The synthesis and characterization of the octahedral Co\textsuperscript{III} complex of a pyrrolopyrrolizine derivative formed with dicyanovinylene-bis-(meso-aryl)dipyrrin\textsuperscript{†}

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A low spin state and diamagnetic Co\textsuperscript{III} complex 1 possessing pyrrolopyrrolizine ligands formed with dicyanovinylene-bis-(meso-aryl)dipyrrin was synthesized via the thermally activated metalation with CoCl\textsubscript{2} and isolated via column chromatography. The nuclear magnetic resonance of complex 1 revealed diamagnetism, thereby confirming the structure of the octahedral Co\textsuperscript{III}-complex of strong-field ligands. The resulting molecular structure of 1 was elucidated by the X-ray diffraction analysis. An arrangement of two pyrrolizine-ligands for the metal chelation was found in the AB–BA order, which was distinct from the case observed during the formation of bis-Ni\textsuperscript{II}-expanded porphyrinoids.

Introduction

Dipyrrin molecules have garnered considerable attention from synthetic and applied chemists due to their proficiency in various wide-ranged applications from medicinal/medical sciences to photo-electronic devices.\textsuperscript{1} Especially, dipyrrin derivative-generated neutral metal complexes, whose separation, purification, and further handling are significantly beneficial.\textsuperscript{2} Thus, dipyrrin segments, have been used in manufacturing either singly expanded molecules or largely assembled arrays/polymers that act as proficient building units.\textsuperscript{3}

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has been a suitable oxidant to completely obtain delocalized π-electron conjugations.\textsuperscript{4} It has been established that DDQ-adducts were formed during the oxidation of dipyrromethane possessing electron-withdrawing meso-aryl. The subsequent transformations of DDQ-adducts were also investigated by treating with Lewis acid in various alcohols and with Lewis base, respectively. Dichlorofuranone-derivatives were formed in a concerted reaction involving the nucleophilic attack of alcohol, the partial elimination of the molecule, followed by the rearrangement of the π-conjugation pathway when treated with Lewis acid (B in Fig. 1).\textsuperscript{5} Dicyanovinylene-derivatives were formed in a concerted reaction involving the initiation by the nucleophilic attack of the Lewis base, the partial elimination of the DDQ-segment, followed by the regeneration of a π-conjugation network when treated with the Lewis base (A in Fig. 1).\textsuperscript{5e}

Furthermore, the nickel metalation of pentafluoro-phenyl-substituted dicyanovinylene compound A–C\textsubscript{6}F\textsubscript{5} afforded

![Fig. 1](https://example.com/fig1.png)

**Fig. 1.** The formation of DDQ adduct and further transformation towards compounds A and B in the presence of Lewis base and Lewis acid.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2.** The formation of bis-Ni\textsuperscript{II}-expanded porphyrinoids during the metalation of A–C\textsubscript{6}F\textsubscript{5} with Ni(OAc)\textsubscript{2}.

\textsuperscript{†}Electronic supplementary information (ESI) available: NMR, Mass, and absorption spectra as well as X-ray packing diagrams. CCDC 1870416. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra09452h

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enantiomeric pairs of regioisomeric pairs of bis-nickel complexes of expanded porphyrinoids (Fig. 2) when treated with a transition-metal Lewis acid such as Ni(OAc)$_2$. It was comprehended that the bicyclic pyrrolizine moiety was functionalized during this transformation. It was reported that the use of a semi-metallic Lewis-acid, BF$_3$OEt$_2$ or a basic-metal Lewis-acid, InBr$_3$, resulted in the formation of pyrrolo Diazepino-pyrrolizine derivatives (Fig. 3) due to a setback in creating sizeable macroyclic structures.\textsuperscript{7}

Other transition-metal sources were then stimulated to foster the investigation of different metal-complexes of cyclic/chain ligands. It is noteworthy to mention that the use of CoCl$_2$ afforded a different alignment (AB–BA order) of ligands as compared with the sequence obtained in the presence of Ni(OAc)$_2$ (AB–AB order). The resulting cobalt complex indicated a low spin, diamagnetic, and octahedral Co$^{III}$ complex formed due to facing two strong-field ligands in the same direction. The formation of bis-nickel(II)-expanded porphyrins, involving cross-condensations and further oxidations were successful within the AB–AB alignment of ligands. Herein, the synthetic and structural details are reported.

Results and discussion

Dicyanovinylene-bis(meso-aryl)dipyrrin (DCVAD) was prepared following a previous method and used in the formation of cobalt complexes with CoCl$_2$ (Scheme 1).

A toluene solution of DCVAD with CoCl$_2$ was heated to 100°C overnight, from which Co$^{III}$ complex 1 was isolated as a yellow fraction via silica gel column chromatography. The low solubility of complex 1 made it difficult to isolate on the silica gel, and the isolation yield was about 10%. A by-product exhibited a larger molecular mass value ($m/z = 2130.82$) than that of complex 1, whose structure was predicted to have two cobalt cations that coordinated with three ligand units. The mass per charge ratio ($m/z$) in the MALDI-TOF mass spectrometry of 1 was 1491.89, which was consistent with [M + H]$^+$ for the molecular formula C$_{68}$H$_{20}$CoF$_{20}$N$_{12}$O$_3$. The growth of single crystals for the X-ray diffraction analysis was achieved with a solvent combination of chloroform and methanol by the interconversion vaporization and slow diffusion of two solvents, which resulted in fine-fit single-crystallization and appropriate diffractions to refine the molecular structure (Fig. 4 and S1–S3$^\dagger$).

As shown in Fig. 4, each molecular origin of A-C$_{6}$F$_{5}$ first formed bicyclo-pyrrolizine, whose initiation inhibited the catalytic reaction of the transition-metal (CoCl$_2$) Lewis-acid, which occurred at vinylene-nitrile. Consequently, the neighboring pyrrole attached the nitrile carbon nucleophilically, resulting in the formation of a bicycle-pyrrolizine segment. Simultaneously, the conjugation pathway of $\pi$-electrons was reorganized for the proficient ligation of the metal-chelation. In the terminal pyrrole rings, the nucleophilic addition of water occurred, and the $\pi$-conjugation pathways were fulfilled by the deprotonation of hydroxyl groups, resulting in 2-pyrrolones. Herein, the cobalt-centre was associated with six coordination sites to complete the ligation, in which one terminal pyrrole out of the four still retained $\alpha$-free confirmation from the nucleophilic addition of water due to the restricted stabilization of the enol-form compared with that of the keto-form. It is noteworthy...
to mention that two distinct terminal pyrroles took a relative orientation to each other and formed intramolecular hydrogen bonds (H-bonds), which did not contribute to metalation, but eventually stabilized the overall structure of compound 1 (dashed lines representing H-bonds in Fig. 4a).

Nevertheless, almost the same ligand was held between two ligands towards the cobalt centre; one possessing a α-free pyrrole-terminal and the other that possessed all pyrrolone-terminals disordered the position of ligands in the crystalline state. The octahedral structure compromising the CoIII centre holds two ligand units, associating with the planarity of two ligands, as shown in Fig. 4b and d. Mean deviations within 20 atoms involved in ligands main skeleton except for the terminal pyrrole/pyrrolone realized hydrogen-bonds and adjacent meso-methin carbons were calculated as 0.174 Å for (b) and 0.137 Å for (d). A ligand unit that places vertically in Fig. 4a is presented in (b) and (c), while the other unit that places horizontally in the figure is presented in (d) and (e). Furthermore, it was implied that terminal pyrroles, which were not involved in the metalation, were standing up from the mean planes of chelating parts due to the following factors. Firstly, the steric interference was induced in individual ligand units; the terminal pyrrole that was not involved in the metal coordination was sterically hindered with the CoIII-coordinating part. Secondly, hydrogen-bonding interactions between terminal pyrrolones, led to the relative orientation. As a result, dihedral angles were measured as 51.23° for the ligand unit (b) and 51.53° for the ligand unit (d) (Fig. 4c and e). Hydrogen-bond lengths for N–H⋅⋅⋅O were 2.871 and 2.909 Å.

The metal-chelating imino-/amino-Ns of fully conjugated multi-pyrrolyl ligands play as strong field ligands, in which a low spin state of CoIII was compromised. The low spin, diamagnetic hexa-coordination of CoIII was exhibited with 1H NMR spectroscopy (Fig. 5). Two terminal pyrroles possessing H-bond interactions, where the amino-Ns of pyrroles acted as the proton donors of H-bonds, resonated two singlet-peaks of NH at a downfield shifted area, 10.48 and 10.21 ppm due to the deshielding effect of H-bond, whose peaks were assigned with the addition of D2O as disappearing peaks (spectra a and c).

Furthermore, the peaks of pyrrole-βHs were assigned to 6.00–7.81 ppm. Because of the distinct structures of the metal-chelating ligands with the CoIII centre, twenty protons and twenty fluorines (four p-Fs and eight each for o- and m-Fs of four pentafluorophenyl groups) were assigned in the 1H and 19F NMR spectra, respectively (Fig. 5 and 6). A few peaks overlapped as random cases. The homonuclear HH-COSY NMR exhibits eight correlation pairs of the β-protons of pyrrole rings and one correlation peak for the α- and β-protons of the α-free terminal pyrrole with nine sets of proton–proton correlations, as shown in Fig. 7. Furthermore, 19F NMR reveals individually located, twenty fluorine peaks (Fig. 6). The fluorine–fluorine correlations are demonstrated with the FF-COSY NMR analysis (Fig. S8†), whose spectrum shows fluorine sets for four meso-pentafluorophenyls as marked with four different symbols. The C=O stretching vibration of 2-pyrrolones of 1 expose broad bands overlapping around 1694 cm⁻¹ in CH2Cl2, which is significant for the 2-pyrrolone carbonyl group inducing a weakened energy vibration frequency as compared to common carbonyl groups (Fig. S9†).

CH2Cl2 solution of 1 exhibits a vastly elongated absorption band of about 1100 nm and demonstrates strong absorbance nearly (log ε = 4.01) at λmax = 795 nm (Fig. 8).
spectrometer using the CDCl₃ solvent and trimethylsilane (TMS) as an internal standard. The X-ray diffraction patterns of the single crystal of Co³⁺ complex 1 were collected at 93 K with a Varimax Saturn N instrument operated with the Rigaku operation software package. The molecular structure was analyzed using direct methods with the aid of SHELXS-97 software, and the refinement was accomplished using the SHELXL-97 program. All hydrogen atoms were placed in calculated positions.

Preparation of Co³⁺ complex 1

The precursor molecule A-C6F₅ was prepared following a previously method. A toluene solution (90 mL) of A-C₆F₅ (60 mg, 86.4 μmol) and CoCl₂·6H₂O (120 mg, 0.924 mmol) was heated to 100 °C for 9 h and then cooled down. The resulting solution was uploaded on aluminium oxide in a column to separate two fractions using eluents having gradually increased polarities, from neat CH₂Cl₂ to 1% MeOH in CH₂Cl₂. The first green fraction was separated to obtain the diazepino-pyrrolizine compound (last structure in Fig. 3) as a failed/retained ligand in cobalt metatation: spectral data elucidated the compound. The second fraction with a yellowish-green colour was then collected and washed with water to remove aluminium oxide dissolved in the increased polar eluent. Using brine and CH₂Cl₂, the organic layer was washed, separated, and dried over anhydrous Na₂SO₄. The residue was then precisely purified on a silica gel using neat CH₂Cl₂. A brownish yellow coloured fraction, fluorescent under the projection of a 365 nm UV lamp was collected to obtain compound 1 (10% yield). The ¹H NMR spectrum of the compound exposes the two significant singlets (10.48 and 10.21 ppm) of amino-NHs, supporting the molecular structure that preserves pyrroles, but not the metatation. Furthermore, the growth of single crystals was achieved with a CHCl₃ solution and MeOH via vapor diffusion.

Spectral data of 1‡

λₘₐₓ (nm (log ε), CH₂Cl₂): 320 (4.34), 456 (4.17), 795 (4.01); δ_H (500 MHz, 298 K, CDCl₃): 10.48 (bs, 1H, NH), 10.21 (bs, 1H, NH), 7.80 (d, J = 4.5 Hz, 1H), 7.66 (d, J = 4.5 Hz, 1H), 6.81 (s, 1H), 6.68 (d, J = 5.4 Hz, 1H), 6.67–6.58 (m, 3H), 6.34 (d, J = 4.8 Hz, 1H), 6.28 (d, J = 3.6 Hz, 1H), 6.27 (d, J = 3.7 Hz, 1H), 6.11 (d, J = 5.6 Hz, 1H), 6.08 (d, J = 3.7 Hz, 1H), 6.06 (d, J = 5.3 Hz, 2H), 6.05 (d, J = 3.7 Hz, 1H), 6.03 (d, J = 5.7 Hz, 1H), 6.01 (d, J = 5.4 Hz, 1H); δ_F (470.57 MHz, 298 K, calibrated with external CF₃COOH): −134.9 (d, J = 23.5 Hz, 1F, α-F), −135.7 (dd, J = 51.8 Hz, J = 3.3 Hz, J = 3.3 Hz, 1F, α-F).

‡ Crystallographic data of 1 (CCDC 1870416): [Co₂H₁₂CoF₂N₅SnO₆], (CHCl₃)·0.38(CH₃OH) Mᵣ = 1623.19, T = 93(2) K, crystal size = 0.09 × 0.09 × 0.01 mm³, Green prism, Mo radiation, triclinic, space group P1 (2), a = 11.204(5) Å, b = 16.844(5) Å, c = 18.838(5)Å, α = 63.767(5)°, β = 83.998(5)°, γ = 77.380(5)°, V = 3115.1(19) Å³, Z = 2, R_exp = 0.1278 g cm⁻³, R(F) = 0.0972 (I > 3σ(I)), wR(F)² = 0.2944 (all), GoF = 1.072. Disordered solvent molecules were refined in one chloroform and around 0.38 methanol molecules per one molecule of 1. Furthermore, one of the terminal pyrroles, positioning the crystal to the terminal pyrrole of the partner ligand in the cobalt complex was also disordered: two terminal parts were disordered and placed close to each other by forming hydrogen bonds, N–H···O.

Experimental

Materials and methods

All reagents obtained from commercial suppliers were used without further purification. Products were column chromatographed on a silica gel (silica gel 300 or 400). The nuclear magnetic resonance (NMR) spectra of synthetic compounds were recorded using a Bruker Avance 300 MHz NMR
Conclusions

In conclusion, the CoIII complex 1 was synthesized and isolated from a toluene solution of dicyanovinylene-bis(meso-aryl) dipyrin via thermal metalation of the pyrrolo-pyrrolizine derivative. The molecular structure of 1 was elucidated by the X-ray diffraction analysis, in which two pyrroline-ligands chelating to the CoIII atom oriented in an AB-BA alignment with the octahedral CoIII complex. Furthermore, NMR spectroscopic and X-ray crystallographic details disclosed the complex 1 to be diamicagnetic, low spin octahedral Co(m)-complex of strong-field ligands.

Conflicts of interest

There are no conflicts of interest to declare.

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