HIGH-FREQUENCY AND -FIELD EPR OF A PSEUDO-OCTAHEDRAL COMPLEX OF HIGH-SPIN Fe(II): BIS(2,2'-BI-2-THIAZOLINE)BIS(ISOTHIOCYANATO)IRON(II)

A. Ozarowski, J. Krzystek, S. A. Zvyagin, Louis-Claude Brunel (NHMFL), William M. Reiff, (Northeastern U., Chemistry), Joshua Telser, (Roosevelt U., Chemistry)

Introduction

High-spin Fe(II) is a non-Kramers (integer spin) ion of typically very large zero-field splitting, on the order of ~5 to 20 cm⁻¹. The allowed EPR transitions thus generally appear at high frequencies, and/or at high magnetic fields. Successful EPR studies on the iron(II) compounds are very infrequent. The title compound can be obtained in two crystalline forms¹, of which one exhibits a thermally driven ‘spin-crossover’ transition becoming diamagnetic below 170 K, while the other form, studied here, remains paramagnetic down to the liquid helium temperatures. The X-Ray structures of both forms are known¹.

Experimental

Magnetic susceptibility was measured over the temperature range 1.8-300 K using a SQUID magnetometer. Mössbauer studies were also performed. EPR spectra were taken at the NHMFL using both the 15/17 Tesla instrument and the 25 Tesla ‘Keck’ magnet equipped with tunable backwards-wave oscillators. Maximum frequency of ca. 700 GHz was employed².

Results and Discussion

The relatively temperature-independent quadrupole splitting of the ⁵⁷Fe Mössbauer spectrum of ~3.0 mm/s is consistent with an isolated, orbitally non-degenerate S=2 ground state of the metal ion. Temperature dependence of the magnetic susceptibility allowed for estimation of the D parameter of the standard spin Hamiltonian: $D \approx +12$ cm⁻¹. The EPR spectra at sufficiently high operating frequencies consist of five strong, well-defined resonances. Rather than fitting the spin Hamiltonian parameters to single-frequency spectra, we obtained a two-dimensional dataset of the resonant fields versus transition energies, as shown by the squares in the Figure. Fitting the standard spin Hamiltonian parameters to that complete dataset of resonances yielded $D = +12.427(12)$, $E = +0.243(3)$ cm⁻¹; $g_x = 2.147(3)$, $g_y = 2.166(3)$, $g_z = 2.01(1)$

Conclusions

The spin Hamiltonian parameters can give initial insight into the electronic structure of Fe(II). We used the full $d^6$ basis set and the following parameters moderately altered from the literature data³, chiefly by including a larger trigonal splitting (values in cm⁻¹): Racah $B = 750$, $C = 3400$; Ballhausen crystal-field, $D_q = 1100$, $D_s = 370$, and spin-orbit coupling, $\zeta = 368$ ($\lambda = -92$), which yield a true spin quintet, orbitally non-degenerate ground state with axial zero-field splitting, $D = +12.5$ cm⁻¹. The heteroleptic nature of our compound as opposed to homoleptic [Fe(im)₆]²⁺ makes an AOM analysis more difficult in our case, and we have not attempted it nor tried to model the small rhombic zero-field splitting term observed.

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References