# 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

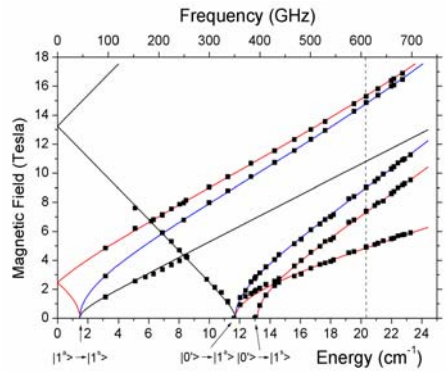
High-spin Fe(II) is a non-Kramers (integer spin) ion of typically very large zero-field splitting, on the order of ~5 to 20 $cm^{-1}$. The allowed EPR transitions thus generally appear at high frequencies, and/or at high magnetic fields. Successful EPR studies on the iron(II) compounds are very infrequent. The title compound can be obtained in two crystalline forms[1], 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 known[1].

## 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 employed[2].

## Results and Discussion

The relatively temperature-independent quadrupole splitting of the $^{57}$Fe 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)




Resonance field vs. microwave quantum energy for EPR transitions. Squares: experimental points. Simulations are shown by blue lines for *x* turning points, red lines for *y* turning points, and black lines for *z* turning points.

## 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 data[3], chiefly by including a larger trigonal splitting (values in $cm^{-1}$): Racah $B$ = 750, $C$ = 3400; Ballhausen crystal-field, $Dq$ = 1100, $Ds$ = 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 $[Fe(im)_6]^{2+}$ in[3] makes an AOM analysis more difficult in our case, and we have not attempted it nor tried to model the small rhombic zero-field splittinhg term observed.

## Acknowledgements

This work was supported by NHMFL through projects 7300-036 and 3000-243. NHMFL is funded by the NSF through Grant DMR-0084173 and the State of Florida. NSF–DMR supported the purchase of a SQUID magnetometer at Northeastern University. The W. M. Keck Foundation funded the high-homogeneity resistive magnet.

## References

[1] Ozarowski, A., *et al*. J. E. *Inorg. Chem.* ***27***, 628-635 (1988).
[2] Ozarowski, A., *et al*. J. Am. Chem. Soc. **126**, 6574-6575 (2004)
[3] Carver, G., *et al*. *Inorg. Chem.* ***42***, 5771-5777 (2003)