Porphyrinoids

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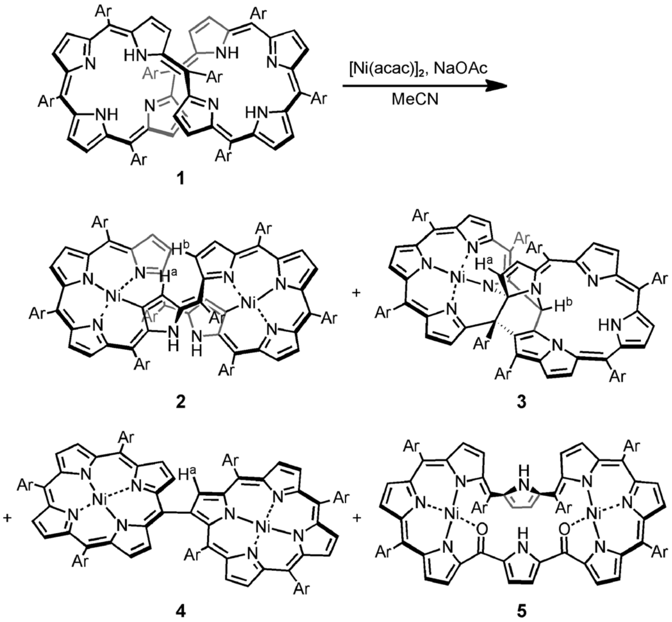
Rearrangements of a [36]Octaphyrin Triggered by Nickel(II) Metalation: Metamorphosis to a Directly meso-β-Linked Diporphyrin**

*Yasuo Tanaka, Hirotaka Mori, Taro Koide, Hideki Yorimitsu, Naoki Aratani, and Atsuhiro Osuka**

In memory of Emanuel Vogel

In recent years, increasing attention has been focused on expanded porphyrins, which consist of more than five pyrrolic subunits.[1] These macrocycles show large conjugated π systems, multiple oxidation states, rich metal-coordination properties, conformational flexibilities, large nonlinear optical properties, and anion-binding abilities. They have been particularly suitable for the realization of Möbius aromatic and antiaromatic systems.[2,3] Beside these features, the metalation of expanded porphyrins has triggered unique skeletal rearrangements. As the first well-characterized examples, Vogel et al. disclosed in 2003 a rearrangement of 5,24-dioxo-octaphyrin(1.1.1.0.1.1.1.0) to a spirodiporphyrin triggered by nickel(II) metalation as well as the formation of a different spirodiporphyrin from a [34]octaphyrin-(1.1.1.0.1.1.1.0) upon its metalation with palladium(II) ions.[4] Later, we found that a dicopper(II) complex of meso-pentafluorophenyl-substituted [36]octaphyrin-(1.1.1.1.1.1.1.1) (**1**) was cleanly split into two copper(II) porphyrins with perfect material balance upon heating.[5] The same splitting reaction proceeded quantitatively with a Co^{II}/Cu^{II} hybrid octaphyrin complex, while the metalation of **1** with $Pd(OAc)_2$ produced several rearranged products.[3a,5d] Curiously, similar metathesis-like splitting reactions have been found with a B^{III}/Cu^{II} hybrid heptaphyrin, which gave a copper(II) porphyrin and a boron(III) subporphyrin.[6] These reactions can be regarded as metamorphoses of expanded porphyrins.[7] Other related examples include rearrangement of [26]hexaphyrin to doubly N-confused [26]hexaphyrin induced by copper(I) metalation[8a] and the rearrangement of [32]heptaphyrin to a palladium(II) complex of N-confused porphyrin triggered by palladium(II) metalation.[8b] Herein we report a novel metamorphosis of **1** to a directly meso-β-linked diporphyrin, which was serendipitously found during the study on the nickel(II) metalation of **1**.



Scheme 1. Metalation of **1** with [Ni(acac)$_2$]. Ar = 2,3,4,5,6-pentafluorophenyl. Acac = acetylacetonate.

A solution of **1** in acetonitrile was heated at reflux in the presence of 10 equivalents of [Ni(acac)$_2$] and NaOAc for 6 h. After usual workup and chromatographic separation, four products **2**, **3**, **4**, and **5** were isolated in 6, 21, 9, and 12 % yields, respectively (Scheme 1). When 100 equivalents of [Ni(acac)$_2$] was used, the yields of **2**, **4**, and **5** were increased to 22, 12, and 20 %, respectively, while the yield of **3** was reduced to 6 %. The high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectrum of **2** indicated a parent ion signal at $m/z = 2062.9559$ ($[M+H]^+$, calcd for $C_{88}H_{17}N_8F_{40}Ni_2$, 2062.9602). The ^1H NMR spectrum of **2** showed a C_2-symmetric species with a singlet at $\delta = 14.31$ ppm and a doublet at $\delta = 8.83$ ppm arising from H^a and H^b (see Scheme 1), respectively. Signals corresponding to the rest of the pyrrolic β protons were observed at $\delta = 6.78$, 6.34, 6.28, 6.06, and 5.61 ppm, and a signal corresponding to the outer NH protons was observed at $\delta = 6.82$ ppm. This is quite similar to the spectrum of the structurally well-characterized

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[*] Dr. Y. Tanaka, H. Mori, T. Koide, Prof. Dr. H. Yorimitsu, Dr. N. Aratani, Prof. Dr. A. Osuka
Department of Chemistry, Graduate School of Science
Kyoto University, Sakyo-ku, Kyoto 606-8502 (Japan)
E-mail: osuka@kuchem.kyoto-u.ac.jp
Dr. N. Aratani
PRESTO (Japan) Science and Technology Agency (Japan)

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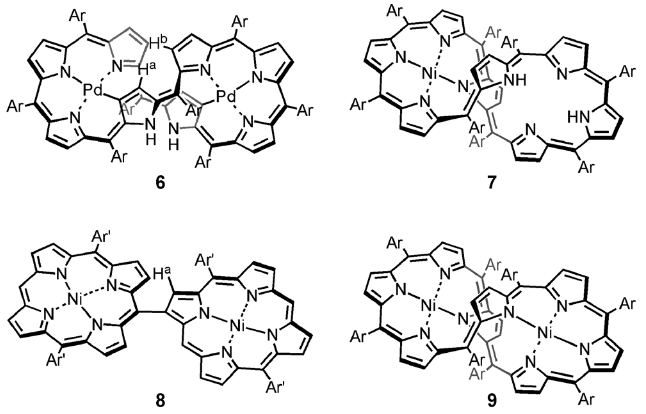


Scheme 2. Compounds **6**, **7**, **8**, and **9**. Ar = 2,3,4,5,6-pentafluorophenyl and Ar′ = 3,5-di-*tert*-butylphenyl.

dipalladium(II) complex **6**,[3a] which showed the signals for H^a and H^b at $\delta = 17.14$ and 8.60 ppm, those for the rest of the pyrrolic β protons in the range $\delta = 6.09$–5.10 ppm, and an NH signal at $\delta = 6.45$ ppm (Scheme 2). These data indicated a weak paratropic ring current for **2**, as seen for **6**, in line with its 36π electronic circuit lying in a figure-of-eight doubly twisted Hückel conformation.

The HR-ESI-TOF mass spectrum of **3** showed the signal for the parent ion at $m/z = 2002.0271$ ([M], calcd for $C_{88}H_{15}N_8F_{40}Ni = 2002.0173$), thus indicating its constitution as the mononickel(II) complex of **1**. The structure of **3** was solved by X-ray diffraction analysis (Figure 1).[9] The nickel(II) atom is bound to the three nitrogen atoms of pyrrole rings A, B, and C as well as the nitrogen atom N(8), which originates from the cleaved pyrrole ring and is also connected to the α-carbon atom C(16) of pyrrole ring D. The nitrogen atom N(4) of pyrrole ring D is transannularly connected with C(38). The other tetrapyrrolic segment consisting of pyrrole rings E, F, and G is metal-free, and pyrrole ring G is fused with the adjacent pyrrole ring to form a pyrrolizine (azapentalene) system. Consistent with the crystal structure, the ^{1}H NMR spectrum recorded in $CDCl_3$ shows a singlet corresponding to the pyrrolic NH proton at $\delta = 10.52$ ppm, a double of doublets for H^a (designated in Scheme 1) at $\delta = 8.37$ ppm, a singlet for H^b at $\delta = 8.14$ ppm, and 13 doublets for the pyrrolic β protons in the range $\delta = 6.52$–4.97 ppm. The considerably low chemical shift of H^b is ascribed to effective intramolecular hydrogen bonding with N(5) of pyrrole ring E. It is apparent that the formation of **3** from **1** requires a large skeletal rearrangement involving cleavage of a pyrrole ring. In a possible reaction route from **1** to **3** (see the Supporting Information), the NNNN-coordinated mononickel(II) complex **7** is postulated as an intermediate to **3**. This putative complex **7**, which was not detected in this reaction, might undergo a cascade reaction sequence as a result of severe strain around the nickel(II) coordination site.

To our surprise, product **4** has been assigned as being a dinickel(II) complex of a directly meso-β-linked diporphyrin on the basis of the following data: 1) the HR-ESI-TOF mass spectrum showed the parent ion signal at $m/z = 1894.9603$ ([M+H]$^+$, calcd for $C_{82}H_{16}N_8F_{35}Ni_2 = 1894.9603$), which was 168 mass units lower than that of the dinickel(II) complex of [36]octaphyrin, 2) the ^{19}F NMR spectrum exhibited only 14 *ortho*-F, 7 *para*-F, and 14 *meta*-F signals. Thus, these data indicated a loss of one pentafluorophenyl substituent ($M = 167$), 3) the ^{1}H NMR spectrum revealed ten doublets and one singlet (H^a) at $\delta = 9.88$ ppm, which nicely resembled that of the dinickel(II) complex of directly meso-β-linked diporphyrin **8**, which showed the H^a signal at $\delta = 9.24$ ppm,[10] and finally 4) the UV/Vis absorption spectrum of **4** showed features characteristic of directly meso-β-linked diporphyrins, such as a moderately broad Soret band arising from exciton coupling and relatively unperturbed Q bands (Figure 2).[10] To

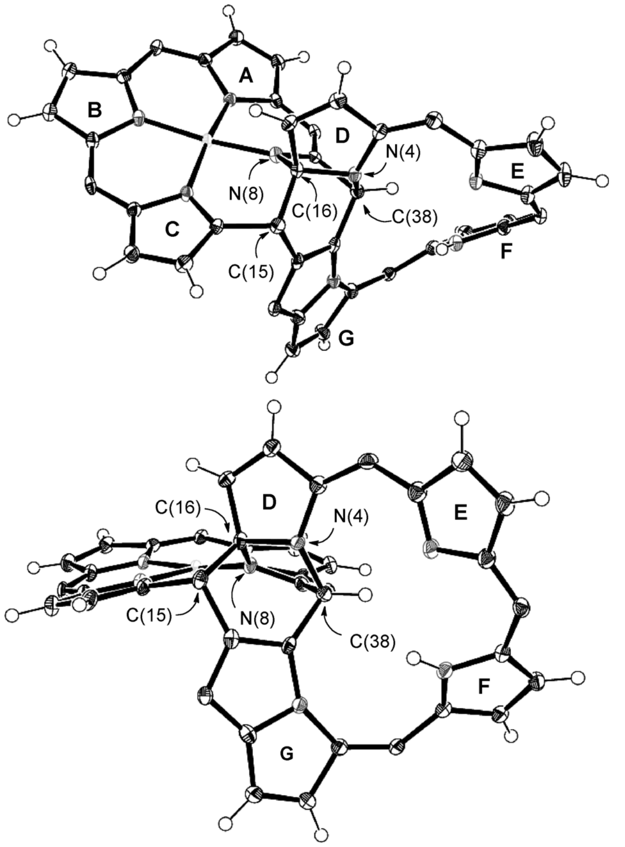


Figure 1. Crystal structure of **3**. Top: top view. Bottom: side view. The thermal ellipsoids are scaled to the 50% probability. meso-Aryl substituents and solvent molecules are omitted for clarity.

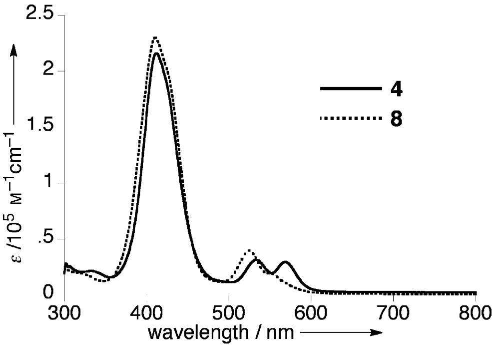
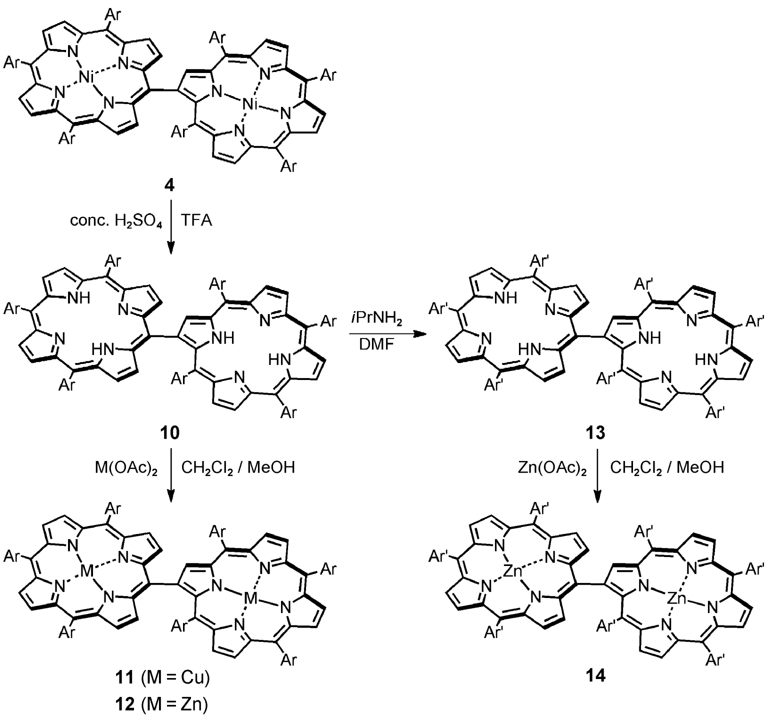


Figure 2. UV/Vis absorption spectra of **4** (solid line) and **8** (dotted line) in CH_2Cl_2.



Scheme 3. Directly meso-β-linked diporphyrins. Ar = 2,3,4,5,6-pentafluorophenyl, Ar′ = 2,3,5,6-tetrafluoro-4-isopropylaminophenyl. TFA = trifluoroacetic acid.

obtain stronger structural evidence, **4** was converted into free-base diporphyrins **10** and its metal complexes **11** and **12** (Scheme 3). Although these diporphyrins displayed absorption spectra that are consistent with the structural assignment (see the Supporting Information), their crystallizations turned out to be difficult. Thus, the diporphyrin **10** was further derivatized by an aromatic nucleophilic substitution reaction with isopropylamine[11] to give **13**, which was subsequently metalated with Zn(OAc)$_2$ to form diporphyrin **14**. Gratifyingly, crystals of **14** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane vapor into a solution of **14** in CH$_2$Cl$_2$, and the directly meso-β-linked diporphyrin structure was determined unambiguously (Figure 3).[9] The two porphyrin rings are connected through a C(meso)−C(β) bond of 1.507 Å and a dihedral angle of 69.9°. The formation of directly meso-β-linked diporphyrin **4** from **1** is interesting from the viewpoint of "chemical connections" in the porphyrinoid family.[7] A possible route to **4** may start from the putative NNNN-coordinated dinickel(II) complex **9** (see the Supporting Information), although this complex was not detected in the reaction mixture. The formation of two aromatic porphyrin segments is probably a driving force for this rearrangement.

Finally, the structure of **5** was determined by X-ray diffraction analysis.[9] The basic octaphyrin(1.1.1.1.1.1.1.1) connection is preserved, but two pentafluorophenyl-substituted methine carbon atoms adjacent to pyrrole ring D are both replaced by carbonyl groups (Figure 4). In line with the structure, the HR-ESI-TOF mass spectrum showed the parent ion signal of **5** at $m/z = 1762.9780$ ($[M{+}\mathrm{H}]^+$, calcd for $C_{76}H_{19}N_8F_{30}Ni_2O_2 = 1762.9815$), which was lower by 300 mass units than that of the dinickel(II) complex of [36]octaphyrin. The two nickel(II) ions are each bound to the three nitrogen atoms of the pyrrole rings and the oxygen atoms of the resultant carbonyl groups in a square-planar manner. Pyrrole rings B, C, D, E, and F are almost coplanar, with a small mean plane deviation of 0.191 Å, while pyrrole ring H is significantly tilted relative to the above-mentioned plane with a dihedral angle of 69.0°. Pyrrole rings D and H, which do not coordinate to the nickel(II) ion, are both amino types. These NH protons are hydrogen bonded with a water molecule in the crystal. The ^{19}F NMR spectrum of **5** is simple, exhibiting six signals for the *ortho*-fluorine atoms, six signals for the *meta*-fluorine atoms, and three signals for the *para*-fluorine atoms, thus indicating an averaged C_s-symmetric structure and the restricted rotation of the meso substituents. The ^{1}H NMR spectrum exhibited eight pyrrolic β-CH signals in the range $\delta = 7.21$–5.81 ppm and two pyrrolic NH signals at $\delta = 11.7$ and 15.3 ppm. The oxygen atoms at the meso positions are considered to be derived from residual water in acetonitrile, since the corresponding experiment in the presence of $H_2{}^{18}O$ yielded the ^{18}O-substituted product (see the Supporting Information). The observed dearylative oxygenation is rare and its mechanism is unclear at present, but may involve the nucleophilic attack of water at the meso position followed by the elimination of a

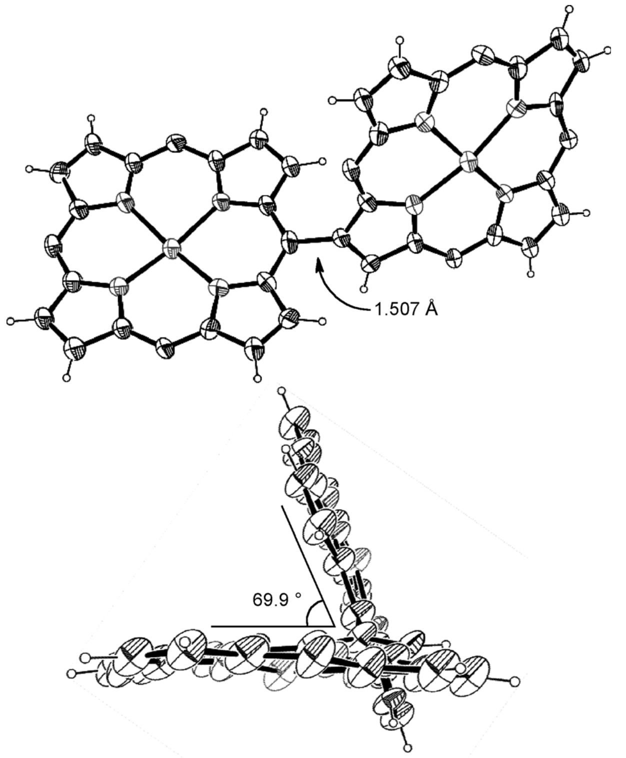


Figure 3. Crystal structure of **14**. Top: top view. Bottom: side view. The thermal ellipsoids are scaled to the 20% probability. meso-Aryl substituents and solvent molecules are omitted for clarity.

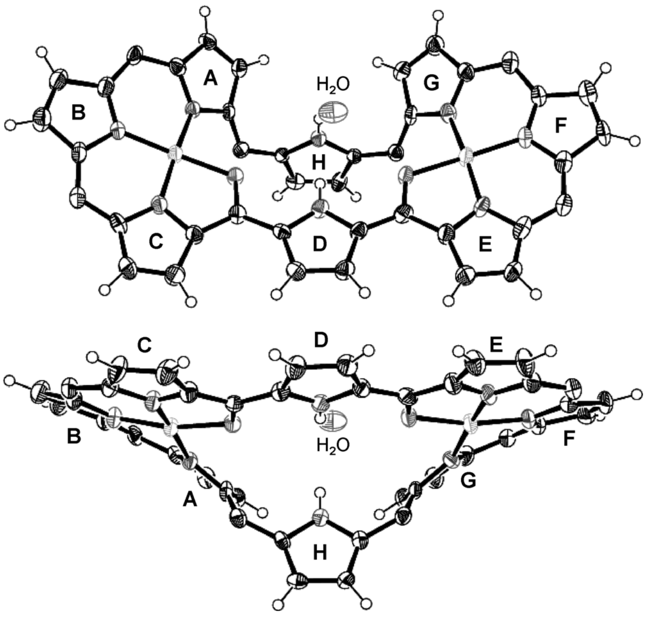


Figure 4. Crystal structure of **5**. Top: top view. Bottom: side view. The thermal ellipsoids are scaled to the 50% probability. meso-Aryl substituents and solvent molecules are omitted for clarity.

pentafluorophenyl group. In fact, when the nickel(II) metalation was conducted with 100 equivalents of [Ni(acac)$_2$] under strictly anhydrous conditions, the formation of **5** was almost suppressed, and the yields of **2** and **4** were increased to 14 and 32%, respectively. Under these conditions, the formation of **3** was also suppressed, probably because of the enhanced second nickel(II) metalation.

Taken together, the nickel(II)-metalation products of **1** can be understood as follows: 1) the nickel(II) metalation can occur at either an NNNC or NNNN ligand, depending on the conformation of **1**, to produce **2** and postulated intermediates **7** and **9**, respectively, 2) the NNNC-coordinated dinickel(II) complex **2** is chemically stable and thus accumulates, 3) the putative NNNN-coordinated mono- and dinickel(II) complexes **7** and **9** undergo further reactions to form **3**, **4**, and **5**. The formation of **3** and **4** are plausibly driven by the transannular electronic interactions enhanced by nickel(II) metalation. The present results underscore the potential of expanded porphyrins for undergoing unprecedented reactions, hence encouraging further study to explore new "chemical connections" in the porphyrinoid world. Further investigation is currently underway in our laboratory.

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Keywords: diporphyrin · metalation · octaphyrin · porphyrinoids · rearrangement

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[9] a) Crystallographic data for **3**: $C_{88}H_{16}F_{40}N_8Ni\cdot(\text{heptane})\cdot(CHCl_3)_3$ ($M_r = 2459.08$), triclinic, space group $P\bar{1}$ (no. 2), $a = 14.9820(12)$, $b = 18.6023(15)$, $c = 20.7235(16)$ Å, $\alpha = 99.544(2)$, $\beta = 109.7090(10)$, $\gamma = 113.2920(10)°$, $V = 4685.7(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.743\ g\,cm^{-3}$, $T = 90(2)$ K, $R_1 = 0.0761$ ($I > 2\sigma(I)$), $R_w = 0.2359$ (all data), GOF = 1.022; b) crystallographic data for **5**: $C_{76}H_{18}F_{30}N_8Ni_2O_2\cdot(\text{toluene})_2\cdot(\text{water})$($M_r$=1962.67), orthorhombic, space group P_{bcn} (no. 61), $a = 19.080(3)$, $b = 39.277(5)$, $c = 20.860(3)$ Å, $V = 15\,633(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.668\ g\,cm^{-3}$, $T = 123(2)$ K, $R_1 = 0.0870$ ($I > 2\sigma(I)$), $R_w = 0.1869$ (all data), GOF = 1.024; c) crystallographic data for **14**: $C_{103}H_{71}F_{28}N_{15}Zn_2\cdot(\text{hexane})_{0.42}\cdot(CH_2Cl_2)_{0.58}$ ($M_r = 2261.06$), triclinic, space group $P\bar{1}$ (no. 2), $a = 13.9016(4)$, $b = 19.0975(5)$, $c = 19.8416(6)$ Å, $\alpha = 110.6778(13)$ $\beta = 101.9521(14)$, $\gamma = 90.9518(11)°$, $V = 4798.3(2)$ Å^3, $Z = 2$, $<\text{Grr}>_{calcd} = 1.565\ g\,cm^{-3}$, $T = 93(2)$ K, $R_1 = 0.0984$ ($I > 2\sigma(I)$), $R_w = 0.3068$ (all data), GOF = 1.077. CCDC 836925 (**3**), 836924 (**5**), and 836923 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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