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Lina K. Blusch

The Siamese-Twin Porphyrin and Its Copper and Nickel Complexes: A Non-Innocent Twist

Doctoral Thesis accepted by
the Georg-August-University Göttingen, Germany

 Springer

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*Believe those who are seeking the truth.
Doubt those who find it.*

André Guide

Supervisor's Foreword

The highly impressive dissertation by Mrs. Blusch describes, for the first time, the formal fusion of two porphyrin-like chromophores into an expanded porphyrin dubbed Siamese-twin porphyrin, whereby the fusion points are pyrazole moieties. The design of expanded porphyrins has become a key topic in contemporary porphyrin chemistry. This is because these systems contribute to the general understanding of the factors controlling the conformation of larger π -conjugated oligopyrrolic macrocycles, and particularly how structural and conformational effects modulate and interconvert aromatic/anti-aromatic/non-aromatic conjugated π -systems.

The Siamese-twin porphyrin structure was long sought-after, but all previous attempts had been unsuccessful and it was only once Mrs. Blusch became involved that this novel expanded porphyrin could firstly be made. The availability of this unprecedented type of macrocycle now opens up an entirely new field of study. As described in this thesis, physicochemical investigations (using multi-nuclear, 1D and 2D NMR spectroscopy, UV-vis spectroscopy, and mass spectrometry) characterize the connectivity of the macrocycle and support the conclusions derived with respect to macrocycle conformation, the electronic coupling of the two near-isolated π -conjugated systems present in the macrocycle, its acid/base properties, and its conformational flexibility. The intrinsically helimeric (chiral) conformation of the twin porphyrin was shown spectroscopically as well as by single crystal diffractometry and rationalized using computational studies.

One more and major aspect of the twin-porphyrins is evaluated: the Siamese-twin porphyrin contains two pseudoplanar $\{N_4\}$ porphyrin-like coordination sites that each can accommodate a transition metal ion. Once metalated, the twin-porphyrin features a bimetallic complex in which the metals are bridged by two pyrazoles. Mrs. Blusch prepared the homobimetallic nickel(II) and copper(II) complexes as well as the heterometallic nickel(II)/copper(II) analog and characterized them by X-ray diffractometry, spectro-electrochemistry, cyclic voltammetry, SQUID magnetometry, X-ray absorption, and MCD spectroscopy, some of this in collaboration with specialty groups. Much of the investigations were focused on defining the degree of electronic coupling of the two metal centers and the involvement of the non-innocent ligand framework in redox events. An unusual ferromagnetic coupling of the two adjacent pyrazolate-bridged copper(II) ions and a sequence of multiple redox processes were found, whereby initial oxidations

appear to be largely ligand-based. This now offers exciting prospects for exploiting novel metal–metal as well as metal–ligand cooperativity effects when activating and transforming substrates at the metalated Siamese-twin porphyrin.

28 February 2013, Göttingen

Prof. Dr. Franc Meyer

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Abbreviations

AM1	Austin model 1
antiferro	Antiferromagnetic
Bn	Benzyl
BP86	Becke–Perdew-1986
Bz	Benzoyl
CA	Chloranil
CD	Circular dichroism
COSY	Correlation spectroscopy
CT	Charge transfer
CV	Cyclic voltammetry
D	Donor atom
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DFc	Decamethylferrocene
DFT	Density functional theory
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EDG	Electron donating group
EPR	Electron paramagnetic resonance
ESI	Electrospray ionization
Et	Ethyl
EWG	Electron withdrawing group
ex	Exchange
EXAFS	Extended X-ray absorption fine structure
Fc	Ferrocene
ferro	Ferromagnetic
h	Hour
HMBC	Heteronuclear multiple-bond correlation
HOMO	Highest occupied molecular orbital
HPLC	High pressure liquid chromatography
HR	High resolution
IAM	Independent atom model
IBX	2-Iodoxybenzoic acid
IR	Infrared

IV	Intervalence
LC	Liquid chromatography
lcp	Left circular polarized
LL	Ligand-to-ligand
LUMO	Lowest unoccupied molecular orbital
m. p.	Melting point
Me	Methyl
min	Minute
MM	Metal-to-metal
MRI	Magnetic resonance imaging
MS	Mass spectrometry
NIR	Near infrared
NLO	Non-linear optics
NMR	Nuclear magnetic resonance
NOE	Nuclear overhauser effect
OAc	Acetate
OEP	Octaethylporphyrin
PDT	Photodynamic therapy
Ph	Phenyl
ppm	Parts per million
PS	Polystyrene
py	Pyridine
pyr	Pyrrole
pz	Pyrazole
r. t.	Room temperature
rcp	Right circular polarized
sMMO	Soluble methane monooxygenase
SQUID	Superconducting quantum interference device
SVP	Split valence polarization
SWV	Square wave voltammetry
t	Total
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TFA	Trifluoroacetic acid
TLC	Thin layer chromatography
TPP	Tetraphenylporphyrin
UV-vis	Ultraviolet-visible
VTVH	Variable temperature variable field
XAS	X-ray absorption spectroscopy
ZFS	Zero field splitting