Chemical Communication

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Supporting Information

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Physical Measurements

Electronic spectra of complexes were recorded with a Perkin-Elmer double-beam photometer (300 to 2000 nm). Cyclic voltammograms were recorded with and EG&G potentiostat/galvanostat.

Magnetic susceptibility data were measured from powder samples of solid material in the temperature range 2 - 300 K by using a SQUID susceptometer with a field of 1.0 T (MPMS-7, Quantum Design, calibrated with standard palladium reference sample, error <2%). The experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants{O'Connor, 1982 #41}{Weast, 1979 #668}, as well as for temperature-independent paramagnetism. The susceptibility and magnetization data were simulated with our own package julX for exchange coupled systems {Bill, 2008 #693}. The simulations are based on the usual spin-Hamilton operator for mononuclear complexes with spin S=2:

$$\hat{H} = g\beta \hat{\vec{S}} \cdot \vec{B} + D[\hat{S}_z^{\,2} - 1/3\, S(S+1) + E/D(\hat{S}_x^{\,2} - \hat{S}_y^{\,2})] \qquad \text{eq. 2}$$

where g is the average electronic g value, and D and E/D are the axial zero-field splitting and rhombicity parameters. Diagonalization of the Hamiltonian was performed with the routine ZHEEV from the LAPACK Library {E.B., 2008 #672}and the magnetic moments were obtained from first order numerical derivative dE/dB of the eigen values. The powder summations were done by using a 16-point Lebedev grid. {Lebedev, 1999 #670}, {Wang, 2003 #671. Intermolecular interactions were considered by using a Weiss temperature, Θ_W, as perturbation of the temperature scale, kT' = k(T-Θ_W) for the calculation. Powder summations were done by using a 16-point Lebedev grid.

References

{O'Connor, 1982 #41}
O'Connor, C. J., Prog. Inorg. Chem. 1982, 29, 203 - 283.

{Weast, 1979 #668}
Weast, R. C.; Astle, M. J., CRC Handbook of Chemistry and Physics. CRC Press Inc.: Boca Raton, Florida, 1979.

{Bill, 2008 #693}
available from E.B.: http://ewww.mpi-muelheim.mpg.de/bac/logins/bill/julX_en.php

{E.B., 2008 #672}
The LAPACK Linear Algebra Package is written in Fortran77 and provides routines for solving systems of simultaneous linear equations, least-squares solutions of linear systems of equations, eigenvalue problems, and singular value problems. The routines are available at http://www.netlib.org/lapack/

{Lebedev, 1999 #670}
Lebedev, V. I.; Laikov, D. N., Doklady Math. 1999, 59, 477.

{Wang, 2003 #671}
A Fortran code to generate Lebedev grids up to order L=131 is available at http://server.ccl.net/cca/software/SOURCES/

NMR spectra were recorded on Varian Mercury 400 MHz instruments at ambient temperature. Mössbauer spectra were simulated by using the program MFIT for Lorentzian line profiles. Mössbauer data were recorded on alternating constant-acceleration spectrometers. The sample temperature was maintained constant in an Oxford Instruments Variox cryostat or an Oxford Instruments Mössbauer-Spectromag cryostat. Isomer shifts are given relative to α-Fe at room temperature. Elemental analyses were performed by the Microanalytical Laboratory, Mülheim an der Ruhr (Germany).

X-Ray Crystallographic Data Collection and Refinement of the Structures

Single crystals of **1** and **2** were coated with perfluoropolyether, picked up with nylon loops, and were mounted in the nitrogen cold stream of the diffractometer. A Bruker-Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo Kα, λ= 0.710 73 Å) was used. Final cell constants were obtained from least-squares fits of all measured reflections. The structures were readily solved by direct methods and subsequent difference Fourier techniques. The Siemens ShelXTL software package was used for solution and artwork of the structure, and ShelXL97 was used for the refinement. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Syntheses and Characterisation

All synthesis were carried out using standard glovebox techniques in the absence of water and dioxygen, unless otherwise stated. Dry solvents were purchased from Fluka and degassed prior to use. The reagents $FeCl_2$, $Ni(COD)_2$ and $ZnCl_2$ were purchased from Strem or Aldrich and used without purification.

N,N'-Bis(6-methyl-2-pyridylmethylene)ethane-1,2-diamine (L)

This compound was prepared as described in the literature[4] and was isolated as pale yellow needles. Yield: 2.05 gm (77%). ^{1}H NMR ($CDCl_3$) δ: 2.52(s, 6H, *Me*); 3.99(s, 4H, *CH_2*); 7.11(d, J_{HH} = 7.5Hz, 2H, Py); 7.55(t, J_{HH} = 7.5Hz, 2H, Py); 7.74(d, J_{HH} = 7.7Hz, 2H, Py); 8.35 (s, 2H, N=C*H*).

^{13}C NMR($CDCl_3$) δ: 24.21(CH_3); 61.36(CH_2); 118.38, 124.27, 136.61, 157.98, 163.57(py, N=C*H*). Anal. Calcd. For $C_{16}H_{18}N_4$: C, 72.18; H, 6.76; N, 21.05. Found: C, 72.03; H, 6.60; N, 21.02.

[Ni^{II}_2 ($L^{\bullet\bullet}$)$_2$] (**1**): To a solution of $Ni(COD)_2$ (COD = cyclooctadiene) (100mg, 36.4mmol) in diethylether (10ml) was added N,N'-bis(6-methyl-2-pyridylmethylene)ethane-1,2-diamine (97mg, 36.4 mmol) and stirred for 24 hr. A dark violet solution was obtained which was evaporated in *vacuo*, washed with CH_3CN (2x 5ml) and extracted with diethylether. A purple black powder was obtained after removing the solvent. Single crystals of X-ray quality were grown from Et_2O at -20 °C. Yield: 188 mg (95%).

^1H NMR (400MHz, toluene-d_8, 213 K) δ: 8.875(s, 1H, imine *CH*); 7.7(t, 4H, J = 6.65 Hz, aryl *H*); 7.64(d, 4H, J = 6.65 Hz, aryl *H*); 6.70(d, 4H, J = 8.09 Hz, aryl *H*); 4.00(d, 4H, J = 12.6 Hz, CH_2); 2.53(d, 4H, J = 12.4 Hz, CH_2); 2.81 (s, 12H, CH_3).

Anal. Calcd. For $C_{34}H_{41}N_8Ni_2O_{0.5}$: C, 59.37; H, 5.96; N, 16.29; Ni, 17.08. Found: C, 59.48; H, 5.82; N, 16.52; Ni, 17.01.

$[Zn_2(L)Cl_4]$ **(2)**: To a solution of N,N'-bis(6-methyl-2-pyridylmethylene)ethane-1,2-diamine (975mg, 3.65mmol) in 5 ml MeCN was added a solution of $ZnCl_2$ (500mg, 3.65mmol) in 5 ml MeCN to obtain a colourless white precipitate. The solution was then filtered and a white precipitate was obtained which was dried under *vacuo*. X-ray quality crystals were grown from a concentrated solution in MeCN at -20° C. Yield: 445 mg (45%).

Anal. Calcd. For $C_{16}H_{18}N_4Cl_4Zn_2$: C, 35.60; H, 3.34; N, 10.39; Cl, 26.35; Zn, 24.20. Found: C, 35.80; H, 3.23; N, 10.37; Zn, 23.51; Cl, 26.38.

$[Fe(L)Cl_2]$ **(3)**: To a solution of N,N'-bis(6-methyl-2-pyridylmethylene)ethane-1,2-diamine (1.05gm, 3.9mmol) in 5 ml MeCN was added a solution of $FeCl_2$ (500mg, 3.9mmol) in 5 ml MeCN. A deep violet solution was obtained which was stirred for 2 days. The solution was filtered and a violet precipitate was obtained which was dried under *vacuo* to get violet powdered compound. Yield: 205 mg (95%).

Anal. Calcd. For $C_{16}H_{18}N_4Cl_2Fe$: C, 48.85; H, 4.58; N, 14.95; Cl, 18.07; Fe, 14.25. Found: C, 48.54; H, 4.68; N, 14.59; Fe, 14.03; Cl, 18.05.

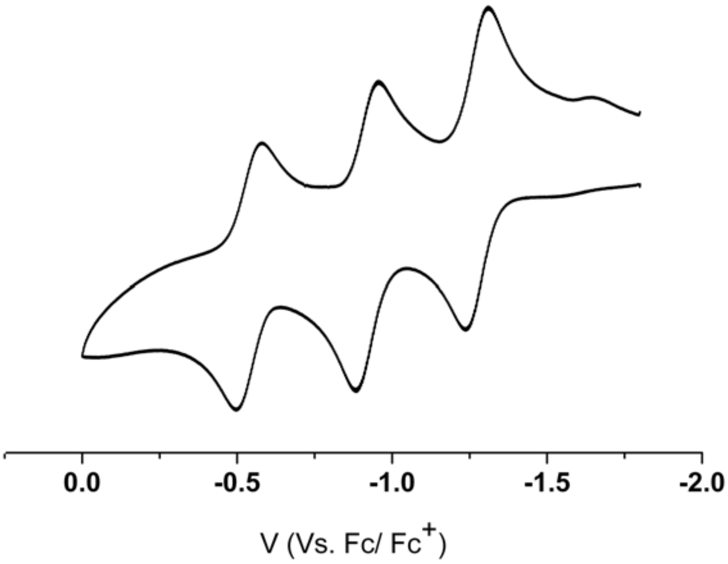

Figure S1. Cyclic voltammograms of **1** in THF, (0.1 M [N(n-Bu)$_4$]BF$_4$) as supporting electrolyte at 22 ^{o}C, glassy carbon working electrode 50mV/s scan rate, internal ferrocene(Fc) standard.

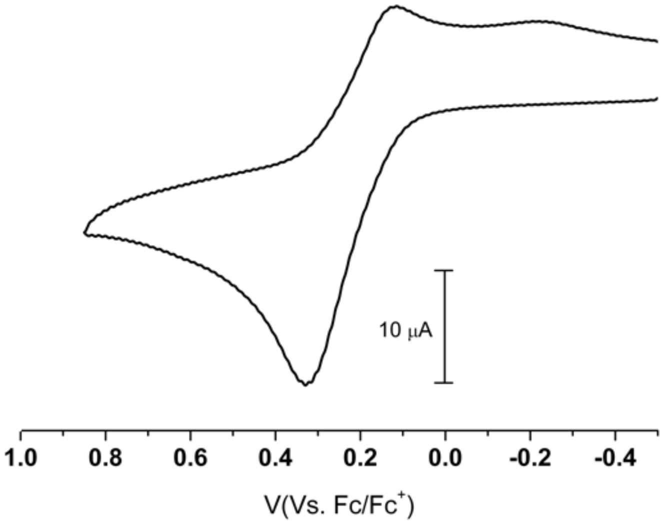

Figure S2. Cyclic voltammograms of **3** in MeOH with (0.1 M [N(n-Bu)$_4$]BF$_4$) as supporting electrolyte at 22 ^{o}C, glassy carbon working electrode 200mV/s , internal ferrocene(Fc) standard.

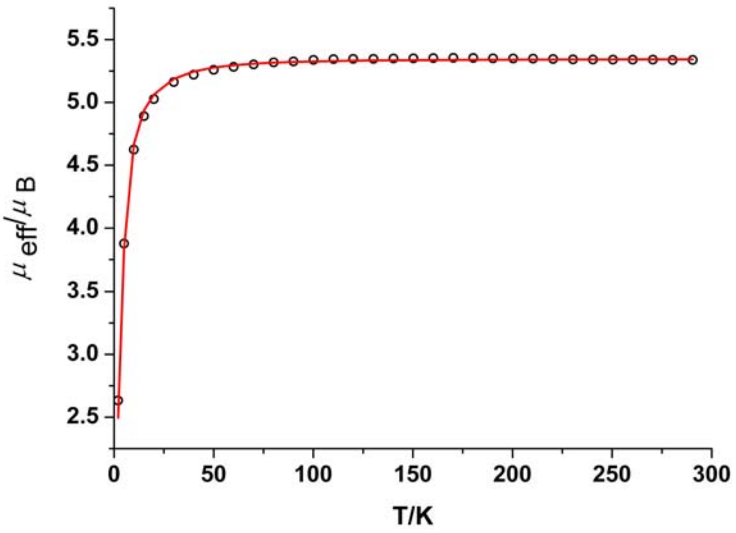

Figure S3. Temperature dependent magnetic moment of **3**, μ_{eff}/μ_B. The solid red line represent the spin-Hamiltonian simulation

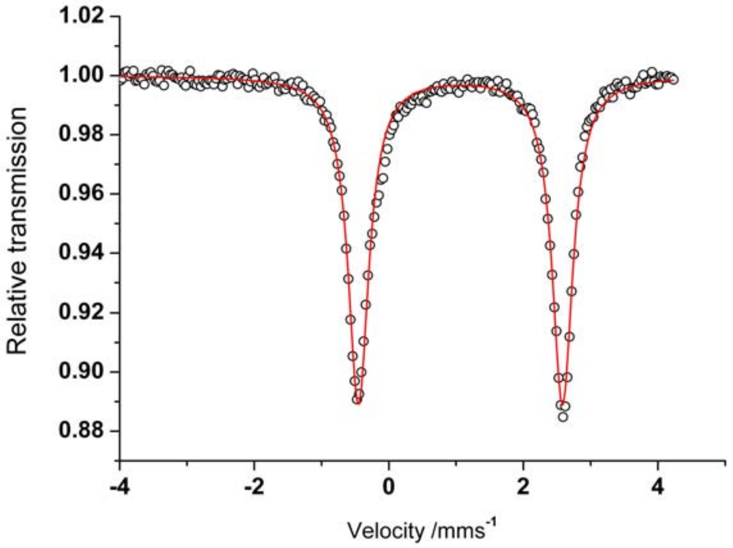

Figure S4. Zero-field Mössbauer spectrum of **3** at 80 K. The fit is shown in red line, with an isomer shift δ of 1.06 mm s^{-1} and a quadruple splitting $|\Delta E_Q|$ = 3.03 mm s^{-1}