

Individual iron(III) glycerolate: synthesis and characterisation

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1. Materials

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%) (Reakhim, Russia), iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%) (Vekton, Russia), glycerol (Vekton, Russia) and sodium hydroxide (NaOH) were used for the synthesis. Fe_3O_4 MNPs were obtained as described previously.¹⁻³

2. General Methods

Elemental Analysis

The C, H and Fe contents were measured on an automatic PE-2400 CHN analyzer, Series II (Perkin Elmer).

IR Spectroscopy

The IR spectra were recorded on a Nicolet 6700 infrared Fourier spectrometer (Thermo Electron Corporation) with a diamond Smart Orbit ATR sampling accessory (scanning area was $400\text{--}4000\text{ cm}^{-1}$).

X-Ray Diffraction Spectroscopy

The phase composition of the synthesized samples was determined by comparing the results of X-ray diffraction analysis (Shimadzu XRD 700, Cu-K α radiation, angle interval $10^\circ \leq 2\theta \leq 70^\circ$). Phases were identified using the Powder Diffraction File JCPDSD-ICDD PDF2 library (set's 1-47). When processing diffractograms, the STOE WinXPow software was used, which includes the possibility of approximate calculation of the percentage of the identified phases.

Mössbauer Spectrometry

Mössbauer spectra were recorded using an advanced MS-2201 spectrometer with a $^{57}\text{Fe}(\text{Cr})$ resonant detector in transmission geometry at a temperature of $T = 295\text{ K}$.⁴ The $^{57}\text{Co}(\text{Rh})$ isotope with an activity of 25 mKu was a source of γ -radiation. The experimental spectra were processed using the Univem MS software. Sodium nitroprusside was taken as reference for calibration. Samples were prepared by deposition from the solution of ethanol and polyvinyl butyral glue to aluminum foil with a diameter of 22 mm.

High-resolution transmission electron microscopy

High resolution transmission electron microscope (HRTEM) observation was performed with a sample prepared by drying a putted drop of ethanol with an ultrasonically dispersed Fe_3O_4 MNPs and Fe_3O_4 MNPs coated with glycerolate **1** on a copper grid in vacuo at room temperature. Picture was taken by a Jeol Jem 2100 high resolution transmission electron microscope with a digital camera Olympus Cantaga G2 and a prefix for microanalysis Oxford Inca EnergyTEM 250 at an acceleration voltage of 200 kV and amperage 105 mA.

3. Synthesis of Iron Glycerolates

Synthesis of iron(III) glycerolate from FeCl₃:

FeCl₃·6H₂O (4.00 g, 14.8 mmol) and NaOH (1.78 g, 44.4 mmol) were added to anhydrous glycerol (50 mL). The reaction mixture was heated under magnetic stirring at 180 °C for 18 h, then poured to distilled water (100 mL) and stirred on a magnetic stirrer for 15 min. The precipitate was filtered off, washed with distilled water (100 mL) and ethanol (25 mL), and oven-dried at 100 °C for 6 h to yield 1.95 g (91%) of iron(III) glycerolate **1**. **Elemental analysis:** Calcd. for FeC₃H₅O₃: C, 24.78; H, 3.81; Fe, 38.54; Found: C, 24.75; H, 3.44; Fe, 38.40. **IR, v/cm⁻¹:** 2925, 2859 (ν(C–H), CH₂, CH); 1460, 1378, 1323, 1249 (δ(C–H), CH₂ and CH); 1120, 1091, 1060, 1004, 971, 955, 914, 857, 825, 712, 607, 507 (ν(C–O), δ(C–O–Fe), γ(C–C)). **XRD:** 12.7° 2θ. **Mössbauer:** Fe³⁺ doublet, δ_{iso} = 0.66 mm/s, Q_S = 0.48 mm/s.

Synthesis of iron(III) glycerolate shell on Fe₃O₄ MNPs: Fe₃O₄ MNPs (0.86 g, 3.7 mmol) were dispersed in glycerol (13.00 g, 0.141 mol). The reaction mixture was stirred at 180 °C for 18 h. The particles were separated by a Nd–Fe–B magnet, washed with absolute ethanol (5 × 15 mL), and dried under reduced pressure at 60 °C to yield 0.99 g. **Elemental analysis,** Found: C, 12.20; H, 1.62. **IR, v/cm⁻¹:** 2940, 2856 (ν(C–H), CH₂, CH); 1450, 1381, 1323, 1253 (δ(C–H), CH₂ and CH); 1120, 1089, 1056, 1002, 961, 915, 859, 822, 714, 708, 582 (ν(C–O), δ(C–O–Fe); γ(C–C); ν(Fe–O), Fe₃O₄ core). **XRD:** 12.6°, 30.0°, 35.6°, 37.1°, 44.6°, 54.4°, 58.9°, 65.3° 2θ. **Mössbauer:** Fe³⁺ doublet, δ_{iso} = 0.66 mm/s, Q_S = 0.51 mm/s.

Synthesis of iron(II,III) glycerolate from FeSO₄: FeSO₄·7H₂O (4.00 g, 14.39 mmol) and NaOH (1.15 g, 28.8 mmol) were added to anhydrous glycerol (50 mL). The reaction mixture was heated under magnetic stirring at 180 °C for 18 h, then poured to distilled water (100 mL) and stirred on a magnetic stirrer for 15 min. The precipitate was filtered off, washed with distilled water (100 mL) and ethanol (25 mL), and oven-dried at 100 °C for 6 h to yield 1.65 g (83%) of iron(II,III) glycerolate **2**. **Elemental analysis:** Calcd. for Fe²⁺₃Fe³⁺₅(C₃H₅O₃)₇: C, 23.57; H, 3.30; Fe, 41.74; Found: C, 23.12; H, 3.20; Fe, 41.89. **IR, v/cm⁻¹:** 2940, 2856 (ν(C–H), CH₂, CH); 1450, 1381, 1323, 1253 (δ(C–H), CH₂ and CH); 1120, 1089, 1056, 1002, 961, 915, 859, 822, 714, 582 (ν(C–O), δ(C–O–Fe), γ(C–C), ν(Fe–O)). **XRD:** 12.7° 2θ. **Mössbauer:** Fe³⁺ doublet, δ_{iso} = 0.66 mm/s, Q_S = 0.46 mm/s, relative content 62%; Fe²⁺ doublet, δ_{iso} = 1.33 mm/s, Q_S = 2.29 mm/s, relative content = 38%.

4. References

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