Structural, Electrochemical, and Photophysical Properties of Gallium(III) 5,10,15-Tris(pentafluorophenyl)corrole**

Jesper Bendix,* Ivan J. Dmochowski, Harry B. Gray,* Atif Mahammed, Liliya Simkhovich, and Zeev Gross*

We have recently reported the first facile synthetic route to *meso*-aryl substituted corroles,[1, 2] which is particularly efficient for the preparation of 5,10,15-tris(pentafluorophenyl)-corrole (H_3(tpfc)).[3, 4] This was followed by a demonstration that the manganese, iron, and rhodium complexes of H_3(tpfc) are potent catalysts for various transformations.[5, 6] In addition, we have shown that a water-soluble derivative of H_3(tpfc) is superior to related porphyrins in cancer-related therapies.[7] These intriguing developments call for an investigation of non-transition metal corroles for the following reasons: firstly, any mechanistic investigation of the catalytic action of transition metal corroles requires a working knowledge of the characteristics of corrole radicals, since during catalysis either the metal or the corrole might be oxidized. Secondly, for many potential applications it is important to know the photophysical properties of corroles, an almost completely unexplored field to date. We are only aware of investigations of corrole–corrole and porphyrin–corrole dyads, which are unstable to light.[8] Zinc(II) complexes with porphyrins have been extensively utilized for both the preparation of cation radicals and for the examination of photophysical properties.[9, 10] Similar investigations of trianionic corroles require a trivalent non-transition metal, but until now only an unstable indium(III) corrole has been reported.[11] According to density functional theory (DFT) calculations of corrole isomers, gallium(III) should be a perfect choice for regular corroles,[12] but an experimental demonstration is still lacking. We have, therefore, prepared the gallium complex of H_3(tpfc) and report herein its X-ray structure, electrochemistry, one-electron oxidation product, photophysical properties, and calculated electronic structure.[13]

Using $GaCl_3$ as the metal source and pyridine (py) as solvent the synthesis of the desired complex was straightforward.[14] Considerable effort was expended in attempts to grow X-ray quality crystals; success finally came when small amounts of pyridine were included in the recrystallization solvent mixture.[15] The X-ray structure of [Ga(tpfc)(py)] (**1**) shows that upon metal binding the corrole adopts a much more conventional geometry (Figure 1) relative to that of

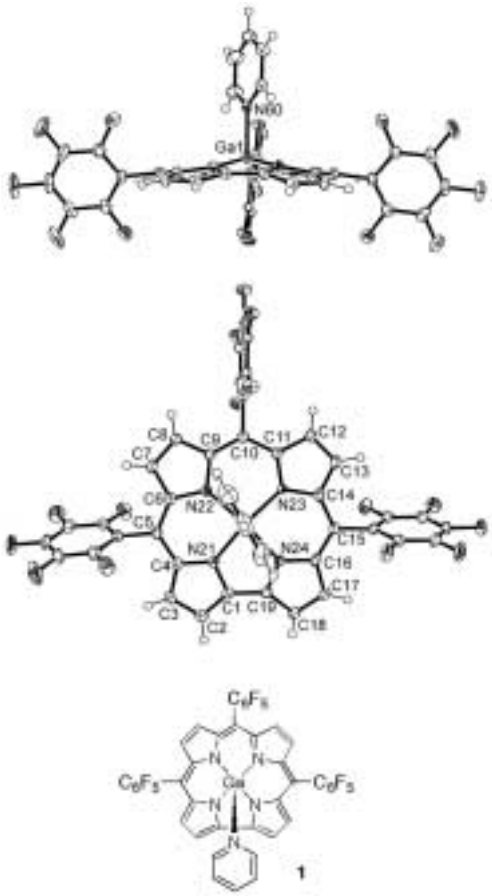


Figure 1. ORTEP plots and structural formula of **1**. Selected bond lengths [Å] and angles [°]: Ga-N21 1.9380(18), Ga-N22 1.9366(17), Ga-N23 1.9441(17), Ga-N24 1.9430(17), Ga-N60 2.0370(17), N21-Ga-N22 88.34(7), N22-Ga-N23 93.51(7), N23-Ga-N24 88.21(7), N21-Ga-N24 79.65(7), N21-Ga-N60 109.83(7), N22-Ga-N60 99.08(7), N23-Ga-N60 94.59(7), N24-Ga-N60 106.51(7). Only data for one of the two independent molecules have been given; they differ significantly only in the rotation of the pyridine ligand around the Ga–N_{py} bond.

H_3(tpfc).[3] The bonding geometry of the metal is pyramidal; the Ga center is displaced 0.4107(9) Å out of the N4 plane which is slightly domed (all the individual pyrrole rings are planar and point toward the metal). The Ga–$N_{corrole}$ bond lengths (average 1.94 Å; Figure 1) are significantly longer than the computed values for unsubstituted gallium corrole (1.909–1.926 Å),[13] but in the range (1.867–1.963 Å) calculated for planar [Ga(tpfc)].[16] The Ga–N_{py} bond is much longer (2.033 Å) than the Ga–$N_{corrole}$ bonds, but, nevertheless, quite short for a gallium–pyridine bond (compare e.g. 2.121–2.151 Å in $[Ga(N_3)_3(py)_3]$).[17] The binding of pyridine to the metal is strong enough for the high-field shifted resonances to be observed by ^{1}H NMR spectroscopy, but also weak enough for the ligand to be displaced by [D_5]pyridine.

[*] Dr. J. Bendix, Prof. Dr. Z. Gross, Dr. A. Mahammed, L. Simkhovich
Department of Chemistry and
Institute of Catalysis Science and Technology
Technion – Israel Institute of Technology
Haifa 32000 (Israel)
Fax: (+972) 4-8233735
E-mail: chr10zg@tx.technion.ac.il

Prof. Dr. H. B. Gray, Dr. I. J. Dmochowski
Beckman Institute
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: (+1) 626-449-4159
E-mail: hgcm@its.caltech.edu

[**] We acknowledge support of this research from the Fund for the Promotion of Research at the Technion (Z.G.), the National Science Foundation (H.B.G.), and the Danish Natural Science Research Council for financial support under grant No. 9800549 (J.B.). We also thank Dr. H. Weihe (University of Copenhagen) for access to computing facilities, and L. M. Henling (Beckman Institute) for assistance with the crystal structure determination.

  0044-8249/00/11222-4214 $ 17.50+.50/0

The cyclic voltammogram of **1** shows a reversible oxidation wave with an $E_{1/2}$ of 0.75 V versus SCE, much lower than the corresponding values of 1.13 and 1.20 V of the related five-coordinate complexes, [Ge(tpfc)(OH)] and [Sn(tpfc)(Cl)], respectively.[18] This is reminiscent of similar observations in metalloporphyrins, in which the redox potential of the macrocycle correlates with the electronegativity of the metal ($Ge^{IV} \geq Sn^{IV} > Ga^{III} > Zn^{II} > Mg^{II}$).[19] The oxidation potential of **1** suggests that it can be oxidized to the corresponding corrole π-cation radical complex, $[Ga(tpfc^{\bullet})(py)]^+$ (**2**) by the commercially available compound tris(4-bromophenyl)-aminium hexachloroantimonate ($E_{1/2} = 1.11$ V). This is indeed the case; Figure 2 shows the UV/Vis spectra of **1** and **2**

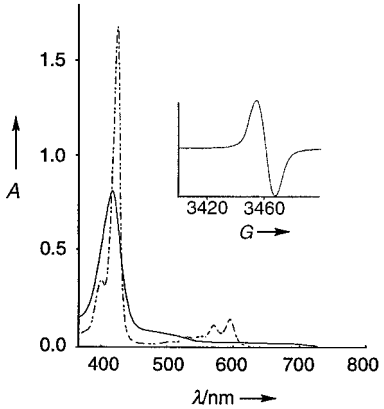


Figure 2. UV/Vis spectra of **1** (broken line) and **2** (full line), and the EPR spectrum of **2** (inset), all in CH_2Cl_2 solution at room temperature. A = Absorbance.

as well as the EPR spectrum of the latter. With respect to the color change from purple to green and the large decrease in the intensity of the Soret band, the corrole radical resembles porphyrin radicals. But, the appearance of new bands at $\lambda >$ 600 nm is much less pronounced in **2** than in porphyrin radicals and there are no hyperfine splittings in the EPR spectrum from coupling to ^{14}N.

The EPR spectra of porphyrin radicals are traditionally analyzed in terms of the HOMO from which the electron is abstracted, with singlets obtained for $^2A_{1u}$ and characteristic nine-line hyperfine splitting for $^2A_{2u}$ states (under D_{4h} symmetry). To gain more insight into the electronic structure of the corrole radical complex, we have optimized the geometries of [Ga(tpfc)] and $[Ga(tpfc^{\bullet})]^+$ (the full complexes were treated, including the pentafluorophenyl substituents) and calculated the two closely spaced HOMOs of both systems by use of gradient corrected DFT.[16] The results for [Ga(tpfc)] are shown in a schematic presentation (Figure 3) and those for $[Ga(tpfc^{\bullet})]^+$ are summarized in Table 1. Close inspection shows that the majority of spin density is located on the *meso*- and α-pyrrole-carbon atoms for the nearly degenerate $b_1(C_{2v})$ and $a_2(C_{2v})$ orbitals, respectively, thus *qualitatively* resembling the $a_{2u}(D_{4h})$ and $a_{1u}(D_{4h})$ orbitals of metalloporphyrins. But, the spin densities on the nitrogen atoms are much smaller in the corrole radical.[20] Actually, the nitrogen splitting constants of the $^2B_1(C_{2v})$ state are calculated from the relation $a_N = 24\rho_N$ to be only 0.46 – 0.62 G, compared to 1.18 G for the $^2A_{2u}(D_{4h})$ state of porphyrins (they are much lower for

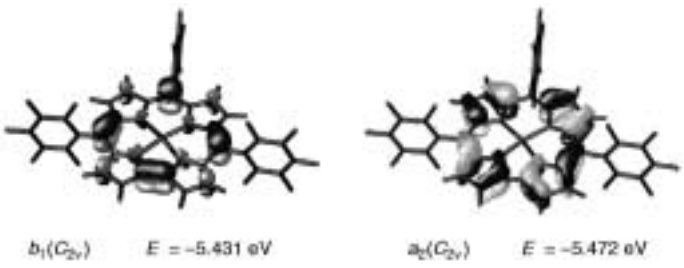


Figure 3. Perspective drawing of the calculated spin densities of the two highest occupied molecular orbitals of [Ga(tpfc)].

Table 1. Gross atomic spin populations of $[Ga(tpfc^{\bullet})]^+$ (see Figure 1 for the numbering system).

Atom	$^2B_1(C_{2v})$ and $^2A_2(C_{2v})$		Atom	$^2B_1(C_{2v})$	$^2A_2(C_{2v})$
C1 (C19)	0.098	0.063	C2 (C18)	– 0.038	0.044
C5 (C15)	0.171	– 0.015	C3 (C17)	0.083	– 0.002
C10	0.225	– 0.054	C7 (C13)	– 0.007	0.050
C4 (C16)	– 0.023	0.140	C8 (C12)	0.068	0.007
C6 (C14)	0.025	0.110	N21 (N24)	0.019	0.002
C9 (C11)	– 0.045	0.151	N22 (N23)	0.026	– 0.025
			Ga1	0.042	0.001

the $^2A_2(C_{2v})$and $^2A_{1u}(D_{4h})$ states). Accordingly, we may conclude that the observed EPR singlets agree well with the computed electronic structure of $[Ga(tpfc^{\bullet})]^+$. We also note that the $^2B_1(C_{2v})$ and $^2A_2(C_{2v})$ states of $[Ga(tpfc^{\bullet})]^+$ are even closer in energy (0.041 eV) than in the (hypothetical) non-substituted gallium corrole (0.095 eV).[13]

In the synthesis of H_3(tpfc), and even more so during its metallation by gallium, we noted a very strong fluorescence. Accordingly, we turned our attention to an examination of the photophysical properties of H_3(tpfc) and **1**, especially in comparison to the extensively studied H_2(tpp) and its metal complexes, Mg(tpp) and Zn(tpp).[4, 21] These results are shown in Figure 4 and summarized in Table 2, which also includes data for various new corroles that we have recently reported.[22, 23] The major points of interest are that the quantum

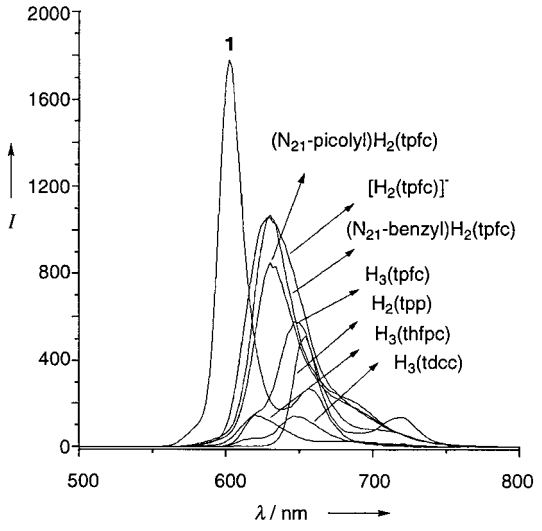


Figure 4. Emission spectra (I = emission intensity) of the porphyrin H_2(tpp), the corroles H_3(tpfc), $[H_2(tpfc)]^-$, **1**, H_3(thfpc), H_3(tdcc), and the *N*-subsituted corroles $(N_{21}$-picolyl)H_2(tpfc), $(N_{21}$-benzyl)H_2(tpfc), all in degassed toluene at room temperature (see Table 2 for the abbrevations).

Table 2. Emission data and quantum yields for several corroles and porphyrins.

Entry	Compound	Integrated intensity	Yield [%][a]	λ_{max} [nm]
1	H_2(tpp)	18.0	11[b]	654, 720
2	[Mg(tpp)]		16.5[b]	
3	[Zn(tpp)]		3.3[b]	
4	H_3(tpfc)	27.3	17	648 (622 sh, 704 sh)
5	$[H_2(tpfc)]^{-}$[c]	56.9	35	628
6	[Ga(tpfc)(py)] (**1**)	51.2	31	602, 656
7	(N_{21}-picolyl)H_2(tpfc)[d]	41.8	26	630 (684 sh)
8	(N_{21}-benzyl)H_2(tpfc)[d]	49.3	30	630 (682 sh)
9	H_3(thfpc)[e]	6.33	3.9	620, 682
10	H_3(tdcc)[f]	7.09	4.3	646 (622, 704 sh)

[a] $\phi_f \times 10^2$. [b] Reference [21]. [c] A solution of H_3(tpfc) in the presence of Et_3N. [d] *N*-Substituted tris(pentafluorophenyl)corroles, see reference [22]. [e] thfpc = 5,10,15-tris(heptafluoropropyl)corrole, see reference [23]. [f] tdcc = 5,10,15-tris(2,6-dichlorophenyl)corrole, see reference [1].

yield of H_3(tpfc) (entry 4) is larger than that of H_2(tpp) (entry 1), that both deprotonation and metallation of H_3(tpfc) (entries 5 and 6, respectively) lead to an increase in the quantum yield (note the quenching effect of zinc in porphyrins, entries 3 and 1), and that *meso*-substitution by either heptafluoropropyl or dichlorophenyl (entries 9 and 10) produces a much lower quantum yield. All these features suggest that H_3(tpfc) and its metal complexes have advantages, yet to be explored, in the many applications where strong fluorescence and high quantum yields are desired. In this regard, noteworthy is that *N*-substitution of H_3(tpfc) (entries 7 and 8) does not quench the fluorescence,[24] which indicates that H_3(tpfc) can be attached by one of its nitrogen atoms to a variety of solid supports without sacrificing useful photophysical properties. Finally, we have also measured the lifetimes of both the excited singlet and triplet states of H_3(tpfc), which were found to be about 4 ns and 870(10) μs, respectively, in degassed toluene.[25] Importantly, the triplet lifetime was reduced to 4.8(3) μs in aerobic solution, indicating an extremely high yield for the production of singlet oxygen.

In conclusion, an easily prepared gallium corrole has been fully characterized; it should serve as a prototype metallocorrole, very much as [Zn(tpp)] does in the metalloporphyrin family. Our study reports the unique photophysical properties of **1**, as well as the characteristic spectroscopic features of its π-cation radical complex and the calculated electronic structure.

Received: June 26, 2000 [Z15331]

[1] Z. Gross, N. Galili, I. Saltsman, *Angew.* **1999**, *111*, 1530; *Angew. Chem. Int. Ed.* **1999**, *38*, 1427.

[2] For the recently reported synthesis of 5,10,15-triphenylcorrole, see: R. Paolesse, L. Jaquinod, D. J. Nurco, S. Mini, F. Sagone, T. Boschi, K. M. Smith, *Chem. Commun.* **1999**, 1307.

[3] a) Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Bläser, K. Boese, I. Goldberg, *Org. Lett.* **1999**, *1*, 599; b) H_3(tpfc) is now commercially available from Strem Chemicals (Illinois); c) (N. Galili-Nachshon, L. Simkhovich, Z. Gross, I. Saltsman (Technion Res. & Dev. Foundation), WO 00/18771, **2000**).

[4] tpfc = the trianion of 5,10,15-tris(pentafluorophenyl)corrole; TPP = dianion of 5,10,15,20-tetraphenylporphyrin..

[5] Z. Gross, L. Simkhovich, N. Galili, *Chem. Commun.* **1999**, 599.

[6] Z. Gross, G. Golubkov, L. Simkhovich, *Angew. Chem.* **2000**, *112*, 4211; *Angew. Chem. Int. Ed.* **2000**, *112*, 4045.

[7] D. Aviezer, S. Cotton, M. David, A. Segev, N. Khaselev, N.Galili, Z. Gross, A. Yayon, *Cancer Res.* **2000**, *60*, 2973.

[8] R. Paolesse, F. Sagone, A. Macagnano, T. Boschi, L. Prodi, L. Montalti, N. Zaccheroni, F. Boletta, K. M. Smith, *J. Porphyrins Phthalocyanines* **1999**, *3*, 364, and references therein.

[9] a) C. M. Barzilay, S. A. Sibilia, T. G. Spiro, Z. Gross, *Chem. Eur. J.* **1995**, *1*, 222; b) N. Ehlinger, W. R. Scheidt, *Inorg. Chem.* **1999**, *38*, 1316.

[10] K. A. Nguyen, P. N. Day, R. Pachter *J. Phys. Chem. A* **1999**, *103*, 9378, and references therein.

[11] R. Paolesse, S. Licoccia, T. Boschi, *Inorg. Chim. Acta* **1990**, *178*, 9.

[12] A. Ghosh, K. Jynge, *Chem. Eur. J.* **1997**, *3*, 823.

[13] After this work was completed (first presented as Poster 23 in *Contemp. Inorg. Chem. II*, March 12–15, 2000, College Station, Texas, and as Paper 293 in the 219th national ACS meeting in San Francisco, March 26–30, 2000), DFT calculations on unsubstituted gallium corrole were published, A. Ghosh, T. Wondimagegn, A. B. J. Parusel, *J. Am. Chem. Soc.* **2000**, *122*, 5100.

[14] A solution of H_3(tpfc) (50 mg) in pyridine (15 mL) was added in large excess of flame-dried $GaCl_3$ and the reaction mixture was heated to reflux for 1 h under argon, followed by evaporation of the solvent. Excess inorganic salts were removed by flash chromatography (silica, *n*-hexane:CH_2Cl_2:pyridine = 100:30:0.5), followed by recrystallization from CH_2Cl_2 and *n*-heptane in the presence of a few drops of pyridine to give 45 mg (76% yield) of purple crystals. MS (CI^+, isobutane (%)) *m/z*: 942 (90) [MH^+], 863 [$MH^+ - py$], MS (CI^-, isobutane): 862 [$M^- - py$]; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 9.20$ (d, $J = 4.05$ Hz, 2H, β-pyrrole H); 8.88 (d, $J = 4.40$ Hz, 2H, β-pyrrole H); 8.74 (d, $J = 4.02$ Hz, 2H, β-pyrrole H); 8.66 (d, $J = 4.56$ Hz, 2H, β-pyrrole H); 4.89 (t, $J = 7.90$ Hz, 1H, *para*-H of pyridine); 4.32 (unresolved t, 2H, *meta*-H of pyridine); 2.84 (unresolved d, 2H, *ortho*-H of pyridine); ^{19}F NMR (C_6D_6, 188 MHz,): $\delta = -138.8$ (dd, $J^1 = 23.9$, $J^2 = 6.0$ Hz, 6F, *ortho*-F); −153.5 (m, 3F, *para*-F); −162.7 (m, 6F, *meta*-F). UV/Vis: CH_2Cl_2, λ_{max}[nm](ε): 398 (5.73×10^4), 420 (2.84×10^5), 568 (1.71×10^4), 594 (2.36×10^4).

[15] Red-purple X-ray quality crystals of [Ga(tpfc)(py)] · 1.5 *p*-xylene were obtained by recrystallization from *p*-xylene/CH_2Cl_2 (1% pyridine). Crystal data: $C_{54}H_{28}F_{15}GaN_5$, $M = 1101.53$, triclinic, space group $P\bar{1}$ with $a = 14.6219(6)$, $b = 17.9135(8)$, $c = 19.6021(9)$ Å, $\alpha = 99.695(1)$, $\beta = 100.236(1)$, $\gamma = 111.384(1)^\circ$, $V = 4549.9(6)$ Å^3, $Z = 4$, $\mu = 0.713$ mm^{-1}, $T = 98$ K. Of 42393 reflections collected ($2\theta_{max} = 57.1^\circ$), 20678 were unique (3 omitted). $R1 = 0.0405$ and $wR2 = 0.0677$ for 14674 reflections with $F_o > 4\sigma(F_o)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147288. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Structure factors may be obtained from xray@caltech.edu.

[16] DFT calculations were performed with the Amsterdam Density Functional (ADF) program suite version 1999. Slater-type orbital basis sets of triple-quality for the valence orbitals were employed with polarization functions on the ligand atoms (2p for H and 3d for C and N centers) and additional valence p orbitals on the metal atoms (ADF basis set IV). Frozen core approximations were used up to 1s on C, N, and F centers and up to 3p on the Ga center. The Vosko–Wilk–Nusair LD correlation functional was employed together with the gradient corrected exchange functional proposed by Becke (B88) and the correlation functional from Perdew(P86). To facilitate the calculations, the symmetries were restrained to C_{2v} with the Ga center in the corrole plane. All reported spin densities are based on Mulliken analyses.

[17] R. A. Fischer, A. Miehr, E. Herdtweck, M. R. Mattner, O. Ambacher, T. Metzger, E. Born, S. Weinkauf, C. R. Pulham, S. Parsons, *Chem. Eur. J.* **1996**, *2*, 1353.

[18] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, *Chem. Eur. J.*, in press.

[19] K. M. Kadish, *Prog. Inorg. Chem.* **1986**, *34*, 435.

  0044-8249/00/11222-4216 $ 17.50+.50/0

[20] J. Fajer, M. S. Davis in *The Porphyrins*, *Vol. IV* (Ed.: D. Dolphin), Academic Press, New York, **1979**, pp. 197–256.
[21] M. Gouterman in *The Porphyrins*, *Vol. III* (Ed.: D. Dolphin), Academic Press, New York, **1979**, pp. 1–165.
[22] Z. Gross, N. Galili, *Angew. Chem.* **1999**, *111*, 2536; *Angew. Chem. Int. Ed.* **1999**, *38*, 2366.
[23] L. Simkhovich, I. Goldberg, Z. Gross, *J. Inorg. Biochem.* **2000**, *80*, 235.
[24] For a high quantum yield for a corrole derivative in which one of the corrole nitrogen atoms is replaced by oxygen (an oxacorrole), see: S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, U. Englich, K. Ruhlandt-Senge, *Org. Lett.* **1999**, *1*, 587.
[25] Measurements were made on solutions of the sample (50 nM) in oxygen-free toluene (degassed by five freeze-pump-thaw cycles) under Ar. For a description of the experimental setup for the triplet-lifetime measurements, see: I. J. Dmochowski, J. R. Winkler, H. B. Gray, *J. Inorg. Biochem.* **2000**, *81*, 221.

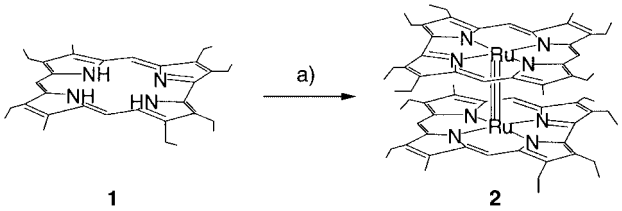
Evidence for the Formation of a Ru^{III}–Ru^{III} Bond in a Ruthenium Corrole Homodimer**

François Jérôme, Béatrice Billier, Jean-Michel Barbe, Enrique Espinosa, Slimane Dahaoui, Claude Lecomte,* and Roger Guilard*

The formation of a ruthenium(II) porphyrin homodimer was first mentioned by Whitten and co-workers in 1975.[1] Nevertheless, the interaction between the two metal centers has been fully evidenced only in 1984 on the basis of an X-ray structure determination of $[\{Ru(oep)\}_2]$.[2, 3] It was shown later that this type of ruthenium porphyrin homodimer can be involved in several catalytic reactions as well as in the coordination of gaseous molecules such as ethylene and carbon monoxide.[4, 5] Furthermore, these complexes are extremely air-sensitive and the one- or two-electron (chemical or electrochemical) oxidation of the dimer easily leads to the formation of the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{III} species, respectively.[6] However, until now, no bisruthenium(III) porphyrin homodimer has been obtained by a direct insertion of the Ru^{III} cation into the porphyrin cavity.

To study the reactivity of tetrapyrrole metal complexes in high oxidation states, we focused on the synthesis and characterization of corrole metal complexes.[7–9] Indeed, the corrole macroring possesses a small four-nitrogen cavity (because of the presence of only three meso carbon atoms) and three NH groups which enhance the stabilization of metal cations in a high oxidation state.[10–12] Although as many as 18 different metal–corrole species are known, ruthenium corroles have never been synthesized. Moreover, many unsuccessful attempts have been made to metalate a corrole with ruthenium(III).[13] Starting from $RuCl_3$ in dimethylformamide, Boschi et al. observed an insertion of a carbonyl group from the solvent into the pyrrole–pyrrole bond leading, after rearrangements, to a ruthenium(III) porphyrin. The same behavior was noted when using $[Ru_3(CO)_{12}]$ in 2-methoxyethanol, again a carbonyl group insertion, this time from the metal carbonyl complex, occurred affording a ruthenium(III) porphyrin.[13]

We have also attempted the metalation reaction of H_3(hedmc)[3, 14] (**1**) with $RuCl_3$ in carbonyl group free solvents with different boiling points, such as pyridine, xylene, benzonitrile and trichlorobenzene. No metalation reaction was noted after 72 h at reflux. The complex $[\{(cod)RuCl_2\}_2]$[3] does not bear a carbonyl group and is more reactive than $RuCl_3$ in many metalation reactions.[15] This Ru^{II} dimer is easily synthesized by the reaction of hydrated $RuCl_3$ with cod[3] in boiling ethanol for 12 h. The reaction of **1** with an excess $[\{(cod)RuCl_2\}_2]$ was carried out in refluxing 2-methoxyethanol with the presence of a trace amount of triethylamine (see Experimental Section). Triethylamine prevents the protonation of **1** by the HCl evolved during the metalation reaction. Furthermore, the reaction is easily carried out in an air atmosphere which enhances the oxidation of Ru^{II} to Ru^{III} necessary to form $[\{Ru(hedmc)\}_2]$ (**2**, Scheme 1).[16]



Scheme 1. The formation of $[\{Ru(hedmc)\}_2]$; a) $[\{(cod)RuCl_2\}_2]$, 2-methoxyethanol, triethylamine, reflux, 30 min.

By UV/Vis spectroscopy one can observe after 30 min of reaction the disappearance of the Q bands of the starting free base corrole and a large blue shift of the Soret band from 396 to 336 nm (Figure 1).

The formation of **2** is demonstrated by both the presence in the MALDI/TOF (matrix assisted laser desorption/ionization time of flight) mass spectrum of a peak pattern in the expected region (largest peak at 1186.53)[16] and the results of a single-crystal X-ray diffraction study.[17] No trace of a monomeric species is evidenced by mass spectrometry, thus confirming the presence of the pure, strongly bound dimer **2**. Figure 2a shows the molecular structure of **2** at $T = 112(2)$ K. In spite of the low-temperature X-ray diffraction measurements the atomic thermal parameters are quite large, resulting probably from a rotation of the dimer around the Ru–Ru axis. As

[*] Prof. Dr. R. Guilard, F. Jérôme, B. Billier, Dr. J.-M. Barbe, Dr. E. Espinosa
LIMSAG, UMR 5633, Université de Bourgogne
Faculté des Sciences "Gabriel"
6 Boulevard Gabriel, 21100 Dijon (France)
Fax: (+33) 3-8039-6117
E-mail: roger.guilard@u-bourgogne.fr
Prof. Dr. C. Lecomte, Dr. S. Dahaoui
LCM3B, Université Henri Poincaré
Boulevard des Aiguillettes
BP 239, 54506 Vandoeuvre-les-Nancy (France)
Fax: (+33) 3-8340-6492
E-mail: lecomte@lcm3b.u-nancy.fr

[**] This work was supported by the CNRS. F.J. gratefully acknowledges the "Region Bourgogne" and Air Liquide for a financial support. The authors also thank Mr. M. Soustelle for technical assistance.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.