Synthesis of 5,10-bis(Trifluoromethyl) Substituted β-Octamethylporphyrins and Central-Metal-Dependent Solvolysis of Their meso-Trifluoromethyl Groups

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Abstract: 5,10-Bistrifluoromethyl substituted β-octamethylporphyrins were synthesized via a scrambling side reaction of a dipyromethane precursor in the presence of a large excess of trifluoroacetic acid. Compared with the trans-analogs, the cis-analogs of meso-trifluoromethyl β-octaalkylporphyrins showed more red-shifted absorption bands. These meso-trifluoromethyl derivatives of β-octaalkylporphyrins underwent smooth metalation, similar to other common porphyrins, however, the corresponding zinc complexes underwent a type of solvolysis, whereby the trifluoromethyl groups were converted into methoxycarbonyl groups by the methanol used as solvent. UV-visible absorption spectra and X-ray crystal structure analyses revealed that the presence of a methoxycarbonyl substituent did not influence the deformation of the molecular framework and its absorption properties; this is because the methoxycarbonyl has a planar and perpendicular geometry, as opposed to the relatively bulky trifluoromethyl substituent.

Keywords: porphyrin; trifluoromethyl; alkoxy carbonyl; solvolysis

1. Introduction

Porphyrins, which are naturally occurring aromatic compounds, are widely distributed in fundamental indispensable biosystems in the form of heme or chlorophyll, and they play essential biological roles. Many scientists have attempted to mimic or improve the functions of porphyrins by modifying their structures and electronic properties. This is because such modifications would allow us to probe the origin of life and aid the design of compounds having potential applications in advanced materials science [1,2]. Incorporating diverse substructures into the porphyrin core is an effective way to induce deformation of the framework, and the consequent non-planarity is one of the prevalent mechanisms for the activation of natural porphyrins [3,4]. The introduction of perfluoroalkyl groups is expected to result in drastic perturbations in the molecule owing to their sterically bulky three-dimensional structure and strong electron-withdrawing nature. Some chemists have demonstrated that meso-perfluoroalkyl-substituted porphyrins have superior functionalities as compared to previously reported examples [5–8]. However, introducing even a trifluoromethyl (CF3) group, the simplest perfluoroalkyl functionality, at the sterically crowded meso-positions of β-alkyl substituted porphyrins is synthetically challenging, thus triggering continual research in this regard [9,10]. Recently, we reported the unexpected formation of...
5-trifluoromethyl-2,3,7,8,12,13,17,18-octaalkylporphyrins and revealed that a trifluoromethyl group has both steric and electronic effects as expected, so that we could access distorted frameworks that show red-shifted light absorption [11]. Herein, we report the synthesis of a meso-CF$_3$ substituted octaalkylporphyrin via another novel and optimized substitution reaction. We also report an inner-metal dependent solvolysis reaction, whereby the CF$_3$ substituents are converted into methoxy-carbonyl groups.

2. Results and Discussion

We investigated various reaction conditions to improve the product yield. Initially, we prolonged the reaction of the β-ethylated dipyrromethane carboxylic acid precursor 2 with TFA, after complete dissolution of the starting solids in TFA (Scheme 1). The reaction mixture was diluted with CHCl$_3$, and the resulting solution was stirred for up to 8 h at room temperature, followed by the addition of DDQ. Unfortunately, no improvement in yields of 6, 7, and 8 was observed. Next, we used the β-methylated dipyrromethylene derivative 1. After 8 h of stirring with TFA, which was a sufficiently long reaction time like that of the previous conditions, followed by the usual oxidation and work-up procedures, a predominant product 9 was obtained. In this case, 3, 4, and 5 were not formed or were detected in only trace amounts (Scheme 2). Purification by silica gel chromatography (CH$_2$Cl$_2$/hexane, 1:1 v/v) gave 9, which eluted as the first olive-green fraction. The colors of 4 and 5 in similar solvents were light green and deep purple, respectively; thus, 9 was deemed different from either 4 or 5 [11].

Scheme 1. Synthesis of meso-CF$_3$ substituted β-octaalkylporphyrins.

Scheme 2. Synthesis of cis-meso-bisCF$_3$ substituted β-octamethylporphyrin.

The UV-visible absorption spectrum of 9 recorded in CH$_2$Cl$_2$ displayed a Soret-band-like band at 415 nm and Q-band-like bands at 537, 575, 616, and 674 nm, indicating that 9 was a type of porphyrin (Figure 1). High resolution electrospray ionization time-of-flight mass spectroscopy (HR-ESI-TOF MS) gave a parent molecular ion peak at 559.2295, which corresponded to the molecular formula C$_{30}$H$_{29}$F$_6$N$_4$ as [M + H]$^+$. The $^1$H-NMR spectrum of 9 showed four sets of singlets due to the β-methyl substituents around the downfield-shifted aliphatic region and only one 2H singlet in the aromatic
region. These results indicated that 9 possessed two CF$_3$ groups at the porphyrinic meso-positions but its spectra were not identical those of 5. Therefore, we assigned the structure of 9 as shown in Scheme 2. The final structure determination was successfully carried out “indirectly” by X-ray diffraction analysis using derivative 12Zn, as will be subsequently discussed.

![Figure 1. UV-visible absorption spectra of 9, 7Zn, 9Zn, 11Zn, and 12Zn in CH$_2$Cl$_2$.](image)

**Figure 1.** UV-visible absorption spectra of 9, 7Zn, 9Zn, 11Zn, and 12Zn in CH$_2$Cl$_2$.

2.1. Metallation Reaction

The meso-CF$_3$ substituted porphyrin derivatives 4, 7, and 9 could encapsulate several ordinary metal ions such as Zn, Cu, Ni, and Pd. When a mixture of 7 and the corresponding metal acetate salt was refluxed within a couple of hours in CHCl$_3$ and methanol (3:1 v/v), the color of the solution turned a vivid blue (Scheme 3). The conversion was almost quantitative in all cases except for zinc, which afforded a minor side product, when it was left for a long time as a mixture. TLC analysis of the reaction showed a reddish impurity spot beside the blue spot corresponding to the desired zinc complex 7Zn; however, this impurity was removed by silica gel column chromatography (CH$_2$Cl$_2$/hexane 1:1 v/v).

![Scheme 3. Metallation and solvolysis of meso-CF$_3$ substituted β-octaalkylporphyrins.](image)

**Scheme 3.** Metallation and solvolysis of meso-CF$_3$ substituted β-octaalkylporphyrins.

2.2. Formation of meso-CO$_2$Me Porphyrins by Solvolysis of CF$_3$ Substituents

Single crystals of zinc complexes 7Zn and 9Zn were grown from CHCl$_3$ solutions by vapor diffusion of methanol. Initially, we believed that we obtained crystals of 7Zn and 9Zn suitable for X-ray diffraction analyses. However, the data generated unusual electron density maps that were different from those of the expected structures. Surprisingly, solvolytic side reactions had occurred such that the CF$_3$ substituents were converted into methoxycarbonyl (CO$_2$Me). Isolated 7Zn and 9Zn also undertook solvolyses without excess zinc salts (Scheme 3), whereas the other metal complexes (Cu, Ni, Pd) did not cause under the similar conditions. Solutions of 11Zn and 12Zn in CHCl$_3$ or other common organic solvents were red in color, as is often seen in the case of common β-alkyl substituted porphyrin zinc complexes. As illustrated in Figure 1, the UV-visible absorption spectrum of 9Zn exhibited a Soret band at 429 nm, which was red-shifted compared to that of the corresponding free base 9, while the lowest energy Q-band was at 623 nm. On the other hand, both the Soret and
the Q-bands of $^{11}$Zn and $^{12}$Zn were remarkably blue-shifted compared to those of $^{9}$Zn (406, 537, 574 nm for $^{11}$Zn; 409, 541, 577 nm for $^{12}$Zn, Table 1), indicating the absence of electronic communication between the macrocycle and the meso-side chain; namely, there was no extension of the $\pi$-conjugation in such a system [12].

Table 1. Wavelengths of absorption bands of 5, 9, 7Zn, 9Zn, 11Zn, and 12Zn in the UV-visible absorption spectra in CH$_2$Cl$_2$.

| Compound | Soret Band (log $\varepsilon$)/nm | Q-Band (log $\varepsilon$)/nm |
|----------|----------------------------------|-----------------------------|
| 5        | 397                              | 575, 671 $^1$              |
| 9        | 415 (5.17)                       | 537 (4.07), 575 (4.23), 616 (3.95), 675 (4.00) |
| 7Zn      | 416 (5.39)                       | 567 (4.01), 611 (4.43)     |
| 9Zn      | 429 (5.15)                       | 578 (3.97), 623 (4.28)     |
| 11Zn     | 406 (5.46)                       | 537 (4.18), 574 (4.22)     |
| 12Zn     | 409 (5.41)                       | 541 (4.18), 577 (4.15)     |

$^1$ These data were quoted from reference [11].

2.3. X-ray Crystal Structures

With the X-ray diffraction data of 11Zn and 12Zn in hand, we examined the structural features of these macrocycles. [13] The structure assigned to 12Zn based on X-ray crystallography provided indirect evidence of the formation of 9 and 9Zn, which have CF$_3$ substituents in a cis-arrangement. We have already reported the relationship between the number of CF$_3$ substituents and the deviation of the macrocycle from planarity in the free-base and nickel-complex forms. As shown in Figure 2, the X-ray crystal structures of 11Zn and 12Zn displayed high planarity, which probably arises from the release of steric strain between the $\beta$- and meso-substituents. This release occurs because a CO$_2$Me substituent is flat and can orient perpendicular against the macrocyclic plane, whereas a CF$_3$ substituent is three-dimensionally bulky. Mean-plane deviations calculated from the core 24 atoms of 11Zn and 12Zn were 0.043 and 0.042 Å, respectively. Figure 3 indicates that the 5-position in compound 7, substituted with the CF$_3$ group, showed a greater deviation from the mean plane than did the other meso-positions of 7. However, since the 5-position of 11Zn or the 5,10-positions of 12Zn were substituted with CO$_2$Me, their skeletons deviated from the mean planes only to a small extent. The angle made by C(5)-CO$_2$Me bond against the mean plane was 9.9° for 11Zn, while those of the C(5)-CO$_2$Me and C(10)-CO$_2$Me bonds were 2.2° and 1.5°, respectively, for 12Zn. Dihedral angles between the CO$_2$Me group and the mean plane were 87° for 11Zn and 89° for 12Zn. The N-Zn distances and the displacement of the Zn atoms from the mean plane were 2.036–2.052 Å and 0.107 Å for 11Zn; 2.057–2.077 Å and 0.001 Å for 12Zn, respectively.

Figure 2. Crystal structures of (a) 11Zn, (b) 12Zn. Upper: top view; lower: side view. $\beta$-substituents of the side views are omitted for clarity. The thermal ellipsoids are set at the 50% probability level.
Figure 3. Mean plane deviation diagrams of 7\[5\], 11Zn, and 12Zn.

3. Experimental Section

3.1. General Information

All reagents were of the commercial reagent grade and were used without further purification. $^1$H-NMR spectra were recorded on an ECX-500 spectrometer (JEOL Ltd., Akishima, Japan), (operating as 500.16 MHz for $^1$H; 470.62 MHz for $^{19}$F) using the residual solvent in CDCl$_3$ as the internal reference for $^1$H ($\delta$ = 7.26 ppm); hexafluorobenzene for $^{19}$F ($\delta$ _T = -164.9 ppm). UV-visible absorption spectra were recorded on a Shimadzu UV-1800 instrument (Shimadzu Corporation, Kyoto, Japan) or a UV-2400 spectrometer (Shimadzu Corporation) in spectroscopic grade CH$_2$Cl$_2$. Mass spectra were recorded on a BRUKER microTOF (Bruker Daltonics K.K., Yokohama, Japan) spectrometer using the positive mode ESI-TOF method on acetonitrile solutions and with sodium formate as the internal reference. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-400HG). Data for single crystal X-ray diffraction analyses were collected on a Rigaku R-AXIS RAPID diffractometer (Rigaku Corporation, Akishima, Japan) using a graphite monochromator with CuK$\alpha$ radiation (λ = 1.54187 Å). Data collection and reduction were performed using RAPID AUTO. The structures for crystallography were solved by direct methods using SHELXL97 [14,15], Sir97 [16], and were refined using SHELXL97 on Yadokari-XG program [17,18].

3.2. Syntheses

5,10-Bis(trifluoromethyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (9). A solution of 1 (3.0 g) in TFA (1.1 mL) was heated at 50 °C in a sealed tube for 8 h. CHCl$_3$ (57 mL) was added and the resulting solution was stirred for 8 h at room temperature, followed by addition of DDQ (2.52 g). After 30 min, the reaction mixture was passed through a short alumina column with CHCl$_3$ and the solution was evaporated to dryness. The residue was chromatographed on silica gel using CH$_2$Cl$_2$-hexane mixed solvent (50%, v/v). The first moving olive-green fraction was collected and evaporated. Recrystalization from CHCl$_3$–MeOH gave 9 as purple solids (23.4 mg 1.1%) $^1$H-NMR (CDCl$_3$): $\delta$ T = -1.40 (brs 2H, NH), 3.15 (s, 6H, CH$_3$), 3.34 (s, 12H, CH$_3$), 3.36 (s, 6H, CH$_3$), and 9.57 (s, 2H, meso) ppm; $^{19}$F-NMR (CDCl$_3$): $\delta$ T = -37.69 (CF$_3$) ppm; UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$($\epsilon$ [M$^{-1}$ cm$^{-1}$]): 415 (150,000), 537 (12,000), 575 (17,000), 616 (8800), and 675 (10,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C$_{30}$H$_{29}$F$_6$N$_4$ ([M + H]+), calcd: 559.2291, found: 559.2295 (100%); Elemental analysis calcd for C$_{30}$H$_{28}$F$_6$N$_4$: C 64.51, H 5.05, N 10.03; found: C 64.45, H 5.15, N 10.31.

5-Trifluoromethyl-2,3,7,8,12,13,17,18-octamethylporphyrin zinc complex (7Zn). A solution of 7 and large excess of zinc acetate in CHCl$_3$ and MeOH (3:1 v/v) zinc acetated was stirred at room temperature until 7 was completely consumed. The resulting solution was washed with water twice and dried over anhydrous sodium sulfate. After removal of the solvent, 7Zn was obtained almost quantitatively. Recrystalization from CHCl$_3$–MeOH gave an analytical sample of 7Zn as purple solids $^1$H-NMR (CDCl$_3$): $\delta$ = 1.70 (t, $J$ = 7.5 Hz, 6H, CH$_2$CH$_3$), 1.80 (t, $J$ = 7.7 Hz, 6H, CH$_2$CH$_3$), 1.82–1.87 (m, 12H,
which are often require harsh conditions such as high temperatures, and/or strongly basic or acidic environments [22–25]. In this regard, the compounds generated via our protocol can be useful scaffolds for novel functional molecular assemblies. Further investigations for utilizing these methodologies are ongoing in our laboratory.

5,10-Bis(trifluoromethyl)-2,3,7,8,12,13,17,18-octamethylporphyrin zinc complex (9Zn). A solution of 9 and large excess of zinc acetate in CHCl3 and MeOH (3:1 v/v) zinc acetated was stirred at room temperature until 9 was completely consumed. The resulting solution was washed with water twice and dried over anhydrous sodium sulfate. After removal of the solvent, 9Zn was obtained almost quantitatively. Recrystallization from CHCl3-MeOH gave an analytical sample of 9Zn as purple solids (7.6 mg, 72%). 1H-NMR (CDCl3): δ = 7.31 (s, 6H, CH3), 7.50 (s, 6H, CH3), 3.92–3.96 (m, 8H, CH2), 3.89–3.93 (m, 4H, CH2), 4.08–4.15 (m, 12H, CH2CH2), 4.53 (s, 3H, OCH3), 10.13 (s, 1H, meso), and 10.21 (s, 2H, meso) ppm; UV-vis (CH2Cl2): λmax (ε [M⁻¹ cm⁻¹])]: 360 (Sh, 29,000), 429 (140,000), 578 (9300), and 623 (19,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C37H43F2N4Zn ([M − F]⁺), calcd: 645.2742, found: 645.2733 (100%); Elemental analysis calcd for C37H43F2N4Zn: C 66.70, H 6.77, N 8.69; found: C 66.71, H 6.51, N 8.41.

5-Methoxycarbonyl-2,3,7,8,12,13,17,18-octamethylporphyrin zinc complex (12Zn). A solution of 9 and large excess of zinc acetate in CHCl3 and MeOH (3:1 v/v) MeOH afforded 12Zn as purple solids (7.3 mg, 74%). 1H-NMR (CDCl3): δ = 1.71 (t, J = 7.5 Hz, 6H, CH2CH3), 1.91–1.96 (m, 18H, CH2CH2), 3.80–3.84 (m, 4H, CH2CH2), 4.08–4.15 (m, 12H, CH2CH2), 4.53 (s, 3H, OCH3) 10.13 (s, 1H, meso), and 10.21 (s, 2H, meso) ppm; UV-vis (CH2Cl2): λmax (ε [M⁻¹ cm⁻¹])]: 338 (Sh, 21,000), 406 (290,000), 537 (15,000), and 574 (17,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C38H46N4O2Zn ([M⁺]), calcd: 654.2907, found: 654.2911 (100%); Elemental analysis calcd for C38H46N4O2Zn: C 69.56, H 7.07, N 8.54; found: C 69.72, H 6.73, N 8.60.

5,10-Bis(methoxycarbonyl)-2,3,7,8,12,13,17,18-octamethylporphyrin zinc complex (11Zn). A solution of 7 and large excess of zinc acetate in CHCl3 (5 mL) and MeOH (5 mL) was refluxed for 1 day. After evaporated to dryness, recrystallization from CHCl3/MeOH afforded 11Zn as purple solids (7.3 mg, 74%). 1H-NMR (CDCl3): δ = 7.31 (s, 6H, CH3), 7.49–7.52 (s, 6H, CH3), 3.89–3.93 (m, 4H, CH2), 4.08–4.15 (m, 12H, CH2CH2), 4.53 (s, 3H, OCH3) 10.13 (s, 1H, meso), and 10.21 (s, 2H, meso) ppm; UV-vis (CDCl3): δ T = −35.12 (CF3) ppm; UV-vis (CH2Cl2): λmax (ε [M⁻¹ cm⁻¹])]: 360 (Sh, 29,000), 429 (140,000), 578 (9300), and 623 (19,000) nm; HR-ESI-TOF-Mass (positive-mode) (%intensity): C38H46N4O2Zn ([M⁺]), calcd: 654.2907, found: 654.2911 (100%); Elemental analysis calcd for C38H46N4O2Zn: C 69.56, H 7.07, N 8.54; found: C 69.72, H 6.73, N 8.60.

5,10-Bis(trifluoromethyl)-2,3,7,8,12,13,17,18-octamethylporphyrin zinc complex (12Zn). A solution of 9 and large excess of zinc acetate in CHCl3 (2 mL), MeOH (10 mL), and H2O (0.5 mL) was refluxed for 1 day. After evaporated to dryness, recrystallization from CHCl3/MeOH afforded 12Zn as purple solids (7.6 mg, 72%). 1H-NMR (CDCl3): δ = 3.33 (s, 6H, CH3), 3.35 (s, 6H, CH3), 3.41 (s, 6H, CH3), 3.54 (s, 6H, CH3), 4.51 (s, 6H, OCH3) and 9.74 ppm; UV-vis (CH2Cl2): λmax (ε [M⁻¹ cm⁻¹])]: 345 (Sh, 23,000), 409 (260,000), 541 (15,000), and 577 (14,000) nm. Elemental analysis calcd for C32H32N4O4Zn: C 63.84, H 5.36, N 9.31; found: C 63.21, H 5.17, N 9.14.

4. Conclusions

We have demonstrated the formation of bis-CF3 substituted β-octamethylporphyrins in a cis-arrangement and the metal-dependent solvolysis of meso-CF3 functionalities. The synthesis of such a cis-configured porphyrin is usually challenging because more complicated oligo-pyrrolic precursors containing CF3 substituent may be required. Compared with its trans-analogue 5, the cis-configured 9 showed more red-shifted absorption bands, suggesting that a cis-arrangement worked more effectively than a trans-arrangement for extension of the absorption range Figure S14). In addition, there are very few reported examples of porphyrins with alkoxycarbonyl substituents at their meso-positions, and even fewer examples with β-octaaldehydeporphyrins [19–21]. Although the exact mechanism of the metal-dependent mild solvolysis of CF3 into CO2Me including the role of the metal is still unclear (Scheme S1), our synthetic protocol is of greater utility compared to existing procedures, which are often require harsh conditions such as high temperatures, and/or strongly basic or acidic environments [22–25]. In this regard, the compounds generated via our protocol can be useful scaffolds for novel functional molecular assemblies. Further investigations for utilizing these methodologies are ongoing in our laboratory.
Supplementary Materials: Supplementary materials can be accessed at: http://www.mdpi.com/1420-3049/21/3/252/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

| Acronym | Description |
|---------|-------------|
| TFA     | Trifluoroacetic acid |
| DDQ     | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone |
| TLC     | solid thin layer chromatography |

References and Notes

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12. The absorption bands of zinc octaethylporphyrin were observed at $\lambda_{\text{max}}$ (log $\varepsilon$) = 331 (4.28), 402 (5.63), 490 (3.51), 532 (4.21), and 569 (4.39) nm in CH$_2$Cl$_2$. These data also support the opinion discussed here. Gong, L.-C.; Dolphin, D. Nitrooctaethylporphyrins: Synthesis, optical and redox properties. Can. J. Chem. 1985, 63, 401–405.
Crystal data for 11Zn: C_{38}H_{46}N_{4}O_{2}Zn = 656, triclinic, space group P-1 (No. 2), a = 10.6883(2) Å, b = 13.0924(2) Å, c = 24.4733(4) Å, \( \alpha = 73.7710(10) \), \( \beta = 89.9650(10) \), \( \gamma = 89.9610(10) \), \( V = 3274.78(10) \text{ Å}^3 \), \( Z = 4 \), \( D_{\text{calc}} = 1.331 \text{ g/cm}^3 \), \( T = -180 ^\circ \text{C} \), \( R_1 = 0.0946 \) (I > 2\( \sigma(I) \)), \( R_W = 0.2274 \) (all data), GOF= 0.859, CCDC-1444312. Crystal data for 12Zn: C_{33}H_{33}Cl_{3}N_{4}O_{4}Zn = 721, triclinic, space group P-1 (No. 2), a = 9.5307(2) Å, b = 12.0063(3) Å, c = 14.4714(3) Å, \( \alpha = 78.7230(10) \), \( \beta = 72.5150(10) \), \( \gamma = 85.381(2) \), \( V = 1548.52(6) \text{ Å}^3 \), \( Z = 2 \), \( D_{\text{calc}} = 1.547 \text{ g/cm}^3 \), \( T = -180 ^\circ \text{C} \), \( R_1 = 0.0921 \) (I > 2\( \sigma(I) \)), \( R_W = 0.2943 \) (all data), GOF= 1.126, CCDC-1444313. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 19 February 2016).

13. Crystal data for 11Zn: C_{38}H_{46}N_{4}O_{2}Zn = 656, triclinic, space group P-1 (No. 2), a = 10.6883(2) Å, b = 13.0924(2) Å, c = 24.4733(4) Å, \( \alpha = 73.7710(10) \), \( \beta = 89.9650(10) \), \( \gamma = 89.9610(10) \), \( V = 3274.78(10) \text{ Å}^3 \), \( Z = 4 \), \( D_{\text{calc}} = 1.331 \text{ g/cm}^3 \), \( T = -180 ^\circ \text{C} \), \( R_1 = 0.0946 \) (I > 2\( \sigma(I) \)), \( R_W = 0.2274 \) (all data), GOF= 0.859, CCDC-1444312. Crystal data for 12Zn: C_{33}H_{33}Cl_{3}N_{4}O_{4}Zn = 721, triclinic, space group P-1 (No. 2), a = 9.5307(2) Å, b = 12.0063(3) Å, c = 14.4714(3) Å, \( \alpha = 78.7230(10) \), \( \beta = 72.5150(10) \), \( \gamma = 85.381(2) \), \( V = 1548.52(6) \text{ Å}^3 \), \( Z = 2 \), \( D_{\text{calc}} = 1.547 \text{ g/cm}^3 \), \( T = -180 ^\circ \text{C} \), \( R_1 = 0.0921 \) (I > 2\( \sigma(I) \)), \( R_W = 0.2943 \) (all data), GOF= 1.126, CCDC-1444313. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 19 February 2016).

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Sample Availability: Samples of the compounds of 7, 9, 7Zn, 9Zn, 11Zn, and 12Zn are available from the authors.