligands exchanged by Odp^- . The lowest melting point is observed for the homoleptic complex 4 at 75 °C, 84 K lower than the melting point of the structurally similar ferric *tert*-butoxide 1. This effect might be due to the bulky organic groups of the Odp^- ligand. The nonpolar alkyl groups shield the polar center of the complex more efficiently and diminish the attractive intermolecular forces. This results in a decreasing melting point with increasing number of Odp^- ligands.

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	1	2	3	4
Fe1…Fe1a	295	298.90(9)	298.19(5)	303.1(1)
Fe101	197	196.80(5)	196.97(3)	198.42(5)
Fe1–O1a	178	196.36(4)	196.78(3)	197.78(5)
Fe1–O2	169	179.65(6)	180.22(6)	180.29(6)
Fe1–O3	178	178.28(8)	178.20(3)	180.60(7)
O3-Fe1-O2	113	117.69(9)	113.82(9)	115.8(1)
01–Fe1–O1a	82	81.02(7)	81.60(7)	80.08(8)

Table 3. Thermal properties of compounds 1–4, obtained from thermogravimetric analysis in argon atmosphere.

	1	2	3	4
Melting point /°C	159	108	88	75
Thermolysis onset /°C	235	254	239	207
Thermolysis end /°C	248	271	263	257
Weightloss exp. 1%	73.1	74.5	72.6	80.0
Weightloss calcd. 1%	71.0	74.8	77.8	80.1



Figure 5. TG-DTA analysis of $[Fe(Odp)_3]_2$ (4), performed in an argon atmosphere, heating rate 10 K·min⁻¹.

Furthermore, the thermolysis reaction of complexes 1–4 was analyzed by TG-DTA. It is characterized by the final temperature of decomposition as well as the weight loss. The final temperature of the decomposition follows a special pattern, where 1 exhibits the lowest final temperature. The observed final temperature of 1 is in agreement with the results of *Mathur* et al.^[1] Exchanging one *tert*-butoxy ligand by Odp^- , the final temperature rises to 271 °C and decreases with more Odp^- ligands to 257 °C for complex 4. The weight loss fits exactly to the calculated values for 2 and 4. The deviation for 3 might be due to partial hydrolysis during sample preparation. While 1 is reported to sublime at 80 °C at 10^{-2} Torr,^[1] 2–4 are less volatile.

The volatile products of the thermal decomposition were analyzed by EI-MS. As volatile products for **1** *iso*-butene and *t*BuOH were found in compliance with results of *Mathur*.^[2] For the heteroleptic compounds **2** and **3**, in addition to *iso*butene and *t*BuOH, the release of 2,4-dimethylpentan-3-ol and 2,4-dimethyl-2-pentene was observed originating in the 2,4dimethylpentan-3-olate ligand. Accordingly, as volatile products of the decomposition of **4** 2,4-dimethylpentan-3-ol and 2,4-dimethyl-2-pentene are formed. These results are also verified by NMR spectra of the trapped volatile thermolysis products (Figures S12, S13, Supporting Information).

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The solid residues of the thermal decomposition (TG-DTA up to 900 °C) of **1–4** were analyzed by PXRD. The diffraction patterns (Figure 6 and Figures S7–S10, Supporting Information) show the phase pure formation of hematite (Fe₂O₃) for the decomposition of all complexes **2–4**.



Figure 6. X-ray powder diffraction patterns of the residues obtained after thermal treatment of 1-4 up to 900 °C in an argon atmosphere in comparison to the simulated pattern based on crystal structure data of hematite.^[12]

Interestingly, PXRD measurements after thermolysis up to 300, 400, and 500 °C show patterns consistent with the formation of magnetite, Fe_3O_4 , or maghemite, γ -Fe₂O₃, which can hardly be distinguished by conventional X-ray diffraction methods.^[13] As expected, the broad peaks get sharper with increasing temperature. Between 500 and 600 °C the color of the solid residue changes from brown-black to red consistent with the transformation to hematite, α -Fe₂O₃, in agreement with the X-ray diffraction pattern measured after heating to 600, 700, and 800 °C (Figure S14, Supporting Information). Since TG-MS experiments do not show any signals in the range above 300 °C and based on the same diffraction patterns observed for thermolysis under inert and atmospheric conditions, the iron oxide phase formed by thermal decomposition of 1-4 is assigned to maghemite, which is transformed to hematite at elevated temperatures.



Conclusions

The new homo and heteroleptic iron(III) alkoxides $[Fe(OtBu)_2(Odp)]_2$ $[Fe(OtBu)(Odp)_2]_2$ (2), (3), and $[Fe(Odp)_3]_2$ (4) were synthesized by a ligand exchange reaction starting from ferric tert-butoxide (1) and 2,4-dimethylpentan-3-ol. Crystal structure analyses confirm the dimeric structure of the complexes as well as their structural similarity to ferric tert-butoxide. By exchanging all tert-butoxy ligands by 2,4-dimethylpentan-3-ol in complex 4 the melting point decreases to 75 °C. The thermal decomposition occurs in one step and results in formation of Fe₂O₃; after thermal treatment (600 °C) the diffraction pattern corresponds to phase pure hematite for all complexes. These results qualify the new iron(III) complexes 2-4 as promising precursors for Fe₂O₃ nanoparticles or thin films and - in combination with other metal compounds - for ternary oxides.

Experimental Section

Materials and Methods: All reactions were carried out under the exclusion of air and moisture using standard Schlenk technique or a MBRAUN UniLab Glovebox in an nitrogen atmosphere. All solvents were dried with sodium and distilled prior to use. Anhydrous FeCl₃ was purchased from Acros Organcis, KOtBu from Alfa Aesar. 2,4-Dimethylpentan-3-ol was dried with CaH₂ and distilled prior to use. The iron(III) *tert*-butoxide dimer **1** was synthesized according to the literature. ^[1]

Thermogravimetric analysis was performed with a Netzsch STA 449 F1 thermobalance in an argon atmosphere (heating rate 10 K·min⁻¹) combined with an Aeolos QMS 403 D mass spectrometer. Elemental analysis was measured with a Vario El-Heraeus, IR spectra (750–4000 cm⁻¹) with a Bruker Tensor27 equipped with ATR attachment, El-mass spectra were measured with a Finnigan MAT 8230.

Crystal Structure Analyses: Single crystal diffraction data were collected on imaging plate diffractometer systems STOE IPDS-1 and IPDS-2T equipped with a sealed Mo X-ray tube and a graphite monochromator crystal [λ (Mo- K_{α}) = 71.073 pm]. Data processing was carried out with STOE X-Area^[14] software including a numerical absorption correction. The structures were solved by direct methods using SHELXS-2014 and refined using SHELXL-2014.^[15] The C atoms of the disordered alkyl groups in **2** are refined with site occupation factors of 0.52(1) and 0.48(1), respectively. All non-hydrogen atoms and non-disordered atoms are refined with anisotropic thermal parameters. The coordinates of the hydrogen atoms were included on idealized positions. The structures are visualized using Diamond 3.2k.^[16]

Measurements of powder XRD patterns were performed with a STOE STADI-P diffractometer system equipped with a sealed Cu X-ray tube and a germanium (111) monochromator crystal $[\lambda(Cu-K_{\alpha 1}) = 154.060 \text{ pm}]$. Samples of **1–4** were measured in transmission mode in capillaries (Hilgenberg, 0.5 mm), thermolysis products were measured as flat samples on polymer films at room temperature. Data processing was carried out with STOE WinXPOW.^[17] Rietveld analysis was performed with Bruker TOPAS 5^[18] using the fundamental parameter approach. The crystallographic data of hematite^[17] used as reference was taken from literature.

Synthesis of [Fe(OtBu)₂(Odp)]₂ (2): 1 (550 mg, 1.0 mmol) was dissolved in 20 mL of toluene and 2,4-dimetylpentan-3-ol (0.28 mL, 2.0 mmol) was added dropwise. The green solution turned brown slowly while heating to 90 °C for 2 h. The solvent was evaporated and the crude product was recrystallized from *n*-pentane to yield the desired product as olive-green crystals (yield 412 mg, 65%). $C_{30}H_{66}O_6Fe_2$: calcd. C 56.8, H 10.5%; found: C 56.3, H 10.1%. **MS**: m/z = 562: [Fe₂(*Odp*)₂(OtBu)₃]⁺, m/z = 520: [Fe₂(*Odp*)(OtBu)₄]⁺, m/z = 448: [Fe₂(*Odp*)₂(OtBu)₂]⁺; m/z = 446: [Fe₂(*Odp*)(OtBu)₃]⁺. **IR**: $\tilde{v} = 1106$ (m), 1177 (s), 1190 (s), 1354 (m), 1364 (m), 1469 (w), 2870 (m), 2927 (m), 2966 (s) cm⁻¹.

Synthesis of $[Fe(OtBu)(Odp)_2]_2$ (3): A solution of 1 (2.75 g, 5.0 mmol) in 50 mL toluene was treated with 2,4-dimetylpentan-3-ol (11.2 mL, 80 mmol, excess). The green solution turned reddish-brown while heating under reflux for 5 h. After stirring for 12 h at room temperature the solvent was evaporated and the crude product was recrystallized from *n*-pentane. The product was obtained as greenbrown crystalline material (yield 2.3 g, 64%). C₃₆H₇₈O₆Fe₂: calcd. C 60.2, H 10.9%; found: C 59.8, H 10.7%. MS: m/z = 603: $[Fe_2(Odp)_3(OtBu)_2]^+$, m/z = 645: $[Fe_2(Odp)_4(OtBu)]^+$, m/z = 488: $[Fe_2(Odp)_2(OtBu)_2]^+$. IR: $\tilde{v} = 1102$ (s), 1110 (s), 1175 (m), 1364 (s), 1378 (m), 1471 (m), 2869 (s), 2905 (s), 2960 (s) cm⁻¹.

Synthesis of [Fe(*Odp*)₃]₂ (4): **1** (550 mg, 1.0 mmol) was dissolved in 25 mL of toluene and an excess of 2,4-dimetylpentan-3-ol (5 mL) was added. The reaction mixture turned reddish-brown and was heated to reflux. While heating, the toluene and *t*BuOH was distilled off and a fresh portion of 25 mL toluene was added to the reaction mixture. This process was repeated and the red crude product was recrystallized from *n*-pentane to obtain the desired compound as brown crystals (yield 400 mg, 50%). C₄₂H₉₀O₆Fe₂: calcd. C 62.8, H 11.3%; found: C 61.8, H 11.3%. **MS**: *m*/*z* = 688: [Fe₂(*Odp*)₅]⁺, *m*/*z* = 572: [Fe₂(*Odp*)₄]⁺, *m*/*z* = 457: [Fe₂(*Odp*)₃]⁺. **IR**: $\bar{\nu}$ = 1100 (m), 1380 (m), 2820 (w), 2871 (m), 2958 (s) cm⁻¹.

Supporting Information (see footnote on the first page of this article): Supporting Information:

Unit cell diagrams of the crystal structures of **2- 4**; TG/DTA analyses; PXRD analyses of the thermal decomposition products; IR spectra of **1- 4**; NMR spectra of the volatile thermolysis products of **2**; PXRD patterns of the solid residues after thermolysis at different temperatures.

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Keywords: Iron(III) alkoxide; Precursor; Fe₂O₃; Iron; Crystal structure; Thermolysis

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