

Electronic supplementary Information for:

Formation and decay of negative ion states up to 11 eV above the ionization energy of the nanofabrication precursor $\text{HFeCo}_3(\text{CO})_{12}$

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Experimental details

Experiments were conducted in a previously described crossed electron/molecular beam instrument¹. In brief, an electron beam (~110 meV resolution) is generated with a trochoidal electron monochromator and crossed with an effusive beam of $\text{HFeCo}_3(\text{CO})_{12}$ supplied through a capillary tube by sublimation at 348-353 K. The electron energy is scanned by ramping the acceleration voltage of the monochromatic electron beam, and the energy scale is calibrated using the SF_6^- signal from SF_6 at 0 eV. Negative ions formed in the interaction zone are extracted by a weak electric field and analyzed with a quadrupole mass spectrometer in perpendicular arrangement to both the electron and molecular beams. The mass spectrometer is set to allow the transmission of the fixed m/z ratio for each negative ion and the electron acceleration voltage is scanned through the relevant energy range to record the respective ion yield curves. All experiments were carried out at a target pressure of about 4×10^{-7} mbar.

Synthesis of $\text{HFeCo}_3(\text{CO})_{12}$

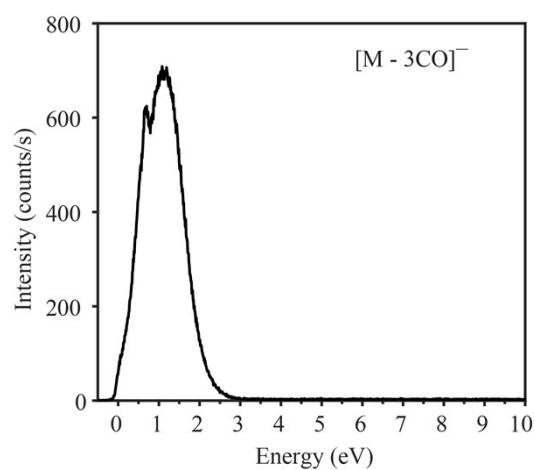
The synthesis was carried out using a procedure slightly modified from the one described by Chini *et al.*² All handling and synthesis procedures were carried out under an inert atmosphere using Schlenk and glove box techniques to prevent oxidation. $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, HCl and acetone were purchased from Sigma Aldrich. Solvents were degassed before use.

In a typical synthesis, 0.50 g (2.6 mmol) $\text{Fe}(\text{CO})_5$ and 1.51 g (4.4 mmol) $\text{Co}_2(\text{CO})_8$ were combined in a three-neck flask and 4.8 ml acetone were added drop wise. After stirring this dark solution at 40 °C for 2 h the temperature was increased to 60 °C for 12 h. All volatile components were removed under reduced pressure (2×10^{-2} mbar; 25 °C) and collected in a cooling trap (liquid N_2). The dark solid residue was dissolved in 10 ml degassed water and filtered in 15 ml HCl conc. (37%), while the yield could be increased by using 5 ml degassed water to transfer the rest of the complex from the filter in the hydrochloric acid. The mixture of the precipitated raw product and HCl was stirred for 1 h at room temperature before the dark purple raw product was separated from the acidic solution via filtration and dried overnight under reduced pressure. Dark purple needles of $\text{HFeCo}_3(\text{CO})_{12}$ were obtained after recrystallization from toluene. Finally, the final product was kept under dynamic vacuum ($\sim 10^{-3}$ mbar; 25 °C) for 2 h to remove toluene adhering to the crystalline solid.

Computational details

Molecular orbital diagrams were calculated with density functional theory using the functional BP86^{3, 4} and the polarized triple-zeta basis set def2-TZVP⁵ using the ORCA quantum chemistry code, version 3.0.3⁶.

Electronic supplementary figures



ESI 1. Negative ion yield curve for the formation of $[M - 3CO]^-$, here M is the neutral molecule $HFeCo_3(CO)_{12}$.

ESI References

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