# Lanthanide(II) and -(III) Porphyrinogens − Rational Synthesis and Derivatisation of Mononuclear, Alkali-Metal-Free Lanthanide(II) and -(III) *meso*-Octaalkylporphyrinogen Complexes

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**Keywords:** Lanthanides / Macrocyclic ligands / Metallocenes / Porphyrinoids / Samarium

Modifying the porphyrinogen framework in lanthanide porphyrinogen complexes by *trans*-*N*,*N*′-dimethylation results in $Sm^{II}$ and $Sm^{III}$ derivatives that are remarkably simple in structure and formulation, and are amenable to highly controllable further reaction chemistry. The $Sm^{II}$ bis(tetrahydrofuran) adduct, $Sm^{III}$ chloride and bis(trimethylsilyl)amide complexes have been synthesised and characterised by elemental analysis, $^1H$ and $^{13}C$ NMR spectroscopy and X-ray crystal structure determinations.

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## Introduction

The metallo-*meso*-octaalkylporphyrinogen complexes of the lanthanides reported to date are structurally diverse, and their unique reactivities have highlighted a range of important potential applications in the area of small-molecule activation and catalysis.[1] The reactivities of $Sm^{II}$ and $Sm^{III}$ complexes have been noted in some cases to exceed those of decamethylsamarocenes, which to date have been the mainstay of organolanthanide-based synthetic transformations and catalysis. Invariably, these complexes have featured (i) the retention of alkali metals arising from metathetical exchange synthetic pathways, and/or (ii) two lanthanides binding within the macrocyclic cavity. These features are clearly the result of the four acidic N−H moieties of the pyrrole units and/or the divergent nature of the macrocyclic cavity in the 1,3-alternate conformation typically adopted when binding large metals by an $\eta^5{:}\eta^1{:}\eta^5{:}\eta^1$- binding mode. The inclusion of alkali metals in these complexes can, in some cases, be seen to have added to the stabilising framework that led to the trapping of reactive species such as $(N_2)^{2-}$, $(N_2)^{4-}$, $(C_2)^{2-}$ and $(C_2H_4)^{2-}$ in stoichiometric reactions.[1b−1h] However, the incorporation of alkali metals (and halides) is generally regarded as limiting the catalytic utility of organolanthanides, as it can lead to the occupation of vital metal coordination sites or, at least, to poorly defined catalytically active species. Significantly, lanthanoid complexes based on tetraanionic porphyrinogens have also proven difficult to derivatise. Indeed, the reaction of the $Y^{III}$ complex $[(THF)_2LiY(L)\cdot LiOEt]$ (where $H_4L$ = *meso*-octaethylporphyrinogen **1**) with lithium reagents led to loss of yttrium from the porphyrinogen.[1a] A single $Sm^{III}$ alkyl complex in which the alkyl group is not involved in bridging with an alkali metal is known, $[(THF)_4(Cl)Li_3(\mathbf{1}-4H)SmMe]$, but its subsequent chemistry is influenced by the incorporation of the alkali metal.[1i] Thus, access to "simple" lanthanocene analogues of the archetypical motif $(L)_nLn^{II/III}R$(solvent) [where $(L)_n$ = a dianionic porphyrinogen-containing unit and R = solvent, alkyl, amide, hydride etc.], often implied in catalysis, has not been realised in the porphyrinogen chemistry of the lanthanide metals. Perhaps then, the full potential of metalloporphyrinogen complexes has not been established in the absence of such desired complexes?

We recently reported that improved structural control is possible through *N*-alkylation of the porphyrinogens by the synthesis of the dipotassium complex **3** derived from *trans*-*N*,*N*′-dimethyl-*meso*-octaethylporphyrinogen **2**.[2] The schematic representation of **3** highlights the steric restraints that the *N*-methyl substituents impose on the macrocyclic cavity in the 1,3-alternate macrocyclic conformation that allows only one potassium cation to bind within the cavity. We report herein the rational synthesis of the first mononuclear, alkali-metal-free metalloporphyrinogens of a lanthanide(II) and -(III) metal, derived from the modified porphyrinogen **2** by metathetical exchange reactions and subsequent derivatisation involving oxidation and halide/amide exchange.

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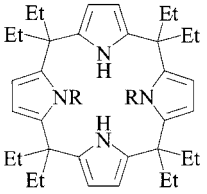
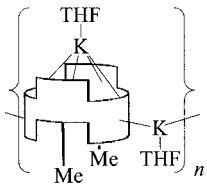


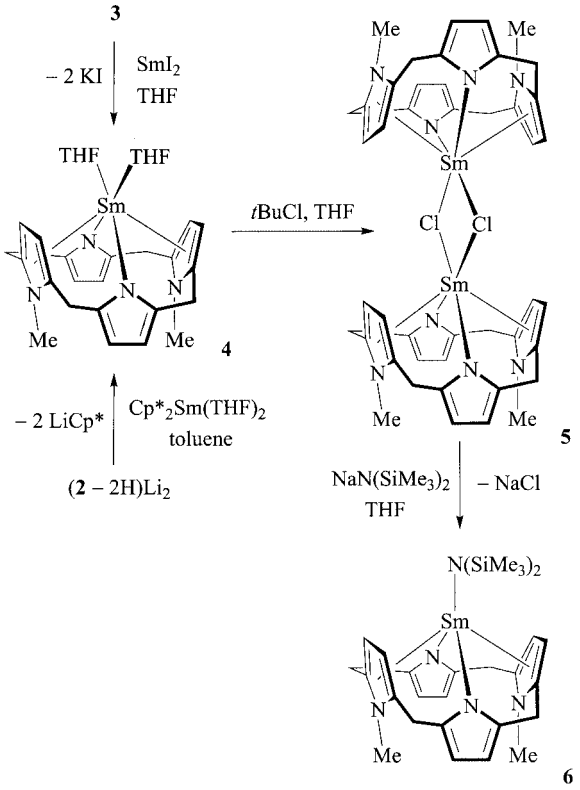
**1** (R = H), **2** (R = Me)



**3**

## Results and Discussion

Complexes **4**−**6** were synthesised according to the route shown in Scheme 1. The reaction of **3** with $SmI_2$ in THF afforded a brown solution of the $Sm^{II}$ complex **4**, which was isolated in high yield as dark purple/brown crystals. Complex **4** was also prepared in low yield by the reaction of the dilithium complex derived from **2**, $(\mathbf{2}-2H)Li_2$, with $[(\eta^5\text{-}C_5Me_5)_2Sm(THF)_2]$ in toluene, where the driving force is presumably the precipitation of the insoluble $[\{(\eta^5\text{-}C_5Me_5)Li\}_n]$. The $Sm^{II}$ complex **4** was oxidised to the $Sm^{III}$ chloride **5** by reaction with *t*BuCl in THF/toluene, which precipitates nearly quantitatively as a brown/red solid, that could be recrystallised from toluene. The $Sm^{III}$ amide **6** was prepared by the reaction of **5** with sodium bis(trimethylsilyl)-amide in THF and isolated as orange crystals in high yield from a solution of the same color. Complexes **4**−**6** were characterised by $^1H$ and $^{13}C$ NMR spectroscopy,[3] microanalysis and X-ray crystal structure determinations.[4]




Scheme 1. Synthesis of $Sm^{II}$ and $Sm^{III}$ complexes (*meso*-octaethyl groups omitted for clarity)

The $^1H$ NMR chemical shifts of **4** and **6** were highly influenced by the paramagnetic shift influence of the $Sm^{II/III}$ centers, covering a wide chemical shift range of 42.19 to −21.07 ppm for the $Sm^{II}$ complex **4** at 25 °C, and a narrower range of 6.10 to −0.17 ppm for the $Sm^{III}$ complex **6** at 25 °C. Variable-temperature $^1H$ NMR experiments established rigid macrocycle conformations for **4** and **6** in toluene, on the basis of the Curie−Weiss Law being obeyed in the temperature range −50 to 50 °C. The $^{13}C$ NMR chemical shifts of **4** and **6** revealed only slight paramagnetic shift influences. The poor solubility of **5** prevented NMR spectroscopic studies.

The crystal structures of **4**−**6** (Figures 1, 2, and 3), show the Sm centers bound within the macrocyclic cavities by $\eta^5$:$\eta^1$:$\eta^5$:$\eta^1$- binding modes. Of particular note are the eclipsed $\eta^5$-interactions to the neutral *N*-methylpyrrole units, with σ-contacts being through the anionic pyrrolide units. $\eta^5$-Bound neutral pyrrole units are uncommon,[5] and unknown in lanthanide chemistry. They are a forced constraint, resulting from either the macrocyclic ring strain or steric interference of the *N*-methyl substituents, which is likely to feature in other bonding situations in which large-radii metals are hosted within the macrocycle. The macrocycle is formally a 16-electron donor, 4 greater than the bis-(cyclopentadienyl) ligand set. The Sm−centroid distance in **4** [$2.75_6$ Å] is longer than in **5** and **6** [$2.63_4$ and $2.65_3$ Å, respectively], reflecting the relative sizes of $Sm^{II}$ and $Sm^{III}$. The ensuing conformational changes to the macrocycle are mainly restricted to the "metallocene bend angle", being $154.4_3°$ in **4** and in the range $160.0_8-162.3_1°$ in **5** and **6** (N−Sm−N angles are within 120.5 ± 1° for **4**−**6**). The $Sm^{III}$ centers in **5** and **6** reside deeper in the macrocyclic cavities as a result. The Sm−N distances in **4**−**6** also correlate with the Sm oxidation states and are greatly influenced (± 0.13 Å) by the details of the chloride and amide coordination in **5** and **6** (vide infra). The metallocene bend angle in **4** is much larger than in $[(\eta^5\text{-}C_5Me_5)_2Sm(THF)_2]$ ($136.7_0°$),[6] but the small β-pyrrole H substituents in **4** effectively result in a wider coordination arc available for ligand binding in the region of the $\eta^5$- bound pyrrole rings, relative to the samarocene. Conversely, the O−Sm−O angle in **4**, 70.13(6)°, is smaller than in $[(\eta^5\text{-}C_5Me_5)_2Sm(THF)_2]$, 82.7(4)°, indicating reduced space for additional ligand binding in the region of the σ-bound pyrrolide units, compared with the samarocene.

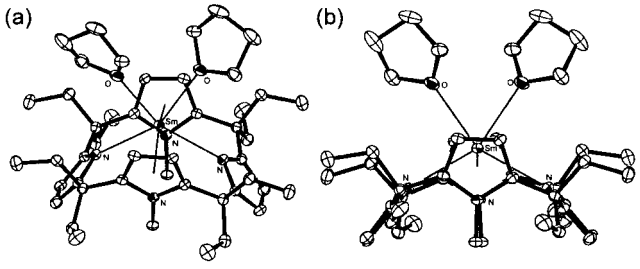



Figure 1. Structure of **4**: (a) general view of **4**, (b) "side" view of **4**

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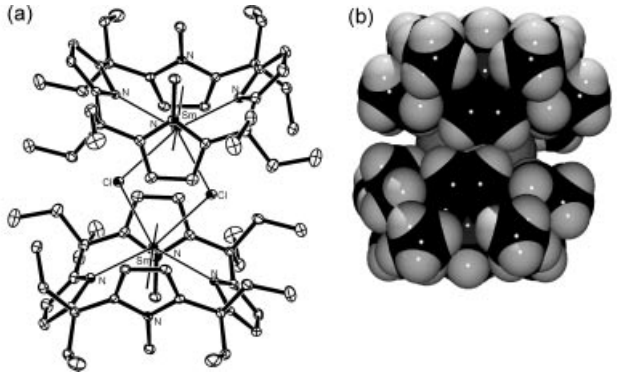


Figure 2. Structure of **5**: (a) general view of **5**, (b) space-filling "side" view of **5**

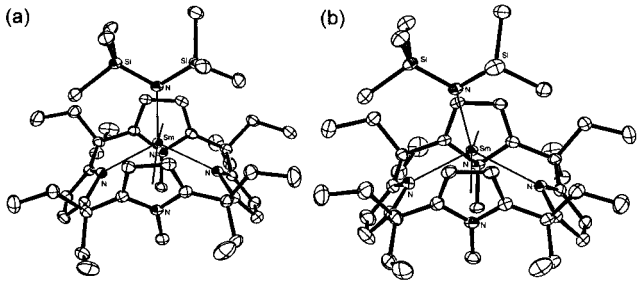


Figure 3. Structure of **6**: (a) general view of a molecule of **6** with a symmetrically bound amide, (b) general view of a molecule of **6** with a "tilted" amide

Both single- and two-fold additional coordination is known for $Sm^{II}$ and $Sm^{III}$ complexes of tetraanionic porphyrinogens, and is seemingly influenced by conformational changes in the macrocycle caused by additional binding of alkali metals and counter-anions in the macrocyclic cavity.[1] Complexes **4** and **5** feature two-fold coordination through THF molecules and two $\mu_2$-Cl ligands, respectively, and **6** displays single-fold coordination through the amide ligand (see Figures 1, 2, and 3).

The Sm−O distances in **4** [2.655(1) Å] are crystallographically equivalent. The Sm−Cl distances in **5** are markedly different [2.7511(5) and 2.9290(5) Å], which is a consequence of the steric interactions between the macrocycles [see Figure 2(b)]. A long terminal Sm−Cl bond [3.15(2) Å] has been reported for a porphyrinogen complex.[1b] The disparate Sm−N(pyrrolide) distances in **5** [2.488(2) and 2.538(2) Å], are also a consequence of the asymmetrically bound chlorides, the former "*trans*" to the short Sm−Cl bond. Decamethylsamarocene(III) chloride forms both a monomeric THF adduct, $[(\eta^5\text{-}C_5Me_5)_2Sm(Cl)(THF)]$, and a more "open" Cl-bridged trimer, $[\{(\eta^5\text{-}C_5Me_5)_2Sm(\mu\text{-}Cl)\}_3]$,[7] whereas non-peralkylated samarocenes, e.g. $[\{[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2Sm(\mu\text{-}Cl)\}_2]$, dimerise by symmetrical $(\mu_2\text{-}Cl)_2$-bridging (Sm−Cl = 2.758(2) and 2.771(2) Å].[8]

In addition to the coordination of the Sm center through the nitrogen center of the amide in **6**, one of the three crystallographically independent molecules exhibits a highly "tilted" amide ligand, diagnostic of a putative weak agostic interaction involving a NSiMe unit, [see Figure 3(b)]. The relevant parameters are: Sm···N 2.314(2), Sm···Si 3.3856(7), Sm···C 3.338(3) Å, Sm−N−Si 113.3(1), N−Si−C 109.5(1)°, and, for the opposite NSiMe unit: Sm···Si 3.6762(9), Sm···C 4.059(3) Å, Sm−N−Si 129.94(9), N−Si−C 114.8(1)°. The Sm···γ-methyl distance is substantially longer than in bona fide agostic interactions of lanthanocene amides featuring a single agostic interaction from a tilted amide, e.g. 2.901(8) Å for $[\{\eta^5,\eta^5\text{-}C_5H_4Si(Me)_2C_{13}H_8\}DyN(SiMe_3)_2]$, but this should be placed in the context of the shorter Dy−N distance of 2.207(5) Å relative to **6**.[9] γ-Agostic interactions in "symmetrically bound" lanthanocene amides where two NSiMe units are inclined towards the metal center, e.g. $[(\eta^5\text{-}C_5Me_5)_2SmN(SiMe_3)_2]$,[10] feature NSiMe···Sm geometries (Sm···N 2.301(3), Sm···Si $3.40_2$, Sm···C $3.24_9$ Å, Sm−N−Si $115.7_5$, N−Si−C $106.3_5$°) similar to those for the silyl group nearest the Sm center in the tilted amide of **6**. Steric interactions between the amide and the macrocycle (absent in lanthanocene amides — recall the discussion of the small O−Sm−O angle in **4**) may be limiting further development of agostic interactions in **6**, or indeed the higher coordination number from the modified porphyrinogen may negate the tendency for the agostic interaction. The putative weak agostic interaction in **6** is "*trans*" to a closely bound σ-bound pyrrolide [Sm−N 2.470(2) Å] [cf. opposite counterpart, 2.604(2) Å]. In comparison, asymmetry is absent in molecules of **6** having non-tilted amides [2.514−2.543(2) Å]. We have yet to delineate the steric and electronic effects on the structure of **6**, and the tendency for the agostic interaction remains an important matter of discussion, of relevance to the reactivity of lanthanide(II) and -(III) complexes of the modified porphyrinogen **2**.

The preparation of the $Sm^{II}$ and $Sm^{III}$ complexes in this report has demonstrated that improved composition, structure and reactivity control is achievable by efforts to match the charge (in its deprotonated form) and steric restraints of a modified porphyrinogen to the metal ions under study. The "simplicity" of the prepared complexes makes this clear. Despite substantial electronic differences that could be expected to exist between the modified porphyrinogen complexes **4**−**6** and both lanthanocenes and unmodified porphyrinogen complexes (viz. $\eta^5$-interactions to neutral pyrrole units) we have demonstrated that imperative structure and reactivity patterns relevant to catalytic applications are common to both systems. A rigid macrocycle conformation in solution for **6** is evident from NMR experiments, thus the macrocycle promises to be an extremely well-defined non-participative ligand for subsequent reactivity studies and applications for which "$(\eta^5\text{-}C_5Me_5)_2Ln^{II/III}R$" systems are utilised. We are continuing synthetic, reactivity and computational studies of this new class of "metallocenes" and related modified porphyrinogen complexes.

## Experimental Section

**Compound 4:** Potassium metal (0.16 g, 4.1 mmol) was added to a solution of **2**[11] (1.14 g, 2.00 mmol) in THF (80 mL) and refluxed

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for 6 h. $SmI_2$ (0.10 M solution in THF, 20 mL, 2.0 mmol) was added dropwise to the crude stirred slurry of **3** over 20 min and allowed to stir for 12 h. The reaction mixture was filtered and the purple solution concentrated in vacuo to ca. 20 mL, giving dark purple/brown crystals (1.38 g, 80 %). $^1$H NMR (399.694 MHz, [D$_6$]benzene, 25 °C): δ = −21.07 (m, 4 H, $CH_2$), −8.15 (t, 12 H, $CH_3$), −4.89 (m, 4 H, $CH_2$), 0.93 (t, 12 H, $CH_3$), 1.12 (s, 4 H, =CH, pyrA), 1.26 (m, 4 H, $CH_2$), 4.51 (br. s, 8 H, $CH_2$, THF), 5.17 (m, 4 H, $CH_2$), 10.83 (br. s, 8 H, $OCH_2$, THF), 19.22 (s, 4 H, =CH, pyrB), 42.91 ppm (s, 6 H, $NCH_3$) ppm. $^{13}$C NMR (100.512 MHz, [D$_6$]benzene, 25 °C): δ = 10.8 (2 × $CH_3$), 21.3 ($CH_2$), 32.0 ($CH_2$), 44.3 (=CH, pyrA), 50.0 ($CEt_2$), 68.2 (=CH, pyrB), 108.7 (=CR, pyrB), 188.0 ppm (=CR, pyrA) ppm. $C_{46}H_{70}N_4O_2Sm$ (861.43): calcd. C 64.14, H 8.19, N 6.50; found C 63.98, H 8.27, N 6.43.

**Alternative preparation of compound 4:** *n*BuLi (6.0 mL, 9.6 mmol) was added to a stirred solution of **2** (2.0 g, 3.5 mmol) in toluene (60 mL) at 0 °C. A colorless solid immediately formed and the mixture was left to stir for 6 h at 50 °C. After being allowed to settle at 20 °C, the solvent was removed by cannula, the colorless solid washed with hexane (20 mL) and dried in vacuo. Toluene (25 mL) was added to a stirred mixture of $[(\eta^5\text{-}C_5Me_5)_2Sm(THF)_2]$[6] (400 mg, 0.718 mmol) and the above-described crude lithium reagent (416 mg, 0.714 mmol) at 20 °C. The mixture was then heated at 50 °C for 4 h to give a dark purple/brown solution. The solution was filtered to remove a colorless solid and the toluene removed in vacuo to give a purple/brown solid. Recrystallisation from THF gave dark purple/brown crystals (163 mg, 27 %) that, by $^1$H NMR spectroscopy, were identical to the product prepared by the alternative route.

**Compound 5:** A solution of *t*BuCl (0.093 g, 1.0 mmol) in THF (10 mL) was added to a stirred solution of **4** (0.86 g, 1.0 mmol) in toluene (50 mL) dropwise over 5 minutes and left to stir for 1 h. The resulting pale brown solid was filtered, washed with toluene and dried in vacuo (0.68 g, 91 %). MS (EI): *m*/*z* (%) = 755 (14) [$M^+$], 726 (64) [$M^+$ − Et], 568 (33) [$\mathbf{2}^+$], 539 (100) [$\mathbf{2}^+$ − Et]. $C_{38}H_{54}ClN_4Sm$ (752.68): calcd. C 60.64, H 7.23, N 7.44; found C 60.68, H 7.18, N 7.39.

**Compound 6:** A solution of *t*BuCl (0.093 g, 1.0 mmol) in THF (10 mL) was added to a stirred solution of **4** (0.86 g, 1.0 mmol) in toluene (50 mL) dropwise over 5 minutes and left to stir for 1 h. $NaN(SiMe_3)_2$ (1.0 M solution in THF, 1.0 mL, 1.0 mmol) was added to the mixture and stirring was continued for 12 h. The solution was filtered and concentrated to ca. 15 mL to give orange crystals (0.64 g, 73 %). $^1$H NMR (399.694 MHz, [D$_6$]benzene, 25 °C): δ = −0.17 (m, 12 H, $CH_3$), 0.75 (m, 12 H, $CH_3$), 0.87 (m, 4 H, $CH_2$), 1.08 (s, 18 H, $CH_3$), 1.37 (m, 4 H, $CH_2$), 1.95 (m, 8 H, $CH_2$), 3.74 (s, 4 H, =CH, pyrMe), 4.87 (s, 6 H, NMe), 6.10 (s, 4 H, = CH, pyr) ppm. $^{13}$C NMR (100.512 MHz, [D$_6$]benzene, 25 °C): δ = 7.9 ($SiCH_3$), 8.1 ($CH_3$), 8.3 ($CH_3$), 23.1 ($CH_2$), 28.7 ($CH_2$), 36.6 ($NCH_3$), 41.7 ($CEt_2$), 100.2 (=CH, pyrMe), 103.5 (=CH, pyr) 139.8 (=CR, pyrMe), 149.9 (=CR, pyr) ppm. $C_{44}H_{72}N_5Si_2Sm$ (877.61): calcd. C 60.22, H 8.27, N 7.98; found C 60.10, H 8.36, N 7.94.

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[3] Full $^1$H and $^{13}$C assignments for **6** were made by gCOSY, gHMBC and gNOESY and VT $^1$H NMR spectroscopy. The *Me*N $^{13}$C resonance of **4** could not be located. A low signal-to-noise ratio caused by paramagnetic line broadening in the gCOSY, gHMQC and gHMBC spectra of **4** did not allow full assignment of $^1$H and $^{13}$C resonances (unique assignment of the pyrrolide and *N*-methylpyrrole units and no conformational information was obtained). Full details of the NMR analyses will be published separately.

[4] Crystallographic data for **4**−**6**: recorded at 123 K (for **4** and **5**) and 150 K (for **6**), with Mo-$K_\alpha$ (0.71073 Å) radiation: **4**: orthorhombic, space group *Pbcn*, *a* = 21.3197(2), *b* = 10.5498(1), *c* = 18.5892(2) Å, *V* = 4181.06(7) Å$^3$, *Z* = 4, *R* = 0.024 for 4197 [$I > 2\sigma(I)$] data and *wR* = 0.069 for 5187 all data; **5**: monoclinic, space group *C*2/*c*, *a* = 19.4523(2), *b* = 13.8795(1), *c* = 26.9726(3) Å, β = 106.1366(4)°, *V* = 6995.37(12) Å$^3$, *Z* = 4, *R* = 0.026 for 6738 [$I > 2\sigma(I)$] data and *wR* = 0.050 for 8572 all data; **6**: triclinic, space group $P\bar{1}$, *a* = 12.1952(7), *b* = 23.2630(10), *c* = 24.728(2) Å, α = 88.925(2), β = 78.125(2), γ = 75.229(2)°, *V* = 6634.0(7) Å$^3$, *Z* = 6, *R* = 0.042 for 41973 [$I > 2\sigma(I)$] data and *wR* = 0.049 for 65461 all data. CCDC 219394−219396 (**4**−**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336033; or deposit@ccdc.cam.ac.uk).

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