$Fe_9O_3(OC_2H_5)_{21}\cdot C_2H_5OH$ − A New Structure Type of an Uncharged Iron(III) Oxide−Alkoxide Cluster

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A new nona iron(III) oxide-alkoxide cluster has been prepared by the treatment of $FeCl_3$ with three equivalents of sodium ethoxide. The molecule is the first example of a neutral iron(III) alkoxide cluster based on OEt ligands and shows a paramagnetic moment of 13.4(1) μ_B at 293 K in the solid state.

Introduction

Iron(III) oxides, alkoxides and hydroxides show a great structural diversity, the most remarkable feature being the formation of charged and uncharged clusters by formal condensation.[1] The iron atoms in such compounds are often linked by oxygen atoms. The remaining ligands on the iron atoms may be hydroxide,[2−5] carboxylate,[4−7] alkoxide,[6,8,9] multipodal amino-organic,[10] or amino hydroxyorganic[2] groups, to mention just a few possibilities. The structural building blocks of such iron oxide clusters are often FeO_6 octahedra (less frequently FeO_5 bipyramids or square pyramids) linked by oxygen atoms, which show twofold to sixfold coordination. The new cluster $Fe_9O_3(OEt)_{21}\cdot EtOH$ described here is the first example of such an aggregate containing, apart from bridging oxygens, only the alkoxide group OEt as ligand.

Results and Discussion

In our attempt to synthesise the alkoxide[11−13] $Fe(OC_2H_5)_3$[14] by reaction of iron(III) chloride with sodium ethoxide following established routes, we noticed that a solid brown compound could be isolated in about 60% yield. The X-ray crystal structure analysis of this molecular compound revealed a new structure type within iron(III) alkoxide clusters (see Figure 1). It also showed that the compound is made up of three oxygen atoms, nine iron(III) atoms, twenty-one alkoxide ligands and an alcohol molecule coordinated to one of the Fe centres. The molecular formulation $Fe_9O_3(OC_2H_5)_{21}\cdot C_2H_5OH$ **(1)** has been confirmed by elemental analysis. The oxygen atoms in the cluster presumably come from the residual water in C_2H_5OH.[15] The molecule has the lowest point symmetry C_1 which is due to asymmetric adduct formation of a neutral ethanol molecule.

Leaving this extra ligand apart an almost *mm*2 (C_{2v}) symmetry can be attributed to the rest of the molecule (neglecting the orientations of the ethyl groups). A pseudo-twofold axis runs through the iron atom Fe(1) and the central oxygen atom O(6) which connects three metal atoms in a trigonal planar coordination sphere. The other two oxygen atoms are in the centres of very distorted Fe_4 tetrahedra, the distortion being due to an important elongation of one of the edges [Fe(2)···Fe(4) and Fe(3)···Fe(5)]. These elongated edges are the only ones which are not bridged by μ_2-OC_2H_5. While most of the iron atoms have one terminal OC_2H_5 ligand, Fe(1), Fe(2) and Fe(3) are completely integrated in the oxygen bridge network, and Fe(6) has an additional C_2H_5OH neutral ligand. At Fe(1) there are four μ_2-OC_2H_5 terminal bridges, while at Fe(2) and Fe(3) there are three. Fe(4), Fe(5) and Fe(6) are almost octahedrally coordinated by oxygen atoms, while all other iron atoms are in distorted trigonal bipyramidal oxygen coordination spheres. The largest deviation from trigonal bipyramidal geometry is found for Fe(1), which is better described as square pyramidal with respect to the nearest oxygen atoms. Altogether there are six terminal OC_2H_5 ligands, fifteen bridging μ_2-OC_2H_5 groups and an additional neutral C_2H_5OH ligand. There is a neat dependence of Fe−O distances and coordination numbers on the atoms involved in the bond as well as on the site of the coordination polyhedron (axial versus equatorial): $Fe-\lambda^4O$ = 201.1(7) pm, $Fe-\lambda^3O$ = 191.1(1)

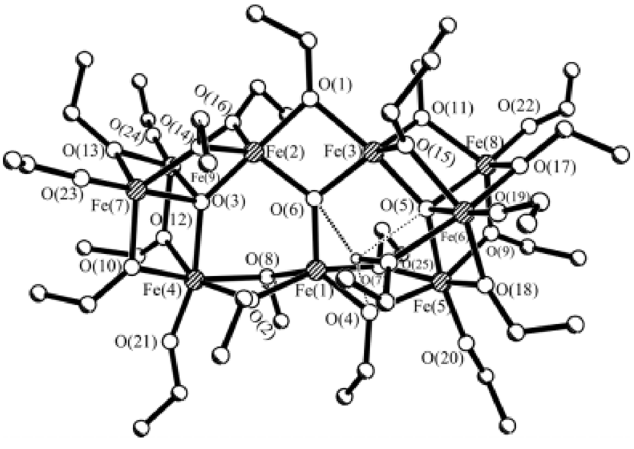

Figure 1. X-ray crystal structure of the iron(III)oxide−alkoxide $Fe_9O_3(OC_2H_5)_{21}\cdot C_2H_5OH$

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pm and Fe$-$OC$_2$H$_5$ (μ_2) = 200.9(0) pm; Fe$-$OC$_2$H$_5$ (terminal) = 178.7(3) pm (mean values). As anticipated, the neutral alcohol ligand at Fe(6) has the longest Fe$-$O bond [219.0(5) pm]. Interestingly, all μ_2-OC$_2$H$_5$ bridges are found at the equatorial sites of the trigonal bipyramidally coordinated iron atoms. The proton of the alcohol ligand can be located and serves as a bridging atom (hydrogen bond) between O(25) and O(4), O(5) and O(6).

The magnetic moment[16−19] of $Fe_9O_3(OC_2H_5)_{21}\cdot C_2H_5OH$ in the solid state is μ_{eff} = 13.4(1) B.M. at 293 K.[20]

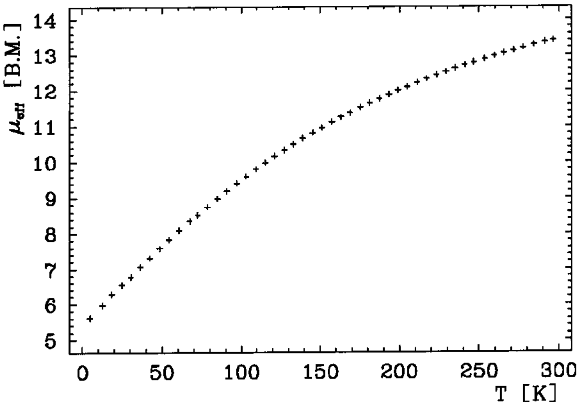

Figure 2. Plot of the magnetic moment (μ_{eff} [B.M.]) of solid **1** versus temperature [K] (see ref.[20])

From the steady shortening of the magnetic moment of crystalline cluster **1** with decreasing temperature (Figure 2) an antiferromagnetic exchange interaction within the molecule can be deduced.[20]

The values found have to be compared to a calculated value for one independent high spin Fe^{3+} ion of μ_{eff} = 5.92 B.M. The crystals seem to be ferrimagnetic, and this is currently being investigated further.[21] Interestingly, the cluster **1** when dissolved in benzene shows a tendency to dissociate. Cryoscopic measurements in the same solvent give a molecular weight of about 510 g/mol. This corresponds to a fragmentation into several species from the original cluster (molecular weight, 1543.0 g/mol) and is more than the simple release of the neutral ethanol ligand. As a solid residue from the benzene solution of cluster **1** we have isolated a compound which analysed as "$Fe_5O(OC_2H_5)_{13}$". We are currently investigating the structural and physical consequences of this decomposition which is driven by simple change of the solvent. Further studies on this system are underway.[21]

Experimental Section

$Fe_9O_3(OC_2H_5)_{21}\cdot C_2H_5OH$ (1): The solvent C$_2$H$_5$OH was distilled from sodium and kept over molecular sieves. Under a dry nitrogen atmosphere anhydrous FeCl$_3$ (4.428 g, 27.3 mmol) was added to a solution of sodium ethoxide [formed in situ from sodium (1.886 g, 82.0 mmol) and C$_2$H$_5$OH (20 mL)] in ethanol. The mixture was stirred under reflux for 100 h. After removing the solvent under reduced pressure the residue was distilled at 200 °C/0.01 Torr; the product crystallizes on cooling as a brown solid. Yield 2.735 g (60%). − $C_{44}H_{111}Fe_9O_{25}$: calcd. C 34.3, H 7.3, Fe 32.6; found C 34.2, H 7.3, Fe 32.1. − M..p.: 90 °C.

X-ray Crystallography

A crystal suitable for X-ray crystallography was isolated from an ethanol solution of **1**. Stoe IPDS diffractometer, Mo-K_α radiation (λ = 71.073 pm), 293 K, crystal size 0.2 × 0.18 × 0.12 mm, triclinic, space group $P1$(bar) with a = 1247.4(2) pm, b = 1746.2(3) pm, c = 1814.1(4) pm, α = 68.02(3)°, β = 84.58(3)°, γ = 88.45(3)°, $V = 3647.7(12) \times 10^6$ pm^3, Z = 2, ρ = 1.405 Mg·m^{-3}, μ = 1.798 mm^{-1}, $2.07° \le \theta \le 24.08°$, $-14 \le h \le 13$, $-19 \le k \le 20$, $-20 \le l \le 20$, 23099 measured reflections, 10729 independent, $R1$ = 0.0627, $wR2$ = 0.1553, GOF = 0.928, no restraints, 483 parameters, remaining electron density max. 0.717×10^{-6} min. -0.652×10^{-6} e·pm^{-3}.

The structure described in this paper was solved with the heavy-atom method and refined towards F^2 for all observed reflections (solution and refinement with SHELXS-97 and SHELXL-97, hydrogen atoms were calculated in an ideal tetrahedral geometry and optimised).

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-149596. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] K. S. Hagen, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1010.
[2] S. L. Heath, A. K. Powell, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 191.
[3] C. J. Harding, R. K. Henderson, A. K. Powell, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 570.
[4] S. M. Gorun, S. J. Lippard, *Nature* **1986**, *319*, 666.
[5] S. M. Gorun, G. C. Papaefthymiou, R. B. Frankel, S. J. Lippard, *J. Am. Chem. Soc.* **1987**, *109*, 3337.
[6] K. L. Taft, S. J. Lippard, *J. Am. Chem. Soc.* **1990**, *112*, 9629.
[7] I. Shweky, L. E. Pence, G. C. Papaefthymiou, R. Sessoli, J. W. Yun, A. Bino, S. J. Lippard, *J. Am. Chem. Soc.* **1997**, *119*, 1037.
[8] A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467.
[9] K. Hegetschweiler, H. W. Schmalle, H. M. Streit, V. Gramlich, H. U. Hund, I. Erni, *Inorg. Chem.* **1992**, *31*, 1299.
[10] V. S. Nair, K. S. Hagen, *Inorg. Chem.* **1992**, *31*, 4048.
[11] R. C. Mehrotra, J. of Non-*Crystalline Solids* **1988**, *100*, 1.
[12] K. G. Caulton, L. G. Hubert-Pfalzgraf, *Chem. Rev.* **1990**, 969.
[13] M. Veith, S. Mathur, V. Huch, *Inorg. Chem.* **1996**, *35*, 7295.
[14] D. C. Bradley, R. K. Multani, W. Wardlaw, *J. Chem. Soc.* **1958**, 126.
[15] A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2716.
[16] R. W. Adams, E. Bishop, R. L. Martin, G. Winter, *Aust. J. Chem.* **1966**, *19*, 207.
[17] K. Hegetschweiler, A. Corina, D. Gatteschi, L. Hausherr-Primo, V. Gramlich, *Inorg. Chem.* **1996**, *35*, 4414.
[18] A. Caneschi, A. Cornia, S. J. Lippard, G. C. Papaefthymiou, R. Sessoli, *Inorg. Chim. Acta* **1996**, *243*, 295.
[19] K. L. Taft, G. C. Papaefthymiou, S. J. Lippard, *Inorg. Chem.* **1994**, *33*, 1510.
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[21] P. Gütlich, J. Ensling, M. Veith, F. Grätz, V. Huch, to be published.

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