

Far-Infrared Magnetic Spectroscopy of a Paramagnetic Cobalt(III) Complex with Perfluorinated Ligands

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Introduction

Transition metal complexes can catalyze a wide variety of desirable chemical processes including selective oxidation of hydrocarbons for fine chemical synthesis and complete oxidation of organohalogen compounds that are environmental pollutants. The oxidation of water, i.e., the ability to mimic the “water splitting” accomplished by the Mn-containing center of the oxygen evolving complex (OEC) of Photosystem II is also a “Holy Grail” of synthetic inorganic chemistry [1]. One approach to developing catalysts that are themselves stable with respect to oxidation is to employ perfluorinated ligands. One such ligand is perfluoropinacolate ($[\text{pin}^{\text{F}}]^{2-}$, dianion of hexafluoro-2,3-bis(trifluoro-methyl)-2,3-butanediol). One metal that is likewise suitable as the basis for oxidation catalysis is cobalt, either as Co(II) ($3d^7$) or Co(III) ($3d^6$) ion. Cobalt(III) is

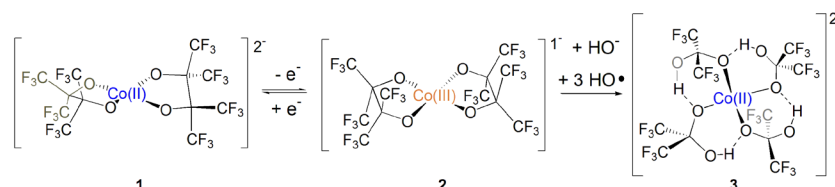


Fig.1 Synthesis and interconversion of **1**, **2**, and **3**.

typically diamagnetic ($S = 0$), but an $S = 1$ or even $S = 2$ ground state is possible in rare cases. Complexes of Co(II) [2] and Co(III) [3] with pin^{F} coordination were prepared and the Co(III) species characterized by far-infrared magnetic spectroscopy (FIRMS), among more conventional spectroscopic techniques, as well as x-ray diffraction.

Experimental

The synthetic route is shown in **Fig.1**. Of interest here is the square-planar Co(III) complex $[\text{Me}_4\text{N}][\text{Co}^{\text{III}}(\text{pin}^{\text{F}})_2]$, **2**. In aerobic solution, **2** eventually reverts to a Co(II) complex, **3**, but **2** is stable as a solid or under N_2 . Complex **2** was studied by HFEPR in the 15/17 T SC magnet of the EMR Facility, and FIRMS in the SCM3 magnet of the DC Facility.

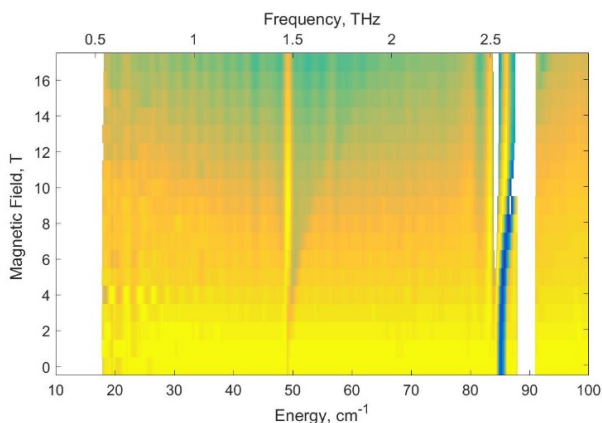


Fig.2 A false color map of FIRMS resonances for **2** at 5 K showing two zero-field transitions at 49.2 cm^{-1} and 85.2 cm^{-1} evolving into powder patterns with applied field.

Results and Discussion

HFEPR of **2** gave no response, but FIRMS was successful and the resulting field-frequency map is shown in **Fig.2**. Two resonances were observed in zero field at 49.2 cm^{-1} and 85.2 cm^{-1} , identified as $D - E$ and $D + E$ transitions, respectively, leading to $D = 67.2 \text{ cm}^{-1}$; $|E| = 18.0 \text{ cm}^{-1}$. The large zero-field splitting (zfs) is consistent with the few other known complexes of Co(III) with square-planar geometry. Quantum chemical (ab initio) and classical ligand-field theory provide an explanation for this large zfs.

Conclusions

An unusual spin triplet square-planar complex of Co(III) has been synthesized and its zfs fully determined by FIRMS. The observed large magnitude zfs ($|D + E| = 85 \text{ cm}^{-1}$) is consistent with detailed computational studies of the complex.

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