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Europium-151 and iron-57 nuclear resonant vibrational spectroscopy of natural abundance KEu(III)Fe(II)$(CN)_6$ and Eu(III)Fe(III)$(CN)_6$ complexes

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Procedures of sample preparation

First, $K_4[Fe(II)(CN)_6]$, $K_3[Fe(III)(CN)_6]$ and $K_3[Co(III)(CN)_6]$ were all obtained from Sigma-Aldrich and used as received without further purification.

Synthesis of KEu(III)[Fe(II)$(CN)_6$]: an aqueous solution of $Eu(NO_3)_3 \cdot 5H_2O$ (1 mM, 15 mL) was added dropwise to an aqueous solution of $K_4[Fe(II)(CN)_6]$ (1 mM, 10 mL) under vigorous stirring. A pale-yellow precipitate was formed slowly, and the reaction was stirred at room temperature for 2 hours before the precipitate was filtered and washed with deionized water and acetone three times each, respectively, to afford an off-white microcrystalline powder.

Synthesis of Eu(III)[Fe(III)$(CN)_6$]: an aqueous solution of $Eu(NO_3)_3 \cdot 5H_2O$ (1 mM, 15 mL) was added dropwise to an aqueous solution of $K_3[Fe(III)(CN)_6]$ (1 mM, 10 mL) under vigorous stirring. A pale-yellow precipitate was formed immediately, and the reaction was stirred at room temperature for 30 minutes before the precipitate was filtered and washed with deionized water and acetone three times each, respectively, to afford an off-white microcrystalline powder.

Synthesis of KFe(II)[Co(III)$(CN)_6$]: an aqueous solution of $FeCl_2 \cdot 4H_2O$ (1 mM, 15 mL) was added dropwise to an aqueous solution of $K_3[Co(III)(CN)_6]$ (1 mM, 10 mL) under vigorous stirring. An off-white precipitate was formed slowly, and the reaction was stirred at room temperature for 8 hours before the precipitate was filtered and washed with deionized water and acetone three times each, respectively, to afford a white microcrystalline powder.

Synthesis of $K^{57}Fe(II)[Co(III)(CN)_6]$: a sample of ^{57}Fe powder was first dissolved in 2 mL concentrated HCl in a small beaker at 50 °C to give a colorless solution. The excess HCl was evaporated at this temperate for 6 hours to dryness before 15 mL deionized water was added to make an aqueous solution of $FeCl_2$ (1 mM). This colorless solution was added dropwise to an aqueous solution of $K_3[Co(III)(CN)_6]$ (1 mM, 10 mL) under vigorous stirring. An off-white precipitate was formed slowly, and the reaction was stirred at room temperature for 8 hours before the precipitate was filtered and washed with deionized water and acetone three times each, respectively, to afford a white microcrystalline powder.

The two degenerated stretching vibrational modes (μ_4) for $[M(CN)_6]^{4-}$: M=metal.