Synthesis of μ-oxo-bridged group 15 element–aluminium heterodinuclear porphyrins [(oep)(Me)M–O–Al(oep)]ClO$_4$ (M = P, As, Sb) and X-ray crystal structure of [(oep)(Me)As–O–Al(oep)]ClO$_4$

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μ-Oxo-bridged group 15 element–aluminium heterodinuclear porphyrins, [(oep)(Me)M–O–Al(oep)]ClO$_4$ (M = P, As, Sb), are synthesized by the reaction of [(oep)(Me)M(OH)]ClO$_4$ with (oep)AlMe.

μ-Oxo-bridged dinuclear porphyrins bearing a transition metal such as Fe, Ru, Mn, V, or Ti have been investigated extensively because of their relation to biological systems.[1,2] Recently, a μ-oxo-bridged dinuclear porphyrin skeleton containing boronic acids has been reported to be useful for molecular recognition of saccharides.[3] However, only a few synthetic methods are available for the synthesis of μ-oxo-bridged dinuclear transition-metal porphyrins, and μ-oxo-bridged dinuclear porphyrins bearing main-group elements have not been reported. Here we report a new synthetic route to μ-oxo-bridged group 15 element–aluminium heterodinuclear porphyrins, [(oep)(Me)M–O–Al(oep)]ClO$_4$ (M = P **1**, As **2**, Sb **3**), and the X-ray crystallographic structure of **2**.

Recently we reported that the hydroxy protons of [(oep)(R)P(OH)]$^+$X$^-$ were relatively acidic and easily removed by treatment with DBU to generate (oep)(R)P=O which were stable, and the double bond character of the P=O bond was confirmed by an X-ray analysis of (oep)(Et)P=O. In fact, the pK_a value of [(oep)(Et)P(OH)]$^+$X$^-$ was determined to be *ca.* 7–8 in water.[4] The corresponding arsenic porphyrins also showed similar behavior in acid–base treatment[5] although the corresponding antimony porphyrins did not show the formation of such double-bonded compounds.[6] Since aluminium porphyrins bearing an alkyl group are known to be reactive towards alcohols and phenols bearing acidic protons,[7] it was of interest to examine whether the acidic hydroxy groups in [(oep)(R)M(OH)]$^+$X$^-$ (M = P, As) were reactive toward (oep)AlMe in spite of the anticipated steric hindrance.

To our delight the reaction of [(oep)(Me)P(OH)]ClO$_4$ **4** with (oep)AlMe **7** proceeded smoothly under reflux in dichloromethane for 1.5 days, and the expected μ-oxo-bridged P/Al heterodinuclear porphyrin **1** was isolated in 62% yield (Scheme 1). The compound was stable to atmospheric moisture and

chromatographic treatment [neutral Al$_2$O$_3$, benzene–CH$_2$Cl$_2$–MeOH (15 : 6 : 1)] and characterization was carried out by elemental analysis and NMR spectroscopy.† The reaction of the corresponding arsenic porphyrin **5** with **7** proceeded slowly and **2** was obtained in 49% yield after 4 days in refluxing dichloromethane. The difference of the reactivity between **4** and **5** can be related to the acidity of the hydroxy group in **4** and **5**, **4** being more acidic than **5** since the methyl protons of **4** shifted upfield faster than those of **5** upon addition of DBU (in portions) to a mixture of **4** and **5** in CDCl$_3$. As expected, the reaction of the least acidic antimony porphyrin [(oep)(Me)Sb(OH)]ClO$_4$ **6** with **7** was very sluggish and only 7% of **3** was obtained after 2 weeks in refluxing 1,2-dichloroethane. ^{1}H NMR of the μ-oxo-bridged heterodinuclear porphyrin [(oep)(Me)M–O–Al(oep)]ClO$_4$ showed characteristic methyl signals at very high fields (δ −7.96 in **1**, −7.94 in **2**, −7.92 in **3**) which were even higher than those of the starting [(oep)(Me)M(OH)]ClO$_4$ (δ −5.79 in **4**, −5.63 in **5**, −6.13 in **6**) probably due to the ring current effect of the aluminium porphyrin nucleus.

Crystals of **2** 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 C2/c group, showing the required twofold axis passed through the C–As–O–Al bond. Fig. 1 shows an ORTEP drawing of a single molecule of **2** (solvent dichloromethane omitted for clarity). Since the As, O and Al atoms lie on the crystallographic twofold axis the As–O–Al bond is explicitly linear. The average torsional angle between N(1)–As–Al–N(3) and N(2)–As–Al–N(4) is 15.3°, the structure of **2** can be represented in terms of a near-eclipsed conformation.[2] The interplanar distance between the mean planes of the porphinato cores is 3.71 Å.

It is interesting that the As–O [1.690(3) Å] and Al–O [1.731(3) Å] bond distances in **2** are shorter than the As–O distance [1.826(6) Å] in **5**,[5] and the reported Al–O distance [1.789(3) Å] in [(diporphyrin biphenylene)CoAl(OEt)],[8] respectively. Similar shortening has been considered to be due to sp hybridization of the oxo oxygen and d$_\pi$(M)–p$_\pi$(O)–d$_\pi$(M)
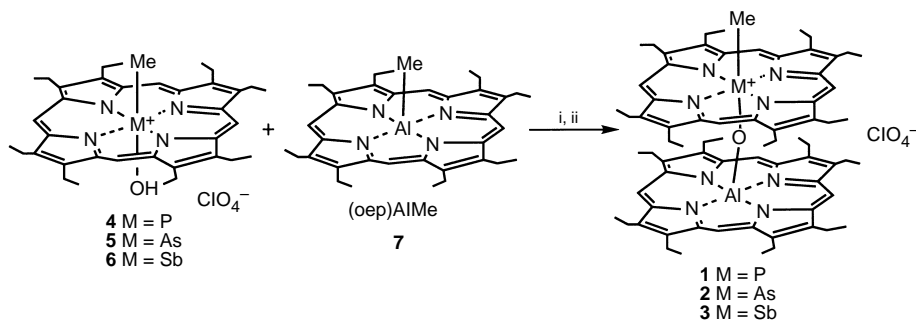
Scheme 1 *Reagents and Conditions:* i, see text; ii, NaClO$_4$, CH$_2$Cl$_2$, MeCN
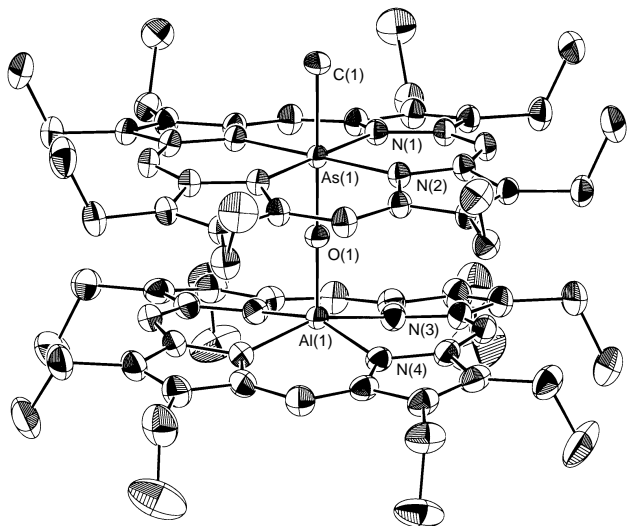
Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): As–C(1) 1.971(4), As–O(1) 1.690(3), As–N(1) 2.028(3), As–N(2) 2.034(3), Al(1)–O(1) 1.731(3), Al(1)–N(3) 2.005(3), Al(1)–N(4) 2.017(3); C(1)–As–N(1) 90.5(1), C(1)–As–N(2) 90.2(1), O(1)–As–N(1) 89.5(1), O(1)–As–N(2) 89.8(1), N(1)–As–N(2) 89.6(1), O(1)–Al(1)–N(3) 101.3(1), O(1)–Al(1)–N(4) 100.8(1), N(3)–Al(1)–N(4) 87.9(2).

interaction in [{(oep)Ru(OH)}$_2$O],[9] however, there is no formal contribution of a d-orbital in **5**. Further synthetic and structural studies are now in progress.

Footnotes

† Compounds, **1**, **2** and **3** gave satisfactory elemental analyses for C, H and N. *Spectroscopic data*: **1**; ^{1}H NMR (CDCl$_3$), δ 9.06 (s, 4 H), 8.42 (s, 4 H), 3.83–4.22 (m, 32 H), 1.82 (t, 24 H), 1.67 (t, 24 H), −7.96 (d, 3 H). **2**; ^{1}H NMR (CDCl$_3$), δ 9.24 (s, 4 H), 9.05 (s, 4 H), 4.09–4.28 (m, 24 H), 3.98 (dq, 8 H), 1.91 (t, 24 H), 1.58 (t, 24 H), −7.94 (s, 3 H). **3**; ^{1}H NMR (CDCl$_3$), δ 9.37 (s, 4 H), 8.90 (s, 4 H), 3.80–4.25 (m, 32 H), 1.91 (t, 24 H), 1.58 (t, 24 H), −7.92 (s, 3 H).

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