

Appendix

Crystallographic Details

Crystals of compound **LCu₂·4 toluene**, **LNi₂·4 toluene** and **LH₂Ni·acetone**, **LH₆²⁺·acetone** and TFA were mounted on a Bruker three circle diffractometer equipped with a SMART 6000 detector and with monochromated Cu-K_α radiation ($\lambda = 1.54 \text{ \AA}$). Integration was performed with SAINT [1], absorption and intensity data were corrected with the SADABS program [2]. The structure was solved using direct methods and refined by full-matrix least-squares procedures against F^2 with SHELX [3]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were added using the riding model.

X-ray data for **[LCu₂(acetone)₂](BF₄)₂ · 2 toluene · 2 acetone** were collected on a STOE IPDS II diffractometer (graphite monochromated Mo-K_α radiation, $\lambda = 0.711 \text{ \AA}$) by use of ω scans. The structure was solved by direct methods and refined on F^2 using all reflections with SHELX [3]. Most non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.2/1.5 Ueq(C). Counterions and solvent molecules were found to be disordered. SADI (d_{B-F} , d_{F-F}) restraints were used to model the disorder of the counterions.

In the case of **LCu₂·4 toluene**, **LNi₂·4 toluene** the asymmetric unit contains half a molecule and two toluene molecules. The two disordered toluene solvent molecules could be refined. FLAT, DFIX, and DANG as well as SIMU, DELU, and ISOR restraints were used, because of complex ligand and solvent disorder. The asymmetric unit of **[LCu₂](BF₄)₂** contains half a molecule and one acetone. For **LH₂Ni·acetone**, **LH₆²⁺·acetone** the refinement was challenging due to several incorporated disordered solvent molecules and in the case of **LH₆²⁺** the presented result is preliminary.

	LH ₆ ²⁺	LH ₂ Ni
Empirical formula	C _{395.62} H _{366.64} F _{21.45} N ₃₂ O _{37.90}	C _{207.90} H _{220.60} N ₁₆ Ni ₂ O _{12.60}
Formula weight	6583.22	3262.41
Temperature	100(2) K	100(2) K
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 19.4383(3) Å <i>α</i> = 66.0039(2)° <i>b</i> = 22.0280(6) Å <i>β</i> = 89.2671(2)° <i>c</i> = 23.8899(7) Å <i>γ</i> = 88.4771(2)°	<i>a</i> = 14.9415(4) Å <i>α</i> = 98.1120(10)° <i>b</i> = 17.0016(4) Å <i>β</i> = 96.8950(10)° <i>c</i> = 19.0343(5) Å <i>γ</i> = 109.7450(10)°
Volume/ Å ³	9341.9(5)	4431.9(2)
<i>Z</i>	1	2
Density (calculated)/Mg/m ³	1.164	1.222
Absorption coefficient/mm ⁻¹	0.672	0.789
<i>F</i> (000)	3443	1737
Crystal size/mm ³	0.02 × 0.01 × 0.01	0.125 × 0.125 × 0.125
<i>θ</i> range for data collection	2.2 to 70.3°	2.384 to 68.245°
Index ranges	-23 ≤ <i>h</i> ≤ 23 -39 ≤ <i>k</i> ≤ 38 -16 ≤ <i>l</i> ≤ 14	-18 ≤ <i>h</i> ≤ 18 -21 ≤ <i>l</i> ≤ 19 -20 ≤ <i>k</i> ≤ 20
Reflections collected	57916	97557
Independent reflections	57916 [<i>R</i> (int) = 0.039]	15835 [<i>R</i> (int) = 0.0393]
Data/restraints/parameters	57913/6336/4618	15835/1523/1284
Goodness-of-fit on <i>F</i> ²	2.63	1.078
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1298, <i>wR</i> 2 = 0.3220	<i>R</i> 1 = 0.0602, <i>wR</i> 2 = 0.1667
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1559, <i>wR</i> 2 = 0.3514	<i>R</i> 1 = 0.0657, <i>wR</i> 2 = 0.1794
Res. el. dens/e/Å ³	-0.66 and 1.73	0.671 and -0.858

	LNi ₂	LCu ₂
Empirical formula	C ₁₂₀ H ₁₁₂ N ₈ Ni ₂	C ₁₂₀ H ₁₁₂ Cu ₂ N ₈
Formula weight	1783.74	1793.26
Temperature	100(2) K	100(2) K
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions	<i>a</i> = 19.5208(9) Å <i>α</i> = 90° <i>b</i> = 21.9198(1) Å <i>β</i> = 109.601(2)° <i>c</i> = 23.3495(1) Å <i>γ</i> = 90°	<i>a</i> = 19.594(3) Å <i>α</i> = 90° <i>b</i> = 22.051(3) Å <i>β</i> = 90° <i>c</i> = 23.455(4) Å <i>γ</i> = 90°
Volume/Å ³	9412.1(3)	9523(3)

(continued)

(continued)

	LNi ₂	LCu ₂
Z	4	4
Density (calculated)/Mg/m ³	1.259	1.251
Absorption coefficient/mm ⁻¹	0.925	0.974
F(000)	3777	3784
Crystal size/mm ³	0.25 × 0.02 × 0.01	0.05 × 0.05 × 0.02
θ range for data collection	3.1 to 73.8°	3.13 to 68.24°
Index ranges	-24 ≤ h ≤ 24 -27 ≤ l ≤ 26 -28 ≤ k ≤ 29	-23 ≤ h ≤ 23 -26 ≤ k ≤ 26 -27 ≤ l ≤ 28
Reflections collected	108147	241142
Independent reflections	9699 [R(int) = 0.030]	8631 [R(int) = 0.0424]
Data/restraints/parameters	8638/400/602	8631 / 2183 / 780
Goodness-of-fit on F ²	3.84	1.05
Final R indices [I > 2σ(I)]	R1 = 0.0296	R1 = 0.0472, wR2 = 0.1334
R indices (all data)	wR2 = 0.038	R1 = 0.0537, wR2 = 0.1425
Res. el. dens/e/Å ³	-0.228 and 0.287	1.157 and -0.447

	[LCu ₂ (acetone) ₂](BF ₄) ₂
Empirical formula	C ₁₁₈ H ₁₂₀ B ₂ Cu ₂ F ₈ N ₈ O ₄
Formula weight	2014.92
Temperature	133(2) K
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 18.8185 (1) Å α = 90° b = 22.3182 (1) Å β = 97.898 (4)° c = 24.6188 (1) Å γ = 90°
Volume/Å ³	10241.7 (9)
Z	4
Density (calculated)/Mg/m ³	1.307
Absorption coefficient/mm ⁻¹	0.488
F(000)	4224
Crystal size/mm ³	0.25 × 0.17 × 0.12
θ range for data collection	1.42 to 24.69°
Index ranges	-21 ≤ h ≤ 22 -26 ≤ k ≤ 26 -27 ≤ l ≤ 28
Reflections collected	45112

(continued)

(continued)

	[LCu ₂ (acetone) ₂](BF ₄) ₂
Independent reflections	8614 [<i>R</i> (int) = 0.1311]
Data/restraints/parameters	8614/257/701
Goodness-of-fit on <i>F</i> ²	1.138
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0849, <i>wR</i> 2 = 0.1590
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1300, <i>wR</i> 2 = 0.1760
Res. el. dens/e/Å ³	0.434 and -0.409

Details on DFT Calculations

DFT Optimizations

DFT calculations were carried out with the ORCA software package [4]. Atom coordinates were obtained from first guess structures drawn with ChemDraw3D. First, coordinates were optimized with the semi-empirical Austin Model 1 (AM1) [5, 6] and then refined using the Becke-Perdew-1986 functional (BP86) [7, 8]. Compounds **LH₄**, **LH₆²⁺** (symmetric and asymmetric protonation motif), **29a**, **29b**, **29c** and **29cH₂²⁺** readily converged.

TDDFT Calculations

Conformational analyses for **LH₆²⁺**, **LCu₂** and **LNi₂** were done using Gaussian09 software package.[96] The geometry optimization for **LH₆²⁺** was repeated using the B3LYP [9, 10] functional and performed for **LCu₂** and **LNi₂** as well. The 6-31G(d,p) basis set [11, 12] was chosen for all first-row elements and the larger 6-311G* [13, 14] basis set for the transition metals Cu and Ni. The TDDFT excited states calculations of the global minima were also performed using Gaussian09. The UV and CD spectra were also simulated with B3LYP/6-31G(d,p) for **LH₆²⁺** (nstates = 50), **LCu₂** (nstates = 40), and **LNi₂** (nstates = 40) while for the transition metals the 6-311G* basis set was used. The UV and CD curves of all compounds were calculated as sums of Gauss functions centered at the wavelength of the corresponding excitations and multiplied by the respective oscillator and rotational strength values (length formalism), with an empirically chosen exponential half width of 0.16 eV. Calculated rotational strength values were multiplied by -1 to get the enantiomeric CD curves. Before comparison of the computational CD curve with the experiments, a UV correction of 5 nm for **LH₆²⁺**, -10 nm for **LNi₂** and -30 nm for **LCu₂** was performed. SpecDis was used for Gauss curve generation, UV correction, plotting and comparison with experimental data [15–17].

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List of Scientific Contributions

Publications

“*The Siamese-Twin Porphyrin: A Pyrazole-Based Expanded Porphyrin Providing a Bimetallic Cavity*” L. K. Frensch, K. Pröpper, M. John, S. Demeshko, C. Brückner, F. Meyer, *Angew. Chem.* **2011**, *123*, 1456–1460; *Angew. Chem. Int. Ed.* **2011**, *50*, 1420–1424.

“*Siamese-Twin Porphyrin: A Pyrazole-Based Expanded Porphyrin of Persistent Helical Conformation*” L. K. Blusch, Y. Hemberger, K. Pröpper, B. Dittrich, F. Witterauf, M. John, G. Bringmann, C. Brückner, and F. Meyer, *Chem. Eur. J.* **2013**, *19*, 5868–5880.

“*Hidden Non-Innocence in an Expanded Porphyrin: Electronic Structure of the Siamese-Twin Porphyrin’s Dicopper Complex in Different Oxidation States*” L. K. Blusch, K. E. Craigo, V. Martin-Diaconescu, E. Bill, A. B. McQuarters, S. Dechert, S. DeBeer, N. Lehnert, F. Meyer, DOI:[10.1021/ja406176e](https://doi.org/10.1021/ja406176e)

Oral Presentations

“*Homo- and Heterobimetallic Complexes of the Siamese-Twin Porphyrin: Story of a Non-Innocent Twist*” Coordination Chemistry Conference (Zing conferences), Cancun, Mexico, December, **2011**.

“*The Siamese-Twin Porphyrin and its Copper Complex: Synthesis, Magnetic and Redox Properties*” Jung-Chemiker Forum (sponsored by GDCh), Göttingen, Germany, July **2011**.

“*The Siamese-Twin Porphyrin and its Copper Complex: Synthesis, Magnetic and Redox Properties*” Koordinationschemie-Treffen, Stuttgart, Germany, March **2011**.

“*Bioinorganic Molecules and Beyond: The Siamese-Twin Porphyrin as an Example*” ISER Pune - Georg-August University Göttingen workshop, Göttingen, Germany, October **2010**.

Poster Presentations

“Persistant Chiral Twists: Protonation Studies and Chiral Resolution of the Siamese-twin Porphyrin and its Homobimetallic Complexes” 16. Vortragstagung der Wöhlerversammlung 2012; Göttingen, September **2012**.

“The Siamese-Twin Porphyrin” International Symposium on Molecular Coordination Chemistry, MPI Mülheim, Germany, November **2010**.

“Synthesis of a Doubleporphyrin: A New Scaffold for Bimetallic Complexes” Summer School: Computational Chemistry and Spectroscopy; Essen, Germany, September **2009**.

Curriculum Vitae

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Academic career

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01/2009	“Diplom” in Chemistry
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