

Intramolecular N-H...Cl Hydrogen Bonding in the Outer Coordination Sphere of a Bipyridyl Bisurea-based Ligand Stabilize a Tetrahedral FeLCl₂ Complex

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Table of Contents

General Experimental.....	S2
Metal Complex Formation.....	S2
X-ray Crystallography Experimental.....	S2
Magnetic Measurements.....	S2
Mass Spectra.....	S4
References.....	S5

General Experimental

All chemical manipulations were carried out in a dry glovebox containing a dinitrogen atmosphere. All solvents were anhydrous unless otherwise noted. All chemicals were obtained from Sigma Aldrich, TCI, or Acros and used as received. Mass spectrometric measurements were performed in the positive ion mode using a Finnigan LCQ Duo mass spectrometer, equipped with an electrospray ion source and a quadrupole ion trap mass analyzer.

Metal Complex Formation

1·FeCl₂. Ligand **1** (0.0109 g, 0.0132 mmol) was suspended in 5 mL of THF. Anhydrous FeCl₂ (0.0028 g, 0.0221 mmol) was added, and the suspension dissipated producing a clear yellow solution. The mixture was stirred under inert atmosphere at 25 °C for 24 h. Upon filtration 0.0051 g of the desired material was obtained as a bright yellow powder. ESI-MS for C₄₈H₄₃Cl₂FeN₈O₆⁺: calc'd 953.2, found 953.9, and for C₄₈H₄₂Cl₂FeN₈O₆⁺: calc'd 952.2, found 952.0.

X-ray Crystallography

Diffraction intensities for **1**·FeCl₂ were collected at -173(2) °C on a Bruker Apex CCD diffractometer using MoK α radiation λ = 0.71073 Å. Space groups were determined based on intensity statistics. Absorption correction was applied by SADABS.¹ Structure was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms in both structures were found from the residual density maps and refined with anisotropic thermal parameters. H atoms were refined in calculated positions using a rigid group model. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.²

Magnetic Measurements

Magnetic susceptibility data on a solid state sample were collected with a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer. In a dinitrogen glovebox, the powder sample was loaded into a gelatin capsule and inserted into a straw. The straws were sealed in a Schlenk tube prior to removal from the glovebox and quickly loaded into the instrument to minimize exposure to air. The presence of ferromagnetic impurities was tested at 100 K by measuring the susceptibility at fields from 1000 to 5000 Oe: a linear dependence indicated any influence of such impurities was quenched above 1000 Oe. Variable temperature susceptibility measurements were carried out in the temperature range of 5 to 295 K under a measuring field of 1000 Oe. The data were corrected by subtracting the measured susceptibility of an empty sample holder. Diamagnetic corrections were calculated by using Pascal's constants.³

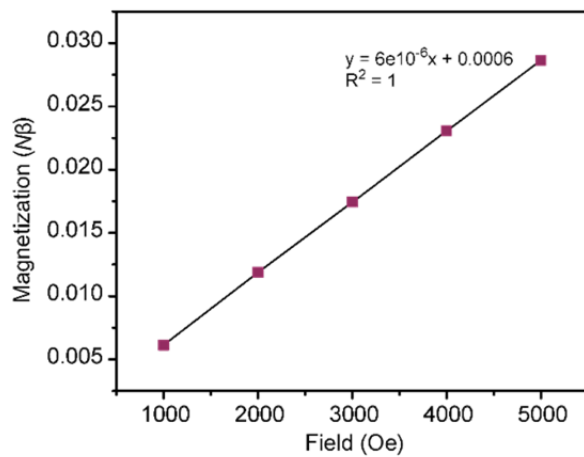


Figure S1 Test for ferromagnetic impurities, carried out at a temperature higher than where any possible weak intermolecular exchange coupling would be observed. The linear dependence ($R^2=1$) of the data confirms the lack of ferromagnetic impurities.

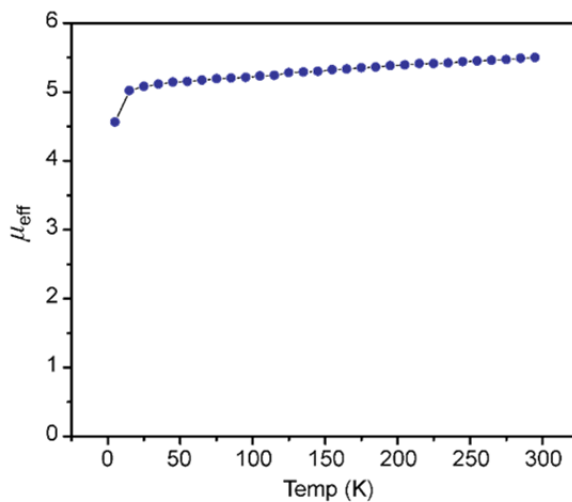


Figure S2 Temperature dependence of the effective magnetic moment for $[\text{FeLCl}_2]$, obtained under a 1000 Oe measuring field.

Mass Spectra

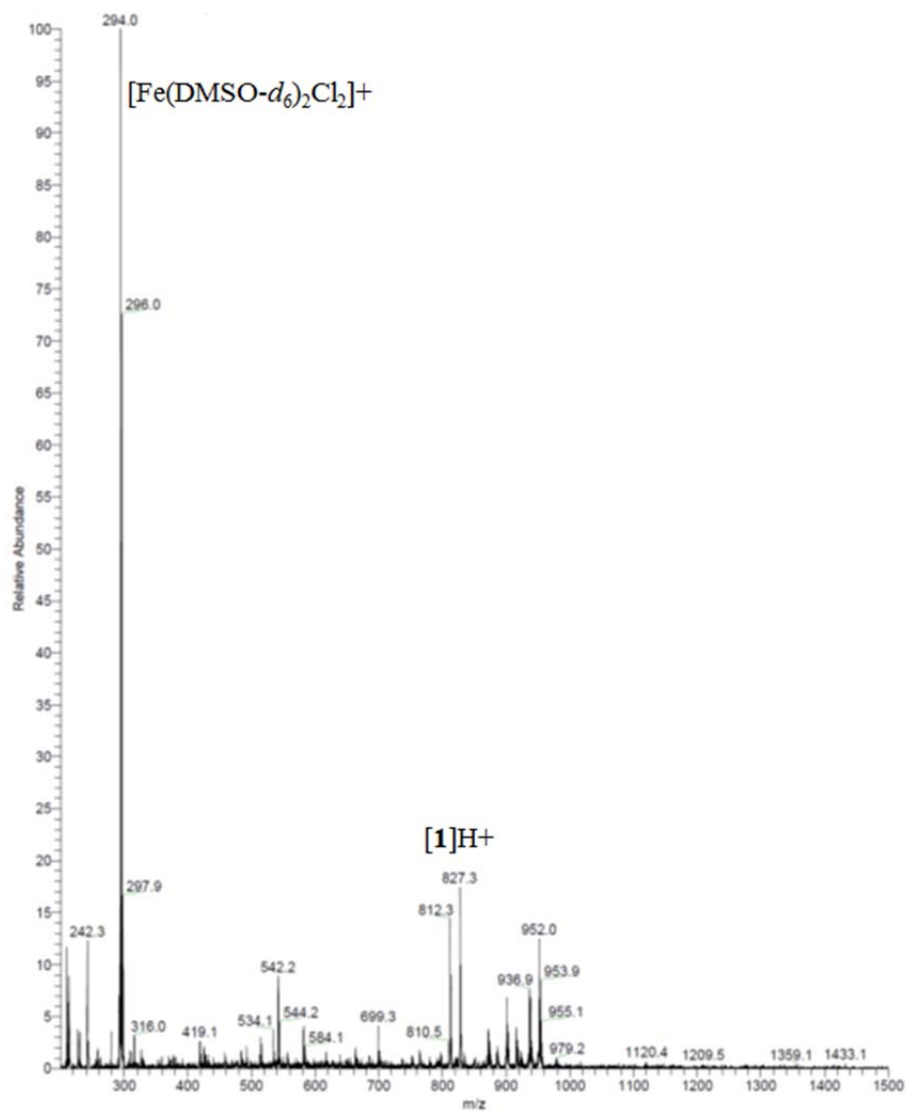


Figure S3 ESI mass spectra of $1 \cdot \text{FeCl}_2$ showing the major peaks are of dissociated metal and **1**.

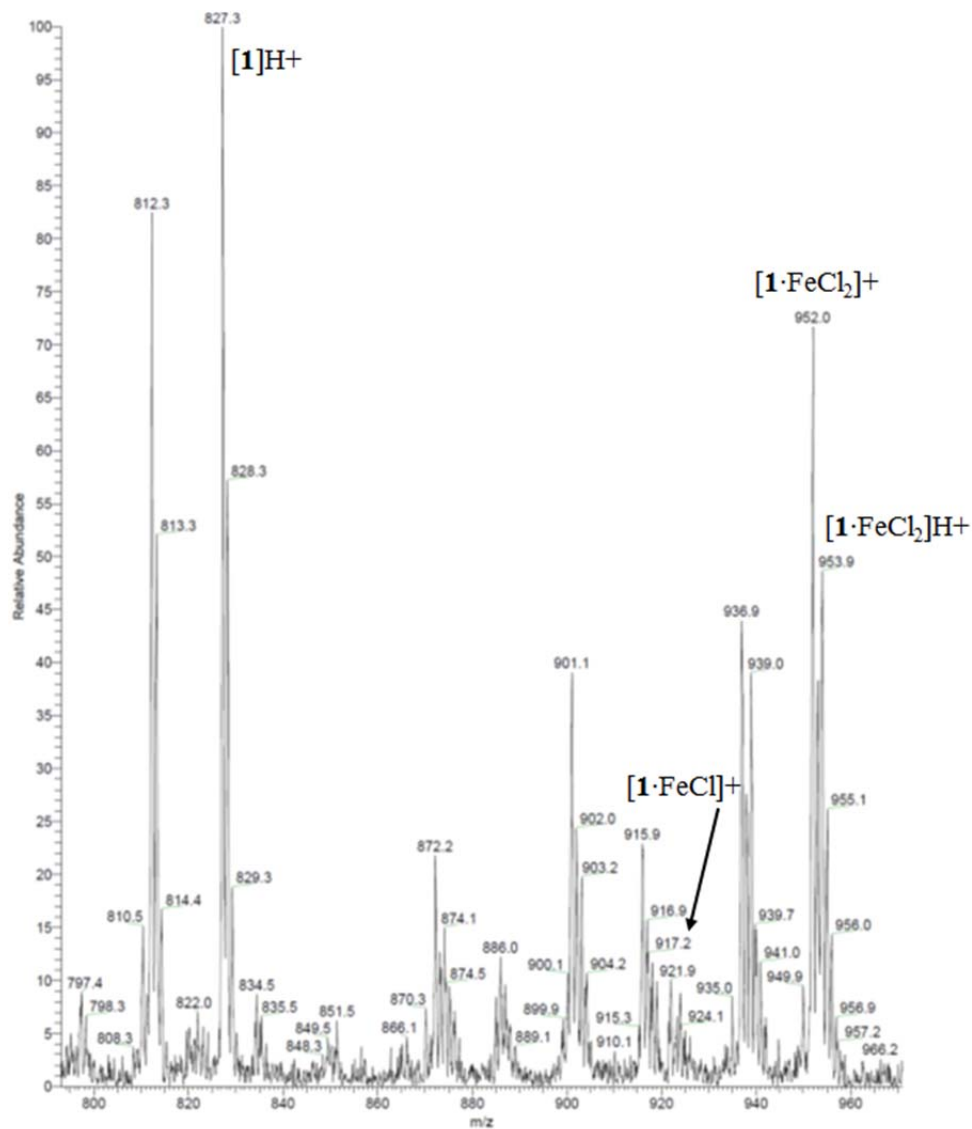


Figure S4 Partial ESI mass spectra on the region from 795-970 m/z indicating coordinated metal complexes

References

1. G. M. Sheldrick, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, 1998.
2. *SHELXTL-6.10 'Program for Structure Solution, Refinement and Presentation'*, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
3. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532–536.