

Electronic Structures and Reactivities of Corrole–Copper Complexes

Inna Luobeznova,^[a] Liliya Simkhovich,^[a] Israel Goldberg,^{*[b]} and Zeev Gross^{*[a]}**Keywords:** Copper / Cyclic voltammetry / Electronic structure / Porphyrinoids / Structure elucidation

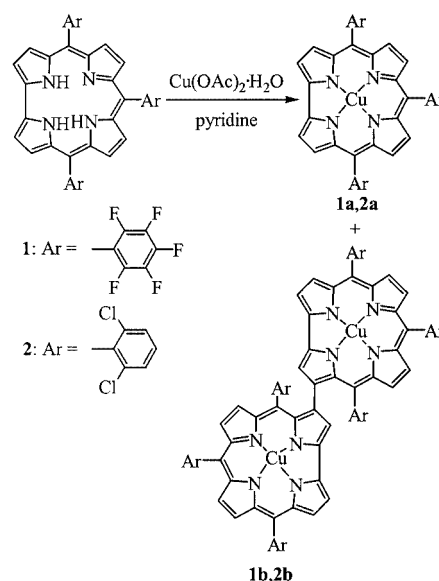
The spectroscopic and electrochemical examination of the mononuclear copper complexes of 5,10,15-tris(pentafluorophenyl)corrole and 5,10,15-tris(2,6-dichlorophenyl)corrole (**1a** and **2a**, respectively) and of the corresponding dinuclear corrole dimers **1b** and **2b** reveal the existence of two almost degenerate electronic states. The lower state consists of copper(III) ions coordinated by closed-shell corrolato trianions and the higher state is composed of copper(II) ions chelated by open-shell corrolato dianions. The contributions from both states are evident in the molecular structure of monomeric

and mononuclear **2a**, which displays a distorted square-planar coordination geometry around the metal ion and short Cu–N bond lengths typical of copper(III), together with some non-equivalence of the C_α–C_{meso} bond lengths that might reflect the open-shell character of the macrocycle. The latter state is most likely to be responsible for the dimerization process.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Recent years have evidenced a real renaissance in the chemistry of corroles,^[1,2] due to the introduction of three facile synthetic methodologies for preparation of triarylcorroles: the solvent-free condensation of pyrrole and aldehydes,^[3] the modified Rothmund procedure,^[4] and the condensation of dipyrromethane with aldehydes.^[5,6] Among all the new corroles, the *meso*-pentafluorophenyl-substituted derivative H₃(tpfc) (**1** in Scheme 1) is by far the most intensively studied. This single corrole and its variants have been shown to support a large variety of metal ions (Cr,^[7] Mn,^[8] Fe,^[9] Ru,^[10] Co,^[9,11] Rh,^[9,12] Ni,^[13] Pd,^[12] Cu,^[12] Zn,^[14] Al,^[15] Ga,^[16] Ge,^[9b] Sn,^[9b] P^[9b]) and many of these complexes have been fully characterized in several oxidation and coordination states. The novel features that were found for **1** and its metal complexes include very high fluorescence quantum yields,^[13,14] easily achieved chirality,^[10,12] potent catalytic activity,^[17] facile methodologies for further functionalization,^[18] and selective interactions with tumor cells.^[19] Another important development is the introduction of corroles with *meso*-aryl groups that contain large *ortho*-phenyl substituents (Cl, CH₃), whose impact in affecting catalysis was demonstrated recently.^[20]



Scheme 1

One of the first metal ions inserted into the N₄ coordination core of corroles was copper,^[21] but both the structural and electronic features of the complexes remained ill-defined for a very long time until, in 1997, Vogel and co-workers provided new insights into these issues by the isolation and full characterization of Cu(tetmc).^[22a] This complex displays a square-planar coordination geometry, consistent with a d⁸ copper(III) ion chelated by a closed-shell corrolato trianion. This appeared to be the ground state in solution as well, although the large shifts and broad signals of the resonances in the ¹H NMR spectra obtained at room

^[a] Department of Chemistry and Institute of Catalysis Science and Technology, Technion – Israel Institute of Technology, Haifa 32000, Israel
Fax: (internat.) + 972-4-829-5703
E-mail: chr10zg@tx.technion.ac.il

^[b] School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel
Fax: (internat.) + 972-3-640-9293
E-mail: goldberg@chemsg7.tau.ac.il

temperature clearly demonstrate that the electronic state with a copper(II) ion coordinated by an open-shell corrole (formally a dianion radical, but usually referred to as a corrole cation radical) is only slightly higher in energy. This coexistence of copper(III) and copper(II) radicals was also predicted by the DFT calculations of Ghosh et al.^[22b] An additional complication exists in the electrochemistry of corrole–copper complexes, as demonstrated by Kadish and co-workers.^[23] Reduction of Cu(oec) provided a simple copper(II) complex, but a dimeric product was formed upon oxidation. The latter was assigned as a non-covalent dimer held together by strong interactions between the π -systems of the corroles. This is reminiscent of the features of metalloporphyrin π -cation radicals,^[24] although definite structural proof is still not available for corroles.

As part of our interest in the preparation and utilization of the metal complexes of **1**, isolation of its copper complex was one of the earliest goals that we wanted to achieve.^[12] Insertion of copper proceeded well, but the corresponding complex, Cu(tpfc) (**1a**), was not stable in solution. Even carefully purified **1a** was converted within a few hours into a mixture of new complexes, which, according to mass spectrometry, are dimeric. This is reminiscent of our recent observation with the cobalt complexes of **1**: pentacoordinate [Co(tpfc)(PPh₃)] and hexacoordinate [Co(tpfc)(pyridine)₂] are very stable complexes, but the tetracoordinate Co(tpfc) is converted in high yield into a single isomer of a C–C-bound corrole dimer with two cobalt(III) ions.^[11] This suggests that the complexes obtained from **1a** are analogous dimers, with a lower selectivity in the C–C bond formation being responsible for the observation of several isomers. In any case, the instability of **1a** in solution significantly hampered further research as it complicates the spectroscopic investigations and interferes with attempts to grow X-ray quality crystals. Because of these shortcomings, we have prepared the copper complex of 5,10,15-tris(2,6-dichlorophenyl)corrole [H₃(tdcc),^[3a,3g] **2** in Scheme 1], anticipating that dimerization of this sterically protected corrole will be a less severe problem. Indeed, the much higher stability of monomeric **2a** allowed for its characterization by X-ray crystallography and the electronic states of the complexes were elucidated by a combination of spectroscopic methods and electrochemistry.

Results and Discussion

Synthesis

All the copper complexes were obtained from the reactions of the corresponding corrole with Cu(OAc)₂·H₂O in pyridine (Scheme 1). The insertion of copper was found to be a facile process for both **1** and **2**, proceeding to completion at room temperature within 30 min, and the red complexes **1a** and **2a** were obtained in 73 and 85% yield, respectively. The lower yield for the formation of **1a** was found to reflect its instability in solution: it is transformed into a mixture of green compounds within a few hours at room temp. All the green complexes display identical mass

spectra, consistent with two copper ions coordinated by a dimeric corrole. This was confirmed by isolation of the major green complex (**1b**), whose spectroscopic features are consistent with the structure shown in Scheme 1. The other green complexes are most likely isomers of **1b** that differ in the identity of the carbon atoms that form the bond between the corroles. Three isomers are possible, even when only the more reactive carbon atoms of rings A and D are taken into account. The red complex **2a** is much more stable: only a minute amount of green dinuclear material is obtained when its solutions in CH₂Cl₂ are left for two weeks at room temp. This allowed us to grow X-ray quality crystals of **2a** and for its characterization by various spectroscopic methods. It was also possible to obtain appreciable amounts of the dinuclear complex **2b** (as a single isomer) by performing the copper insertion reaction at higher temperatures.

Electrochemistry

The cyclic voltammograms (CVs) of **1a** (freshly prepared) and **2a** displayed in Figure 1 show that the half-wave potentials of the former complex are more positive (easier to reduce and harder to oxidize) than for the latter, as expected for a corrole with more electron-withdrawing *meso* substituents. Based on a comparison with non-transition-metal complexes of **1**, wherein corrole-centered reductions occur below –1.0 V, the reduction waves [Cu(tpfc): $E_{1/2}$ = 0.22 V; Cu(tdcc): $E_{1/2}$ = 0.06 V] may be confidently assigned as reflecting metal-centered processes. The processes occurring with $E_{1/2}$ of 1.01 and 0.92 V for **1a** and **2a**, respectively, were assigned as reflecting corrole-centered oxidations based on the similarity of the oxidation potentials to that of gallium(III) complexes of **1** and **2**. The quite different spacing of the redox couples in **1a** (0.79 V) and **2a** (0.86 V) is also consistent with different centers involved in the reduction and oxidation processes. Taken together, the CVs of **1a** and **2a** indicate that while their reduction is metal-centered, the oxidation is corrole-centered. This was further confirmed

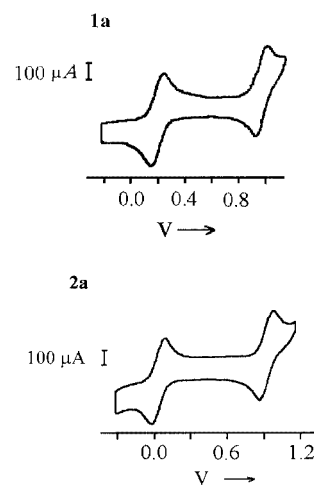


Figure 1. Cyclic voltammograms of Cu(tpfc) (**1a**: $E_{1/2}$ = 0.22 V and 1.01 V) and Cu(tdcc) (**2a**: $E_{1/2}$ = 0.06 and 0.92 V), in benzonitrile/ 5×10^{-4} M TBAP

for **2a** by its chemical reduction ($\text{Na}_2\text{S}_2\text{O}_4$, $\text{EtOH}/\text{H}_2\text{O}/\text{Ar}$) and oxidation $\{[(4\text{-Br-C}_6\text{H}_5)\text{N}]^+\text{SbCl}_6^-, \text{CH}_2\text{Cl}_2\}$: the EPR spectra (see below for more details) are characteristic of corrole–copper(II) and –copper(III) radicals, respectively.

The CV of **2b** (Figure 2) shows that the subunits of the dinuclear dimeric corrole are not strongly interacting. Both the reduction and the oxidation waves are partially resolved, with $E_{1/2} = -0.17, 0.05$ V and $0.82, 0.95$ V, respectively. The similarities of the redox potentials of **2b** to those of **2a** suggest that the former complex undergoes stepwise reduction of the copper(III) ions at low potentials and stepwise oxidation of the corrole subunits at more positive potentials.

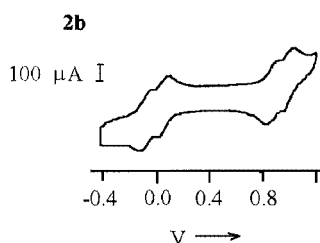


Figure 2. Cyclic voltammogram of the dinuclear corrole dimer **2b** ($E_{1/2} = -0.17, 0.05$ V and $0.82, 0.95$ V) in benzonitrile/ 5×10^{-4} M TBAP

Spectroscopy

Complexes **1a** and **2a** are EPR-silent and their NMR spectra at low temperature (Figure 3a, c) display resonances that are sharp enough to determine the characteristic vicinal coupling constants of the β -pyrrole hydrogen and the *meso*- C_6F_5 fluorine atoms ($J_{\text{H,H}} \approx 4$, $J_{\text{F,F}} \approx 23$ Hz). This data is consistent with expectations for diamagnetic square-planar d^8 complexes, suggesting that **1a** and **2a** contain low-

spin copper(III) ions coordinated by closed-shell corroles. The first clue that this description might be oversimplified is that the ^1H NMR chemical shifts are at higher field ($\delta = 6.9\text{--}7.7$ ppm) than in the corresponding free-base corroles and their complexes with other diamagnetic metal ions ($\delta = 8.2\text{--}9.2$ ppm).^[3–5,11,15,16] What is more, both the ^1H and the ^{19}F NMR resonances are much broader in the spectra recorded at higher temperatures (Figure 3b, d). These changes are fully reversible, suggesting a coexistence of diamagnetic and paramagnetic electronic states, with the former being dominant at lower temperatures. There are three conceivable possibilities that might explain the indications for diamagnetism at low temperatures and paramagnetism at high temperatures: a low-spin vs. high-spin corrole–copper(III) complex, a dimeric (cofacial) vs. monomeric corrole–copper(II) radical, and a corrole–copper(III) complex vs. a corrole–copper(II) radical. The first suggestion is the least likely: the large ligand field stabilization energy (LFSE) of copper(III) enforces a d^8 low-spin configuration in square-planar geometry, while higher coordination numbers should actually be less populated at high temperatures. The second proposal is more probable, especially since similar temperature effects have been observed for porphyrin–copper(II) radicals. However, non-covalent dimerization of π -cation radical complexes (of porphyrins and corroles) is only effective in the absence of prohibitive steric effects.^[24] This is not the case for **1a** and **2a**, as proven by the crystal structure of the latter (vide infra). Accordingly, the only reasonable explanation that remains is that the ground state of the corrole–copper(III) complex is only slightly lower in energy than that of the corrole–copper(II) radical (Scheme 2). The contribution of the latter state increases with temperature, exactly as proposed by Vogel and co-workers for the copper complex of β -alkyl-substituted

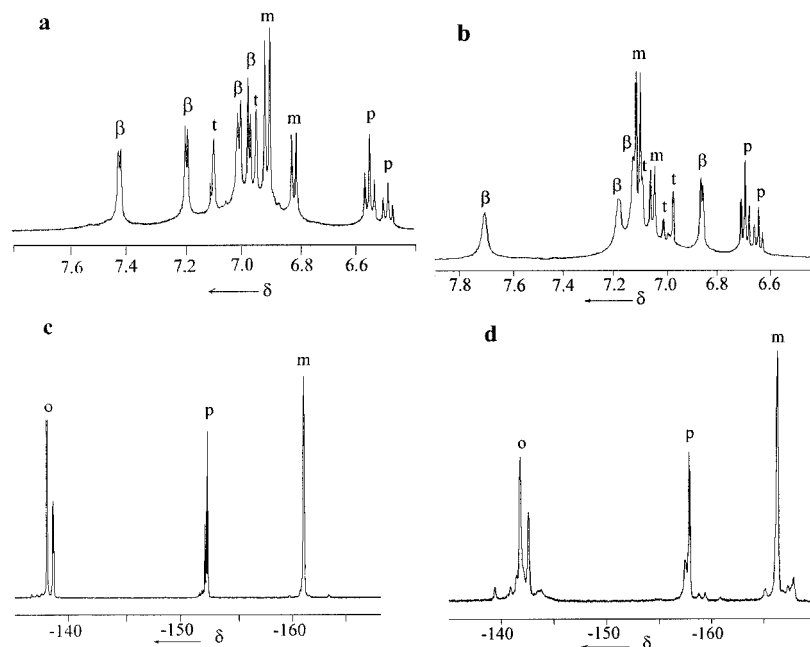
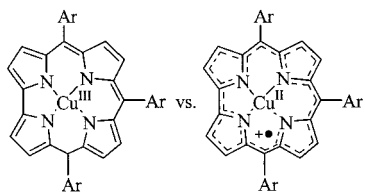


Figure 3. ^1H NMR spectra of **2a** at (a) 240 K and (b) 297 K (β = β -pyrrole CH, p = *para*-H, m = *meta*-H, t = $[\text{D}_7]\text{toluene}$), and ^{19}F NMR spectra of **1a** at (c) 240 K and (d) 355 K (o = *ortho*-F, p = *para*-F, m = *meta*-F), in $[\text{D}_8]\text{toluene}$

corroles.^[22] The small difference between the electronic states could also account for the apparent sensitivity of the electronic absorption spectra of triarylcorrole–copper complexes to substitution on the aryl groups.^[25]



Scheme 2

The mass spectra of **1b** and **2b** correspond to $[(1a)_2-2H]$ and $[(2a)_2-2H]$, respectively, and are consistent with two copper ions coordinated by covalently bound corrole dimers (Scheme 1). The seven rather than eight β -pyrrole hydrogen atoms that are evident in the NMR spectra of **2b** (Figure 4) confirm the loss of two protons upon dimerization. What is more, since there is only a total number of seven different β -pyrrole hydrogen atoms in each of the complexes, substitution must have occurred at the same carbon atom in each of the subunits, otherwise 14 different β -pyrrole hydrogen atoms should be apparent. The same conclusion holds for **1b**, whose ^{19}F NMR spectrum (Figure 4) reveals three rather than six types of C_6F_5 rings. Unfortunately, we were not able to grow X-ray quality crystals of **1b** or **2b**. However, the independently demonstrated high reactivity of C3 in other metal complexes of corrole **1** and

the full characterization of the cobalt(III) analog of **1b**,^[11,18] suggest that the single bond in **1b** and **2b** is also between the C3 atoms of the subunits.

Since all isolated complexes are EPR-silent, we turned our attention to the spectra of the reduced and oxidized complexes. Chemical reduction of **2a** leads to a spectrum that is typical of copper(II) (Figure 5a). The spectrum is centered at $g = 2.033$, with a four-line hyperfine splitting due to the $I = 3/2$ ^{63}Cu ion, with $a_{Cu} = 207.12$ G. The expected nine-line superhyperfine splitting from the ^{14}N atoms of the corrole is best seen in the high-field part of the spectrum, with $a_N = 17.64$ G. These values are similar to those obtained by Kadish and co-workers for $[(oec)Cu]^-$, where $a_{Cu} = 227$ G.^[23,26] The spectrum of one-electron-oxidized **2a** ($[2a]^+$) is very different (Figure 5b). It contains a single and quite sharp line, resembling that of the corrole–gallium(III) radical $[Ga(tpfc+)]^+$.^[16] In addition, a comparison between the electronic spectra of $[2a]^+$ and **2a** reveals that the Soret-like band of the former is less intense and blue-shifted and that it contains a new band at long

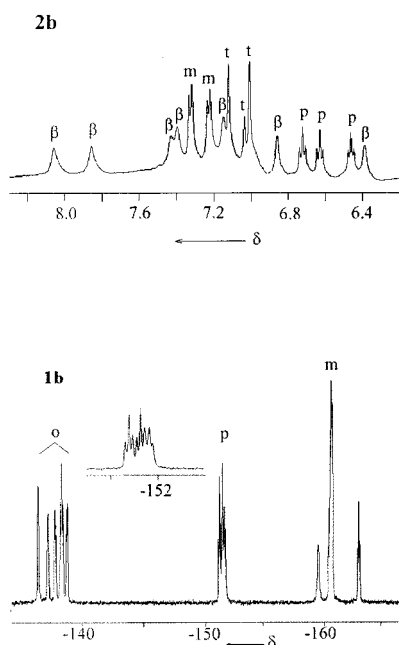


Figure 4. 1H NMR spectrum of **2b** at 320 K (β = β -pyrrole CH, p = *para*-H, m = *meta*-H, t = $[D_7]$ toluene), and ^{19}F NMR spectrum of **1b** at 275 K, in $[D_8]$ toluene; inset: extension of the *para*-F resonances

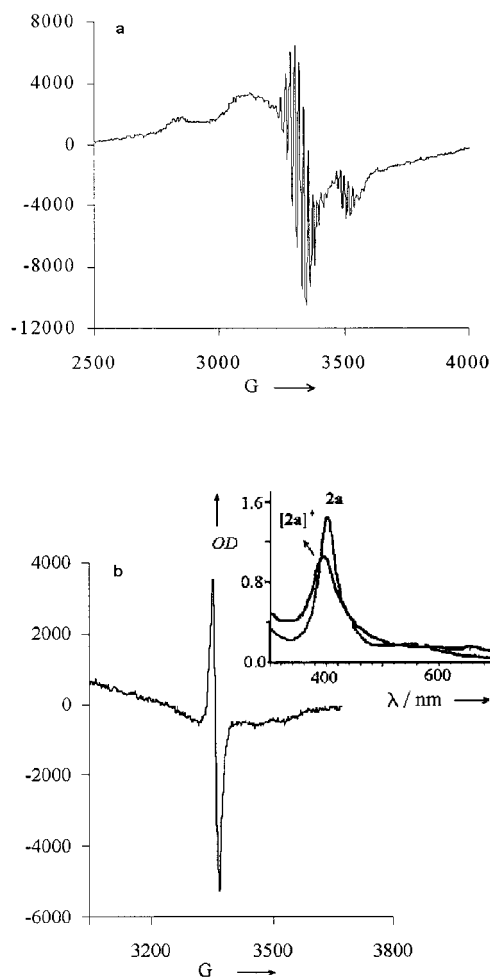


Figure 5. EPR spectra of (a) reduced **2a** (by $Na_2S_2O_4$ in EtOH/ H_2O /Ar; instrument settings: power 20.070 mW, modulation frequency 100 kHz, modulation amplitude 10 G, $T = 150$ K) and (b) oxidized **2a** {by $[(BrC_6H_4)_3N]^+SbCl_6^-$, recorded in CH_2Cl_2 ; instrument settings: power 0.635 mW, modulation frequency 100 kHz, modulation amplitude 10 G, $T = 150$ K}; inset: UV/Vis spectra of **2a** and its oxidation product in CH_2Cl_2

wavelengths ($\lambda_{\max} = 654$ nm; Figure 5b, inset). This data allows for quite a confident identification of $[2a]^+$ as a corrole–copper(III) cation radical. This is remarkably different from the situation for β -pyrrole-alkylated corroles, which dimerize to as yet unidentified products.^[23]

Structural Aspects

The X-ray structure of **2a** determined at ca. 110 K is presented in Figure 6. There are two structurally similar but crystallographically independent molecules of the corrole in the asymmetric unit (labeled as unprimed and primed atoms). The 23-atom corrole macrocycle is significantly ruffled, the individual atoms deviating from the mean plane by between -0.28 and $+0.21$ Å in one species and between -0.22 and $+0.23$ Å in the other unit (the r.m.s. of these deviations is 0.13 Å). The copper ion resides at the center of the corrole ring and, as is commonly observed for porphyrinoid–copper systems (see below), is four-coordinate. The Cu–N(pyrrole) bond-length range is 1.874(3)–1.891(3) Å in one unit and 1.880(3)–1.890(3) Å in the other unit. In the crystal, the monomeric units of **2a** are arranged in columns along the *b* axis, alternating in their relative orientation (Figure 6b). The dihedral angle between the mean planes of neighboring corrole rings is 44° . This allows the copper center of any given moiety to form van der Waals contacts from above and below with one of the chlorine substituents of the adjacent corroles in the column. The corresponding contact distances are Cu $\cdots$ Cl' 3.366 and 3.521 Å and Cu' $\cdots$ Cl 3.663 and 3.730 Å. There is no interaction between the antiparallel inversion-related columns in the triclinic crystal, and the *n*-heptane crystalli-

zation solvent is included between them. The Cu–N coordination distances in **2a** are similar to those observed in Cu(tetmc), the only other corrole–copper complex for which crystallographic data are available.^[22] In the latter, the d^8 Cu^{III} ion is four-coordinate as well, and the observed Cu–N bonds are within 1.866–1.896 Å. However, due to the apparent π – π dimerization of the Cu(tetmc) molecules, at 3.43 Å between the parallel and overlapping units within the dimer, their central corrole framework is somewhat less corrugated (with deviations of individual atoms from the corrole plane confined within -0.21 to $+0.17$ Å, and r.m.s. deviation of 0.08 Å) than **2a**.

It is of further interest to compare the current findings with those observed for the copper complex of tetra(2,6-dichlorophenyl)porphyrin.^[24b] In this compound the porphyrin ring is only slightly saddled (r.m.s. deviation of the porphyrin atoms from their mean plane is 0.11 Å), with the four-coordinate copper ion residing at the center of the ring. However, the Cu–N bonds within the porphyrin macrocycle (1.957–2.019 Å) are significantly longer than in the corrole. Adjacent porphyrin units in this structure are also markedly inclined with respect to each other, but no specific interaction is evident between them. Moreover, in many tetracoordinate Cu^{II} complexes of tetraarylporphyrins the Cu–N bond lengths are within a similar general range of 1.97–2.00 Å, irrespective of the intermolecular organization.^[27] Based on the above, and related evidence from other square-planar Cu^{III}–N₄ complexes with noncyclic ligands,^[28] we may thus safely conclude that the much shorter Cu–N bonds in **2a** are supportive of the corrole–copper(III) electronic state.

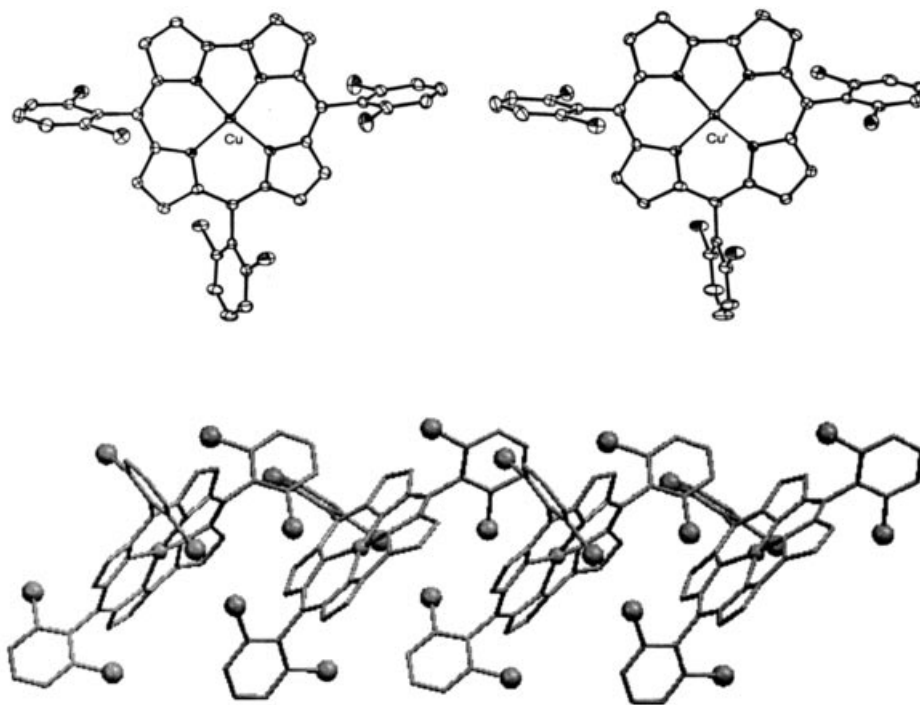


Figure 6. (top) ORTEP illustration of the two crystallographically independent corrole species of **2a** (the atomic displacement parameters are represented by 50% probability ellipsoids); (bottom) the columnar intermolecular organization of the corroles along the *b* axis of the crystal, showing that the corrole ring is approached from both sides by the chlorine substituents

Another interesting comparison can be made with the copper complexes of octaethyltetraphenylporphyrin, where both the Cu^{II} and formally Cu^{III} complexes are available.^[24c] In this case, due to the steric crowding around the molecular periphery caused by the substitution of eight alkyl and four aryl residues, the porphyrin core is severely distorted from planarity, adopting a highly puckered S4-saddle conformation. This seems to have little effect on the coordination distances of the copper ions positioned at the center, which are within 1.966–1.980 Å in the porphyrin– Cu^{II} complex and within 1.968–1.979 Å in the oxidized porphyrin–Cu perchlorate moiety, mostly due to the fact that the oxidation of this system is porphyrin-centered rather than metal-centered.

In porphyrins, an alternation of shorter and longer bonds within the inner 16-membered ring π -network (comprised of the N, α -C and *meso*-C) atoms is one of the criteria for oxidation of the macrocycle.^[29] Although not always present, it provides a strong indication that oxidation of the copper(II) complex of octaethyltetraphenylporphyrin affects the porphyrin rather than the metal ion, resulting in a porphyrin– Cu^{II} cation radical species. In the same context, we have examined the distribution of bond lengths within the two crystallographically independent corrole rings of **2a**, as displayed in Figure 7. The observed structure clearly

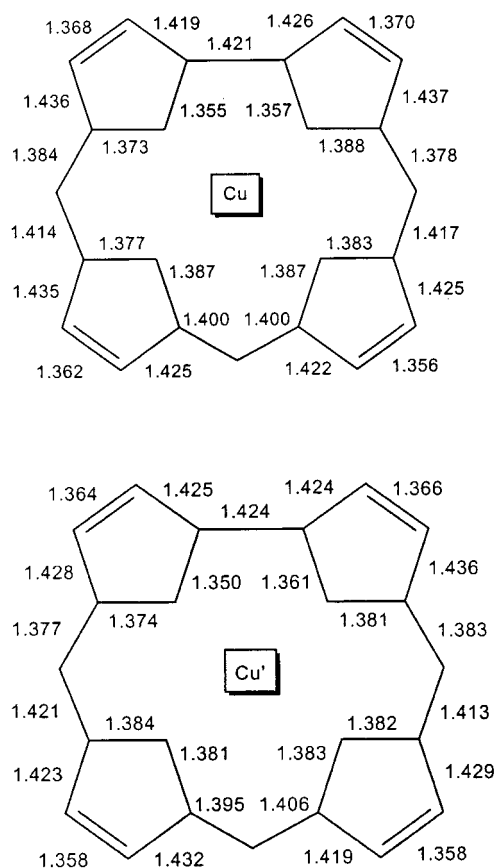


Figure 7. Observed distribution of bond lengths within the central corrole ring of **2a**; the estimated standard deviations for the shown values are 0.005 Å; two crystallographically independent species of the asymmetric unit are shown

shows a portion of an alternating bond length pattern in the “upper” section of the ring close to the C1–C19 bond. This pattern consists of systematically short C_α –N (av. 1.356 Å), long N– C_α (av. 1.379 Å), short C_α – C_{meso} (av. 1.380 Å) and long C_{meso} – C_α (av. 1.416 Å) bonds, while for a closed-shell fully delocalized corrolato trianion one might expect all bond lengths within the N– C_α and the C_{meso} – C_α sets to be equivalent. The observed structural data are thus consistent with the related spectroscopic evidence described above, that the paramagnetic corrole–copper(II) radical state contributes to the structure of **2a** even at the low applied temperature. A different aspect that is emphasized in Figure 7 is that the β -pyrrole bonds are much shorter than all other C–C bonds — they have the characteristics of non-aromatic double bonds. This is a common feature in all crystallographically characterized corroles,^[9–11,20] apparently responsible for the facile electrophilic substitution at those positions.

In a broader sense, and of particular relevance to ongoing debates about the assignment of oxidation states in corrole complexes with transition metal ions,^[9c,13,30] it is of interest to examine this aspect with the increasing number of crystallographically characterized complexes of **1** and **2**.^[31] Accordingly, we have summarized the available data in Table 1.

Inspection of these data reveals that the differences in C_α – C_{meso} bond lengths are smallest in [Ga(tpfc)(py)] (average 0.004 Å), the prototype of closed-shell corrolato–metal complexes, and largest in **2a** (average 0.028 Å), for which the evidence for contribution of open-shell electronic states is the strongest. Within the limit of experimental errors (average ESD of the relevant bond lengths being 0.005 Å), the complexes may be classified by the average difference between C_α – C_{meso} bond lengths: less than 0.01 Å in [Co(tpfc)(py)₂], [Ga(tpfc)(py)], [Fe(tpfc)(py)₂], and [Ru(tpfc)NO], 0.01–0.014 Å in [Rh(tpfc)(PPh₃)(py)], [Rh(tpfc)(PPh₃)], and [Rh(tdcc)(PPh₃)(py)], and 0.019–0.028 Å in [Fe(tdcc)(NO)], [Fe(tpfc)(NO)], [Fe(tpfc)(Cl)], and [Cu(tdcc)]. Based on this criterion only, this could be indicative for ranking the complexes in terms of the contribution of open-shell electronic states therein. However, one must keep in mind that in all the corrole complexes the $\text{C}_{\beta\text{-pyrrole}}$ – $\text{C}_{\beta\text{-pyrrole}}$ bonds are particularly short, the average differences in C_α –N bond lengths are quite similar, and that even the largest average difference between C_α – C_{meso} bond lengths (0.028 Å) is significantly smaller than in porphyrin radical complexes (> 0.04 Å).

Summary and Conclusions

The reactions of 5,10,15-tris(pentafluorophenyl)corrole and 5,10,15-tris(2,6-dichlorophenyl)corrole with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ lead to the tetracoordinate mononuclear copper complexes **1a** and **2a**, respectively, which can be further transformed into the corresponding dinuclear corrole dimers **1b** and **2b**. All complexes are EPR-silent, and electrochemical measurements coupled with EPR spectroscopy revealed that their reduction and oxidation pro-

Table 1. Differences in bond lengths [$\text{\AA}$] between the carbon atoms bound to *meso*-carbon (C5, C10, C15) and nitrogen (N21, N22, N23, N24) atoms in various complexes of **1** (tpfc) and **2** (tdcc)

	C–C5–C	C–C10–C	C–C15–C	C_{α} – C_{meso} , average	C–N21–C	C–N22–C	C–N23–C	C–N24–C	C_{α} –N, average	Ref.
Cu(tdcc)	0.030	0.011	0.044	0.028	0.020	0.001	0.003	0.024	0.012	this work
Rh(tdcc)(PPh ₃)(py)	0.021	0.006	0.004	0.010	0.014	0.014	0.024	0.014	0.016	[20]
Rh(tpfc)(PPh ₃)(py)	0.008	0.004	0.025	0.012	0.014	0.036	0.031	0.000	0.020	[20]
Rh(tpfc)(PPh ₃)	0.017	0.018	0.007	0.014	0.004	0.008	0.018	0.024	0.013	[9a]
Fe(tdcc)(NO)	0.021	0.010	0.025	0.019	0.025	0.002	0.006	0.007	0.010	[9c]
Fe(tpfc)(NO)	0.027	0.000	0.043	0.023	0.020	0.004	0.020	0.006	0.013	[9c]
Fe(tpfc)(py) ₂	0.009	0.007	0.002	0.006	0.031	0.015	0.010	0.024	0.020	[9b]
Fe(tpfc)(Cl)	0.026	0.007	0.040	0.024	0.003	0.004	0.005	0.015	0.007	[9a]
Ru(tpfc)NO	0.019	0.007	0.001	0.009	0.012	0.015	0.002	0.015	0.011	[10]
Co(tpfc)(py) ₂	0.001	0.004	0.002	0.002	0.001	0.027	0.029	0.005	0.016	[11]
Ga(tpfc)(py)	0.000	0.003	0.009	0.004	0.007	0.023	0.018	0.007	0.014	[16]

cesses are metal- and corrole-centered, leading to corrole–copper(II) and –copper(III) radicals, respectively. The temperature-dependent NMR spectra of **1a** and **2a** revealed the existence of two almost degenerate electronic states. The diamagnetic ground states, favored at lower temperatures, were analyzed as consisting of copper(III) coordinated by closed-shell corrolato trianions and the paramagnetic state as being composed of copper(II) chelated by open-shell corrolato dianions. The contributions from both states are evident in the molecular structure of **2a**, which displays a distorted square-planar coordination geometry around the metal ion and short Cu–N bond lengths typical of copper(III), together with some non-equivalence of the C_{α} – C_{meso} bond lengths that might reflect the open-shell character of the macrocycle. The radical character is also likely to be responsible for the facile C–C coupling process that leads to the dimerization products. Nevertheless, the contribution of the copper(II) radical state is much lower than in analogous complexes of porphyrins and octaethylbilindione (a noncyclic tetrapyrrole with three protonated N atoms as in corroles),^[32] where the Cu–N bonds are much longer. The latter case may be considered at the opposite extreme, based on its magnetic moment and the very large paramagnetic isotopic shifts in its NMR spectrum.

Experimental Section

Physical Methods: The ^1H and ^{19}F NMR spectra were recorded with a Bruker AM 200, operating at 200 MHz for ^1H and 188 MHz for ^{19}F , a Bruker AM 300, operating at 300 MHz for ^1H and 282 MHz for ^{19}F , or a Bruker AM 500, operating at 500 MHz for ^1H . Chemical shifts are reported in ppm relative to residual hydrogen atoms in the deuterated solvents: $\delta = 7.24, 7.15, 7.00$ ppm for chloroform, benzene and toluene, respectively, for the ^1H NMR spectra and relative to CFCl_3 ($\delta = 0.00$ ppm) in the ^{19}F NMR spectra. The electronic spectra were recorded with an HP 8452A diode array spectrophotometer and gas chromatographic analysis was performed with an HP-5890 GC equipped with an HP-5 capillary column and FID detector. Mass spectrometry was performed with a Finnigan mat TSQ 70 instrument with isobutane as carrier gas and IR measurements with an FT-IR Bruker Vector 22. The redox potentials were determined by cyclic voltammetry (CV) at ambient temperatures with a home-made voltammograph, using

$\text{C}_6\text{H}_5\text{CN}$ solutions, 0.05 M in tetra-*n*-butylammonium perchlorate (TBAP, Fluka, recrystallized three times from absolute ethanol) and about 0.5 mM in substrate. Ag/AgCl was used as the reference electrode. The other experimental conditions are reported in the captions of the corresponding spectra.

Materials: $\text{C}_6\text{H}_5\text{CN}$ (BioLab Ltd.), dichloromethane (Bio-Lab Ltd.), pyridine (Merck), ethanol (Bio-Lab Ltd.), *n*-heptane (Carlo-Erba), *n*-hexane (Bio-Lab Ltd.), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (Riedel–de Haën), $\text{Na}_2\text{S}_2\text{O}_4$ (Merck), $(\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6$ (Aldrich) and deuterated solvents (Aldrich and Cambridge Isotopes products) were used as received.

Synthetic Methods: The synthetic details for the preparation of $\text{H}_3(\text{tpfc})$ and $\text{H}_3(\text{tdcc})$ are provided in previous publications.^[3a,3b,3c–3g]

Cu(tpfc) (1a) and the Dinuclear Complex 1b: An approximate three-fold excess of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (66 mg, 0.34 mmol) was added to a solution of **1** (100 mg, 0.126 mmol) in pyridine (5 mL) in one portion. TLC examinations (silica gel; *n*-hexane/ CH_2Cl_2 , 2:1) revealed that the starting material was fully consumed at room temp. within 30 min. The solvents were evaporated from the red-green mixture and **1a** was obtained as a red powder (75 mg, 73% yield) after column chromatography (silica gel; *n*-hexane/ CH_2Cl_2 , 4:1), together with trace amounts of **1b**. When an identical reaction mixture was heated to reflux for 10 min, both **1a** (32 mg, 30% yield) and **1b** (42.8 mg, 40% yield) could be isolated by column chromatography (silica gel; *n*-hexane/ CH_2Cl_2 , 10:3). Complexes **1a** and **1b** could not be further purified by recrystallization because of their transformation (within hours) into a mixture of green compounds, all of which were analyzed by mass spectrometry as dinuclear complexes of dimeric corrole (isomers of **1b**).

1a: UV/Vis (benzene): λ_{max} ($\epsilon \times 10^{-4}$) = 410 (6.17), 550 (0.81) nm. MS (DCI^-): m/z (%) = 856 (100) [M^-]. ^1H NMR (toluene, 500 MHz, room temp.): $\delta = 7.76$ (br. s, 2 H), 7.23 (br. s, 2 H), 7.14 (br. s, 2 H), 6.93 (br. s, 2 H) ppm. ^1H NMR (toluene, 200 MHz, 233 K): $\delta = 7.67$ (d, $J = 3.99$ Hz, 2 H), 7.32 (d, $J = 3.98$ Hz, 2 H), 7.23 (unresolved d, 2 H), 7.18 (unresolved d, 2 H) ppm. ^{19}F NMR (CDCl_3 , 300 MHz, room temp.): $\delta = -137.11$ (d, m, 4 F, *o*-F), -137.97 (m, 2 F, *o*-F), -152.12 (t, $J = 21.2$ Hz, 1 F, *p*-F), -152.35 (t, $J = 21.2$ Hz, 2 F, *p*-F), -160.89 (m, 6 F, *m*-F) ppm.

1b: UV/Vis (benzene): λ_{max} ($\epsilon \times 10^{-4}$) = 412 (10.95), 566 (1.44) nm. MS (DCI^-): m/z (%) = 1710 (100) [M^-]. ^1H NMR (CDCl_3 , 200 MHz, room temp.): $\delta = 7.84$ (br. s, 2 H), 7.58 (br. s, 2 H), 7.33 (br. s, 2 H), 7.21 (br. s, 2 H), 7.14 (br. s, 2 H), 6.94 (m, 4 H) ppm.

^{19}F NMR ($[\text{D}_8]\text{toluene}$, 300 MHz, room temp.): $\delta = -136.04$ (s, 2 F, *o*-F), -136.98 (d, $J = 21.17$ Hz, 2 F, *o*-F), -137.56 (d, $J = 21.17$ Hz, 2 F, *o*-F), -138.12 (m, 4 F, *o*-F), -138.62 (d, $J = 21.17$ Hz, 2 F, *o*-F), -151.62 (t, $J = 21.17$ Hz, 2 F, *p*-F), -152.01 (dt, 4 F, *p*-F), -159.79 (s, 2 F, *m*-F), -160.81 (m, 8 F, *m*-F), -163.06 (t, $J = 21.17$ Hz, 2 F, *m*-F) ppm.

Cu(tdcc) (2a) and the Dinuclear Complex 2b: A threefold excess of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (25 mg, 0.12 mmol) was added to a solution of **2** (30 mg, 0.04 mmol) in pyridine (5 mL) in one portion and mixed for 30 min at room temp. After solvent evaporation and column chromatography (silica gel; *n*-hexane/ CH_2Cl_2 , 4:1), **2a** was isolated as a red powder (26 mg, 85% yield). X-ray quality crystals were obtained by recrystallization from CH_2Cl_2 /*n*-heptane. When an identical reaction mixture was heated to reflux for 30 min, **2a** (15 mg, 45% yield) and **2b** (14 mg, 42% yield) were separated by column chromatography (silica gel; *n*-hexane/ CH_2Cl_2 , 10:3).

2a: UV/Vis (benzene): λ_{max} ($\epsilon \times 10^{-4}$) = 406 (4.71), 548 (0.56) nm. MS (DCI^-): m/z (%) = 794 (100) [M^-]. ^1H NMR (toluene, 500 MHz, room temp.): $\delta = 7.69$ (br. s, 2 H), 7.26 (br. s, 2 H), 7.17 (br. s, 2 H), 6.86 (unresolved d, 2 H), 7.10 (d, $J = 8$ Hz, 4 H, *m*-H), 7.04 (d, $J = 8$ Hz, 2 H, *m*-H), 6.68 (t, $J = 8.25$ Hz, 2 H, *p*-H), 6.63 (t, $J = 8.25$ Hz, 1 H, *p*-H) ppm. ^1H NMR (toluene, 500 MHz, 240 K): $\delta = 7.43$ (d, $J = 4.37$ Hz, 2 H), 7.19 (d, $J = 4.37$ Hz, 2 H), 7.01 (d, $J = 4.77$ Hz, 2 H), 6.97 (d, $J = 4.77$ Hz, 2 H), 6.92 (d, $J = 8.34$ Hz, 4 H, *m*-H), 6.83 (d, $J = 8.34$ Hz, 2 H, *m*-H), 6.56 (t, $J = 8.25$ Hz, 2 H, *p*-H), 6.50 (t, $J = 8.25$ Hz, 1 H, *p*-H) ppm.

2b: UV/Vis (benzene): λ_{max} ($\epsilon \times 10^{-4}$) = 410 (12.8), 560 (2.14) nm. MS (DCI^-): m/z (%) = 1584 (100) [M^-]. ^1H NMR (toluene, 500 MHz, room temp.): $\delta = 7.77$ (br. s, 4 H), 7.64 (br. s, 4 H), 6.86 (d, $J = 4$ Hz, 4 H), 6.53 (unresolved d, 4 H), 7.19 (unresolved d, 6 H, *m*-H), 7.06 (unresolved d, 4 H, *m*-H), 6.67 (d, $J = 8$ Hz, 2 H, *m*-H), 6.68 (t, $J = 8$ Hz, 2 H, *p*-H), 6.58 (t, $J = 8.25$ Hz, 2 H, *p*-H), 6.40 (t, $J = 8$ Hz, 2 H, *p*-H) ppm. ^1H NMR (toluene, 500 MHz, 235 K): $\delta = 7.38$ (br. s, 2 H), 7.33 (d, $J = 3.97$ Hz, 2 H), 7.26 (d, $J = 3.97$ Hz, 2 H), 6.85 (d, $J = 4.37$ Hz, 2 H), 6.73 (d, $J = 4.77$ Hz, 2 H), 6.44 (unresolved d, 2 H), 7.01 (unresolved d, 2 H), 6.98 (m, 6 H, *m*-H), 6.79 (m, 6 H, *m*-H), 6.54 (t, $J = 8$ Hz, 2 H, *p*-H), 6.54 (t, $J = 8.25$ Hz, 2 H, *p*-H), 6.25 (t, $J = 8$ Hz, 2 H, *p*-H) ppm. ^1H NMR (toluene, 500 MHz, 320 K): $\delta = 8.06$ (br. s, 2 H), 7.86 (br. s, 2 H), 7.42 (br. s, 2 H), 7.38 (br. s, 2 H), 7.15 (br. s, 2 H), 6.86 (br. s, 2 H), 6.39 (br. s, 2 H), 7.32 (d, $J = 7.9$ Hz, 6 H, *m*-H), 7.23 (d, $J = 7.8$ Hz, 6 H, *m*-H), 6.72 (t, $J = 8.07$ Hz, 2 H, *p*-H), 6.63 (t, $J = 8.07$ Hz, 2 H, *p*-H), 6.45 (t, $J = 8.07$ Hz, 2 H, *p*-H) ppm.

Chemical Oxidation of [Cu(tdcc)] (2a): Solid $(\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6$ (13 mg, 18 μmol) was added in one portion to a well-stirred solution of **2a** (5 mg, 6 μmol) in CH_2Cl_2 . The color changed to yellow-green within a few minutes, after which the solution was filtered and used for the spectroscopic examinations.

Chemical Reduction of [Cu(tdcc)] (2a): A saturated solution of $\text{Na}_2\text{S}_2\text{O}_4$ (2 mg, 0.011 mmol) in H_2O (2 mL) was added in one portion to a 50-mL three-necked, round-bottomed flask containing a solution of **2a** (5 mg, 6 μmol) in ethanol (2 mL). The mixture was stirred under Ar for 5 min, during which time the color changed from red to green. This solution was used for the EPR measurements, still under Ar.

Electrochemistry: The cyclic voltammograms of the complexes were measured for approximately 0.5 mm substrate in 0.05 M TBAP/ $\text{C}_6\text{H}_5\text{CN}$ solutions at scan rates of 100 V/s with Ag/AgCl reference electrode. The redox potentials are reported vs. the ferrocene/ferrocenium redox couple observed at 0.4 V vs. Ag/AgCl.

X-ray Crystallography of [Cu(tdcc)] (2a): The crystalline sample of **2a** was covered with a thin layer of light oil and cooled to 110 K in order to minimize the escape of the volatile crystallization solvent and minimize thermal motion/structural disorder effects. The intensity data were corrected for absorption. The structure was solved and refined by standard crystallographic techniques. All non-hydrogen atoms of the corroles were refined anisotropically. The hydrogen atoms were located in calculated positions, and were refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2 U_{ij}(\text{eq.})$ for the atom to which they are bonded]. Complex **2a** crystallized as an *n*-heptane solvate. $2\text{C}_{37}\text{H}_{17}\text{Cl}_6\text{N}_4\text{Cu} \cdot 1/2\text{C}_7\text{H}_{16}$, $M = 1637.68$, triclinic, space group $P\bar{1}$, $a = 12.3630(2)$, $b = 16.5760(3)$, $c = 17.8710(4)$ Å, $\alpha = 93.615(1)^\circ$, $\beta = 92.401(1)^\circ$, $\gamma = 97.352(1)^\circ$, $V = 3401.9(1)$ Å³, $Z = 2$, $T = 110(2)$ K, $D_c = 1.599$ g·cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.15$ mm⁻¹, 15035 unique reflections to $2\theta_{\text{max}} = 56.6^\circ$, 902 refined parameters, $R_1 = 0.055$ for 120571 observations with $I > 2\sigma(I)$, $R_1 = 0.096$ ($wR_2 = 0.108$) for all unique data, $\Delta\rho \leq 0.64$ e/Å³. The asymmetric unit consists of two corrole species and half of the *n*-heptane solvate molecule which is located on, and disordered about, a center of inversion. CCDC-206173 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This research was supported by the Israel Science Foundation under Grants 368/00 (Z. G.) and 68/01 (I. G.). A postdoctoral fellowship for L. S. by the Institute of Catalysis Science and Technology of the Technion is acknowledged as well.

- [1] For reviews that cover the chemistry of corrole up to 1999, see: [1a] J. L. Sessler, S. J. Weghorn, in *Expanded, Contracted & Isomeric Porphyrins*, Pergamon, Oxford, **1997**, pp. 11–85. [1b] R. Paolesse, in *The Porphyrin Handbook*, vol. 2 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, chapter 11, pp. 201–231. [1c] K. M. Kadish, in *The Porphyrin Handbook*, vol. 2 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, chapter 12, pp. 233–295.
- [2] For only the two triarylcorroles that were reported prior to 1999, see: [2a] N. M. Loim, E. V. Grishko, N. I. Pysnograeva, E. V. Vorontsov, V. I. Sokolov, *Izv. Akad. Nauk. Ser. Khim.* **1994**, 5, 925. [2b] E. Rose, A. Kossanyi, M. Quelquejeu, M. Soleilhavoup, F. Duwavan, N. Bernard, A. Lecas, *J. Am. Chem. Soc.* **1996**, 118, 1567.
- [3] [3a] Z. Gross, N. Galili, I. Saltsman, *Angew. Chem. Int. Ed.* **1999**, 38, 1427. [3b] Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Bläser, R. Boese, I. Goldberg, *Org. Lett.* **1999**, 1, 599. [3c] L. Simkhovich, I. Goldberg, Z. Gross, *J. Inorg. Biochem.* **2000**, 80, 235. [3d] E. Steene, T. Wondimagegn, A. Ghosh, *J. Inorg. Biochem.* **2002**, 88, 113. [3e] L. Simkhovich, I. Goldberg, Z. Gross, *Org. Lett.* **2003**, 5, 1241. [3f] J. P. Collman, R. A. Decreau, *Tetrahedron Lett.* **2003**, 44, 1207. [3g] D. T. Gryko, B. Koszarna, *Org. Biomol. Chem.* **2003**, 1, 350.
- [4] [4a] R. Paolesse, L. Jaquinod, D. J. Nurco, S. Mini, F. Sagone, T. Boschi, K. M. Smith, *Chem. Commun.* **1999**, 1307. [4b] R. Paolesse, S. Nardis, F. Sagone, R. G. Khoury, *J. Org. Chem.* **2001**, 66, 550.
- [5] [5a] J.-W. Ka, C.-H. Lee, *Tetrahedron Lett.* **2000**, 41, 4609. [5b] J.-W. Ka, W.-S. Cho, C.-H. Lee, *Tetrahedron Lett.* **2000**, 41, 8121. [5c] D. T. Gryko, *Chem. Commun.* **2000**, 2243. [5d] D. T. Gryko, K. Jadach, *J. Org. Chem.* **2001**, 66, 4267. [5e] R. P.

- Brinas, C. Bruckner, *Synlett* **2001**, 3, 442. ^[5f] C. V. Asokan, S. Smeets, W. Dehaen, *Tetrahedron Lett.* **2001**, 42, 4483. ^[5g] R. A. Decreau, J. P. Collman, *Tetrahedron Lett.* **2003**, 44, 3323.
- [6] For synthesis of corrole-like molecules, see: ^[6a] B. Sridevi, S. J. Narayanan, T. K. Chandrashekar, U. Englisch, K. Ruhlandt-Senge, *Chem. Eur. J.* **2000**, 6, 2554. ^[6b] B. Ramdhanie, C. L. Stern, D. P. Goldberg, *J. Am. Chem. Soc.* **2001**, 123, 9447. ^[6c] M. Broering, C. Hell, *Chem. Commun.* **2001**, 22, 2336.
- [7] ^[7a] A. E. Meier-Callahan, H. B. Gray, Z. Gross, *Inorg. Chem.* **2000**, 39, 3605. ^[7b] A. E. Meier-Callahan, A. J. Di Bilio, L. Simkhovich, A. Mohammed, I. Goldberg, H. B. Gray, Z. Gross, *Inorg. Chem.* **2001**, 40, 6788.
- [8] ^[8a] Z. Gross, G. Golubkov, L. Simkhovich, *Angew. Chem. Int. Ed.* **2000**, 39, 4045. ^[8b] J. Bendix, G. Golubkov, H. B. Gray, Z. Gross, *Chem. Commun.* **2000**, 1957. ^[8c] G. Golubkov, J. Bendix, H. B. Gray, A. Mohammed, I. Goldberg, A. J. DiBilio, Z. Gross, *Angew. Chem. Int. Ed.* **2001**, 40, 2132. ^[8d] S. P. de Visser, F. Ogliaro, Z. Gross, S. Shaik, *Chem. Eur. J.* **2001**, 7, 4954.
- [9] ^[9a] L. Simkhovich, N. Galili, I. Saltsman, I. Goldberg, Z. Gross, *Inorg. Chem.* **2000**, 39, 2704. ^[9b] L. Simkhovich, A. Mohammed, I. Goldberg, Z. Gross, *Chem. Eur. J.* **2001**, 7, 1041. ^[9c] L. Simkhovich, I. Goldberg, Z. Gross, *Inorg. Chem.* **2002**, 41, 5433.
- [10] L. Simkhovich, I. Luobeznova, I. Goldberg, Z. Gross, *Chem. Eur. J.* **2003**, 9, 201.
- [11] A. Mohammed, I. Giladi, I. Goldberg, Z. Gross, *Chem. Eur. J.* **2001**, 7, 4259.
- [12] L. Simkhovich, P. Iyer, I. Goldberg, Z. Gross, *Chem. Eur. J.* **2002**, 8, 2595.
- [13] Z. Gross, *J. Biol. Inorg. Chem.* **2001**, 6, 733.
- [14] Z. Gross, N. Galili, *Angew. Chem. Int. Ed.* **1999**, 38, 2366.
- [15] A. Mohammed, Z. Gross, *J. Inorg. Biochem.* **2002**, 88, 305.
- [16] J. Bendix, I. J. Dmochowski, H. B. Gray, A. Mohammed, L. Simkhovich, Z. Gross, *Angew. Chem. Int. Ed.* **2000**, 39, 4048.
- [17] ^[17a] Z. Gross, L. Simkhovich, N. Galili, *Chem. Commun.* **1999**, 599. ^[17b] L. Simkhovich, Z. Gross, *Tetrahedron Lett.* **2001**, 42, 8089. ^[17c] J. Grodkowski, P. Neta, E. Fujita, A. Mohammed, Z. Gross, *J. Phys. Chem. A* **2002**, 106, 4772. ^[17d] R. A. Eikey, S. I. Khan, M. M. Abu-Omar, *Angew. Chem. Int. Ed.* **2002**, 41, 3592.
- [18] ^[18a] A. Mohammed, I. Goldberg, Z. Gross, *Org. Lett.* **2001**, 3, 3443. ^[18b] I. Saltsman, A. Mohammed, I. Goldberg, E. Tkachenko, M. Botoshansky, Z. Gross, *J. Am. Chem. Soc.* **2002**, 124, 7411. ^[18c] Z. Gross, A. Mahammed, *J. Porphyrins Phthalocyanines* **2002**, 6, 553.
- [19] D. Aviezer, S. Cotton, M. David, A. Segev, N. Khaselev, N. Galili, Z. Gross, A. Yaron, *Cancer Res.* **2000**, 60, 2973.
- [20] L. Simkhovich, I. Goldberg, Z. Gross, *J. Porphyrins Phthalocyanines* **2002**, 6, 439–444.
- [21] ^[21a] A. W. Johnson, I. T. Kay, *J. Chem. Soc.* **1965**, 1620. ^[21b] R. Grigg, A. W. Johnson, G. Shelton, *J. Chem. Soc., C* **1971**, 2287.
- [22] ^[22a] S. Will, J. Lex, E. Vogel, H. Schmicker, J.-P. Gisselbrecht, C. Hauptmann, M. Bernard, M. Gross, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 357; *Angew. Chem.* **1997**, 109, 367. ^[22b] A. Ghosh, T. Wondimagegn, A. B. Parusel, *J. Am. Chem. Soc.* **2000**, 122, 5100.
- [23] K. M. Kadish, V. A. Adamian, E. Van Caemelbecke, E. Guelletii, S. Will, C. Erben, E. Vogel, *J. Am. Chem. Soc.* **1998**, 120, 11986.
- [24] ^[24a] Y. Ni, S. Lee, B. B. Wayland, *Inorg. Chem.* **1999**, 38, 3947. ^[24b] N. Ehlinger, W. R. Scheidt, *Inorg. Chem.* **1999**, 38, 1316. ^[24c] M. W. Renner, K.M. Barkigia, Y. Zhang, C. J. Medforth, K. M. Smith, J. Fajer, *J. Am. Chem. Soc.* **1994**, 116, 8582.
- [25] I. H. Wasbotten, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* **2002**, 124, 8104.
- [26] The a_N of 3.3 G reported in the text of ref.[23] must be erroneous, as judged from examination of the relevant figure therein.
- [27] R. Krishna Kumar, S. Balasubramanian, I. Goldberg, *Inorg. Chem.* **1998**, 37, 541; Y. Diskin-Posner, S. Dahal, I. Goldberg, *Angew. Chem. Int. Ed.* **2000**, 39, 1288.
- [28] ^[28a] R. Ruiz, C. Surville-Barland, A. Aukauloo, E. Anxolabehere-Mallart, Y. Journaux, J. Cano, M. C. Munoz, *J. Chem. Soc., Dalton Trans.* **1997**, 745. ^[28b] M. Melnik, M. Kabesova, *J. Coord. Chem.* **2000**, 50, 323.
- [29] W. R. Scheidt, *J. Biol. Inorg. Chem.* **2001**, 6, 727.
- [30] ^[30a] O. Zakharieva, V. Schunemann, M. Gerdan, S. Licoccia, S. Cai, F. A. Walker, A. X. Trautwein, *J. Am. Chem. Soc.* **2002**, 124, 6636. ^[30b] A. Ghosh, P. R. Taylor, *Curr. Opin. Chem. Biol.* **2003**, 7, 113. ^[30c] F. A. Walker, *Inorg. Chem.* **2003**, 42, 4526.
- [31] For another triarylcorrole–copper complex that was published while this manuscript was in the referee process, see: C. Bruckner, R. P. Brinas, J. A. Krause-Bauer, *Inorg. Chem.* **2003**, 42, 4495.
- [32] A. L. Balch, M. Mazzanti, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1993**, 115, 12206.

Received November 3, 2003

Early View Article

Published Online March 9, 2004