First characterization of arsenic porphyrins: synthesis and X-ray structure of $[(oep)AsMe(OH)]^+ClO_4^-$

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$[(oep)As(OH)_2]ClO_4$ is synthesized in good yields by non-nucleophilic oxidative treatment of (oep)AsCl with pyridinium tribromide followed by hydrolysis and is converted to $[(oep)AsMe(OH)]ClO_4$ with $AlMe_3$.

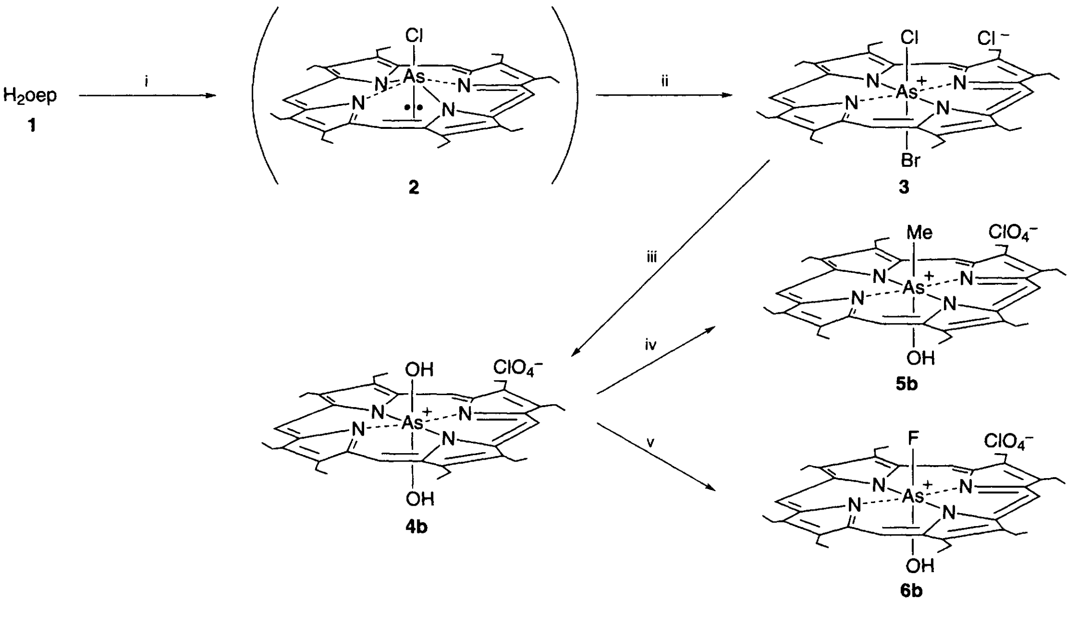
Group 15 element porphyrins are of interest because two valence states are accessible to the central atom,[1] and redox electrochemistry[2,3] and photochemistry[4,5] of phosphorus and antimony porphyrins have attracted considerable attention recently in addition to the structural effects of ruffling and bonding due to electronegativity of axial ligands.[6]

In contrast, there has been no reliable result on the synthesis of arsenic porphyrins. Formation of arsenic octaethylporphyrin, $[(oep)As(OH)_2]^+$, has been reported[1,7] by the reaction of H_2oep with $AsCl_3$ in pyridine, followed by hydrolysis and air oxidation of the resultant (oep)AsCl; however, in these reports the products were not well characterized. Recently, Brothers and co-workers re-examined the preparation of arsenic porphyrins, but this resulted in failure.[8] We also tried to follow the reaction by use of aqueous hydrogen peroxide for the oxidation of (oep)AsCl but obtained only a trace of $[(oep)As(OH)_2]OH$ while almost all the (oep)AsCl was demetallated to give H_2oep.

We rationalized that the difficulty for isolation of the arsenic porphyrins may be due to two reasons: (*i*) (oep)AsCl is not oxidized easily by air from a lower oxidation state, As^{III}, to a higher one, As^{V}, in contrast to the corresponding phosphorus porphyrins[1,4] and (*ii*) the arsenic(III) porphyrin, (oep)AsCl, is much more unstable towards nucleophiles in comparison with the antimony(III) porphyrin, (oep)SbCl.[9]

Our new synthetic method for the preparation of arsenic porphyrins is based on non-nucleophilic oxidative conversion of unstable arsenic(III) porphyrins into arsenic(V) prophyrins by use of halogenating reagents because we believe group 15 element porphyrins should be much more stable in the high oxidation state (V) than in the lower one (III) based on our experience.[6,9] We investigated XeF_2, $Hpy^+Br_3^-$, *N*-bromosuccinimide, *N*-chlorosuccinimide and $NMe_3(CH_2Ph)^+Br_3^-$ as oxidising agents for (oep)AsCl as shown in Scheme 1. Of these $Hpy^+Br_3^-$ and $NMe_3(CH_2Ph)^+Br_3^-$ gave the best results although good yields of the arsenic(V) porphyrin were obtained in all cases.

Typical experimental procedures to obtain $[(oep)As(OH)_2]ClO_4$ **4b** are as follows. To a solution of (oep)AsCl **2**, which was prepared by the reaction of H_2oep **1** (75 mg, 0.14 mmol) with $AsCl_3$ (0.3 ml, 3.56 mmol) in the presence of 2,6-dimethylpyridine (0.75 ml, 6.45 mmol), was added an equimolar amount of $Hpy^+Br_3^-$ (45 mg, 0.14 mmol) at room temperature. The resultant $[(oep)AsCl(Br)]Cl$ **3** was treated with dilute HCl to afford $[(oep)As(OH)_2]Cl$ **4a** (72 mg) in 76% overall yield. **4a** was thermally stable and could be purified by chromatographic treatment [neutral Al_2O_3, benzene–CH_2Cl_2–MeOH (15 : 6 : 1)], and was obtained pure as **4b** for elemental analysis.† One of the hydroxy groups of **4a** was substituted by a methyl group by the reaction of **4a** with oxalyl bromide followed by treatment with excess trimethylaluminium in dichloromethane to yield $[(oep)AsMe(OH)]Cl$ **5a** in 71% yield according to the method recently reported by us for antimony porphyrins. The ^1H NMR spectrum of **5a** showed a characteristic methyl signal at very high field (δ −5.79) due to the large



Scheme 1 *Reagents and conditions*: i, $AsCl_3$ 2,6-dimethylpyridine, CH_2Cl_2, room temp., 12 h; ii, $Hpy^+Br_3^-$, room temp., 12 h; iii, dilute HCl, H_2O, then $NaClO_4$, H_2O, CH_2Cl_2; iv, $(COBr)_2$, CH_2Cl_2, room temp., 1 h, then $AlMe_3$ in hexane, CH_2Cl_2, reflux, 1 d; v, $(COBr)_2$, CH_2Cl_2, room temp., 1 h, then $AgBF_4$, CH_2Cl_2, room temp., 12 h

ring current effect of the porphyrin nucleus, close to that (δ −6.10) for [(oep)SbMe(OH)]PF_6.[9]

Crystals of [(oep)AsMe(OH)]ClO_4 **5b** suitable for X-ray analysis were obtained by recrystallization from dichloromethane–dibutyl ether. 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. Fig. 1 shows the ORTEP drawing (solvent dichloromethane omitted for clarity). The arsenic lies in the porphyrin plane with two axial ligands completing its octahedral coordinations. This is the first concrete characterization of an arsenic porphyrin by X-ray analysis. In addition [(oep)AsF(OH)]ClO_4 **6b** was obtained in 68% yield by the reaction of **4b** with silver tetrafluoroborate. After **5a** was treated with Na_2SO_4 or with DBU, a characteristic methyl signal shifted upfield from δ −5.79 to −6.22. This result suggests the formation of [(oep)AsMe(=O)] with a unique six-coordinate hypervalent bonding system (12-As-6) similar to that for phosphorus porphyrins.[6] Further synthetic and structural studies are now in progress.

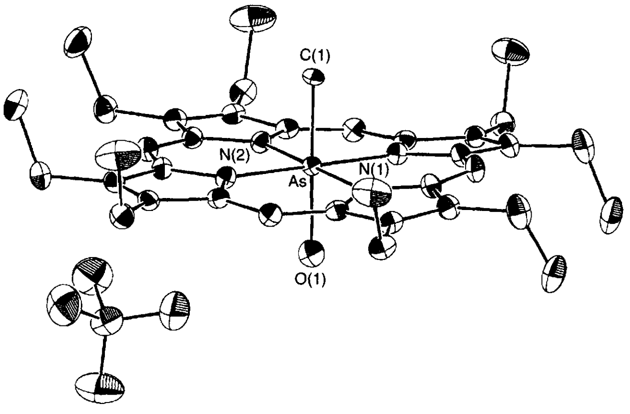


Fig. 1 Molecular structure of **5b**·CH_2Cl_2. Selected bond lengths (Å) and angles (°): As–C(1) 1.870(6), As–O(1) 1.826(6), As–N(1) 2.002(4), As–N(2) 2.005(4); O(1)–As–N(1) 89.3(2), O(1)–As–N(2) 90.8(2), N(1)–As–N(2) 89.6(2), N(2)–As–C(1) 89.5(3).

Footnotes

† Compounds, **4b**, **5b** and **6b** gave satisfactory elemental analyses for C, H and N. *Spectroscopic data*: **4b**; ^{1}H NMR ($CDCl_3$): δ 10.38 (s, 4 H), 4.19 (q, 16 H), 2.01 (t, 24 H), −2.88 (s, 2 H). **5b**; ^{1}H NMR ($CDCl_3$): δ 10.51 (s, 4 H), 4.22 (q, 16 H), 2.00 (t, 24 H), −5.79 (s, 3 H). **6b**; ^{1}H NMR ($CDCl_3$): δ 10.23 (s, 4 H), 4.18 (q, 16 H), 2.01 (s, 24 H).

‡ *Crystal data* for **5b**·CH_2Cl_2 : $C_{38}H_{50}AsCl_3N_4O_5$, M = 824.12 monoclinic, space group $P2_1/m$, a = 12.419(4), b = 16.864(4), c = 9.493(3) Å, β = 106.08(2)°, U = 1910.5(9) Å^3, Z = 2, D_c = 1.43 g cm^{-3}, T = 297 K. Data were collected on a Mac Science MXC-3 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The structure was solved using the Crystan-GM (Mac Science) system and refined by full-matrix least- squares. The data were corrected for absorption.[10] Final $R1$ = 0.056 (R_w = 0.061) for 3053 observed reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/242.

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