Synthesis of Arsenic(V) Octaethylporphyrins and X-ray Crystal Structure of [(OEP)As(Me)(OH)]ClO_4

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[(OEP)As(OH)$_2$]ClO_4 (**4-ClO$_4$**) and [(OEP)As(Ph)(OH)]ClO_4 (**12-ClO$_4$**) are synthesized in good yields by oxidative conversion of (OEP)AsCl (**2**) and (OEP)AsPh (**10**), respectively, with pyridinium tribromide followed by hydrolysis and counteranion exchange. **4-Cl** is converted to [(OEP)As(R)(OH)]ClO_4 (**6-ClO$_4$**, R = Me; **8-ClO$_4$**, R = Et) and [(OEP)As(R)$_2$]X (**7-ClO$_4$**, R = Me; **9-PF$_6$**, R = Et) by the reaction with $(COBr)_2$ followed by treatment with trialkylaluminum (alkyl = Me, Et) and counteranion exchange. The reaction of **6-Cl** with PCl_3 gives the corresponding chloride [(OEP)As(Me)(Cl)]Cl (**13-Cl**), from which [(OEP)As(Me)(OR)]ClO_4 (**14-ClO$_4$**, R = Me; **15-ClO$_4$**, R = Et; **16-ClO$_4$**, R = *i*-Pr), [(OEP)As(Me)(NH-*n*-Bu)]ClO_4 (**17-ClO$_4$**), [(OEP)As(Me)(NH-*p*-$CH_3C_6H_4$)]ClO_4 (**18-ClO$_4$**), and [(OEP)As(Me)(Et)]ClO_4 (**19-ClO$_4$**) are synthesized. These compounds are stable toward air and moisture. The OH protons of [(OEP)As(R)(OH)]Cl (**6-Cl**, R = Me; **8-Cl**, R = Et, **12-Cl**, R = Ph) are acidic enough to generate [(OEP)As(R)(=O)] (**20**, R = Me; **21**, R = Et, **22**, R = Ph) by treatment of a solution of **6-Cl**, **8-Cl**, and **12-Cl** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). **6-Cl**, **8-Cl**, and **12-Cl** are regenerated by treating a solution of **20**, **21**, and **22** with dilute HCl. The first characterization of an arsenic porphyrin 6-ClO_4, by X-ray crystallographic analysis is presented.

Introduction

The porphyrin ligand has been demonstrated to have coordinating ability toward most of the metallic elements.[1,2] Although the main studies have been focused on transition-metal porphyrins, some unique properties of main-group-element porphyrins have attracted recent interest.[3] As for group 15 element porphyrins, photoelectronic properties of Sb(III),[4] Sb(V),[5] and P(V) porphyrin oligomers[6−12] and redox electrochemistry[13−17] have been reported, and some of these compounds have been utilized as photochemical oxygenating reagents.[18−24] Characteristic UV−visible spectra have been observed for the high-valent (V) and the low-valent (III) complexes of group 15 element porphyrins.[3,4,25] It has been concluded that the former porphyrins show normal-type spectra, whereas the latter complexes have *p*-type hyper spectra which are very similar to that of cytochrome P-450,[26,27] although the assignment of these porphyrins has been revised from preliminary reports.[28,29] A number of phosphorus[6−14,30−45] and antimony[13,15,20,24,28,29,46,47]porphyrins have been prepared,

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and some of the compounds have been characterized by X-ray analyses, but only a few papers have been published to claim the synthesis of arsenic porphyrins, and there has been no reliable result on the preparation of arsenic porphyrins. In one report the product is incorrectly assigned[28] and experimental details are not given in one review[3] and only UV−visible data are given in a dissertation.[48] In our preliminary communication, we reported successful synthetic procedures to give arsenic octaethylporphyrins.[49] Here we describe full experimental details for preparations of arsenic(V) porphyrin derivatives and X-ray crystallographic analysis of [(OEP)As(Me)(OH)]ClO_4 (**6-ClO_4**; OEP = octaethylporphyrin(2−)).

Experimental Section

Materials and Measurements. All solvents were dried and distilled prior to use. All reactions were carried out under an argon atomosphere, and subsequent isolation and purification procedures were carried out in air. Melting points were measured with a Yanagimoto micromelting point apparatus and were uncorrected. ^{1}H NMR (400 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^{1}H spectra. UV spectra (λ values in nm) were recorded on a Shimadzu UV-2200 spectrophotometer. Elemental analyses were performed by a Perkin-Elmer 2400 CHN elemental analyzer. Column chromatography was carried out on Merck neutral alumina (No. 1077).

Preparation of [(OEP)As(OH)$_2$]ClO_4 (4-ClO_4). To a solution of $(OEP)H_2$ (100 mg, 0.19 mmol) in dry dichloromethane (10 mL) was added 2,6-lutidine (1 mL) and arsenic trichloride (0.5 mL, 5.94 mmol) at room temperature under Ar. The mixture was stirred at room temperature for 12 h under Ar. Pyridinium tribromide (61 mg, 0.19 mmol) was added to the solution. The mixture was stirred at room temperature for 12 h under Ar. After removal of the solvent and arsenic trichloride *in vacuo*, the residue was dissolved in *dry* dichloromethane (10 mL) and water (10 mL) was added. The mixture was stirred at room temperature for 1 day. Extraction with dichloromethane (10 mL × 2) and removal of the solvent yielded a purple solid, which was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:6:1). After removal of the solvents the residue was dissolved in dichloromethane (20 mL) and the solution was washed with aqueous HCl (pH 4, 20 mL). Counteranion exchange of the resulting [(OEP)As(OH)$_2$]Cl with sodium perchlorate in dichloromethane/acetonitrile (1:1) gave [(OEP)As(OH)$_2$]ClO_4 (**4-ClO_4**; 105 mg, 76%): mp 230−234 °C dec; UV (CH_2Cl_2) λ (log ϵ) 345 (4.21), 401 (5.54), 533 (4.15), 572 (4.16); ^{1}H NMR ($CDCl_3$) −2.88 (s, 2 H), 2.01 (t, 24 H, J = 7.7 Hz), 4.19 (q, 16 H, J = 7.7 Hz), 10.38 (s, 4 H). Anal. Calcd for $C_{36}H_{46}N_4O_6ClAs$: C, 58.34; H, 6.26; N, 7.56. Found: C, 58.05; H, 6.13; N, 7.45.

Preparation of [(OEP)As(Me)(OH)]ClO_4 (6-ClO_4). To a solution of [(OEP)As(OH)$_2$]Cl (75 mg, 0.11 mmol) in dry dichloromethane (5 mL) was added 0.3 mL (2.12 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the residue was dissolved in dry dichloromethane (10 mL). Trimethylaluminum (15% solution in *n*-hexane, 0.76 mL, 1.1 mmol) was added to the solution at 0 °C under Ar. The mixture was refluxed for 3.5 h and was poured into ice. After filtration through Celite, the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with water (20 mL). After removal of the solvent, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:6:1) and the solvent then evaporated. The residue was dissolved in dichloromethane (40 mL), and the solution was washed with aqueous HCl (30 mL, pH 4). Evaporation of the solvent gave [(OEP)As(Me)(OH)]Cl (**6-Cl**, 53 mg, 71%). Counteranion exchange of [(OEP)As(Me)(OH)]Cl with sodium perchlorate gave [(OEP)As(Me)(OH)]ClO_4 (**6-ClO_4**) quantitatively: mp 238−241 °C dec; UV (CH_2Cl_2) λ (log ϵ) 358 (4.47), 411 (5.48), 539 (4.20), 575 (4.06); ^{1}H NMR ($CDCl_3$) −5.62 (s, 3 H), 2.05 (t, 24 H, J = 8.1 Hz), 4.30 (q, 16 H, J = 8.1 Hz), 10.60 (s, 4 H). Anal. Calcd for $C_{37}H_{48}N_4O_5ClAs\cdot CH_2Cl_2$: C, 55.38; H, 6.12; N, 6.80. Found: C, 55.38; H, 6.13; N, 6.61. (OEP)As(Me)(=O) (**20**) was prepared by treatment of a solution of **6-ClO_4** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU): UV (CH_2Cl_2) λ (log ϵ) 351 (4.52), 418 (5.35), 542 (4.12), 576 (3.92); ^{1}H NMR ($CDCl_3$) −6.13 (s, 3 H), 2.02 (t, 24 H, J = 7.7 Hz), 4.22 (q, 16 H, J = 7.7 Hz), 10.45 (s, 4 H).

Preparation of [(OEP)As(Me)$_2$]ClO_4 (7-ClO_4). To a solution of [(OEP)As(OH)$_2$]Cl (135 mg, 0.20 mmol) in dry dichloromethane (30 mL) was added 0.19 mL (1.0 mmol) of oxalyl bromide at room temperature under Ar. The mixture was refluxed for 1 h. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (40 mL). Trimethylaluminum (15% solution in *n*-hexane, 1.0 mL, 1.45 mmol) was added to the solution at 0 °C under Ar. The mixture was refluxed for 1 day under Ar and was poured into ice. After filtration through Celite, the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:12:1) and the solvent then evaporated to give [(OEP)As(Me)$_2$]OH (51 mg, 40%). Counteranion exchange of [(OEP)As(Me)$_2$]OH with sodium perchlorate gave [(OEP)As(Me)$_2$]ClO_4 (**7-ClO_4**) quantitatively: mp >300 °C; UV (CH_2Cl_2) λ (log ϵ) 366 (4.60), 424 (5.45), 551 (4.23), 585 (3.86); ^{1}H NMR ($CDCl_3$) −6.15 (s, 3 H), 2.07 (t, 24 H, J = 7.6 Hz), 4.31 (q, 16 H, J = 7.6 Hz), 10.63 (s, 4 H). Anal. Calcd for $C_{38}H_{50}N_4O_4ClAs\cdot H_2O\cdot CH_2Cl_2$: C, 55.75; H, 6.48; N, 6.67. Found: C, 56.03; H, 6.25; N, 6.46.

Preparation of [(OEP)As(Et)(OH)]ClO_4 (8-ClO_4). To a solution of [(OEP)As(OH)$_2$]Cl (102 mg, 0.15 mmol) in dry dichloromethane (6 mL) was added 0.41 mL (2.90 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the residue was dissolved in dry dichloromethane (10 mL). Triethylaluminum (15% solution in *n*-hexane, 0.83 mL, 1.8 mmol) was added to the solution at 0 °C under Ar. The mixture was stirred at room temperature for 6 h and was poured into ice. After filtration through Celite,

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the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:3:1) and the solvent then evaporated. The residue was dissolved into dichloromethane (40 mL) and the solution was washed with aqueous HCl (30 mL, pH 4). Evaporation of the solvent gave [(OEP)As(Et)(OH)]Cl (29 mg, 28%). Counteranion exchange of [(OEP)As(Et)(OH)]Cl with sodium perchlorate gave [(OEP)As(Et)(OH)]ClO_4 (**8-ClO_4**) quantitatively: mp 233−235 °C dec; UV (CH_2Cl_2) λ (log ϵ) 360 (4.30), 412 (5.28), 539 (3.97), 575 (3.78); ^{1}H NMR ($CDCl_3$) −5.68 (q, 2 H, J = 7.6 Hz), −4.63 (t, 3 H, J = 7.6 Hz), 2.04 (t, 24 H, J = 7.6 Hz), 4.29 (q, 16 H, J = 7.6 Hz), 10.60 (s, 4 H). Anal. Calcd for $C_{38}H_{50}N_4O_5ClAs\cdot 0.5H_2O$: C, 59.88; H, 6.75; N, 7.35. Found: C, 60.00; H, 6.77; N, 7.11. (OEP)As(Et)(═O) (**21**) was prepared by treatment of a solution of **8-ClO_4** with DBU: UV (CH_2Cl_2) λ (log ϵ) 352 (4.56), 420 (5.34), 543 (4.18), 576 (3.96); ^{1}H NMR ($CDCl_3$) −6.20 (q, 2 H, J = 7.3 Hz), −4.91 (t, 3 H, J = 7.3 Hz), 1.97 (t, 24 H, J = 7.3 Hz), 4.20 (q, 16 H, J = 7.3 Hz), 10.37 (s, 4 H).

Preparation of [(OEP)As(Et)$_2$]PF_6 (9-PF_6). To a solution of [(OEP)As(OH)$_2$]Cl (120 mg, 0.18 mmol) in dry dichloromethane (10 mL) was added 0.5 mL (3.50 mmol) of oxalyl bromide at room temperature under Ar. The mixture was refluxed for 1 h. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (10 mL). Triethylaluminum (15% solution in *n*-hexane, 1.0 mL, 2.2 mmol) was added to the solution at 0 °C under Ar. The mixture was refluxed for 1 day under Ar and was poured into ice. After filtration through Celite, the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:12:1) and the solvent then evaporated to give [(OEP)As(Et)$_2$]OH (77 mg, 64%). Counteranion exchange of [(OEP)As(Et)$_2$]OH with potassium hexafluorophosphate gave [(OEP)As(Et)$_2$]PF_6 (**9-PF_6**) quantitatively: mp >300 °C; UV (CH_2Cl_2) λ (log ϵ) 367 (4.64), 428 (5.44), 553 (4.25), 586 (3.81); ^{1}H NMR ($CDCl_3$) −6.27 (q, 4 H, J = 7.3 Hz), −4.98 (t, 6 H, J = 7.3 Hz), 2.06 (t, 24 H, J = 7.6 Hz), 4.33 (q, 16 H, J = 7.6 Hz), 10.64 (s, 4 H). Anal. Calcd for $C_{40}H_{54}N_4F_6PAs\cdot H_2O\cdot 0.5CH_2Cl_2$: C, 55.83; H, 6.60; N, 6.43. Found: C, 55.68; H, 6.42; N, 6.24.

Preparation of [(OEP)As(Ph)(OH)]ClO_4 (12-ClO_4). To a solution of $(OEP)H_2$ (100 mg, 0.19 mmol) in dry dichloromethane (7.5 mL) was added 2,6-lutidine (1.2 mL) and phenylarsenic dichloride[55] (1 g, 4.5 mmol) at room temperature under Ar. The mixture was stirred at room temperature for 12 h under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in dry dichloromethane (10 mL) under Ar. Pyridinium tribromide (61 mg, 0.19 mmol) was added to the solution. The mixture was stirred at room temperature for 12 h under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (10 mL) and water (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:6:1) and the solvent then evaporated. The residue was dissolved in dichloromethane (20 mL), and the solution was washed with aqueous HCl (pH 4, 20 mL). Evaporation of the solvent gave [(OEP)As(Ph)(OH)]Cl (101 mg, 75%). Counteranion exchange of [(OEP)As(Ph)(OH)]Cl with sodium perchlorate gave [(OEP)As(Ph)(OH)]ClO_4 (**12-ClO_4**) quantitatively: mp 224−225 °C dec; UV (CH_2Cl_2) λ (log ϵ) 357 (4.57), 413 (5.45), 539 (4.24), 577 (4.04); ^{1}H NMR ($CDCl_3$) −0.03 (d, 2 H, J = 8.0 Hz), 1.99 (t, 24 H, J = 7.4 Hz), 4.19 (m, 16 H), 4.87 (t, 2 H, J = 8.0 Hz), 5.48 (t, 1 H, J = 8.0 Hz), 10.41 (s, 4 H). Anal. Calcd for $C_{42}H_{50}N_4O_5ClAs\cdot 0.5CH_2Cl_2$: C, 60.49; H, 6.10; N, 6.64. Found: C, 60.37; H, 6.17; N, 6.63. (OEP)As(Ph)(═O) (**22**) was prepared by treatment of a solution of **12-ClO_4** with DBU: ^{1}H NMR ($CDCl_3$) −0.26 (d, 2 H, J = 8.0 Hz), 1.99 (t, 24 H, J = 7.4 Hz), 4.19 (m, 16 H), 4.75 (t, 2 H, J = 8.0 Hz), 5.38 (t, 1 H, J = 8.0 Hz), 10.42 (s, 4 H).

Preparation of [(OEP)As(Me)(OMe)]ClO_4 (14-ClO_4). To a solution of [(OEP)As(Me)(OH)]Cl (50 mg, 0.074 mmol) in dry dichloromethane (5 mL) was added 0.26 mL (3.01 mmol) of PCl_3 at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (5 mL). Dry methanol (0.5 mL) was added to the solution at room temperature under Ar. The mixture was stirred at room temperature for 12 h. After removal of the solvent *in vacuo*, the residue was dissolved in dry dichloromethane (10 mL) and water (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:12:1) and the solvent then evaporated to give [(OEP)As(Me)(OMe)]OH (50 mg, quantitative). Counteranion exchange of [(OEP)As(Me)(OMe)]OH with sodium perchlorate gave [(OEP)As(Me)(OMe)]ClO_4 (**14-ClO_4**) quantitatively: mp >300 °C; UV (CH_2Cl_2) λ (log ϵ) 358 (4.49), 412 (5.46), 539 (4.18), 575 (4.06); ^{1}H NMR ($CDCl_3$) −5.62 (bs, 3 H), −3.35 (s, 3 H), 2.06 (bt, 24 H), 4.30 (bq, 24 H), 10.60 (s, 4 H). Anal. Calcd for $C_{38}H_{50}N_4O_4ClAs\cdot CH_2Cl_2$: C, 55.89; H, 6.25; N, 6.68. Found: C, 55.69; H, 6.36; N, 6.52.

Preparation of [(OEP)As(Me)(OEt)]ClO_4 (15-ClO_4). To a solution of [(OEP)As(Me)(OH)]Cl (54 mg, 0.08 mmol) in dry dichloromethane (5 mL) was added 0.26 mL (3.01 mmol) of PCl_3 at room temperature under Ar. The mixture was stirred for 1 h. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (5 mL). Dry ethanol (0.5 mL) was added to the solution at room temperature under Ar. The mixture was stirred at room temperature for 12 h under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in dry dichloromethane (10 mL) and water (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:12:1) and the solvent then evaporated to give [(OEP)As(Me)(OEt)]OH (49 mg, 90%). Counteranion exchange of [(OEP)As(Me)(OEt)]OH with sodium perchlorate gave [(OEP)As(Me)(OEt)]ClO_4 (**15-ClO_4**) quantitatively: mp 239−242 °C dec; UV (CH_2Cl_2) λ (log ϵ) 357 (4.08), 412 (5.48), 540 (4.17), 576 (4.05); ^{1}H NMR ($CDCl_3$) −5.65 (s, 3 H), −3.83 (q, 2 H, J = 6.6 Hz), −2.76 (t, 3 H, J = 6.6 Hz), 2.04 (bt, 24 H), 4.29 (bq, 16 H), 10.54 (s, 4 H). Anal. Calcd for $C_{39}H_{52}N_4O_5ClAs\cdot 0.5H_2O$: C, 60.35; H, 6.88; N, 7.21. Found: C, 60.58; H, 6.71; N, 6.95.

Preparation of [(OEP)As(Me)(O-*i*-Pr)]ClO_4 (16-ClO_4). To a solution of [(OEP)As(Me)(OH)]Cl (54 mg, 0.08 mmol) in dry dichloromethane (5 mL) was added 0.26 mL (3.01 mmol) of PCl_3 at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (5 mL). Dry 2-propanol (0.5 mL) was added to the solution at room temperature under Ar. The mixture was stirred at room temperature for 12 h under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in dry dichloromethane (10 mL) and water (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:6:1) and the solvent then evaporated to give [(OEP)As(Me)(O-*i*-Pr)]OH (38 mg, 68%). Counteranion exchange of [(OEP)As(Me)(O-*i*-Pr)]OH with sodium perchlorate gave [(OEP)As(Me)(O-*i*-Pr)]ClO_4 (**16-ClO_4**)

quantitatively: mp 237−239 °C dec; UV (CH_2Cl_2) λ (log ϵ) 358 (4.50), 412 (5.50), 538 (4.21), 576 (4.09); ^{1}H NMR ($CDCl_3$) −5.69 (s, 3 H), −4.72 (m, 1 H), −3.16 (d, 6H, J = 5.9 Hz), 2.04 (t, 24 H, J = 7.3 Hz), 4.27 (q, 16 H, J = 7.3 Hz), 10.57 (s, 4 H). Anal. Calcd for $C_{40}H_{54}N_4O_5ClAs\cdot H_2O\cdot CH_2Cl_2$: C, 55.69; H, 6.61; N, 6.33. Found: C, 55.76; H, 6.28; N, 6.50.

Preparation of [(OEP)As(Me)(NH-*n*-Bu)]ClO_4 (17-ClO_4). To a solution of [(OEP)As(Me)(OH)]Cl (54 mg, 0.08 mmol) in dry dichloromethane (5 mL) was added 0.26 mL (3.01 mmol) of PCl_3 at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (5 mL). *n*-Butylamine (0.47 mL, 4.8 mmol) was added to the solution at 0 °C under Ar. The mixture was stirred at room temperature for 12 h. After removal of the solvent *in vacuo* the residue was dissolved in dry dichloromethane (10 mL) and water (20 mL) was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:6:1) and the solvent then evaporated to give [(OEP)As(Me)(NH-*n*-Bu)]OH (47 mg, 82%). Counteranion exchange of [(OEP)As(Me)(NH-*n*-Bu)]OH with sodium perchlorate gave [(OEP)As(Me)(NH-*n*-Bu)]ClO_4 (**17-ClO_4**) quantitatively: mp 229−232 °C dec; UV (CH_2Cl_2) λ (log ϵ) 360 (4.59), 417 (5.37), 543 (4.25), 578 (3.98); ^{1}H NMR ($CDCl_3$) −5.93 (s, 3 H), −4.55 (t, 2 H, J = 7.3 Hz), −2.23 (t, 2 H, J = 7.3 Hz), −1.57 (t, 2 H, J = 7.3 Hz), −0.76 (t, 3 H, J = 7.3 Hz), 2.04 (t, 24 H, J = 7.6 Hz), 4.30 (q, 16 H, J = 7.4 Hz), 10.58 (s, 4 H). Anal. Calcd for $C_{41}H_{57}N_5O_4ClAs\cdot 0.5H_2O$: C, 61.30, H, 7.28; N, 8.71. Found: C, 60.91; H, 7.09; N, 8.42.

Preparation of [(OEP)As(Me)(Et)]ClO_4 (19-ClO_4). To a solution of [(OEP)As(Me)(OH)]Cl (32 mg, 0.047 mmol) in dry dichloromethane (3 mL) was added 0.03 mL (0.35 mmol) of PCl_3 at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the residue was dissolved in dichloromethane (3 mL). Triethylaluminum (15% solution in *n*-hexane, 0.36 mL, 0.78 mmol) was added to the solution under 0 °C under Ar. The mixture was stirred for 2 days at room temperature under Ar and was poured into ice. After filtration through Celite, the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layer was washed with water (20 mL). After the solvent was evaporated, the residue was chromatographed on neutral alumina (benzene/dichloromethane/methanol; 15:6:1) and the solvent then evaporated to give [(OEP)As(Me)(Et)]OH (28 mg, 89%). Counteranion exchange of [(OEP)As(Me)(Et)]-OH with sodium perchlorate gave [(OEP)As(Me)(Et)]ClO_4 (**19-ClO_4**) quantitatively: mp >300 °C; UV (CH_2Cl_2) λ (log ϵ) 367 (4.37), 426 (5.38), 552 (4.22), 585 (3.84); ^{1}H NMR ($CDCl_3$) −6.28 (s, 3 H), −6.20 (q, 2 H, J = 7.3 Hz), −4.98 (t, 3 H, J = 7.3 Hz), 2.04 (t, 24 H, J = 7.3 Hz), 4.30 (q, 16 H, J = 7.3 Hz), 10.62 (s, 4 H). Anal. Calcd for $C_{39}H_{52}N_4O_4ClAs\cdot CH_2Cl_2$: C, 57.46; H, 6.51; N, 6.70. Found: C, 57.49; H, 6.59; N, 6.60.

X-ray Structure Determination of [(OEP)As(Me)(OH)]-ClO_4 (6-ClO_4). Crystal data of the structure determination are given in Table 1. Crystals suitable for X-ray structure determination were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) for data collection. Lattice parameters were determined by least-squares fitting of 31 reflections with 46° < 2θ < 50°. Data were collected with the 2θ/ω scan mode. All data were not corrected for absorption. The structures were solved by a direct method with the SIR 92 program[61] in the Crystan-GM package. Refinement on F was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table 1. Crystallographic Data for [(OEP)As(Me)(OH)]$^+ClO_4^-$ (6-ClO_4)[a]

formula	$C_{37}H_{48}N_4O_5ClAs\cdot CH_2Cl_2$
mol wt	824.12
cryst syst	monoclinic
space group	$P2_1/m$
cryst dimens, mm	0.60 × 0.35 × 0.20
color	violet
habit	plate
a, Å	12.419(4)
b, Å	16.864(4)
c, Å	9.493(3)
α, deg	90
β, deg	106.08(2)
γ, deg	90
V, Å^3	1910.5(9)
Z	2
D_{obs}, D_{calc}, g cm^{-3}	−, 1.43
abs coeff, cm^{-1}	35.655
F(000)	860
radiation; λ, Å	Cu Kα; 1.541 78
temp, °C	23 ± 1
$2\theta_{max}$, deg	130
scan rate, deg min^{-1}	3.0
linear decay, %	
data collected	±h,+k,+l
total no. of data collcd, obsd	3594, 3005 ($I > 4\sigma(I)$)
no. of params refined	269
R, R_w, S	0.087, 0.098, 6.65
max shift in final cycle	0.003
final diff map, max, e Å^{-3}	2.01 (near As)

[a] The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)^2]$, in which $w = 1.0/[(\sigma|F_o|^2 + 0.0003|F_o|^2]$. $R = \Sigma[(||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

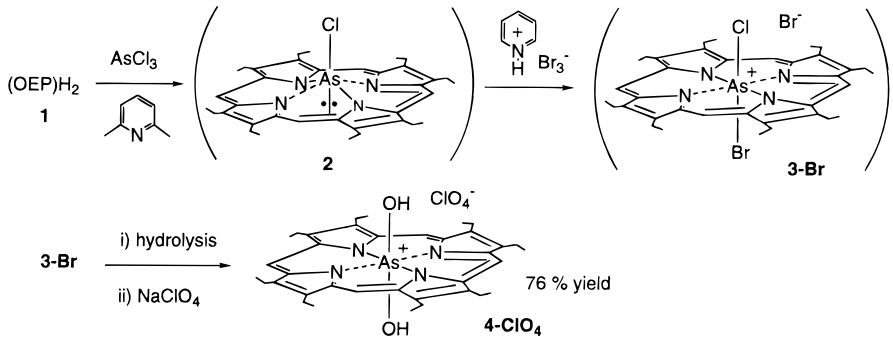
Hydrogen atoms were included in the refinement on calculated positions (C−H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters, except the hydrogen of the OH group in **6-ClO_4**, which could be found on a difference Fourier map; the coordinate was included in the refinement. All the computations were carried out on an Indigo 2 computer.

Results and Discussion

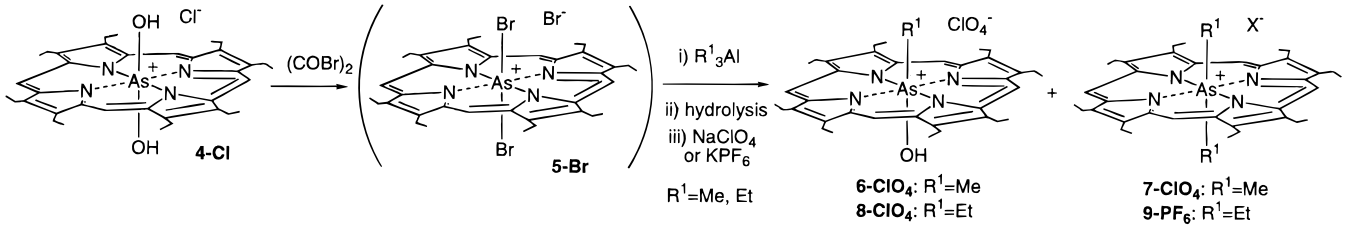
Preparation of [(OEP)As(OH)$_2$]ClO_4 (4-ClO_4). The arsenic octaethylporphyrin [(OEP)As(OH)$_2$]OH (**4-OH**) has been reported to be prepared by the reaction of (OEP)H_2 (**1**) with $AsCl_3$ in refluxing pyridine followed by air oxidation of the resultant arsenic(III) complex (OEP)AsCl (**2**).[48] However, elemental analyses, yields, and spectroscopic data except for UV−vis data have not been reported.[3,48] Recently, Brothers and co-workers re-examined the preparation of arsenic porphyrins by use of tetra-*p*-tolylporphyrin ((TTP)H_2) with $AsCl_3$, AsI_3, and As_2O_5 under similar conditions but resulted in failure.[46] Our similar attempt to insert an arsenic atom into the porphyrin ligand by the reaction of (OEP)H_2 (**1**) with $AsCl_3$ in dichloromethane in the presence of 2,6-lutidine, which was shown to be superior to pyridine in the insertion reaction of antimony tetraphenylporphyrin,[15] indicated that (OEP)AsCl (**2**) was clearly formed, on the basis of the characteristic UV−vis spectrum.[3] However, the arsenic(III) porphyrin was very unstable toward hydrolysis/oxidation in air and treatment with aqueous hydrogen peroxide. Only a trace amount of [(OEP)As-(OH)$_2$]Cl (**4-Cl**) was obtained in both cases, and almost all **2** was demetalated to afford (OEP)H_2 in the reaction with air oxidation and with hydrogen peroxide. We thought that **2** was reluctant to be oxidized by air, and the strong nucleophilicity of hydrogen peroxide should be the reason for the demetalation. Our new synthetic approach for the preparation of arsenic porphyrins is

(50) Kajigaeshi, S.; Kakinami, T.; Okamoto, T.; Nakamura, H.; Fujikawa, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4187.

Scheme 1



Scheme 2



based on oxidative conversion of unstable arsenic(III) porphyrins into arsenic(V) complexes by use of less-nucleophilic halogenating reagents. Group 15 element porphyrins in a higher oxidation state (V) should be much more stable than those in a lower one (III).

$Hpy^+Br_3^-$, $NMe_3(CH_2Ph)^+Br_3^-$,[50] *N*-bromosuccinimide, and *N*-chlorosuccinimide were chosen as the oxidizing reagents for (OEP)AsCl (**2**). Each reagent was added to the dark brown solution of **2**, which was obtained by the reaction of **1** with $AsCl_3$ in dichloromethane in the presence of 2,6-lutidine at room temperature for 12 h. The color of the solution changed to bright purple. After hydrolytic treatment with dilute HCl the reaction mixture was examined by ^{1}H NMR. The reactions with $Hpy^+Br_3^-$ and $NMe_3(CH_2Ph)^+Br_3^-$ showed good results, giving almost entirely [(OEP)As(OH)$_2$]Cl (**4-Cl**). Some other unidentified compounds in addition to **4-Cl** were observed in the reaction with *N*-bromosuccinimide and *N*-chlorosuccinimide. **4-Cl** was finally isolated in 76% yield after the reaction of **2** with an equimolar amount of $Hpy^+Br_3^-$ was carried out at room temperature, followed by hydrolytic treatment with the resultant [(OEP)As(Cl)(Br)]Br (**3-Br**) (Scheme 1). **4-Cl** was stable to column chromatography. The characterization of **4-ClO$_4$** was carried out by elemental analysis after counteranion exchange of **4-Cl**.

Preparation of [(OEP)As(Me)(OH)]ClO$_4$ (6-ClO$_4$), [(OEP)As(Me)$_2$]ClO$_4$ (7-ClO$_4$), [(OEP)As(Et)(OH)]-ClO$_4$ (8-ClO$_4$), [(OEP)As(Et)$_2$]ClO$_4$ (9-ClO$_4$), and [(OEP)As(Ph)(OH)]ClO$_4$ (12-ClO$_4$). With **4-Cl** in hand arsenic porphyrins bearing arsenic−carbon σ bonds were prepared. Porphyrins bearing metal−carbon bonds have attracted intense interest in relation to porphyrins with iron−carbon bonds, which are intermediates in the metabolism of cytochrome P-450 complexes.[51−54]

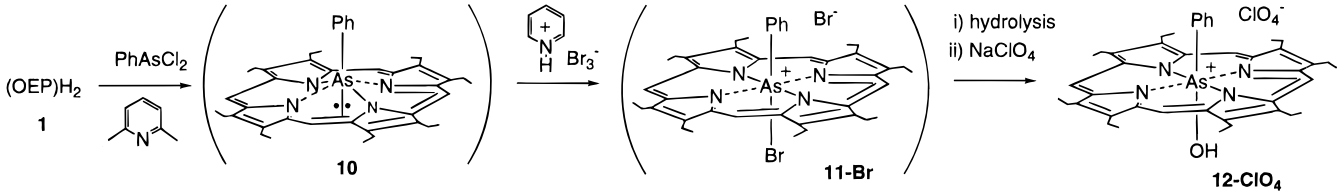
The synthesis of arsenic porphyrins bearing arsenic−carbon σ bonds could be carried out by similar procedures reported by us for antimony and phosphorus porphyrins.[15,45,47] The reaction of **4-Cl** with oxalyl bromide gave moisture-sensitive [(OEP)As(Br)$_2$]Br (**5-Br**), which was treated *in situ* with excess trimethylaluminum in dichloromethane under reflux for 3.5 h. [(OEP)As(Me)(OH)]ClO$_4$ (**6-ClO$_4$**) was obtained as the sole product in 71% yield after counteranion exchange (Scheme 2). The extended reaction time in the reaction of **5-Br** with trimethylaluminum to 1 day yielded the dimethylated product [(OEP)As(Me)$_2$]OH (**7-OH**) in 40% yield. The ^{1}H NMR spectrum of **6-ClO$_4$** showed a characteristic methyl signal at very high field (δ −5.62) due to the large ring current effect of the porphyrin nucleus. The chemical shifts were comparable to those (δ −6.10 and −5.74) for [(OEP)Sb(Me)(OH)]PF$_6$[47] and [(OEP)P(Me)(OH)]PF$_6$,[45] respectively.

Similar procedures were applied for the preparation of [(OEP)As(Et)(OH)]Cl (**8-Cl**); however, [(OEP)As(Et)$_2$]-OH (**9-OH**) was also formed accompanied by **8-Cl**. **8-Cl** was obtained in 28% yield, together with a 20% yield of **9-OH** by the reaction of **5-Br** with triethylaluminum in dichloromethane at room temperature for 6 h. In refluxing dichloromethane for 1 day, only **9-OH** was obtained in 64% yield.

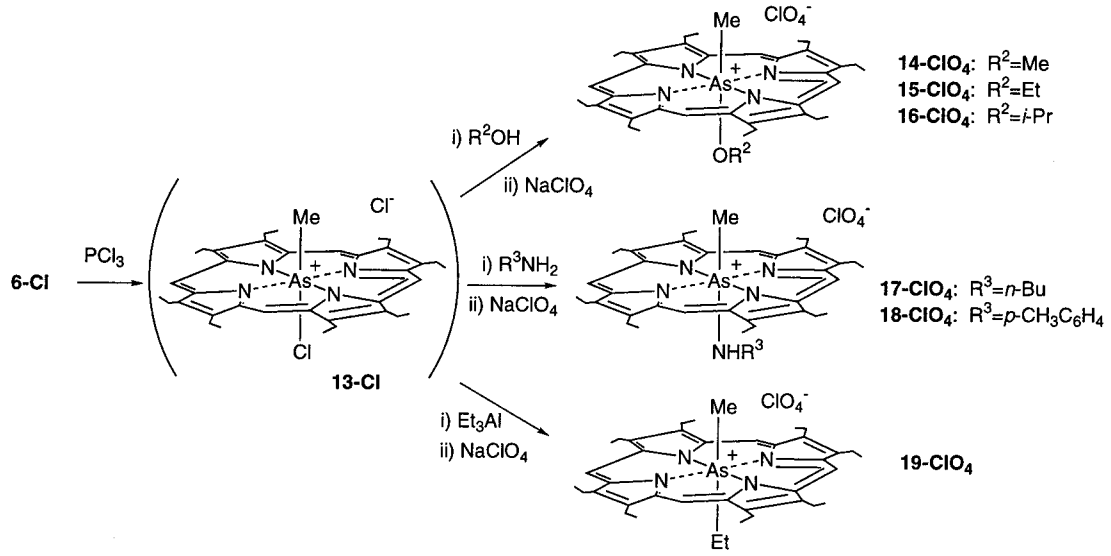
In order to prepare arsenic porphyrins bearing an arsenic−phenyl bond, the use of phenylarsenic dichloride for the reaction with (OEP)H$_2$ (**1**) was found to be more convenient than the use of commercially unavailable triphenylaluminum for the reaction with **5-Br**. Phenylarsenic dichloride was prepared from phenylarsonic acid with $SOCl_2$.[55] The treatment of **1** with a large excess of phenylarsenic dichloride in dichloromethane in the presence of 2,6-lutidine at room temperature for 12 h gave an unstable arsenic(III) porphyrin bearing an arsenic−phenyl bond, (OEP)AsPh (**10**). The oxidative conversion of **10** with an equimolar amount of pyridinium tribromide *in situ* afforded [(OEP)As(Ph)-

(51) Augusto, O.; Kunze, K. L.; Ortiz de Montellano, P. R. *J. Biol. Chem.* **1982**, *257*, 6231.
(52) Ortiz de Montellano, P. R.; Kunze, K. L. *J. Am. Chem. Soc.* **1981**, *103*, 6534.
(53) Guilard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121.
(54) Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding (Berlin)* **1987**, *64*, 205.
(55) Steinkopf, S. *Chem. Ber.* **1928**, *61*, 676.
(56) Takido, T.; Kobayashi, Y.; Itabashi, K. *Synthesis* **1986**, 779.

Scheme 3



Scheme 4

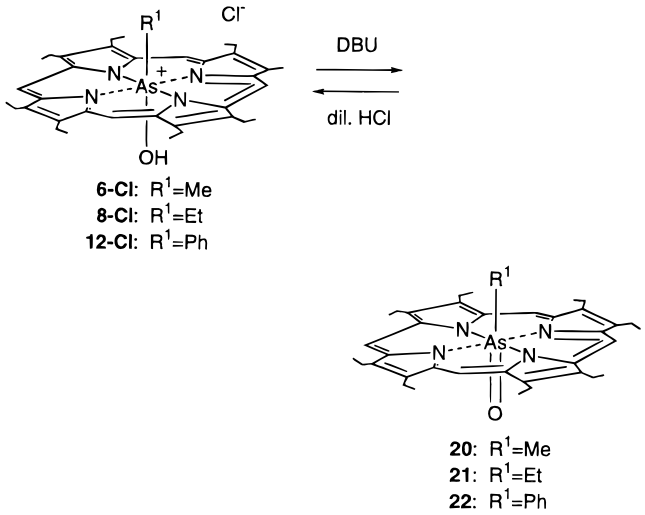


(OH)]ClO_4 (**12-ClO$_4$**) in 75% yield after hydrolytic treatment of the resultant [(OEP)As(Ph)(Br)]Br (**11-Br**) and counteranion exchange (Scheme 3).

Preparation of Unsymmetrically Substituted Arsenic(V) Porphyrins Bearing an Axial Methyl Group and an Axial Alkoxy, an Amino, and an Ethyl Group. The hydroxy group of **6-Cl** could be converted to the corresponding chloride [(OEP)As(Me)(Cl)]Cl (**13-Cl**) by treatment with PCl_3. Alcohols and some nucleophiles reacted with **13-Cl** to form the corresponding alkoxy derivatives [(OEP)As(Me)(OR)]Cl (**14-Cl**, R = Me; **15-Cl**, R = Et; **16-Cl**, R = *i*-Pr) in good yields (Scheme 4). These compounds were characterized as perchlorate salts after counteranion exchange. Even [(OEP)As(Me)(NH-*n*-Bu)]ClO_4 (**17-ClO$_4$**), [(OEP)As(Me)(NH-*p*-$CH_3C_6H_4$)]ClO_4 (**18-ClO$_4$**), and [(OEP)As(Me)(Et)]ClO_4 (**19-ClO$_4$**) could be also prepared by treatment of **13-Cl** with *n*-butylamine, *p*-toluidine, and triethylaluminum, respectively, but the reaction with diethylamine did not afford [(OEP)As(Me)(NEt_2)]OH, probably because of the bulkiness of the amine. **18-ClO$_4$** showed the characteristic methyl and phenyl signals in the ^{1}H NMR (in $CDCl_3$: −5.85 (s, 3 H), 1.21 (d, 2 H, J = 8.1 Hz), 2.03 (t, 24 H, J = 7.3 Hz), 4.30 (m, 16 H), 5.37 (d, 2H, J = 8.1 Hz), 10.57 ppm (s, 4 H)) but **18-ClO$_4$** could not be obtained in pure form because it was gradually converted to **14-OH** by chromatographic treatment.

Preparation of (OEP)As(R)(=O) (20, R = Me; 21, R = Et; 22, R = Ph). Recently we reported the preparation and X-ray structural analysis of (OEP)P(Et)(=O) with a phosphorus−oxygen double bond.[45] The bonding around the phosphorus atom of the porphyrin could be regarded as a hypervalent 12-P-6 system[57,58] with a P=O double bond, and the compound constituted

Scheme 5



the first experimentally characterized example of a hypervalent 12-P-6 compound bearing a P=O double bond. The compound was prepared by treating [(OEP)P(Et)(OH)]Cl with DBU, and the chemical shifts in the ^{1}H NMR and the wavelengths in the UV−vis spectra changed on addition of DBU. However, a similar change in the spectra was not observed in the corresponding antimony compounds.[47] Therefore, it was of

(57) For designation see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(58) Recent reports on hypervalent compounds of group 15 and group 16 elements: Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **1996**, *118*, 12866. Ohkata, K.; Ohsugi, M.; Yamamoto, K.; Ohsawa, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **1996**, *118*, 6355. Yamamoto, Y.; Chen, X.; Kojima, S.; Ohdoi, K.; Kitano, M.; Doi, Y.; Akiba, K.-y. *J. Am. Chem. Soc.* **1995**, *117*, 3922. Yamamoto, Y.; Chen, X.; Akiba, K.-y. *J. Am. Chem. Soc.* **1992**, *114*, 7906.

Table 2. ^{1}H NMR of Arsenic and Phosphorus Porphyrins

	[(OEP)AsMe(OH)]	(OEP)AsMe(=O)	[(OEP)AsEt(OH)]	(OEP)AsEt(=O)	[(OEP)AsPh(OH)]	(OEP)AsPh(=O)
axial protons	−5.62 (s, 3H)	−6.13 (s, 3H)	−5.68 (q, 2H) −4.63 (t, 3H)	−6.20 (q, 2H) −4.91 (t, 3H)	−0.03 (d, 2H) 4.87 (t, 2H) 5.48 (t, 1H)	−0.26 (d, 2H) 4.75 (t, 2H) 5.38 (t, 1H)
meso protons	10.60 (s, 4H)	10.45 (s, 4H)	10.59 (s, 4H)	10.37 (s, 4H)	10.41 (s, 4H)	10.42 (s, 4H)
	[(OEP)PMe(OH)][a]	(OEP)PMe(=O)[a]	[(OEP)PEt(OH)][a]	(OEP)PEt(=O)[a]	[(OEP)PPh(OH)][a]	(OEP)PPh(=O)[a]
axial protons	−5.74 (d, 3H)	−6.37 (d, 3H)	−5.70 (q, 2H) −4.52 (t, 3H)	−6.39 (dq, 2H) −5.08 (dt, 3H)	0.53 (d, 2H) 4.78 (t, 2H) 5.47 (t, 1H)	−0.02 (dd, 2H) 4.54 (dt, 2H) 5.18 (dt, 1H)
meso protons	9.68 (s, 4H)	9.95 (s, 4H)	9.72 (s, 4H)	10.20 (s, 4H)	9.43 (s, 4H)	9.60 (s, 4H)

[a] Reference 45.

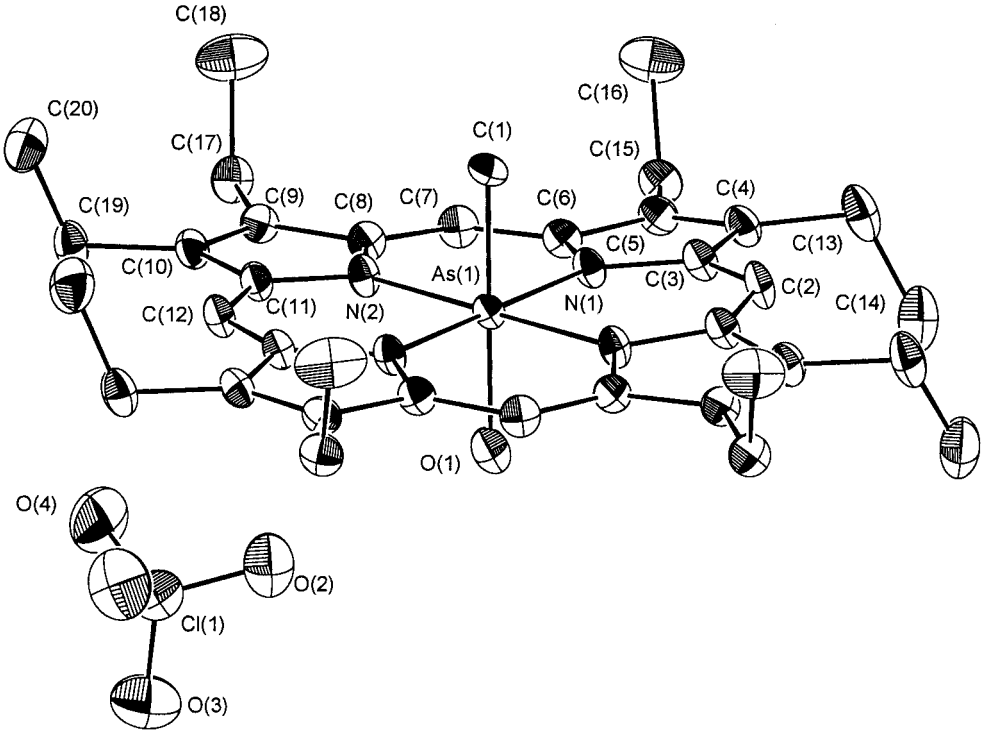


Figure 1. ORTEP diagram (30% probability ellipsoids) for **6-ClO$_4$**.

interest to examine the ability of the corresponding arsenic porphyrins to form a stable arsenic−oxygen double bond by monitoring the chemical shift change upon addition of bases.

When **6-ClO$_4$** in $CDCl_3$ was treated with DBU, the characteristic methyl signal shifted upfield from δ −5.62 to −6.13 as shown in Table 2. In addition, notable upfield shifts of axial ethyl protons from δ −5.68 (q) and −4.63 (t) to δ −6.20 (q) and −4.91 (t) were observed by treatment of a solution of **8-ClO$_4$** in $CDCl_3$ with DBU. Treatment of **12-ClO$_4$** with DBU also showed upfield shifts of the phenyl protons from δ −0.03 (d), 4.87 (t), and 5.48 (t) to δ −0.26 (d), 4.75 (t), and 5.38 (t). These changes were found to be reversible when the basic solution was treated with dilute HCl (pH 4). These results indicated that [(OEP)As(R)(=O)] compounds were formed by treatment with DBU and could be converted to [(OEP)As(R)(OH)]Cl by addition of HCl. The ^{1}H NMR chemical shifts of corresponding phosphorus compounds are shown in Table 2, and it is clear that the degree of the ^{1}H NMR chemical shift differences ($\Delta\delta$) of axial groups between [(OEP)M(R)(=O)] and [(OEP)M(R)(OH)]X is larger in the phosphorus compounds than that in the corresponding arsenic porphyrins ($\Delta\delta$: R = Me, 0.63 in P, 0.51 in As; R = Et (CH_3), 0.69 in P, 0.52 in As; R = Et (CH_2), 0.56 in P, 0.28 in As; R = Ph (ortho), 0.55 in P, 0.23 in As; R = Ph (meta), 0.24 in P, 0.12 in As; R = Ph (para), 0.29 in P, 0.10 in As). In the phosphorus compounds X-ray structural results showed that the porphyrin core of [(OEP)P(Et)(=O)] was almost planar; in contrast, [(OEP)P(Et)(OH)]ClO_4 was severely ruffled.[45] Therefore, the ring current effects of the porphyrin core should be different between [(OEP)P(R)(=O)] and [(OEP)P(R)(OH)]X. Since the X-ray structural analysis of [(OEP)As(Me)(OH)]ClO_4 (**6-ClO$_4$**) shows that the porphyrin core is almost planar (*vide infra*), the chemical shift differences in the arsenic porphyrins are considered to originate from the pure electronic effects of the axial ligands. In fact, downfield shifts were observed for the meso protons from [(OEP)P(R)(OH)]X to [(OEP)P(R)(=O)], indicating that the ring current effect of the core was larger in the planar [(OEP)P(R)(=O)] than that of the ruffled [(OEP)P(R)(OH)]X. In contrast, the corresponding arsenic analogue showed upfield shifts of the meso protons from [(OEP)As(R)(OH)]X to [(OEP)As(R)(=O)], probably due to the electron donation from the axial oxide without considerable change of ruffling.

UV−Visible Spectra. The electronic absorption spectral data for the arsenic porphyrins are shown in the Experimental Section and are summarized in Table 3 (see the Supporting Information). The porphyrins

synthesized above all exhibited normal type UV−vis spectra with a Soret band in the range 401−428 nm and two Q bands in the ranges 533−553 and 572−586 nm. The absorption maxima varied with the electron-donating nature of the axial ligand; i.e., the more donating the axial ligand, the longer the wavelength maxima. There is a 23−27 nm red shift for the Soret band of $[(OEP)As(R)_2]ClO_4$ and a 13−20 nm shift for the Q bands in relation to $[(OEP)As(OH)_2]ClO_4$. Similar shifts have already been reported for germanium[59] and silicon[60] dihydroxy- and dialkylporphyrins.

X-ray Crystal Structure of 6-ClO_4. Crystals of **6-ClO_4** suitable for X-ray analysis were obtained by recrystallization from dichloromethane/di-*n*-butyl ether (2:1). X-ray structural analysis of the compound was carried out on the basis of the centrosymmetric $P2_1/m$ space group, in which the As atom and the axial atoms are on a crystallographic mirror plane. Refinement led to the final values of $R = 0.087$ and $R_w = 0.098$. In this case the solvent dichloromethane was incorporated in the crystal lattice. Figure 1 shows the ORTEP drawing, and the solvent is omitted for clarity. This is the first concrete characterization of an arsenic porphyrin by X-ray analysis. The oxygen atom of the axial OH group is hydrogen-bonded with the perchlorate anion (the length between the hydrogen atom of the OH group and the closest oxygen atom in the perchlorate anion is 2.10 Å). The hydrogen bond clearly distinguishes the axial OH group from the axial methyl group in **6-ClO_4**. Thus, the perchlorate anion was a better counteranion than hexafluorophosphate in this case, since in [(TPP)-Sb(Me)(OH)]PF_6 the hexafluorophosphate anion did not form a hydrogen bond with the axial OH group. As a result, Sb−CH_3 and Sb−OH could not be differentiated due to the alternate inverse arrangement of the molecule in the crystal.[15] Selected bond lengths and bond angles for **6-ClO_4** are listed in Table 4. The arsenic atom exhibits approximate octahedral geometry. The length of the As−O bond (1.830(2) Å) is shorter than that of the As−C bond (1.864(3) Å). The average As−N bond length is 2.009(2) Å, which is longer than the average P−N bond length (1.884(3) Å) in severely ruffled $[(OEP)P(Et)(OH)]ClO_4$ and is slightly longer than the threshold length (ca. 1.95 Å) between the extensively ruffled porphyrin core and the planar one.[45] Thus, the arsenic porphyrin **6-ClO_4** shows the planar porphyrin core but a ruffled arsenic porphyrin core may be possible by tuning the electron-withdrawing property of the axial substituents. Further structural studies are in progress.

Table 4. Selected Bond Lengths and Angles for 6-ClO_4

Bond Lengths (Å)			
As−C(axial)	1.864(3)	As−O(axial)	1.830(2)
As−N(1)	2.009(2)	As−N(2)	2.009(2)
Bond Angles (deg)			
C(axial)−As−O	179.6(1)	O(axial)−As−N(1)	89.5(1)
C(axial)−As−N(1)	90.2(1)	O(axial)−As−N(2)	90.8(1)
C(axial)−As−N(2)	89.4(1)	N(1)−As−N(2)	89.4(1)

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Supporting Information Available: Tables of UV−visible data for arsenic porphyrins in CH_2Cl_2 (Table 3) and positional and of thermal parameters and interatomic distances and angles for **6-ClO_4** (14 pages). Ordering informaiton is given on any current masthead page.

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