Electronic Supplementary Information for Dalton Transactions

Supporting Information For:

Manipulating the crystal packing of pyDTDA radical ligand coordination complexes with Mn(II) and Ni(II)

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Experimental Details of Crystallography

*Complex **4**:*
Crystals of **4** arrived from the University of Guelph. A dark, block was mounted on a goniometer head. Data were collected at low temperature (-163 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data and systematic absences were consistent with a monoclinic space group: P2(1).

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by direct methods. The complex consisted of individual molecules of $[Mn(C_5HF_6O_2)_2(\mu\text{-}C_7H_3N_4S_2)]$. There were close contacts between the cyano group and neighbouring sulphur atoms. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.608 e/Å^3) was associated with the Mn atom. Full-matrix least squares refinement on F^2 gave $R_1 = 6.17$ for 2σ data and $wR_2 = 15.33$ for all data (GOOF = 1.096).

*Complex **5**:*
Crystals of **5** arrived from the University of Guelph. A dark, block was mounted on a goniometer head. Data were collected at low temperature (-163 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data and systematic absences were consistent with a monoclinic space group: P2(1)/c.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by Patterson methods. The data set was very weak and there were not sufficient observed data to give a decent data-to-parameter ratio. The complex consisted of individual molecules of $[Ni(C_5HF_6O_2)_2(\mu\text{-}C_7H_3N_4S_2)]$. There were close contacts between the cyano group and neighbouring sulphur atoms. The molecules were disordered at two of the $-CF_3$ sites and they were each modeled at a 56/44 ratio. Only the Ni and S atoms were refined with anisotropic thermal parameters. This gave a data to parameter ratio of about 7. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.950 e/Å^3) was associated with one of the $-CF_3$ units. Full-matrix least squares refinement on F^2 gave R_1 = 13.17 for 2σ data and wR_2 = 30.04 for all data (GOOF = 1.169).

*Complex **6**:*

Crystals of **6** were grown by sublimation. A purple block was mounted on a glass fibre. Data were collected at low temperature (-123 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data were consistent with a triclinic space group: P(-1).

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by Patterson methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. Distinct molecules were formed. The complex was well ordered except for one of the $-CF_3$ groups. It was modeled as a 53/47 mixture of isotropic fluorine atoms. The cyano group points towards the S-S bond of an adjacent molecule. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.521 e/Å^3) was associated with the disordered $-CF_3$ group. Full-matrix least squares refinement on F^2 gave R_1 = 5.14 for 2σ data and wR_2 = 13.48 for all data (GOOF = 1.025). The final solution was submitted to the IUCR checkCIF program and 2 Alert level B's. These were associated with the isotropic disorder and the close contact between the cyano group and the sulphur atoms.

Complex 7:

Crystals of **7** arrived from the University of Guelph. The red, plate was mounted on a goniometer head. Data were collected at low temperature (-163 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data were consistent with a triclinic space group: P(-1).

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by direct methods. The complex consisted of individual molecules of $[Ni(C_5HF_6O_2)_2(\mu\text{-}C_7H_3N_4S_2)]$. There were close contacts between the cyano group and neighbouring sulphur atoms. The R-value could not be reduced below 25.2 % and there were definite signs of twinning. A possible Twin Law was suggested by ROTAX. This caused an improvement in R1, wR2, GOOF, K, standard uncertainties and the size of top Q-peak. Thus, confirming the correctly chosen Twin Law. All of the non-hydrogen atoms, except C5, C8, and C12, were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.431 e/Å^3) was associated with one of the nitrogen atoms. Full-matrix least squares refinement on F^2 gave R_1 = 7.34 for 2σ data and wR_2 = 21.60 for all data (GOOF = 1.052). Some weak high angle data was discarded and the fact that the molecule was twinned led to some oblate and/or prolate ellipsoids.

*Complex **8**:*

Crystals of **8** arrived from the University of Guelph. A dark, wine plate was selected and mounted on a goniometer head. Data were collected at low temperature (-173 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data and systematic absences were consistent with a monoclinic space group: C2/c.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure using direct methods. There were two molecules in the asymmetric unit. There were three deviations from a well-ordered structure and all were disordered CF_3 ligands. One was modeled as a .43/.57 mixture, one at .54/.46 and one at .41/.59. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.431 e/Å^3) was associated with one of the perfluorobutyl moieties. Full-matrix least squares refinement on F^2 gave R_1 = 4.55 for 2σ data and wR_2 = 11.54 for all data (GOOF = 0.989).

Magnetic Characterization of Complex 6

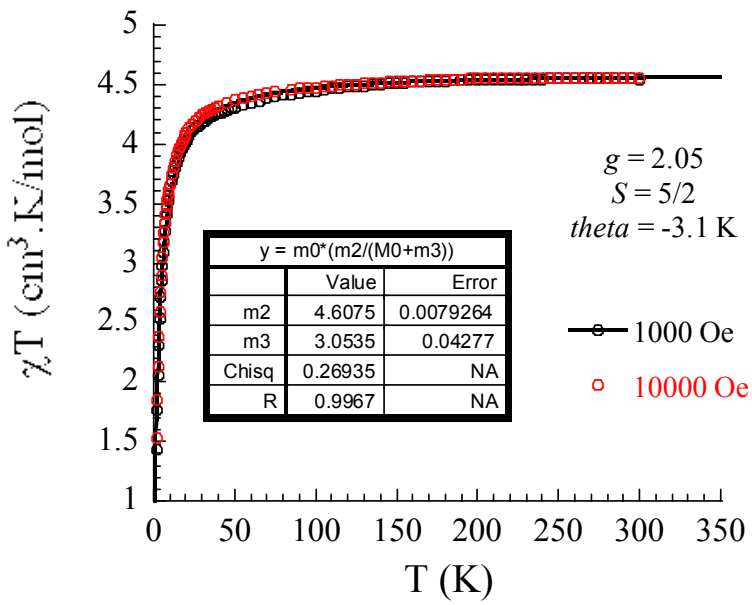

Figure S-1. χT vs T plot for **6** measured at 1000 Oe (black circles) and 10000 Oe (red circles), and best-fit parameters generated from Curie-Weiss model (black line).