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Evidence for A [17] π-Electronic Full-Fledged Non-Innocent Gallium(III)-Corrole Radical

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Abstract: One-electron oxidation of a Ga^{III}-corrole with N(4-BrC$_6$H$_4$)$_3$SbCl$_6$ resulted in an air-stable non-innocent Ga^{III}-corrole radical. The single crystal X-ray crystallography of [2,17-bis-formyl-5,10,15-tris(pentafluorophenyl)corrolato gallium(III)(chloride)] radical (**[3-Cl]$^\bullet$**) revealed delocalization of the unpaired electron, which was further confirmed by electron spin resonance (ESR) spectroscopy and spin density distribution plot. In addition, the nucleus-independent chemical shift (NICS), anisotropy induced-current density (AICD) and harmonic oscillator model of aromaticity (HOMA) supported a [17] π-electron conjugated (or antiaromatic) radical.

Corrole macrocycle is a contracted porphyrinoid having a 2,2′-bipyrrolic unit and three inner NH hydrogens, first reported by Johnson and Kay in 1965.[1] The rich and intriguing properties of corrole remained largely unexplored until the development of efficient methodologies for the synthesis of *meso*-arylcorroles in the late nineties.[2] One of the most intriguing features of corrole is the non-innocence character, predominantly observed with transition-metals, where corrole exists as a dianionic corrole radical (corrolato$^{\bullet 2-}$).[3] In the last few decades, elegant computational and experimental results provided overwhelming support to the non-innocence character for corrole macrocycle.[4,5] A large variety of metallocorroles (M = Cu,[4,5a-b] FeCl/FeNO,[5c-g] MnPy/MnCl,[5h-j] Ag,[5k-l] Co(Ph),[5m-n] Pt(Ar)$_2$[5o], Ni[4a,5p]) have been synthesized, which exhibit moderate to full-fledged non-innocent character. The ligand non-innocence in transition-metal corrole is mainly mediated through the interaction of a metal d-orbital ($d_{x^2-y^2}$ or d_{z^2} or d_π) and HOMO ("a$_{2u}$-type") of corrole radical, facilitated by a saddle geometry.[3,4,5]

On the other hand, the existence of free-base [2H]corrole radical was speculated to manifest in solution under oxidizing conditions.[6] However, its unambiguous characterization was rather elusive until recently, when Bröring and co-workers reported a stable [2H]corrole radical.[7] They serendipitously isolated 3,17-dichloro-5,10,15-trimesitylcorrole radical (4-7%) in an attempt to achieve a tungsten corrole complex using WCl$_6$/W(CO)$_6$ (2:1) in benzonitrile at 200°C for 8 hours.

However, the structure of substantially stable radical of corrole (*i,e*., dianionic radical) with main-group element is not familiar. This impelled us to think about the possibilities of existence of a stable main-group corrole radical, which can be a missing link between radicals of transition-metal and free-base corroles. The pertinent question is the stability and electronic structure of main-group (filled d-orbitals) corrole-radical, and the differences with the transition-metal (partially filled d-orbitals) complexes. Therefore, it would be worthy to investigate the nature of the radical if a non-transition metal is present in the core. Importantly, Fu and co-workers[8] generated putative [(TPFC)Ge^{III}] radical intermediate by the photolysis of (TPFC)Ge^{IV}-H and characterized by electron spin resonance (ESR) spectroscopy. The spin density distribution analysis showed a large contribution from the Ge^{III} centre. Thus, an unambiguous proof of a full-fledged non-innocent corrole with main-group remains inexplicit. Notably, *in-situ* formation of trianionic [(TPFC)Ga^{III}]$^{\bullet +}$SbCl$_6^-$ as proposed by one electron chemical oxidation of (TPFC)Ga^{III} with N(4-BrC$_6$H$_4$)$_3$SbCl$_6$.[9] The isotropic ESR signal and the absence of hyperfine splitting supported the delocalized corrole cationic radical species. However, the identical ESR signal can arise from two distinct species as depicted in Figure 1. After expulsion of one electron, corrole ligand (**I**) can either exist as a trianionic radical cation (**II**) as in the case of [(corrolato^{3-})Ga^{III}]$^{\bullet +}$A$^-$ or a non-innocent dianionic radical (**III**) as in the case of [(corrolato$^{\bullet 2-}$)Ga^{III}-A], where A is a mono-anionic ligand.

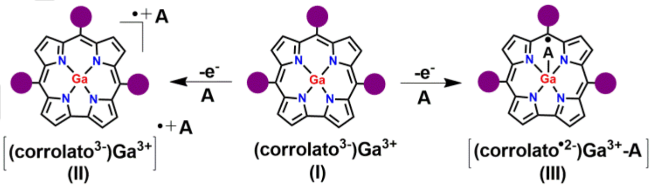

Figure 1: Schematic representation of probable products (**II** and **III**) after one electron chemical oxidation of Ga^{III}-corrole (**I**). A is a mono-anionic ligand.

Thus, the structural ambiguity in solution has prevented detailed assessment of electronic structure of the radical. From this perspective, we decided to investigate one electron chemical oxidation of three Ga^{III}-corrole complexes (**1**, **2** and **3**, Scheme 1) with N(4-BrC$_6$H$_4$)$_3$SbCl$_6$ (Magic Blue, $E_{oxi}^{0/1}$ = 1.1 V *vs* SCE).[9,11] Herein, we report the existence of a full-fledged non-innocent Ga^{III}-corrole radical that revealed the [17] π-electron conjugated (or antiaromatic) radical.

The compounds **1**, **2** and **3** were synthesized as reported[2c,9,10] (Scheme 1 and see supporting information) and characterized by mass spectrometry, ^{1}H and ^{19}F NMR spectroscopies (Figure S1-S8, supporting information). The reaction of **1** ($E_{oxi}^{0/1}$ = 0.78 V *vs* SCE, Scheme 1)[9] with equimolar Magic Blue was probed by ESR and high resolution mass spectroscopy-electron spray ionization (HRMS-ESI). The X-band ESR studies in toluene/CHCl$_3$ at 110 K indicated the formation of radical species with g_{iso} value of 2.0054 (Figure S16). Surprisingly, the mass spectral analysis indicated the formation of species with isotopic patterns resembling chlorinate

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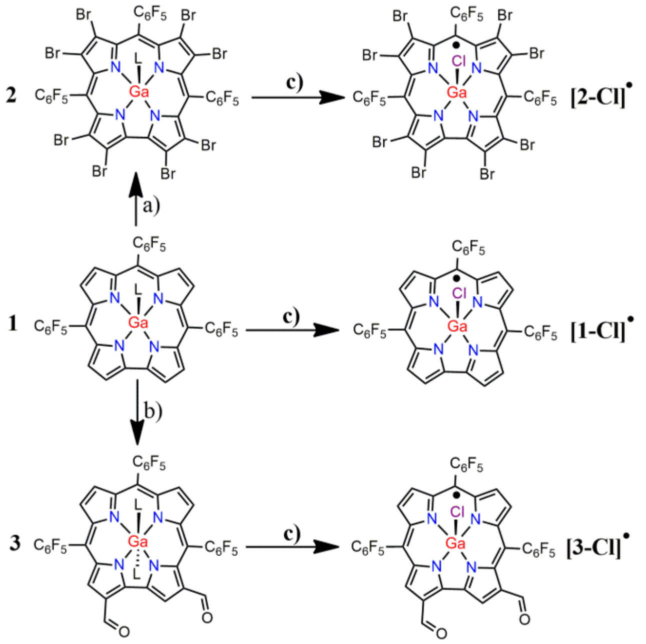


Scheme 1: Synthesis of Ga^{III}-corrole derivatives (**1**, **2** and **3**, L = pyridine) and corresponding Ga^{III}-corrole radical (**[1-Cl]$^•$** **[2-Cl]$^•$** and **[3-Cl]$^•$**); (a) Br_2/DCM, dark, 12 hrs, 88%, (b) DMF/$POCl_3$, CH_2Cl_2, 1 h, H_2O/K_2CO_3, 12 hrs, 62%, (c) $N(4\text{-}BrC_6H_4)_3SbCl_6$ (1 equiv.), toluene/$CHCl_3$, *in-situ* investigations/crystallization.

-d monomer and dimers.The ion-peaks corresponding to m/z = 896.9474[M^+], 1756.9047[M_2^+], 1792.8844[$(M_2+H)^+$] and 1871.9221[$(M_2+H)^+$] can be assigned to the compounds having empirical formulae of $C_{37}H_8F_{15}GaN_4Cl$, $C_{74}H_{14}F_{30}Ga_2N_8Cl$, $C_{74}H_{15}F_{30}Ga_2N_8Cl_2$ and $C_{79}H_{20}F_{30}Ga_2N_8Cl_2$ respectively (Figure SI10-S11). The *β*-pyrrolic positions of corrole are susceptible towards electrophilic substitution.[12,13] Thus, at first instance, the *β*-chlorinated corroles have emerged to us as the most probable products. In order to prevent any possible chlorination[13b] and to avert dimerization of the formed radical,[13f-g] two distinct Ga^{III}-corrole were preferred, where the *β*-pyrrolic positions have been blocked. In compound **2** ($E_{oxi}^{0/1}$ = 0.99 V *vs* SCE),[11] all the eight *β*-pyrrolic positions have been substituted with bromine. Similarly, in compound **3** ($E_{oxi}^{0/1}$ = 0.84 V *vs* SCE),[11] the most reactive bipyrrolic positions have been deactivated by the insertion of formyl group. To our surprise, in both the scenarios despite highly deactivated corroles, the mass spectral analysis showed the formation of chlorinated species (Figure S12-S15). Furthermore, the X-band ESR studies in toluene/$CHCl_3$ at 110 K indicated the radical species with g_{iso} value of 2.0093 and 2.0068 respectively for **2** and **3** on reaction with Magic Blue (Figure S17 and Figure S18).

The structure of Ga^{III}-corrole radical was confirmed from the single crystal X-ray diffraction study obtained for **[3-Cl]$^•$** (Figure 2 and Figure S19). The separation and crystallization attempts were unsuccessful for **[1-Cl]$^•$** and **[2-Cl]$^•$** due to the gradual decomposition and the formation of uncharacterizable species along with the chlorinated products. The slow evaporation of the filtrate obtained from the reaction of **3** and Magic Blue in toluene/$CHCl_3$ at room temperature resulted in dark green colored single crystal of **[3-Cl]$^•$**.

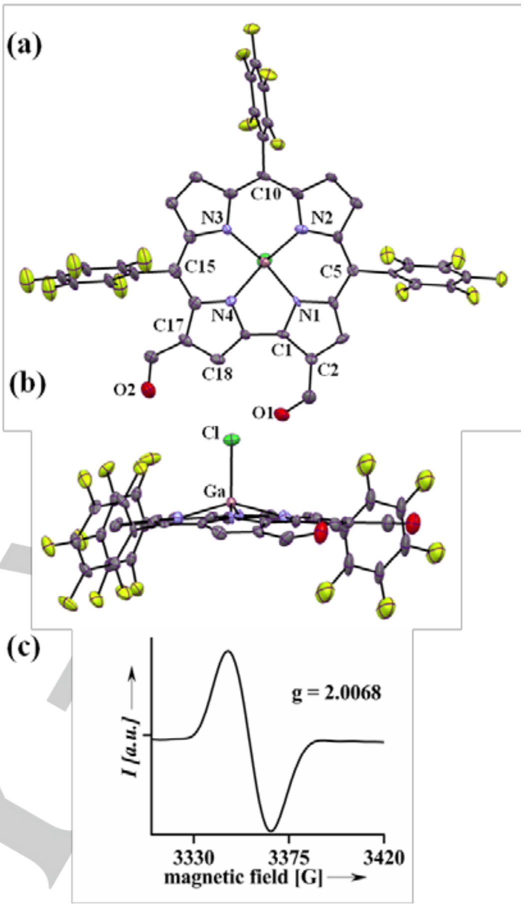
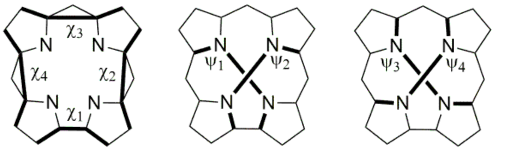


Figure 2: Single crystal X-ray structure of **[3-Cl]$^•$**: (a) front view, (b) side view; hydrogen atoms and solvent residue (pyridine) were omitted for clarity; thermal ellipsoids set to 50% probability, CCDC-1564991. (c) X-band ESR spectra of crystals of **[3-Cl]$^•$** in toluene/$CHCl_3$ (2:1, *v/v*) at 110 K.

Table 1: Selected saddling (χ) and ruffling (ψ) dihedrals angles (defined below, [Å]) of **[1-Cl]$^•$**, **[2-Cl]$^•$**, **[3-Cl]$^•$** and of selected triarylcorroles.



Compounds	χ_1	χ_2	χ_3	χ_4	ψ_1	ψ_2	ψ_3	ψ_4
[1-Cl]$^{•a}$	0.1	18.9	3.4	21.4	6.4	5.0	9.0	7.5
[2-Cl]$^{•a}$	27.7	25.4	30.6	41.4	5.2	2.1	3.6	3.7
[3-Cl]$^•$	7.2	9.9	3.5	16.1	1.8	5.2	1.1	6.4
Ga[TPFC][9]	5.0	27.9	2.9	15.7	8.1	6.5	9.4	7.7
Bi[TPFC][15c]	7.4	26.8	3.6	15.3	6.1	3.7	18.0	11.9
Cu[TPC][5b]	25.0	41.3	48.0	52.5	6.3	5.2	3.8	3.1
Cu[Br_8TpMePC][5l]	44.7	61.0	57.3	71.0	1.0	3.8	6.3	11.7
Ag[Br_8TpMePC][5l]	45.0	75.1	63.5	61.8	3.4	0.7	10.6	5.1
Au[TpFPC][16a]	13.8	25.7	24.5	20.5	3.1	1.3	4.80	4.8
H_3[TFPC][15c]	21.1	67.8	14.1	28.3	18.2	13.7	28.0	15.4
H_3[Br_8TPFC][16b]	31.1	82.3	50.4	1.7	3.9	4.5	29.7	29.5
H_2[Cl_2T(Mesityl)C][7]	4.7	8.9	1.4	3.2	0.2	2.5	11.1	4.6

^{a}calculated based on DFT optimized geometry

Interestingly, a chlorine atom was found to be coordinated with Ga^{III} centre with a bond length of 2.215(2) Å, which is in the range of Ga^{III}-Cl bond distances of 2.1915(6)-2.440(3) Å for five

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and six coordinated Ga^{III}-complexes.[14] The Ga^{III} ion adopted a distorted square pyramidal geometry, exhibiting a deviation of ~0.66 Å above the corrolic 23-atom mean-plane, which is similar to that observed in the case of pentacoordinated metallocorroles.[15] Furthermore, inspection of the crystal structure of **[3-Cl]**$^{\bullet}$ revealed a dianionic radical character of corrole ligand as hinted by the absence of counter ions in the crystal packing. The C-C and C-N bond length alteration in **[3-Cl]**$^{\bullet}$ was found to be similar to that observed in the case of neutral corrole complexes as reported,[9,15] suggesting the delocalization of unpaired electron. The delocalized nature of the radical was further supported by X-band ESR spectra obtained from crystals dissolved in toluene/CHCl$_3$ (2:1,*v/v*) at 110 K (Figure 2c) exhibiting a g_{iso} value of 2.0068. An important feature of the crystal structure of **[3-Cl]**$^{\bullet}$ is the relatively smaller nonplanar distortion of the macrocycle in comparison with the transition-metal corrole complexes.[5,16] The comparison of saddling (χ) and ruffling (ψ) dihedral angles with known structures of selected metallocorroles and free-base corroles are presented in Table 1.

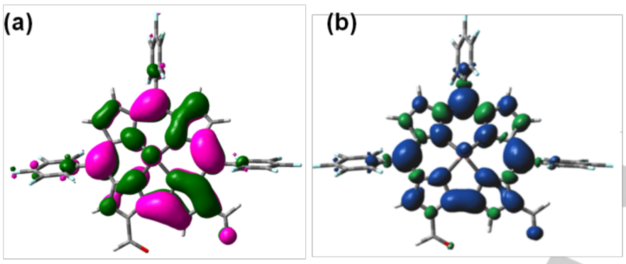

Figure 3: Graphical representations of (a) singly occupied molecular orbital (SOMO) and (b) spin density of **[3-Cl]**$^{\bullet}$ from DFT at UB3LYP/6-31G*(C,H,N,O,Cl) + LANL2DZ(Ga) level; Isosurface value at 0.01.

Density functional theory (DFT)[17] calculation at UB3LYP/6-31G*(C,H,N,O,Cl) + LANL2DZ(Ga) level were performed to understand the electronic structure of **[3-Cl]**$^{\bullet}$ based on optimized geometry taken from the single crystal X-ray structure. The singly occupied Kohn-Sham orbitals (SOMOs) and spin density distribution plot of **[3-Cl]**$^{\bullet}$ are entirely distributed over the whole π-system of corrole ligand with no contribution from Ga^{III} centre (Figure 3 and Figure S20-S23). Thus, suggested a full-fledged non-innocent [(corrolato$^{\bullet 2-}$)Ga^{III}-Cl] complex rather than partially non-innocent [{(corrolato^{3})(Ga^{III})}$^{\bullet}$-Cl] or a [(corrolato^{3-})(Ga^{IV})$^{\bullet}$-Cl] complex.

Aromaticity indices would be of help to estimate the extent of cyclic conjugation in **[3-Cl]**$^{\bullet}$. The harmonic oscillator model of aromaticity (HOMA)[18] for the single crystal structure of **[3-Cl]**$^{\bullet}$ was calculated to be 0.701 (Figure S24). Infact, the HOMA value for those of the genuine conjugated/aromatic compounds **H$_3$(TPFC)** and **(TPFC)Ga^{III}** are 0.789[19c] and 0.770, respectively (Figure S24). These values indicated a [17] π-electron conjugated electronic circuit in **[3-Cl]**$^{\bullet}$. It should be noted that the existing definition of Hückel′s aromaticity donot include the odd-electrons and/or open-shell cyclic conjugated systems.[19] However, in accordance with the energy criteria of Hückel′s (anti)aromaticity, whether a cyclic conjugation stabilizes or destabilizes a system is independent of whether there is an odd or even number of electrons. On this basis, the extension of the concept of Hückel′s aromaticity to odd-electrons cyclic conjugated systems ([4n+1]π or/and [4n+3]π) have been demonstrated, although the practice may be in its infancy.[13g,19] Similarly, the concept of aromaticity in open-shell of even-electrons ([4n+1]/[4n+1]π) was predicted by Baird[20] and suggested that the aromatic versus antiaromatic character may be reversed between singlet and triplet species. On this standpoint, we calculated nucleus-independent chemical shift (NICS)[18] values to understand the aromaticity of **[3-Cl]**$^{\bullet}$. Large and positive NICS(0) values for the crystal structure of **[3-Cl]**$^{\bullet}$ were calculated to be 19.1, 19.5, 18.3 and 19.4 (Figure S25) at the midpoint of two C-N bond inside the tetrapyrrolic ring. Furthermore, anisotropy induced-current density (AICD)[18,21] plot of **[3-Cl]**$^{\bullet}$ showed the presence of a strong anticlockwise current (Figure S26-S28). Thus, the compound **[3-Cl]**$^{\bullet}$ may be categorized as antiaromatic due to its large positive NICS(0) values and the presence of a strong anticlockwise current as visualized by AICD.

The Uv-vis-NIR spectra were monitored in acetonitrile during the formation of radical. The observed spectral change was characteristic of formation of the radical.[9] Addition of Magic Blue (upto 1.2 equiv.) to **3** resulted in the decrease in absorption coefficient of Soret-band, and more prominently the Q-band (Figure 4a and Figure S29-S30). Furthermore, the appearance of a new broad absorption in the range of ~700-800 nm was also observed. The formation of radical also resulted in the diminished corrole-centred emission at λ_{emis}= 658 nm with the addition of Magic Blue in acetonitrile (Figure 4b).

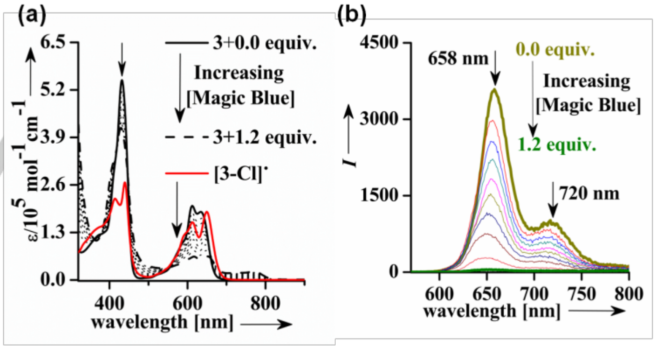

Figure 4: Change in (a) UV-vis-NIR absorption and (b) Flouroscent emission of compound **3** in acetonitrile with gradual addition (0 to 1.2 equiv.) of Magic Blue.

The presented experimental results established the non-innocent dianionic Ga^{III}-corrole radical (**III**). However, *in-situ* formation of trianionic Ga^{III}-corrole radical cation (**II**) in presence of oxidizing agent (Magic Blue or Ag^{+}) was speculated as an intermediate responsible for the regioslective nitration at 3,17 β-pyrrolic positions.[12,13h] This is in contrast to the electrophilic substitution at 2,17-positions leading to the *bis*-formyl and *bis*-sulphonyl derivatives.[12] Very interestingly, a similar regioslective substitution pattern was observed in the formation of 3,17-dichloro-5,10,15-trimesitylcorrole radical.[7] This finding gives an indication that the [(corrolato^{3-})Ga^{III}]$^{\bullet +}$SbCl$_6^{-}$ is the initial product of a chemical oxidation, which probably then electronically rearranged to give [(corrolato$^{\bullet 2-}$)Ga^{III}-Cl], with an axial chloride ion (Figure 1).

In conclusion, a Ga^{III}-corrole radical was unambiguously characterized for the first time, a paradigm of full-fledged non-innocent character of corrole ligand with main-group elements. The extrapolation of this result led us to state a few observations; (i) Eventhough dianionic corrole radical is not ubiquitous among main-group but it is appeared to have a stable thermodynamic sink. (ii) This apparent stability could be inferred from the existence of [2H]corrole radical (*i,e.,* resembling [2H]porphyrin) at various circumstances,[6,7,19c-d] probably due to the higher electron density and acidic NH hydrogens of [3H]corrole. (iii) Thus, the predominance of dianionic corrole radical with transition-metals can be understood as a consequence of an extra stability imparted by the interaction between a HOMO (“a_{2u}-type”) of corrole and a d-orbital of transition-metal,[3,4,5] although it is not the sole stabilizing factor. We hope this development can open up a new avenue in the direction of corrole-based magnetic materials. Further, the exploration and investigation of neutral corrole radical with other main-group elements are ongoing in our laboratory.

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Keywords: corrole • radical • non-innocence • antiaromatic

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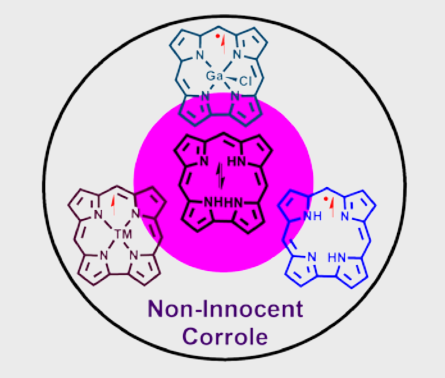
COMMUNICATION

Existence of a Ga^{III}-corrole radical was unambiguously established, a paradigm of full-fledged non-innocent corrole with main-group elements



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Evidence for A [17] π-Electronic Full-Fledged Non-Innocent Gallium(III)-Corrole Radical