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Template-assisted self assembly of two lipophilic polyion aggregates derived from sodium tetraphenyl imidodiphosphinate-complexes containing sodium ions in four different coordination environments†

Perla Román-Bravo,[a] Marcela López-Cardoso,[a] Patricia García y García,[a] Herbert Höpfl[a] and Raymundo Cea-Olivares*[b]

[a] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca 62210, México*

[b] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México D.F. 04510, Mexico. E-mail: cea@servidor.unam.mx; Fax: (52-55)56162203; Tel: (52-55)56224505*

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The molecular structures of two lipophilic polyion aggregates derived from tetraphenyl imidodiphosphinate are described: $[Na(crown\ ether)]\{MNa_2[Ph_2P(O)NP(O)Ph_2]_4\}$ with crown ether = 15-crown-5 for 1 and benzo-15-crown-5 for 2 (M = Na^+ for 1 and $Na(H_2O)^+$ for 2).

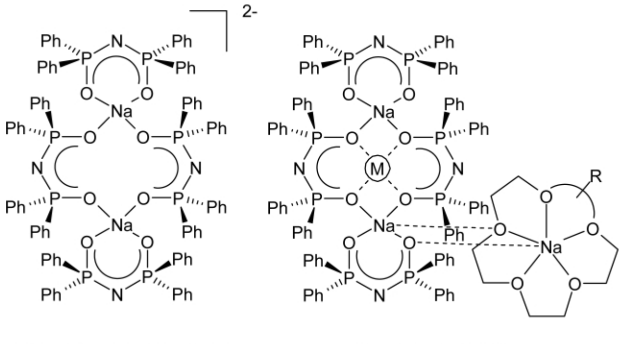
The structural features that are responsible for the high selective transport of metal ions like sodium and potassium through ion channels are still not completely understood.[1] It is known that within the protein structures of ion channels amide carbonyl groups form part of the selectivity filter and that several metal ions are bound simultaneously in order to guarantee high transport rates.[2] Imidodiphosphinates have highly flexible structures[3] and can therefore mimic the spatial distribution of the carbonyl groups in a peptide. So far, the alkaline metal salts of imidodiphosphinates, $M[R_2P(X)NP(X)R_2]$ (with M = alkaline metal, R = alkyl, or aryl and X = O, S, Se, Te), have been used mainly as starting materials for the preparation of complexes with transition and main group elements.[4–5] Little is known on their molecular structures, although this knowledge may provide useful information on the complexing abilities of alkaline metals, not only with oxygen, but also with the heavier homologues of this element.[6–15]

Herein, we report on the synthesis and molecular structures of two polyion aggregates having the formula $[Na(crown\ ether)]\{MNa_2[Ph_2P(O)NP(O)Ph_2]_4\}$ with crown ether = 15-crown-5 for **1** and benzo-15-crown-5 for **2** (M = Na^+ for **1** and $Na(H_2O)^+$ for **2**). Interestingly, in this complex the sodium ions adopt a series of different coordination numbers and unusual geometries with the same ligand.

The title compounds **1** and **2** crystallized from dichloromethane–hexane solutions containing sodium tetraphenyl imidodiphosphinate, $Na[Ph_2P(O)NP(O)Ph_2]$, and an equimolar amount of the corresponding crown ether. Compounds **1** and **2** are readily soluble in organic solvents such as chloroform and ethanol, but insoluble in water and hexane. The molecular structures were determined by elemental analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and X-ray crystallography.‡ These data indicate that the sodium salt had reacted with the crown ethers in a 4 : 1 proportion instead of the generally observed 1 : 1 ratio[15] to give the molecular structures of **1** and **2** outlined in Chart 1. Analysing the structure it can be supposed that sodium ions are capable of acting as templates in the self assembly process of tetraphenylimidodiphosphinates to build a so far unknown $\{Na_2[Ph_2P(O)NP(O)Ph_2]_4\}^{2-}$ dianion with a 12-membered inorganic ring (Chart 1). The $[Na(crown\ ether)]^+$ complexes apparently function as counterions for the so formed host–guest-complexes in order to provide charge neutrality in the solid-state. Until now only one further related sodium polyion aggregate has been known, which has been prepared by Bock *et al.* from $Na[(PhO)_2P(O)NP(O)(OPh)_2]$. In that case a hexameric complex with a lipophilic 'hydrocarbon skin' composed of 24 phenyl rings and a central $[Na_6O_{12}]^{6+}$ core had formed.[13a] The analogous lithium complex has been described also.[13b]

That the sodium complexes **1** and **2** possess certain stability could be proved by the FAB^+ mass spectrum of **1**, which showed peaks for $[M - 15\text{-crown-}5]^+$ (m/z = 1758) and $[M - 15\text{-crown-}5]^{2+}$ (m/z = 879). Peaks were also observed at m/z = 1342 for the $[M - 15\text{-crown-}5 - Ph_2P(O)NP(O)Ph_2]^+$ ion and at m/z = 1319 for the $[M - 15\text{-crown-}5 - Na[Ph_2P(O)NP(O)Ph_2]]^+$ ion.

Apart from the coordination to different crown ethers, there is one interesting difference in the solid-state molecular structures of compounds **1** and **2** that consists in the coordination of an additional water molecule to the central sodium ion in compound **2**, which is absent in compound **1**. This fact and the observation that the $[Na(crown\ ether)]^+$ complexes are coordinated to one of the further two sodium ions, breaking thus the molecular symmetry of the anion, indicate that the tetra-coordinate sodium ions in $\{MNa_2[Ph_2P(O)NP(O)Ph_2]_4\}^-$ (with M = Na^+ for **1** and $Na(H_2O)^+$ for **2**) are coordinatively unsaturated and can still function as Lewis acidic sites. This is in agreement with the results obtained by Bock *et al.* for the $\{Na[(PhO)_2P(O)NP(O)(OPh)_2]\}_6$ hexamer, in which each sodium ion is surrounded by four close oxygen centers (2.23–2.50 Å) and two further oxygen atoms at a longer distance (2.65–3.05 Å).[13a] Fig. 1 shows the molecular structure of the inorganic host formed from sodium tetraphenyl imidodiphosphinate including the central sodium ion, which acted probably as template ion during the self assembly process. This supposition is confirmed by the observation that with lithium, potassium, rubidium and caesium only monomeric structures of the composition $\{[Na(crown\ ether)][Ph_2P(O)NP(O)Ph_2]\}$ are obtained.[15] The $[Na_3O_8]^{3+}$ and $[Na_3O_9]^{3+}$ cores, respectively, are embedded in lipophilic $H_{80}C_{96}$ capsules of 16 phenyl groups, providing kinetic stability. Fig. 2 shows the central part of the complete molecular structure of **1** including the coordinated $[Na(crown\ ether)]^+$ cation.[16]



$\{Na_2[Ph_2P(O)NP(O)Ph_2]_4\}^{2-}$

1 M = Na^+, R = CH_2CH_2
2 M = $Na(H_2O)^+$, R = $o\text{-}C_6H_4$

Chart 1

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† Electronic supplementary information (ESI) available: preparative methods, spectroscopic data, complete tables of X-ray data, detailed discussion of the coordination geometries for **1** and **2**. See http://www.rsc.org/suppdata/cc/b4/b406817c/

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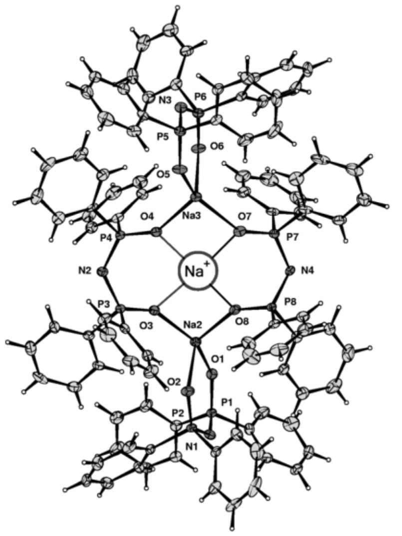

Fig. 1 Perspective view of the self-assembled $\{Na_2[Ph_2P(O)NP(O)Ph_2]_4\}_2^-$ dianion with the templating sodium ion in the center of the $Na_2O_4N_2P_4$ inorganic heterocyclic ring.

According to the nomenclature established for the description of the different coordination modes of imidodiphosphinates,[4] three different coordination patterns can be identified in the molecular structures of **1** and **2**. Ligand L1 acts as monometallic biconnective ligand, L4 as bimetallic triconnective and L2 and L3 as trimetallic tetraconnective ligands (Fig. 2). L1 and L4 are connected between each other by the bridging ligands L2 and L3, thus forming an inorganic framework of the formula $\{[Na(O_2NP_2)]_2O_4N_2P_4\}$ with a 12-membered $Na_2O_4N_2P_4$ ring in the central part (see Fig. 1 and the figures in the ESI†). The $Ph_2P(O)NP(O)Ph_2$ moieties present complete delocalization within the framework as evidenced by the P–O and P–N bond lengths, which show no significant variations. The four oxygen atoms of the bridging ligands are coordinated to the central sodium ion, Na1, which adopts a square-planar coordination geometry in **1** and a square-pyramidal coordination geometry in **2**. The difference consists in the apical ligation of a water molecule to the sodium ion in **2**. Ligand L4 forms one further bridge to the corresponding $[Na(crown\ ether)]^+$ cation, which at the same time is coordinated to Na2 through one of its oxygen atoms. Due to this arrangement compounds **1** and **2** provide the exceptional opportunity to analyse the geometry of four sodium ions at a time, each being embedded in a different coordination environment, but surrounded by the same type of ligand. The Na2, Na3 and Na4 sodium ions have distorted square-pyramidal, tetrahedral and pentagonal-pyramidal coordination geometries. A detailed description is given in the ESI.†

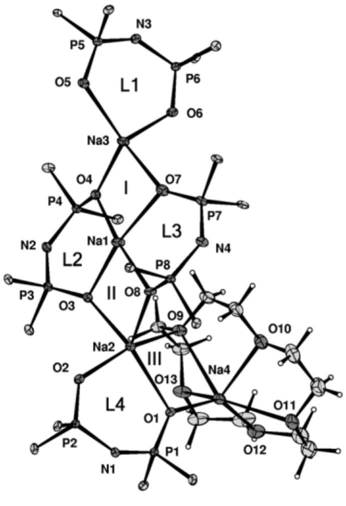

Fig. 2 Perspective view of $[Na(15\text{-crown-}5)]\{Na_3[Ph_2P(O)NP(O)Ph_2]_4\}$, **1**. For clarity the P-phenyl groups are only represented by the *ipso*-carbon atoms.

In conclusion, this contribution has shown that sodium tetraphenyl imidodiphosphinate can assemble to a lipophilically wrapped $\{MNa_2[Ph_2P(O)NP(O)Ph_2]_4\}^-$ anion, through a process that is most probably induced by the templating effect of a sodium ion. This process seems to be highly selective, since by using the same ligand with other alkaline metal ions, only monomeric complexes could be isolated.

Notes and references

‡ Crystal data: **1**, $C_{106}H_{100}N_4Na_4O_{13}P_8{\cdot}CH_2Cl_2$, $M = 2062.55$, triclinic, $a = 13.9644(7)$, $b = 14.4020(8)$, $c = 15.3266(8)$ Å, $\alpha = 64.0460(10)$, $\beta = 68.6120(10)$, $\gamma = 72.1590(10)°$, $U = 2540.7(2)$ Å^3, $T = 293(2)$ K, space group $P1$, $Z = 1$, μ(Mo-Kα) = 0.71073 Å, 18474 reflections measured, 15149 reflections observed, $I > 2\sigma(I)$. Final R values: $R_1 = 0.063$, $wR_2 = 0.165$ (all data). **2**, $C_{110}H_{102}N_4Na_4O_{14}P_8$, $M = 2043.68$, monoclinic, $a = 15.8021(9)$, $b = 13.9991(8)$, $c = 13.9991(8)$ Å, $\beta = 92.411(1)°$, $U = 5127.9(5)$ Å^3, $T = 100(2)$ K, space group Pn, $Z = 2$, μ(Mo-Kα) = 0.71073 Å, 42259 reflections measured, 9905 reflections observed, $I > 2\sigma(I)$. Final R values: $R_1 = 0.056$, $wR_2 = 0.103$ (all data). CCDC 236540–236541. See http://www.rsc.org/suppdata/cc/b4/b406817c/ for crystallographic data in .cif or other electronic format.

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16 The ESI† includes the molecular structure of **2**.