

Recognition of Giant Cluster Anions by a Protonated Porphyrin Trimer: Detection by Fast-atom Bombardment (FAB) Mass Spectrometry

Harry L. Anderson and Jeremy K. M. Sanders*

Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Anions such as $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{Os}_{10}\text{C}(\text{CO})_{24}^{2-}$ are recognised and bound by a porphyrin cyclic trimer of complementary size and charge; these second-sphere coordinate cluster complexes were detected by FAB mass spectrometry.

Many receptors have been designed for simple anions,¹ but recognition of large anions is much rarer;[†] we now report that the protonated form of the porphyrin trimer host **1**[‡] binds giant anions such as Keggin-type polyoxometallate (POM) anions and anionic high-nuclearity metal carbonyl clusters. Organic structures capable of binding heavy-metal clusters such as these are of particular interest because of their potential for development into selective stains for electron microscopy. Such assemblies may also exhibit interesting electron-transfer properties since both components are redox-active. Fast-atom bombardment (FAB) mass spectrometry is a technique that is widely used for probing supramolecular interactions and second sphere coordination,^{3,4} but we are not aware of its previous use for studying anion binding.

Molecular mechanics calculations⁵ on the protonated porphyrin trimer **1**[‡] indicate that it has a cavity with an internal van der Waals surface diameter of approximately 13 Å. Thus it has a positively charged concave surface which should be complementary to the convex, negatively charged surface of a Keggin heteropolytungstate anion such as $\text{PW}_{12}\text{O}_{40}^{3-}$ which has a mean van der Waals diameter of 12.7 Å.⁶ This complementarity prompted us to look for binding between the anion and protonated trimer. A slight excess of

the acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was added to a 0.1 mmol dm⁻³ solution of **1** in 3-nitrobenzyl alcohol (*m*-NOBA) until the porphyrin was fully protonated, and a positive-ion FAB mass spectrum was obtained using a primary beam of 15 keV Cs^+ ions. The high-mass region of the spectrum [Fig. 1(a)] shows peaks due to the free host at m/z 2032,[‡] the $\text{H}_{12}\text{I}^{6+} \cdot \text{PW}_{12}\text{O}_{40}^{3-}$ complex at m/z 4915 (calc. 4914)[§] and the corresponding Cs adduct at m/z 5047. The dodecasilicotungstate anion, $\text{SiW}_{12}\text{O}_{40}^{4-}$, has an identical van der Waals surface to that of $\text{PW}_{12}\text{O}_{40}^{3-}$, and again a 1:1 complex with the porphyrin trimer was detected (observed m/z , 4914; calc., 4911).[§]

In control experiments where trimer **1** was replaced by monomeric porphyrin **2**, no complexation was detected either with $\text{PW}_{12}\text{O}_{40}^{3-}$ or $\text{SiW}_{12}\text{O}_{40}^{4-}$. This indicates that $\text{XW}_{12}\text{O}_{40}^{n-}$ anions show a specific binding interaction with the protonated trimer, to give an adduct which presumably has the structure shown in Fig. 2. Further evidence that this binding is selective for anions which have good shape-, size- and charge-complementarity was provided by the decaosmium

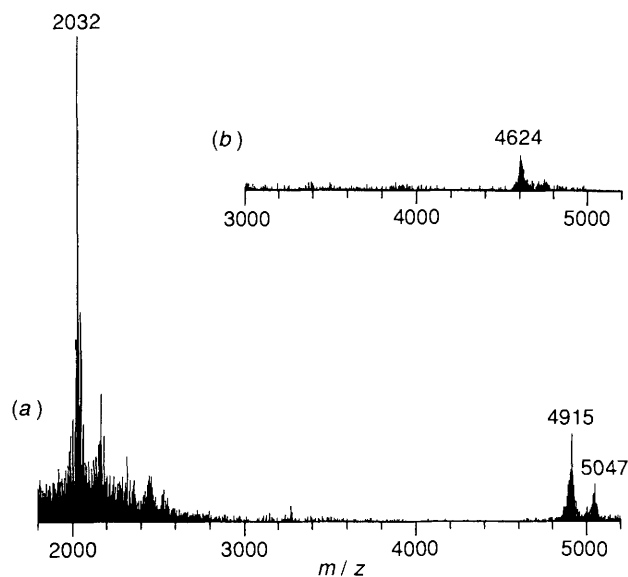
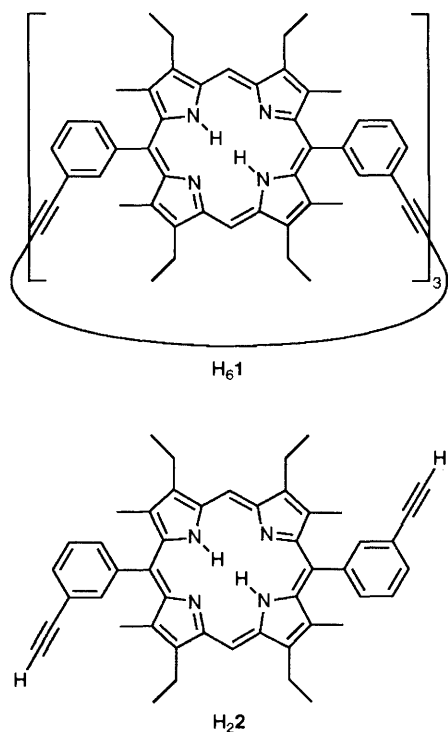


Fig. 1 (a) High mass region of the FAB mass spectrum of a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and **H₆1** in a *m*-NOBA matrix. (b) Insert showing the corresponding molecular ion region for the adduct of $\text{H}_{12}\text{I}^{6+}$ and $\text{Os}_{10}\text{C}(\text{CO})_{24}^{2-}$, plotted with the same vertical intensity for the m/z 2032 peak as in (a). Masses were calibrated with CsI .

[‡] The spectra of **H₆1** and **H₂2** show singly charged molecular ions due to M^+ , MH^+ and MH_2^{2+} in ratios that reflect oxidation potentials and the matrix pH.⁷ Also, the spectrum of trimer **H₆1** contains prominent peaks for multiply charged ions at m/z 1015 (H_6I^{2+}) and 677 (H_6I^{3+}), each porphyrin unit bearing a charge independently.

[§] It is not clear precisely how many protons are carried by the molecular ion of the cluster adducts; if the host is fully protonated then the overall assembly must also gain electrons from the matrix to give a singly charged species. Peaks due to multiply charged adduct molecular ions are very weak.

[†] Apart from the rather different recognition of polyanions such as DNA by histones and other polycations.

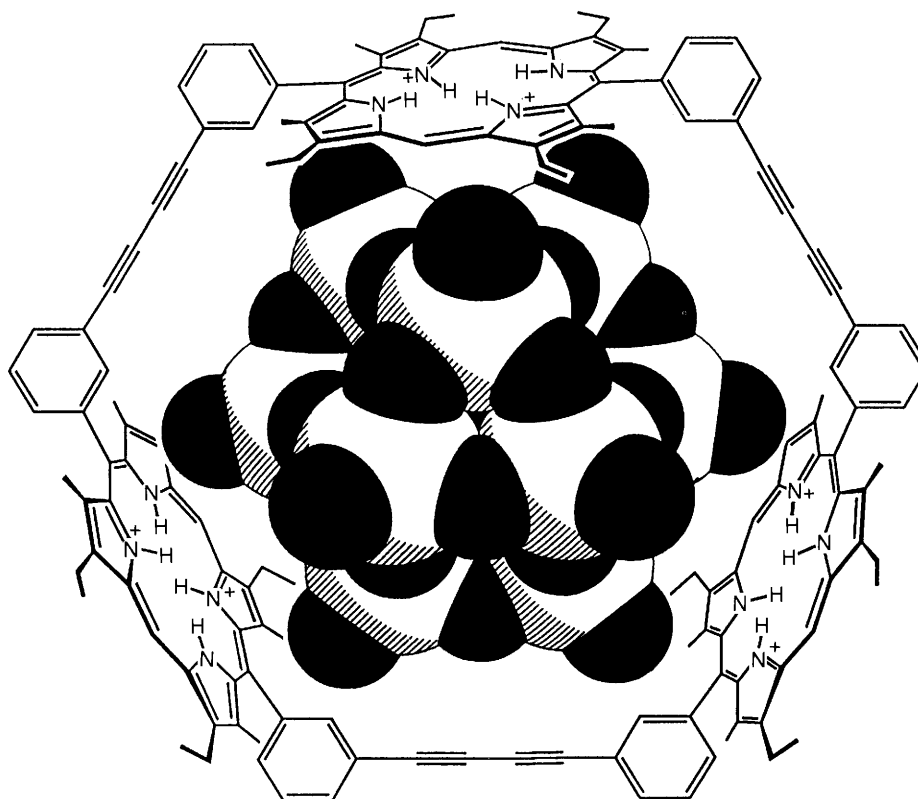


Fig. 2 Schematic illustration of the proposed $H_{12}I^{6+} \cdot PW_{12}O_{40}^{3-}$ adduct

carbido dianion, $Os_{10}C(CO)_{24}^{2-}$.⁸ The internal structure of this anion is quite different from that of Keggin POM anions, but its van der Waals surface has a similar size (12.3 Å diameter), shape (roughly spherical with T_d symmetry) and composition; both anions have surfaces dominated by non-basic oxygen atoms. The FAB mass spectrum of a 1 : 1 mixture of $H_{12}I^{6+} \cdot 6CF_3CO_2^-$ and $Os_{10}C(CO)_{24}^{2-} \cdot 2(Ph_3P)_2N^+$ gave a reproducible signal corresponding to the 1 : 1 complex [Fig. 1(b); obs. m/z 4624; calc., 4623.2]. Again, a control experiment with protonated monomer showed no peaks attributable to anion complexation.

Crystal structures of protonated porphyrins often show hydrogen bonds to simple counter-anions such as chloride,⁹ but the FAB mass spectra of compounds such as $H_{12}I^{6+} \cdot 6X^-$ and $H_4I^{2+} \cdot 2X^-$ (where X is Cl^- , $CF_3CO_2^-$ or $0.5 SO_4^{2-}$) show no peaks due to anion complexation. Given that complexes of anions such as Cl^- are likely to be at least as volatile as those of cluster anions, the second sphere complexes formed between $H_{12}I^{6+}$ and the cluster anions must be substantially more stable than those formed with simple anions. To date, the small complexation shifts observed in UV or NMR spectra have prevented the measurement of reliable binding constants.

In summary we have shown that a protonated cyclic porphyrin trimer binds giant cluster anions in a way that depends on shape complementarity with the guest rather than on the details of internal bonding. This raises the intriguing possibility of separating clusters according to size by use of different hosts.

We thank Dr L. H. Gade for a sample of $Os_{10}C(CO)_{24}[(Ph_3P)_2N]_2$ and for valuable discussion, and the SERC for financial support.

Received, 15th April 1992; Com. 2101979E

References

- 1 M. W. Hosseini, A. J. Blacker and J.-M. Lehn, *J. Am. Chem. Soc.*, 1990, **112**, 3896; J. L. Sessler, D. A. Ford, M. J. Cyr and H. Furuta, *J. Chem. Soc., Chem. Commun.*, 1991, 1733; A. Müller, E. Krickemeyer, M. Penk, R. Röhlfing, A. Armatage and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1674; J. Aragó, A. Bencini, A. Bianchi, A. Domenech and E. Garcia-España, *J. Chem. Soc., Dalton Trans.*, 1992, 319; P. H. Boyle, M. A. Convery, A. P. Davis, G. D. Hosken and B. A. Murray, *J. Chem. Soc., Chem. Commun.*, 1992, 239; E. v. Aken, H. Wynberg and F. V. Bolhuis, *J. Chem. Soc., Chem. Commun.*, 1992, 629; P. D. Beer, D. Heseck, J. Hodakova and S. E. Stokes, *J. Chem. Soc., Chem. Commun.*, 1992, 270.
- 2 H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1989, 1715.
- 3 P. R. Ashton, J. F. Stoddart and R. Zarzychi, *Tetrahedron Lett.*, 1988, **29**, 2103; N. Malhotra, P. Roepstorff, T. K. Hansen and J. Becher, *J. Am. Chem. Soc.*, 1990, **112**, 3709; K. Laali, *Chem. Ber.*, 1990, **123**, 1433; K. Yamada, S. Matsutani, A. Uchitama and T. Takahashi, *J. Incl. Phenomena*, 1991, **11**, 49.
- 4 Electrospray mass spectrometry has also been used to study non-covalent complexes: B. Ganem, Y.-T. Li and J. D. Henion, *J. Am. Chem. Soc.*, 1991, **113**, 7818.
- 5 Energy minimised structures were calculated on a DEC microVAX 3600 using MacroModel V2.5.
- 6 M.-R. Spirlet and W. R. Bushing, *Acta Crystallogr., Sect. B*, 1978, **34**, 907.
- 7 S. Naylor, C. A. Hunter, J. A. Cowan, J. H. Lamb and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 6507; S. Naylor, J. A. Cowan, J. H. Lamb, C. A. Hunter and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 2*, 1992, 411.
- 8 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 224.
- 9 E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1974, 1236; H. Ogoshi, E. Watanabe and Z. Yoshida, *Tetrahedron*, 1973, **29**, 3241; A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, 1968, **90**, 2735.