



Tris(pentafluorophenyl)corrolatoindium(III) – A Long-awaited Metalloporphyrin: Synthesis and Characterization

Ali Tuna^{1,2*} , Pekka Peljo¹ , Roberto Paolesse³ , Günther Knör^{4*} 

¹Department of Mechanical and Materials Engineering, University of Turku (UTU), Vesilinnantie 5, FI-20014 Turku, Finland.

²Institute of Chemical Sciences and Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Rue de l'Industrie 17, Case Postale 440, Sion CH-1951, Switzerland.

³Department of Chemical Science and Technologies, University of Rome "Tor Vergata" (UniRoma2), Via della Ricerca Scientifica 1, Roma I-00133, Italy.

⁴Department of Environmental Technology Magistrate Linz, Hauptplatz 1-5, Linz A-4041, Austria.

Abstract: The first attempts at the synthesis of an indium corrole compound were synthesized in the late 80s, but it has not been possible to obtain and characterize such complex completely, and the indium part of metalloporphyrin's periodic table remained unfilled. In this work, an efficient insertion of indium into the 5,10,15-tris(pentafluorophenyl)corrole was achieved. The obtained 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) derivatives has been successfully characterized by relevant analytical techniques and some photophysical and electrochemical features were studied and investigated for the first time. As a novel research, ¹⁹F-¹⁹F COSY NMR technique was employed for the first time in corrole chemistry and the obtained results were further compared to the geometry-optimized molecular structure via density functional theory (DFT) calculations.

Keywords: corrole, indium, metalloporphyrin, NMR, ¹⁹F-¹⁹F COSY

Submitted: January 26, 2024. **Accepted:** March 2, 2024.

Cite this: Tuna A, Peljo P, Paolesse R, Knör G. Tris(pentafluorophenyl)corrolatoindium(III) – A Long-awaited Metalloporphyrin: Synthesis and Characterization. JOTCSA. 2024;11(2):803-12.

DOI: <https://doi.org/10.18596/jotcsa.1425456>

***Corresponding author's E-mail:** ali.tuna@utu.fi, knoer.guenther@web.de

1. INTRODUCTION

Corroles are ring-contracted porphyrin derivatives, with a conjugated 18 π -electron aromatic ring system carrying one direct pyrrole-pyrrole linkage. Many metal complexes of corrole ligands have been successfully synthesized in the last decades, and their molecular as well as electrochemical and photophysical properties have been investigated (1).

The coordination chemistry behavior of corrole is quite different from the corresponding porphyrin derivatives (Figure 1) and most of these variations can be related to the ligand charge, being while porphyrins are dianionic species, free-base corrole molecules are trianionic ligands, and to the contracted size and electron-rich character of the corrole ring. These features have important consequences for the stability and chemical properties of the corresponding metalated corrole derivatives (1).

For example, the coordinated central ions of metalloporphyrins are better stabilized in their high-valent oxidation states, due to the triply negative charge of the fully deprotonated ligand core. The available size of the metal-binding cavity is a second important criterion of distinction between corrole and porphyrin molecules, which leads to modified coordination chemistry (2).

In many cases, the contracted core and the electron distribution of the trianionic corrole ligand joined with the positive charge of the coordinated metal cation may induce a ligand-to-metal type re-distribution of electron density, which is characteristic for the non-innocent behavior of corrole as a ligand. This feature has caused a difficult elucidation of the dominant electronic structure of various metal complexes of corrole (2).

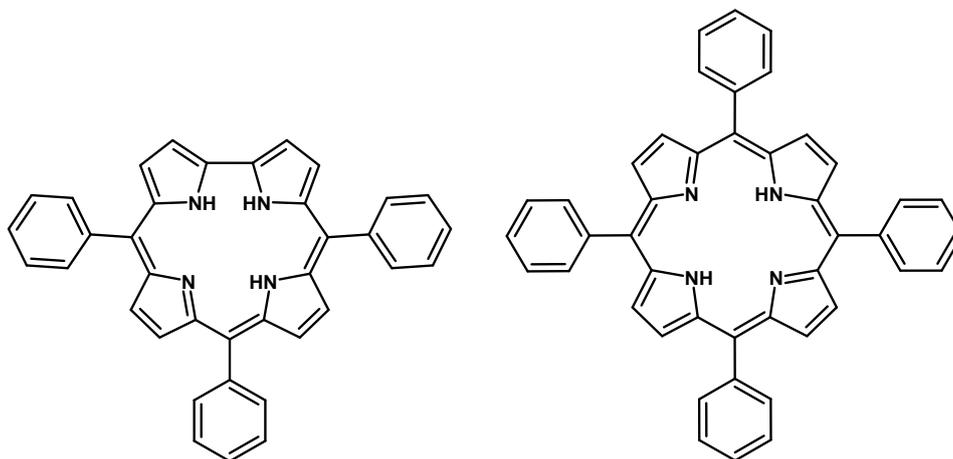


Figure 1: The basic molecular structures of 5,10,15-triphenylcorrole (left) and 5,10,15,20-tetraphenylporphyrin (right).

The characterization of different types of main group and transition metal corrole complexes has been reported, and their diverse properties have been investigated by many specialized research groups active in the field (2,3).

These efforts also include several examples of group 13 elements (B, Al, and Ga), which are already very well characterized. The corresponding corrole complexes of the heavier elements of this main group of the periodic table, however, are still mainly unexplored. Although first systematic attempts to synthesize such compounds started quite early in the field (4), a detailed characterization of an indium corrole molecule has not been published in the literature so far. We herein wish to report our recent progress in this direction.

2. EXPERIMENTAL

5,10,15-Tris(pentafluorophenyl)corrole as free base ligand molecule was synthesized from the condensation reaction between 2,3,4,5,6-pentafluorobenzaldehyde and freshly distilled pyrrole in acidic media and the obtained free-base corrole ligand was purified according to the published procedure (5).

Indium(III) chloride was purchased from ABCR Chemie, Germany. All NMR solvents were purchased from ARMAR Isotopes, Germany. Other solvents, chemicals and supplements were purchased from VWR, Finland and Magasin EPFL, Switzerland. Commercially available reagents were used without further purifications.

The obtained indium corrole species were characterized by UV-vis (Specord plus, Analytik Jena), MS (Q-TOF, Bruker and Orbitrap, Exploris), CV (Gamry 600+ Potentiostat/Galvanostat), IR (Vertex 70 FTIR-ATR, Bruker), Fluorescence (FLS1000 spectrofluorometer, Edinburgh Instruments) and NMR (400 MHz, Bruker) techniques. Full details are given in the supporting information.

2.1. Synthesis of bis(*d*₅-pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III)

To a solution of 5,10,15-tris(pentafluorophenyl)corrole (51 mg, 64 μmol, 1 eq) in *d*₅-pyridine (15 mL), an excess amount of indium(III) chloride was added and the reaction mixture was refluxed under Ar atmosphere. The reaction was monitored by UV-vis spectroscopy. Once metalation completed as no further spectral change observed, the reaction mixture was cooled down to room temperature and the reaction mixture was purified by microcolumn chromatography using silica gel and *d*₅-pyridine as an eluent to give bis(*d*₅-pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) as a dark green solution. The obtained indium corrole molecule was characterized by various analytical techniques.

¹H-NMR (400 MHz, 278 K, *d*₅-py, ppm): δ= 9.12-8.99 (m, 5H), 8.97-8.82 (m, 3H); ¹⁹F NMR (376 MHz, 278 K, *d*₅-py, ppm): δ= -137.4-139 (m, 6F, o-Ar-F), -153-156.2 (m, 3F, p-Ar-F), -163.2-164.2 (m, 6F, m-Ar-F); UV/Vis (pyridine, nm, ε (mol⁻¹dm³cm⁻¹)): λ_{max}= 411 (39700), 433 (174000), 516 (6740), 544 (9300), 585 (16000), 610 (19700); fluorescence (pyridine): λ_{ex}= 410 nm; λ_{em}= 617, 669.5 nm; MS: m/z calcd for [M-(*d*₅-py)+H]⁺: 993.0357, found: 993.0366; m/z calcd. for [M+H]⁺: 1077.1093, found: 1077.1112; FTIR (*d*₅-py): ν̃= 1790 (s) cm⁻¹ (In-N=C).

2.2. Synthesis of 5,10,15-tris(pentafluorophenyl)corrolatoindium(III)

Previously obtained solution of bis(*d*₅-pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in *d*₅-pyridine was slowly evaporated in a two-necked round bottom flask under reduced pressure at room temperature, then *d*-chloroform was added via the septum to give 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) as a dark green solution. The obtained indium corrole molecule was characterized by various analytical techniques.

¹H-NMR (400 MHz, 278 K, *d*₃-AcN, ppm): δ= 8.87 (s, 2H), 8.73 (s, 2H), 8.56 (s, 2H), 8.44 (s, 2H); ¹⁹F NMR (278 MHz, 263 K, *d*₃-AcN, ppm): δ= (m, 6F, Ar-F); UV/Vis (acetonitrile, nm, ε (mol⁻¹dm³cm⁻¹)): λ_{max}= 411 (178500), 549 (39400), 600 (37100), 656 (28800), 708 (22600); fluorescence (acetonitrile):

$\lambda_{\text{ex}} = 410 \text{ nm}$; $\lambda_{\text{em}} = 617, 661.5, 718 \text{ nm}$; MS: m/z calcd for $[M+H]^+$: 908.9621, found: 908.9417.

2.3. NMR Measurements

The 1D- and 2D-NMR experiments were performed using AVANCE 400 MHz Bruker NMR spectrometers equipped with relevant (cryo) probes. D_5 -pyridine (d_5 -py) or d_3 -acetonitrile (d_3 -AcN) were used as the solvent and relevant corrole compounds were dissolved in 300-500 μL of the solvent and placed in a high accuracy 500 mm (7-inch) NMR tubes with PTFE septum. The NMR spectra were observed in various temperatures from 253 K to 298 K in order to study kinetic peak resolutions. At the end, we only report the NMR spectra were observed at around 278 K (approximately 5°C).

The ^{19}F - ^{19}F COSY experiments were performed using AVANCE-III-HD 400 MHz Bruker NMR spectrometer equipped with a BBO2: BB {1H} 5mm (ATMA) (Z136881/10) probe. D_5 -pyridine or d_3 -acetonitrile were used as the solvent, and 5,10,15-tris(pentafluorophenyl)corrole and/or relevant indium corrole complexes were dissolved in 400 μL of the solvent and placed in a high accuracy 500 mm (7-inch) NMR tubes with PTFE septum.

The resulting spectra were processed using TOPSPIN (Bruker) software. The FID was Fourier transformed using relevant commands and window functions, and the resulting spectrum was phase-corrected, baseline-corrected, and referenced to the d-TFA and CFCl_3 resonances. The ^{19}F - ^{19}F COSY spectrum was analyzed to determine the correlations between different sets of fluorine nuclei in the sample. The chemical shifts and coupling constants were measured, and the resulting data were used to determine the molecular structure and aid in the characterization of the compound.

2.4. Photophysical Measurements

The UV-Vis measurements were performed in a quartz fluorescence cuvette at room temperature in pyridine or chloroform. Steady-state fluorescence intensity (365 nm or 410 nm) and excitation (at 650 nm) measurements were performed using FLS1000 spectrofluorometer (Edinburgh Instruments) with an excitation source of a pulsed (μsec) Xe-arc lamp at ambient temperature with a same cuvette in pyridine or chloroform. The emission spectra were set to limit at 850 nm due to the saturation of the detector (no peak formation). The obtained photophysical data were evaluated and visualized over Origin and Microsoft Excel.

2.5. Electrochemical Measurements

The cyclic voltammetry experiments were performed in Gamry 600+ Potentiostat/Galvanostat using a four-hole-three-electrode glass cell (24 mm x 62 mm, 10 mL). Cyclic voltammograms were obtained at room temperature under Ar atmosphere (10 minutes of purging) using with 3 mm glassy carbon as working electrode, Pt wire as counter (auxiliary) electrode and Ag wire dipped in 100 mM AgNO_3 (in anhydrous pyridine) as reference electrode, together with 100 mM tetrabutylammonium perchlorate

(TBAP) as supporting electrolyte and ferrocene (Fc) as an internal standard. The data were analyzed over Echem Analyst (Gamry) software.

2.6. Computational Methods

The DFT calculations were performed with the Gaussian 16 using the hybrid functional B3LYP along with the basis set of LANL2DZ as well as fine integration grids and tight SCF and geometry optimization criteria were used throughout with the implicit effects from pyridine taken into account (6–9). TD-NMR values were calculated using the method implemented in the Gaussian 16 and GaussView 6.0 software was used for the visualization (10). For more details on the DFT calculations please see the supporting information.

3. RESULTS AND DISCUSSION

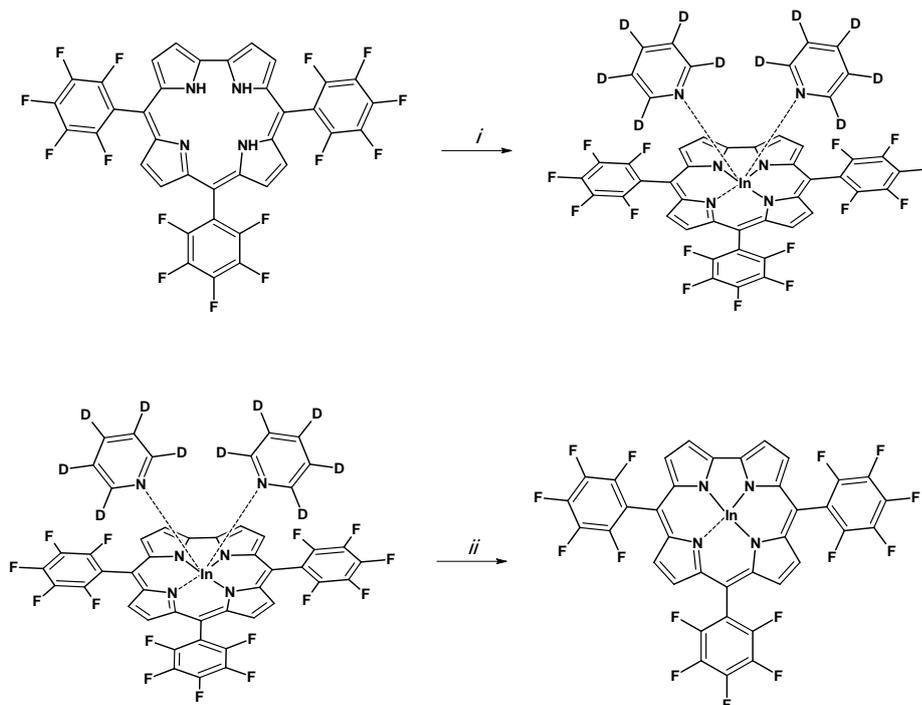
The 5,10,15-tris(pentafluorophenyl)corrolatoindium (III) and a corresponding bis(d_5 -pyridine) coordinated complex were successfully synthesized and characterized with different spectroscopic techniques (Scheme 1).

The synthetic methodologies were modified systematically and, the preparation strategy was optimized and repeated several times to study the influence of different reaction conditions with variations in solvents, reagents, optimal temperature, and reaction time.

In contrast to our initial assumptions derived from the well-known properties of aluminum- and gallium-corrole complexes (11), it turned out that the corresponding indium compound could be obtained and characterized without the attachment of additional axial ligands such as pyridine.

Our experimental studies and analytical results revealed that 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) exists as either in a six-coordinate pyramidal with two d_5 -pyridine units on the same side or four-coordinate parent complex in non-coordinating solvents such as chloroform and that it is metastable under certain conditions, as could be clearly demonstrated by MS and NMR techniques.

Such structural motif seems to be quite common for heavier main group element corrolato complexes with tricationic central ions, as already observed with bismuth as the central metal, where a four-coordinate species was isolated and crystallized (12). Although different crystallization techniques (solvent diffusion, under oil treatment, slow solvent evaporation, etc.) were also tried out several times in the case of the indium corrolato complex, unfortunately, no successful formation of a sample suitable for single crystal diffraction was achieved up to now. The solidified and dried green compound showed decomposition to give a mixture of white indium oxide/hydroxide and green residue as free base corrole ligand in the presence of air. However, it was possible to characterize 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in solution.



Scheme 1: The syntheses of indium corrole molecules; bis(d_5 -pyridine)-5,10,15-tris(pentafluorophenyl)corolatoindium(III) (top, i: InCl_3 in d_5 -pyridine) and 5,10,15-tris(pentafluorophenyl)corolatoindium(III) (bottom, ii: vacuum at r.t.)

Metalation of the free-base corrole with an excess of indium salts was performed in pyridine solution. As soon as 5,10,15-tris(pentafluorophenyl)corrole was dissolved in pyridine, we observed a deprotonation of the free-base corrole ligand indicated by the absorption spectroscopic signature of the corresponding corrolato anion. This observation was further corroborated by analyzing the ^1H -NMR spectra in d_5 -pyridine, where the characteristic signals of the inner protons experiencing a strong shielding effect of the macrocyclic aromatic ring current of the corrole core were disappearing. A similar phenomenon in porphyrin chemistry can be

also seen in the course of porphyrinato anion formation under alkaline conditions (13,14).

For our present study of new indium compounds with a fluorinated macrocyclic ligand system, we introduced a relevant ^{19}F - ^{19}F COSY NMR technique, which to the best of our knowledge was not used before for any corrole complex in accordance to today's known literature. With this technique, we characterized both our free-base corrole ligand of 5,10,15-tris(pentafluorophenyl)corrole and its two new indium complexes to understand and analyze the correlations between all F atoms (Figure 2).

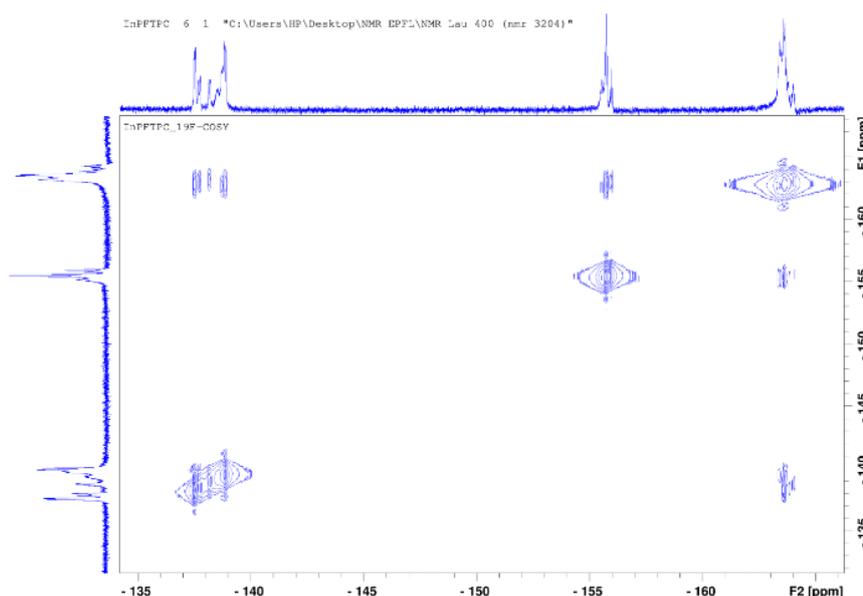


Figure 2: The ^{19}F - ^{19}F COSY NMR spectrum of bis(d_5 -pyridine)-5,10,15-tris(pentafluorophenyl)corolatoindium(III) in d_5 -pyridine.

After insertion of indium, the $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ peaks of the axially coordinated d_5 -pyridine complex of the 5,10,15-tris(penta-fluorophenyl)corrolato indium(III) molecule formed were unequally distributed indicating a top-sitting complex structure where two d_5 -pyridine molecules were actually placed on the same side. However, when losing both axial d_5 -pyridine ligands, in deuterated chloroform a $^1\text{H-NMR}$ spectrum of 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) was obtained, indicating a more symmetrical structure resembling the one of 5,10,15-tris(pentafluorophenyl)corrolatobismuth (III).

The possible exploitation of the In-NMR technique for the characterization of the corrole complex has been considered. However, indium has naturally abundant two NMR active nuclei, ^{113}In and ^{115}In which both present a quadrupolar (with 9/2 spin) behavior. In most cases, NMR measurements yield in very broad signals which give an increased signal width over the chemical shift range even if the molecules have highly symmetric chemical environments. All these properties limit to study the chemical environment of indium as giving too broad signals and requiring very long measurement times together with very fast relaxation times (μs) which are not suitable for indium peak observation by an In-NMR spectroscopy (15,16).

Considering all experimental and instrumental parameters, it was concluded that the use of In-NMR technique is not applicable for our molecular system due to molecular asymmetry. In order to understand the effect of this asymmetry, we did run $^{19}\text{F-}^{19}\text{F}$ COSY NMR spectroscopy measurements and found that the

geminal pyridine molecules were localized on the same side and as a result the asymmetry was increased to be yielded in the formation of unequal F peaks as well as having different atomic interactions between the F atoms of meso-aryl units and D atoms of axially coordinated pyridine molecules.

In the same group elements, as Al and Ga corrole complexes, this phenomenon occurs somewhat two pyridine molecules are positioned axially but in opposite directions such one is up and one is down. This situation can be associated with the size of the ionic diameter. In rare cases, axial units can be positioned in the same direction which can be also exemplified by obtaining some tantalum, tungsten, molybdenum, uranium, and thorium corrole molecules in a monomeric or dimeric form(s) (17–19).

During the prediction, if two pyridine molecules were positioned relative to their surroundings (above and below), a symmetrical structure would emerge as they would interact equally with the F atoms of the corrole ligand and the pyrrole H in the beta position. A similar interaction was also observed in the $^1\text{H-NMR}$ spectrum, where H peaks interacted to different degrees with pyridine molecules in the same direction (geminal). However, all H and F atoms of the formed indium corrole structure with two axial pyridine ligands were distributed unequally, which indicates that an asymmetric molecule as we deceived was present. This situation was further simulated geometry-optimization molecular structure via density functional theory (DFT) calculations (Figure 3).

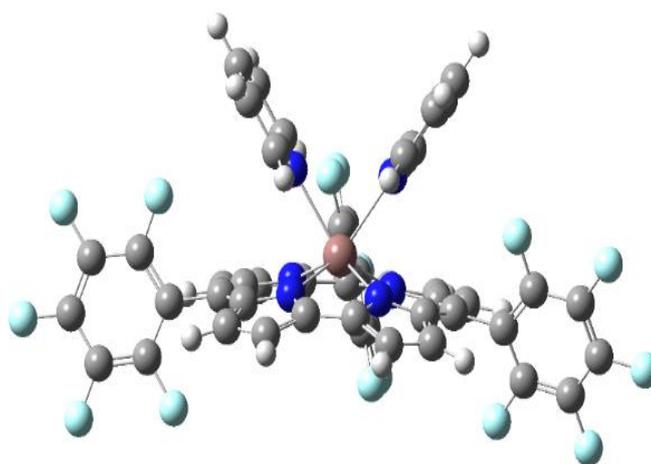


Figure 3: The DFT optimized molecular structure of bis(pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in pyridine.

Considering the structure of geminal two pyridine-coordinated indium corrole, the optimized distance between the closest F and the D atom of the one pyridine units of two geminal pyridine is approximately 3.231 Å, while this distance with the H atom in the beta position is approximately 4.029 Å.

As a result, $^{19}\text{F-}^{19}\text{F}$ COSY experiment is more favorable than $^1\text{H-}^1\text{H}$ COSY experiment due to the

considered bond lengths where D atoms of axial pyridine ligand(s) have more impact on F atoms on meso positions.

The DFT-assisted obtained $^{19}\text{F-NMR}$ spectrum also showed very similar images that F atoms interacted differently in the same ring which cause different peak formations in the obtained both experimental and theoretical spectrum (Figure 4).

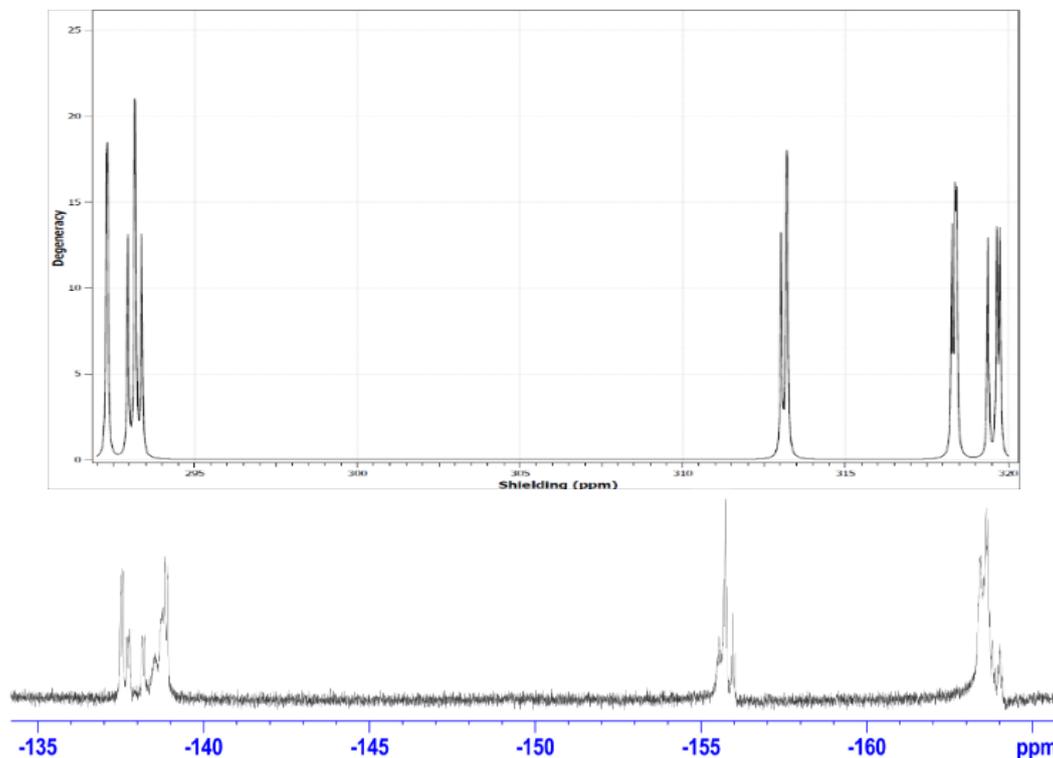


Figure 4: The DFT ^{19}F -NMR spectrum of the optimized molecular structure of bis(pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in pyridine (top) and experimental ^{19}F -NMR spectrum of bis(d_5 -pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in d_5 -pyridine (bottom).

As it can be easily seen that the similarity between DFT and experimental ^{19}F -NMR spectra of two pyridine coordinated 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) structure in pyridine, two pyridine units are coordinated on the same side instead of axially to create unsymmetrical interactions through meso-substituted aryl-fluorine atoms as well as they are yielded in more peak formations.

A preliminary study of indium corrole luminescence spectra could also be carried out. The emission properties of bis(d_5 -pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in pyridine solution at room temperature are shown (Figure 5), together with the corresponding excitation spectrum.

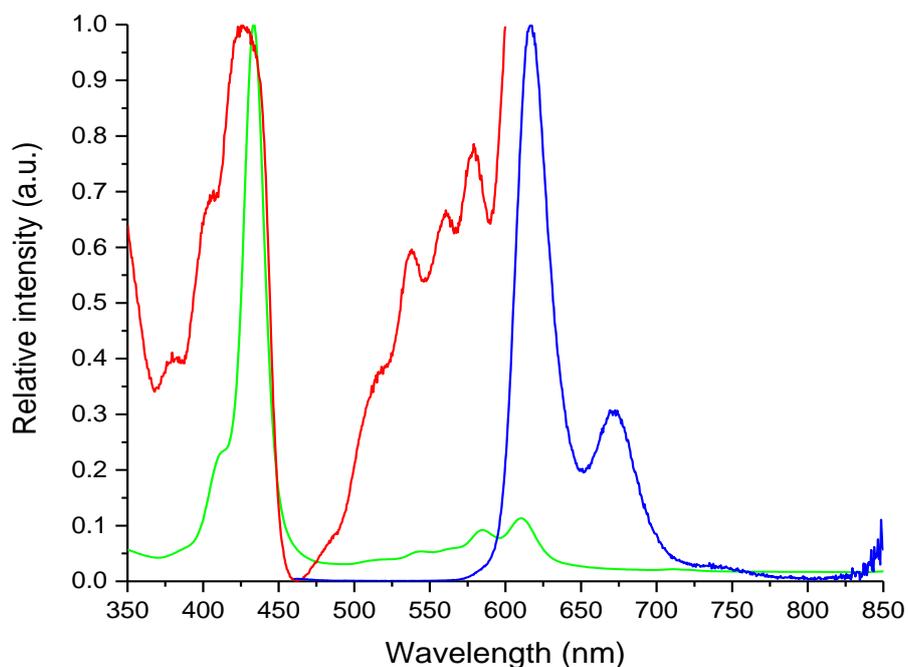


Figure 5: Absorbance (green), excitation (red), and fluorescence (blue) spectra of bis(d_5 -pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) in pyridine.

All luminescence features reported here were checked for authenticity by analyzing the corresponding excitation spectra of Figure 5 above. Remarkably, in addition to the expected Soret- and

Q-band patterns of the indium corrole complex, the fluorescence excitation spectrum shows an additional shoulder at around 482 nm, which is not dominant in the absorption spectrum below (Figure 6).

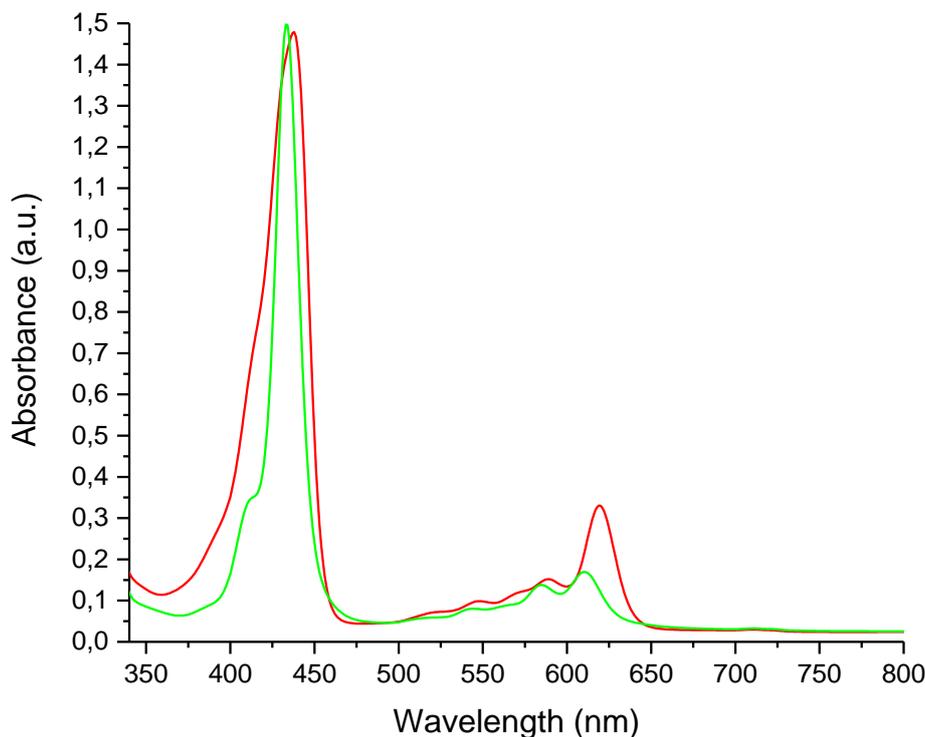


Figure 6: UV-Vis spectra of the 5,10,15-tris(pentafluorophenyl)corrolato anion (red) and of bis(d_5 -pyridine)-5,10,15 tris(pentafluorophenyl)corrolato indium(III) (green) in pyridine.

The indium corrole complex displays a normal-type ligand-centered fluorescence arising from the lowest π - π^* excited singlet state with a quantum yield of $\phi = 0.25$ and electronic energy level of $E_{0-0}(S_1) = 2.06$ eV.

At the same time, the Stokes-shift of the fluorescence band is calculated to be found around 200 cm^{-1} in d_5 -pyridine. Due to the general reactivity trends in the main group 13 element series with an increasing oxidation power of the heavier trivalent cations, it can be rationalized that this unique feature of In(III)-corrole might indicate the presence of a low-lying ligand-to-metal charge transfer (LMCT) excited state level in the visible spectral region, which is not accessible in the case of the related Al(III)- and Ga(III)-corrole derivatives.

Although more detailed studies will be necessary to finally corroborate such a tentative assignment, the currently available luminescence results seem to indicate the accessibility of lower oxidation states of the central metal. Therefore, a reversible metal centered two-electron photoredox chemistry, as typical for heavier main group element derivatives containing tetrapyrrole ligands might also be expected in the case of indium corrole complexes (12,20,21).

To explore the possibility of reaching lower oxidation states at the central metal, the new compounds were investigated by cyclic voltammetry. All electrochemical experiments were carried out in Ar-purged anhydrous pyridine and performed versus Ag/AgNO₃ in the presence of TBAP as a supporting electrolyte. In contrast to more common solvents usually preferred for cyclovoltammetry studies, pyridine is limited to a rather narrow potential window (22), but had to be chosen in our case due to the much better stability of the indium complexes in this solvent as we obtained the mass spectra of mono- and di-pyridine coordinated indium corrole complexes.

For the indium corrole complex carrying axial pyridine, except from axial ligand reduction, only one irreversible cathodic peak at -1.51 V was obtained. Interestingly, this peak shifted to -1.42 V after addition of ferrocene as an internal standard, while at the same time a pseudo-reversible electron transfer behavior occurred. This might indicate an unexplored switch in electron transfer pathways via interaction of the corrole complex with ferrocene. The first oxidation of the indium corrole complex in pyridine solution occurs at an anodic peak potential around 0.6 V . All cyclovoltammetric waves were compared with the literature data available for the Al and Ga complexes of 5,10,15-tris(pentafluorophenyl)corrole, respectively (Table 1).

Table 1: Comparison of redox potentials of the tris(pentafluorophenyl)corrole complexes of Al, Ga, and In.

	Al	Ga	In
2nd Oxidation	-	1.14 V*	-
1st Oxidation	0.55 V*	0.68 V*	~ 0.6**
1st Reduction	- 0.88 V*	- 0.81 V*	- 0.78 V**
2nd Reduction	-1.58 V*	-1.55 V*	-1.51 V** (-1.42 V***)

(*: in dichloromethane (22), **: in pyridine versus Ag/AgNO₃ in pyridine, ***: after ferrocene addition in pyridine versus Ag/AgNO₃ in pyridine.

From the first oxidation peak and the data given in Table 1, an approximately calculated HOMO-LUMO gap of ~2.1 V can be derived, which is in good agreement with our spectroscopic results and the electrochemical data of other group 13 metallocorrole complexes such as 5,10,15-tris(pentafluorophenyl)corrolatoaluminum(III) (23).

Along with the photophysical data obtained, the redox properties of the indium corrole complex in the first excited singlet state can also be estimated. A clear trend can be observed for all known values in the series Al, Ga and In, where the indium corrole derivative is the one which is easier to reduce and harder to oxidize (22,23). This can also be seen from the possible oxidation states of the metal center, indium can have In(I), In(II), and In(III) oxidation states but for gallium and aluminum, these are quite exceptional in special conditions.

In our attempts to characterize the onset of the ring-centered reductions of the indium corrole system by measuring further into the cathodic region of the given solvent window, we observed very interesting results indicating the accessibility of metal-centered electron transfer steps.

According to the literature on main group element tetrapyrroles, the first electrochemical reduction should occur at the macrocyclic ligand system to form an In(III)-corrole π -radical anion. These species may then interconvert into a redox-isomeric In(II)-corrole complex with an open-shell s₁-electronic configuration at the central metal, thus forming a short-lived radical intermediate. In general, such types of In(II) complexes can be stabilized by an intermolecular disproportionation process or undergo dimerization, however, we did not observe any dimerization in our studies. In addition, a further In(II)/In(I) reduction may easily occur by capturing an electron in follow-up chemical steps due to the close redox potentials. This finally leads to a low-valent diamagnetic complex with an In(I) oxidation state and a "carbene-analogous" s₂-electron configuration at the central metal (24–26).

In our preliminary studies, unfortunately, the electron transfer steps following the first metal-centered redox process in solution were not fully reversible and resulted in demetallation of the indium corrole complex and we observed cyclic voltammograms indicating some deposition of elemental indium on the working electrode (25). This lack of stability in the low-valent form is probably due

to the fact that In(I) becomes too large for the corrole ligand system and no longer fits well into the macrocyclic core. The indium redox behaviors were also compared to the standard electrode potential values (27). It should also be outlined here that more comprehensive electro-chemical investigations necessary were not yet within the scope of our present study.

Moreover, we are planning to further explore the very interesting metal-centered redox processes not accessible with the lighter group 13 central metals, and to study the potential presence of low-lying charge transfer (CT) excited states that could be populated by visible light excitation. These efforts are mainly motivated by the importance of controlled formation of low-valent indium complexes and to study the potential of driving In(I)/In(III) interconversion processes as a further example main group element related two-electron redox chemistry. This might become quite useful for the (photo)catalysis of multielectron conversions with carbon-based substrates (e.g. CO₂ reduction, C-C coupling etc.) and interesting other applications in the future.

4. CONCLUSIONS

As a result, two new 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) complexes were successfully synthesized and characterized their structures and basic properties by several analytical techniques. The synthetic approach was refined several times to optimize the minimum conditions for successful indium corrole formation.

In addition to one-dimensional ¹H- and ¹⁹F-NMR techniques, ¹⁹F-¹⁹F COSY NMR technique was employed for the first time in corrole chemistry. Thus, we were able to better understand the characteristic peaks and to compare our new indium corrole complexes with the free-base corrole ligand in different deuterated solvents. By means of NMR-spectroscopy, we could characterize the formation of a pyramidal top-sitting indium corrole complex in d₅-pyridine which gives several and different proton and fluorine peaks in accordance the atomic interactions.

Our ESI-MS results also showed the presence of one and two axially linked d₅-pyridine units to the indium corrole. Once we removed these pyridines under reduced pressure, we also observed 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) as a

four-coordinate species and it showed different analytical responses than its pyridine derivatives.

Cyclic voltammetry technique was attempted in order to understand redox behavior of the formed indium corrole molecule in pyridine. Unfortunately, we observed immediate decomposition of indium corrole molecules in dichloromethane, benzonitrile, acetonitrile, tetrahydrofuran, and toluene. Although the bis(*d*₅-pyridine)-5,10,15-tris(pentafluorophenyl)corrolatoindium(III) and 5,10,15-tris(pentafluorophenyl)corrolatoindium(III) complexes are readily soluble in chloroform, unfortunately it did not allow us to perform any further electrochemical measurements.

To increase our knowledge on group 13 metallocorroles, we also have aimed to synthesize a series of different other indium complexes. The formation of some new indium corrole complexes had been just and recently confirmed by some preliminary spectroscopic data. We are currently conducting our experimental and theoretical studies for further investigations, however in this study, we report successful synthesis and characterization of two new indium corrole molecules together with DFT-assisted calculations.

5. AUTHOR CONTRIBUTIONS

Tuna A: Data curation, formal analysis, investigation, methodology, validation, visualization, writing – original draft, writing – review & editing.

Peljo P: Resources, supervision, validation, writing – review & editing.

Paolesse R: Conceptualization, supervision, resources, validation, writing – review & editing.

Knör G: Conceptualization, data curation, investigation, supervision, validation, writing – original draft, writing – review & editing.

6. CONFLICTS OF INTEREST

All authors read and commented on the manuscript, and have no conflicts of interest to declare.

7. ACKNOWLEDGEMENTS

We would like to thank to the Academy of Finland (Suomen Akatemia, Funding Decision Number 334828), University of Turku (UTU) and the École Polytechnique Fédérale de Lausanne (EPFL) to support our PhD student, Ali Tuna for his projects. We would also like to thank to Dr. Jeremy Weaver, University of Wisconsin – Madison, USA) who carried out his PhD thesis on the investigation of indium corrole formation and discussions, and NMR specialists Aurélien Bornet (EPFL, Switzerland) and Jani Rahkila (Bruker, Finland) for establishing ¹⁹F-¹⁹F COSY NMR technique for detailed analytical characterization, and Dr. Ian Pompermayer Machado (UTU, Finland) for fluorescence spectroscopy measurements.

8. REFERENCES

- Kadish K, Smith KM, Guillard R. The Porphyrin Handbook, Volume 2. New York, USA: Academic Press; 1999.
- Nardis S, Mandoj F, Stefanelli M, Paolesse R. Metal complexes of corrole. *Coord Chem Rev* [Internet]. 2019 Jun 1;388:360–405. Available from: [<URL>](#).
- Mahammed A, Gross Z. Milestones and Most Recent Advances in Corrole's Science and Technology. *J Am Chem Soc* [Internet]. 2023 Jun 14;145(23):12429–45. Available from: [<URL>](#).
- Paolesse R, Licocchia S, Boschi T. Towards the periodic table of metallocorrolates: synthesis and characterization of main group metal complexes of octamethylcorrole. *Inorganica Chim Acta* [Internet]. 1990 Dec 3;178(1):9–12. Available from: [<URL>](#).
- Orłowski R, Gryko D, Gryko DT. Synthesis of Corroles and Their Heteroanalogues. *Chem Rev* [Internet]. 2017 Feb 22;117(4):3102–37. Available from: [<URL>](#).
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 16, Revision C. 01. Wallingford, CT: Gaussian, Inc.; 2016.
- Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* [Internet]. 1993 Apr 1;98(7):5648–52. Available from: [<URL>](#).
- McLean AD, Chandler GS. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z = 11–18. *J Chem Phys* [Internet]. 1980 May 15;72(10):5639–48. Available from: [<URL>](#).
- Tomasi J, Mennucci B, Cammi R. Quantum Mechanical Continuum Solvation Models. *Chem Rev* [Internet]. 2005 Aug 1;105(8):2999–3094. Available from: [<URL>](#).
- Reed AE, Curtiss LA, Weinhold F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem Rev* [Internet]. 1988 Sep 1;88(6):899–926. Available from: [<URL>](#).
- Kowalska D, Liu X, Tripathy U, Mahammed A, Gross Z, Hirayama S, et al. Ground- and Excited-State Dynamics of Aluminum and Gallium Corroles. *Inorg Chem* [Internet]. 2009 Mar 16;48(6):2670–6. Available from: [<URL>](#).
- Reith LM, Stiftinger M, Monkowius U, Knör G, Schoefberger W. Synthesis and Characterization of a Stable Bismuth(III) A₃-Corrole. *Inorg Chem* [Internet]. 2011 Jul 18;50(14):6788–97. Available from: [<URL>](#).
- Shen J, Ou Z, Shao J, Gałęczowski M, Gryko DT, Kadish KM. Free-base corroles: determination of deprotonation constants in non-aqueous media. *J Porphyr Phthalocyanines* [Internet]. 2007 Apr 25;11(04):269–76. Available from: [<URL>](#).

14. Weaver J. Corroles [PhD Thesis]. [California, USA]: Technical University of California; 2005.
15. McGarvey BR, Trudell CO, Tuck DG, Victoriano L. Coordination compounds of indium. 37. Indium-115 NMR studies of anionic indium species in nonaqueous solution. *Inorg Chem* [Internet]. 1980 Nov 1;19(11):3432–6. Available from: [<URL>](#).
16. NMR Lab [Internet]. 2023 [cited 2024 Jan 23]. NMR Lab. Available from: [<URL>](#).
17. Ward AL, Buckley HL, Lukens WW, Arnold J. Synthesis and Characterization of Thorium(IV) and Uranium(IV) Corrole Complexes. *J Am Chem Soc* [Internet]. 2013 Sep 18;135(37):13965–71. Available from: [<URL>](#).
18. Ziegler JA, Buckley HL, Arnold J. Synthesis and reactivity of tantalum corrole complexes. *Dalton Trans* [Internet]. 2017 Jan 17;46(3):780–5. Available from: [<URL>](#).
19. Vazquez-Lima H, Conradie J, Johansen MAL, Martinsen SR, Alemayehu AB, Ghosh A. Heavy-element–ligand covalence: ligand noninnocence in molybdenum and tungsten Viking-helmet Corroles. *Dalt Trans* [Internet]. 2021 Sep 28;50(37):12843–9. Available from: [<URL>](#).
20. Knör G. Photocatalytic reactions of porphyrin-based multielectron transfer sensitizers. *Coord Chem Rev* [Internet]. 1998 Apr 1;171:61–70. Available from: [<URL>](#).
21. Schöfberger W, Lengwin F, Reith LM, List M, Knör G. Lead corrole complexes in solution: Powerful multielectron transfer reagents for redox catalysis. *Inorg Chem Commun* [Internet]. 2010 Oct 1;13(10):1187–90. Available from: [<URL>](#).
22. Fang Y, Ou Z, Kadish KM. Electrochemistry of Corroles in Nonaqueous Media. *Chem Rev* [Internet]. 2017 Feb 22;117(4):3377–419. Available from: [<URL>](#).
23. Mahammed A, Gross Z. Corroles as triplet photosensitizers. *Coord Chem Rev* [Internet]. 2019 Jan 15;379:121–32. Available from: [<URL>](#).
24. Tuck DG. The lower oxidation states of indium. *Chem Soc Rev* [Internet]. 1993 Jan 1;22(4):269. Available from: [<URL>](#).
25. Hill MS, Hitchcock PB, Pongtavornpinyo R. Oxidative Addition Reactions of Alkyl Halides with the Group 13 Carbene Analogue [In{N(Dipp)C(Me)}₂CH] (Dipp = 2,6- i Pr 2 C 6 H 3). *Inorg Chem* [Internet]. 2007 Apr 30;46(9):3783–8. Available from: [<URL>](#).
26. Hill MS, Hitchcock PB. A mononuclear indium(i) carbene analogue. *Chem Commun* [Internet]. 2004 Aug 9;2004(16):1818–919. Available from: [<URL>](#).
27. Cramer SD, Covino BS, editors. *Electrochemical Series*. In: *Corrosion: Materials* [Internet]. ASM International; 2005. p. 665–71. Available from: [<URL>](#).