Mössbauer Spectroscopic Investigation of the Cesium Suboxoferrate(III) Cs_9FeO_4

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^{57}Fe Mössbauer spectroscopic studies have shown that in cesium suboxoferrate, Cs_9FeO_4, the iron atom has the formal oxidation state +III. The isomer shift $\delta = 0.10(1)$ is in very good agreement with that of a large number of ionic ferrates(III). The same holds for geometrical details of the $[FeO_4]^{5-}$ anion, which shows only a small deviation from ideal tetrahedral symmetry giving rise to a quadrupole splitting of $\Delta E_Q = 0.36(2)$ mm/s.

Key words: Suboxometallates, Cesium, Ferrates, Mössbauer Spectroscopy

Introduction

Suboxometallates of cesium and rubidium are an interesting class of new subvalent compounds [1]. They all have the common composition A_9MO_4, where A is cesium which can be partially substituted by rubidium, and M is a trivalent metal. The formal electron counting $(Cs^+)_9(M^{+3})(O^{-2})_4 \cdot 4\ e^-$ shows the subvalent character of the compounds, and electronic structure calculations suggest that one of the four crystallographic Cs positions is best described as Cs^- [2]. For M = Al, Ga, In and Sc the oxidation state +3 in these compounds is no surprise. However, in the suboxoferrate the oxidation state of the iron atom is subject to some discussion. Here we present spectroscopic evidence for the presence of Fe(III) in Cs_9FeO_4.

Experimental Section

Sample preparation

Powder samples of phase-pure Cs_9FeO_4 were prepared by reacting stoichiometric mixtures of Fe_2O_3 (ChemPur, 99.9 %), Cs_2O (prepared from Cs metal and HgO, as described in [1b]) and Cs metal (triply distilled) in tantalum crucibles under argon. The reaction mixtures were heated to 180 °C within 3 h, and after a reaction time of 1 h the furnace was turned off. The purity of the reaction product was subsequently analyzed by X-ray powder diffraction.

As samples prepared with natural Fe_2O_3 showed a very low Mössbauer signal due to the large absorption effects of cesium and the low cross section of Cs_9FeO_4, samples with Fe_2O_3 with a ^{57}Fe content of 95.74 % (American Elements) were prepared. These samples showed a high extinction due to the high isotopic purity, and therefore for the final samples equal parts of Cs_9FeO_4 prepared from natural and from enriched Fe_2O_3 were mixed, and diluted with quartz powder in a ratio 30 : 130 [w/w].

^{57}Fe Mössbauer spectroscopy

A ^{57}Co/Rh source was available for the ^{57}Fe Mössbauer spectroscopic investigation. The air- and moisture-sensitive Cs_9FeO_4 sample was placed in a thin-walled glass container and sealed under argon atmosphere to prevent hydrolysis. The measurement was performed in the usual transmission geometry at 298 K. The total counting time was approximately three weeks (see Fig. 2). Fitting of the spectra was performed with the NORMOS-90 program system [3].

Results and Discussion

The crystal structure of the alkali metal suboxometallates A_9MO_4 can formally be divided into two substructures [1]. One consists of $[MO_4]^{5-}$ anions coordinated by distorted cuboctahedra of 12 cesium atoms forming columns parallel to [001] by sharing common edges, and the second one consists of face-sharing cubes built up from 8 cesium atoms (Fig. 1). These cubes are centered by a further cesium atom having no direct contact to the anion. According to eletronic structure calculations it can best be described as Cs^-

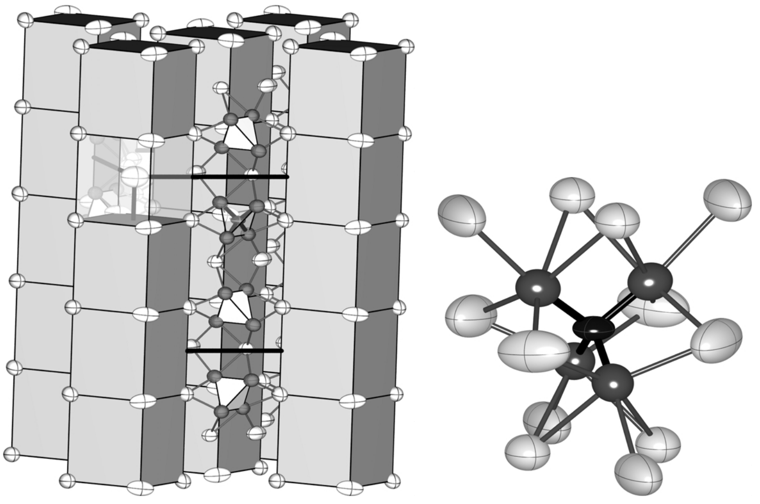

Fig. 1. Left: the crystal structure of Cs_9FeO_4. Grey spheres: O atoms, light-grey spheres: Cs atoms. Light-grey tetrahedra depict orthoferrate anions $[FeO_4]^{5-}$ (one is drawn transparent), grey cubes are drawn for the metallic $[Cs_8Cs]$ building blocks (again, one is drawn transparent). Bold black lines are drawn for the unit cell, thin grey lines show the coordination of the orthoferrate anion by its next Cs neighbors. For all atoms displacement ellipsoids are drawn at a probability level of 80 % [7]. Right: detailed view of the orthoferrate anion with point symmetry $\bar{4}2m$ and its coordination by cesium atoms.

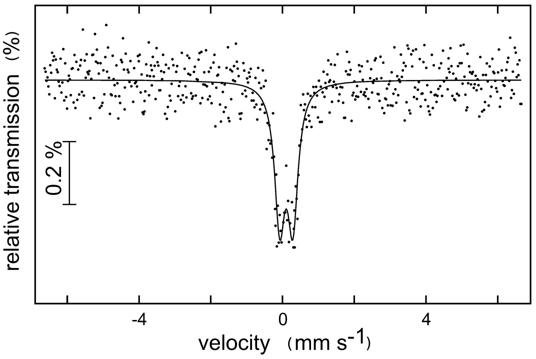

Fig. 2. Room-temperature ^{57}Fe Mössbauer spectrum of Cs_9FeO_4. The isomeric shift of δ = 0.10(1) mm s^{-1} clearly indicates the presence of Fe(III). The quadrupole splitting of ΔE_Q = 0.36(2) mm s^{-1} results from the small deviation from ideal tetrahedral symmetry of the $[FeO_4]^{5-}$ anion.

[2]. This negatively polarized cesium atom can partially be substituted by rubidium. The anion and its direct coordination polyhedron shows geometrical details very similar to those found in purely ionic orthoferrates(III) [4]. The similarity of the anions in Cs_9FeO_4 and Cs_5FeO_4 (distances d_{Fe-O} = 190(2) pm for Cs_9FeO_4, 188.3 – 191.3 pm for α-Cs_5FeO_4, and 188.9 – 190.4 pm for β-Cs_5FeO_4 [4]), together with the isotypic crystal structures of Cs_9FeO_4 and $Cs_9M^{III}O_4$ (M = Al, Ga, In, Sc), strongly suggest the presence of Fe^{III}. The presence of an oxidizing agent such as Fe^{III} embedded in a metallic cesium matrix must imply a thermodynamic instability of the suboxoferrate. As a consequence, DTA studies on Cs_9FeO_4 show an exothermic decomposition at about 190 ℃ into cesium ferrates(II) [5], whereas thermodynamically stable suboxoferrates such as Cs_9InO_4 show congruent melting behavior [1]. A narrow range between formation and decomposition is serendipitiously realized in Cs_9FeO_4, but in other examples the respective temperature ranges where reaction sets in and thermal decomposition occurs overlap. If cesium metal is for example brought to reaction with CrO_3 or Cs_2CrO_4 under comparable conditions with the aim of preparing $Cs_9Cr^{VI}O_4$, surprisingly no reaction whatsoever takes place up to about 180 ℃. However, when the reaction finally sets in, the redox process leading to chromates with oxidation states lower than +VI for the chromium atom [5] is already induced. Therefore $Cs_9Cr^{VI}O_4$ cannot be obtained in this way. Moreover, mixtures of cesium metal and $CsMnO_4$ react vigorously at r. t.

Spectroscopic evidence for the presence of Fe(III) in Cs_9FeO_4 has now been obtained by Mössbauer spectroscopic studies. The r. t. ^{57}Fe Mössbauer spectrum of Cs_9FeO_4 (Fig. 2) shows a signal with an isomer shift of δ = 0.10(1) mm s^{-1}, an experimental line width of Γ = 0.35(3) mm s^{-1} and a quadrupole splitting of ΔE_Q = 0.36(2) mm s^{-1}. The isomer shift is in excellent agreement with the value expected for isolated $[Fe^{III}O_4]$ polyhedra [6]. The quadrupole splitting reflects the small deviation from ideal tetrahedral symmetry (actual point symmetry for the $[FeO_4]^{5-}$ anion is $\bar{4}2m$, angles O–M–O ranging from 105 to 112°). Due to the large interatomic distance of two neighboring Fe atoms in the crystal structure (d_{Fe-Fe} = 628.6(5) pm), no hyperfine splitting of the signal is observed at temperatures as low as 4 K.

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