

Supporting Information for

Photo-induced excited state structure of a hetero-bimetallic ionic pair complex, $\text{Nd}(\text{DMA})_4(\text{H}_2\text{O})_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, analyzed by single crystal X-ray diffraction

Helle Svendsen,^a Jacob Overgaard,^a Yu-Sheng Chen,^b Bo B. Iversen^{*a}

^a *Centre for Materials Crystallography, Department of Chemistry and iNANO, University of Aarhus, DK-8000 Århus C, Denmark. Fax: (+) 45 - 8619 6199; E-mail: bo@chem.au.dk*

^b *ChemMatCARS beam line, The University of Chicago, Advanced Photon Source, Argonne, IL 60439, USA.*

Experimental Section

Synthesis

The compound NdFeDMA was synthesized by mixing $\text{K}_3[\text{Fe}(\text{CN})_6]$ (1 mmol) with water (10 mL). The lanthanide salt, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol), dissolved in DMA (5 mL) was then added down the side of the glass very slowly. Green-yellow crystals precipitated and crystals suitable for single crystal X-ray analysis were obtained after evaporation. The compound crystallizes in the $\text{P2}_1/\text{n}$ space group and has four asymmetric ($[\text{Nd}(\text{C}_4\text{H}_9\text{NO})_4(\text{H}_2\text{O})_4]\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) units per unit cell. The metal centers are connected to each other through hydrogen bonds formed with the crystal water molecule.

Photocrystallography

Single crystal X-ray diffraction experiments with and without UV illumination have been conducted at the ChemMatCARS beamline (ID-15) at the Advanced Photon Source, Argonne National Lab, IL, USA. Data were measured at a Bruker D8 diffractometer equipped with a Bruker APEXII CCD detector. A helium cryostat (Pinkerton type cooling device)¹ was used for cooling the crystal down to approximately 15 K. The X-ray wavelength was 0.41328 Å (30 keV).

The UV light used for excitation was a CUBE laser diode with a wavelength of 375 nm a power output of 4 mW. The UV light was focused on to the sample using a light guide and a lens. The dimension of the crystal was $\sim 50 \mu\text{m}$. It was attached with oil on a goniometer head before mounting on the diffractometer. First, a ground state data collection was measured (GS. data collection). After turning on the UV light identical small data collections of a few minutes were repeated until no further changes were observed in the unit cell parameters. The data collection used for the ground state determination was then repeated (EXC. data collection) – also with continuous UV illumination.

The data were integrated using the software SAINT+ and further processed and corrected for empirical absorption using SADABS.² The data were merged in SORTAV.³ The structures were refined with SHELXL-97.² All non-water hydrogen atoms were refined as riding on the parent C atom. The ground state data collection was refined using a single conformer with full occupancy on all sites except for the three disordered DMA molecules. The overlapping atoms in the disorder were fixed to identical positions and their ADPs were kept identical. The sum of the occupancies of the two disordered parts was fixed to unity. The occupancy of the major components was 60%, 79%, and 64% for DMA groups 20, 30, and 40, respectively. All atoms except hydrogen were treated anisotropically. The ground state fractional coordinates and ADPs were then imported into the refinement of the excited state data collection where two conformers were co-refined; an excited state structure and a fixed ground state structure. The sum of their occupancies was constrained to unity. No disorder was modeled for any of the DMA groups in the excited state conformer. The four DMA groups in the excited state were modeled using isotropic ADPs while the rest of the non-hydrogen atoms are modeled anisotropically. It was not possible to locate the hydrogen atoms in the water molecules in the excited state.

An analysis of the data using only one conformer has also been performed, thereby obtaining an average structure of the ground state and the excited state structure. These average models showed the exact same bond lengths tendencies as the excited state structures obtained from the two conformer models, though not as evident.

In order to investigate the reversibility of the structural changes, the UV light was turned off after the excited state data were collected. No changes were afterwards observed in the cell parameters. All crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 823987-823988.

GS data collection: Space group $P2_1/c$, $a = 14.364(1) \text{ \AA}$, $b = 14.075(1) \text{ \AA}$, $c = 17.803(1) \text{ \AA}$, $\beta = 91.295(2)^\circ$, $V = 3598.4(5) \text{ \AA}^3$, No. of measured reflections = 106328, No. of unique reflections = 17531, $R_{\text{int}} = 0.0458$, Refinement: $N_{\text{obs}}(I > 2\sigma) = 13054$, $N_{\text{par}} = 505$, $R_{\text{all}} = 0.0499$, $R(I > 2\sigma) = 0.0303$, $wR(I > 2\sigma) = 0.0725$

EXC data collection: Space group $P2_1/c$, $a = 14.188(1) \text{ \AA}$, $b = 14.022(1) \text{ \AA}$, $c = 17.873(1) \text{ \AA}$, $\beta = 91.441(2)^\circ$, $V = 3554.7(4) \text{ \AA}^3$, No. of measured reflections = 104191, No. of unique reflections = 17290, $R_{\text{int}} = 0.0501$, Refinement: $N_{\text{obs}}(I > 2\sigma) = 9534$, $N_{\text{par}} = 287$, $R_{\text{all}} = 0.1271$, $R(I > 2\sigma) = 0.0642$, $wR(I > 2\sigma) = 0.143$

1. Hardie, M. J.; Kirschbaum, K.; Martin, A.; Pinkerton, A. A., *J. Appl. Crystallogr.* **1998**, *31*, 815-817.
2. Sheldrick, G. M. *SAINT+, SADABS, XPREP and SHELXTL programs included in the Bruker SMART CCD software*, 2003.
3. Blessing, R. H., *J. Appl. Crystallogr.* **1997**, *30*, 421-426.