Supplimentary Information

Spin Crossover Behaviour of Asymmetrical Iron(III) Schiff Base Complexes from Ethylenediamine

Dawit Tesfaye ^{a,b,c,d}, Mamo Gebrezgiabher ^{a,b}, Jonas Braun ^e, Taju Sani ^{a,b}, Abbasher Gismelseed ^f, Tim Hochdörffer ^g, Volker Schünemann ^g, Juraj Kuchár ^d, Juraj Černák ^d, Christopher E. Anson ^e, Madhu Thomas ^{a,b*} and Annie K. Powell ^{e*}

^aDepartment of Industrial Chemistry, College of Natural and Applied Sciences, Addis Ababa Science and Technology University, Addis Ababa P.O. Box 16417, Ethiopia.

^bNanotechnology Center of Excellence, Addis Ababa Science and Technology University, Addis Ababa P.O. Box 16417, Ethiopia.

^eDepartment of Chemistry, College of Natural Sciences, Salale University, Fitche P.O.Box 245, Ethiopia.

^dDepartment of Inorganic Chemistry, Institute of Chemistry, P. J. Šafárik University in Košice, Moyzesova 11, 041 54 Košice, Slovakia.

^eInstitute of Inorganic Chemistry (AOC), Institute of Nanotechnology (INT) and Institute for Quantum Materials and Technologies (IQMT) Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany.

^fDepartment of Physics, College of Science, Sultan Qaboos University, P.O.Box 50 Al-khod, Oman.

^gDepartment of Physics, University of Kaiserlautern-Landau, Erwin-Schrödinger-Strasse 46, 67663, Kaiserlautern, Germany.

X-ray Crystallography

Experimental

X-ray diffraction measurement for 1 was performed at 173 K (1-173) on a Xcalibur diffractometer from Rigaku OD equipped with Sapphire2 CCD detector with graphitemonochromated MoK α sealed-tube as source ($\lambda = 0.71073$ Å) and at 299 K (1-299) on a Gemini diffractometer from Rigaku OD equipped with AtlasS2 CCD detector with graphite-monochromated MoK α sealed-tube as source ($\lambda = 0.71073$ Å). Inspection of additional single crystals from the synthetic batch has revealed that another studied single crystal was composed of two phases, i.e. that of complex 1 along and of complex 2 exhibiting the same composition as complex 1 but without methanol solvate molecule.

This single crystal was studied on a diffractometer used for data collection of complex 1-173 at the same temperature. It was possible to gather diffraction data of both phases but here we present the results of complex 2 as the complex 1 was already studied at two different temperatures. The data collections were done using the CrysAlisPro software package ¹. The data were corrected for absorption using numerical absorption correction based on analytical integration over a multifaceted crystal model 2 with $T_{\text{min}}=0.746$ and $T_{max} = 0.852$ for **1-173**, $T_{min} = 0.607$ and $T_{max} = 0.883$ for **1-299**, and $T_{min} = 0.719$ and T_{max} = 0.891 for 2. The structures of 1-173, 1-299 and 2 were solved by direct methods and refined by full-matrix least-squares techniques on F² using programs SHELXT and SHELXL ^{3–5} that is incorporated in the WinGX program package. ⁶ All non-hydrogen atoms including the well-defined methanol solvate molecule were refined with anisotropic thermal parameters. Hydrogen atoms on the Schiff base type ligands were placed in the calculated positions and allowed to ride on the parent atoms with isotropic thermal parameters tied with the parent atoms ($U(H) = 1.2U(CH_2)$ and $U(H) = 1.5U(CH_3)$), while the positional coordinates of the hydroxyl hydrogen atoms in methanol (O6 atoms) solvate molecule were refined with application of restrained O-H distances. The positional parameters of the hydrogen atoms bound to the methine carbon atoms were refined. Structural figures were drawn using Diamond program.⁷ Crystal data and refinement results

for both complexes are summarized in **Table 1** and the selected bond lengths and bond angles of the complexes are presented in **Table 2**

Structure [ML6]	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
Complex (1-173)	30.912	28.610	0.204	15.343	31.940
Complex (1-299)	30.947	28.473	0.202	15.181	31.835
Complex 2	32.159	22.113	1.883	10.983	25.818

Table S1. Shape calculations results for 1-173 and 1-299 and 2

HP-6 1 D	6h Hexagon
----------	------------

PPY-6 2 C5	Pentagonal pyramid
------------	--------------------

- OC-6 3 Oh Octahedron
- TPR-6 4 D3h Trigonal prism
- JPPY-6 5 C5v Johnson pentagonal pyramid J2

Table S2. Possible hydrogen bond interactions for 1-299

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C1-H1A…O6	0.97	2.59	3.350(9)	135.3
N1-H1C…O3	0.89	2.12	2.927(7)	150.9
N1-H1D····O4 ⁱ	0.89	2.03	2.916(7)	173.2
N3-H3A…O3	0.89	2.36	3.230(8)	166.9
N3-H3A…O5	0.89	2.44	3.175(9)	139.5
N3-H3B····O6 ⁱⁱ	0.89	2.24	3.083(7)	158.4
O6-H6A…O2	0.82	1.95	2.773(6)	177.0





Fig. S2. View of the coordination polyhedra of the Fe(III) atoms in 1-173 (left), 1-299 (middle) and 2 (right).



Fig. S3. Overlay of the two complex cations of **1-173** (blue) and **2** (red). The two complex cations were overlayed so that the Fe central atoms, respective O1 and O2 donor atoms and respective N2 donor atoms are as close as possible. Hydrogen atoms are omitted for clarity.



Fig. S4. Simulated Powder XRD pattern of the mixture of [Fe(saen)₂]NO₃·CH₃OH (1) (monoclinic)-red and [Fe(saen)₂]NO₃ (2) (triclinic) –blue. Experimental –black.

The ESI-MS spectrum was recorded in positive mode. The molecular peak at m/z = 382.11 corresponds to the singly-charged complex and the observed isotopic pattern is in excellent agreement with the simulated pattern. The minor features centred at m/z = 388.09 and 394.68 show much smaller separations between the constituent peaks than those for the molecular peak, and may be assigned to multiply-charged species resulting from aggregation of the complex molecules. ⁸



Fig.S5. ESI-MS of the complexes 1 and 2

References

- 1 R. CrysAlis^{Pro} (1.171.41.93a), *Oxford Diffraction*, Oxford Diffraction Ltd, England, 2020.
- 2 R. C. Clark and J. S. Reid, *Acta Crystallogr. Sect A*, 1995, **51**, 887–897.
- G. M. Sheldrick, *Acta Crystallogr. Sect A Found Crystallogr*, 2015, **71**, 3–8.
- 4 G. M. Sheldrick, *Acta Crystallogr Sect C Struct Chem*, 2015, **71**, 3–8.
- 5 G. M. S.-97 Sheldrick, Crystal structure refinement with SHELXL, Bruker AXS Inc,

Madison, WI, WI, 1997, vol. version 5.

- 6 L. J. Farrugia, J Appl Crystallogr., 2012, 45, 849–854.
- 7 Dr. H. Putz, D. K. B. Brandenburg GbR, and Kreuzherrenstr, Diamond Crystal and Molecular Structure Visualization, Crystal Impact, 102, 53227 Bonn, Germany, 2022.
- 8 J. S. McIndoe and K. L. Vikse, *J Mass Spectrom*, 2019, **54**, 466–479.