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The pentadecadentate phosphazenate $[\{2\text{-}(MeO)C_6H_4N\}_6P_3N_3]^{6-}$: chelation of twelve lithium ions by a single ligand

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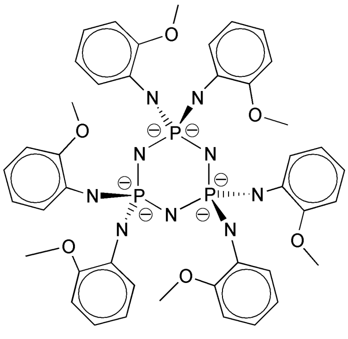
The hexaprotic phosphazene $\{2\text{-}(MeO)C_6H_4NH\}_6P_3N_3$ reacts with 12 equivalents of Bu^nLi in thf to give the monomeric dodecanuclear complex $(thf)_6Li_{12}[\{2\text{-}(MeO)C_6H_4N\}_6P_3N_3](CH_2{=}CHO)_6$ which contains six enolate anions resulting from fragmentation of thf; the hexaanionic pentadecadentate phosphazenate ligand $[\{2\text{-}(MeO)C_6H_4N\}_6P_3N_3]^{6-}$ accommodates a total of twelve lithium ions in bidentate chelation sites.

Ligands able to carry a high metal load (> 10 metal centres) have scarcely been investigated, although such systems bear the potential to stabilise well-defined multinuclear metal arrays. In contrast, a multinuclear metal arrangement held together by several counter ions in an oligomeric complex usually shows pronounced dynamic behaviour. Particularly, alkaline metal complexes are highly fluxional and their oligomerisation grades strongly depend on the nature of donor additives.[1] Recently, we have shown that cyclophosphazenes equipped with primary amino groups act as multiprotic acids in the presence of organometallic reagents yielding multianionic phosphazenates, highly charged ligands which complex multinuclear metal arrangements.[2–5] We observed that lithiated phosphazenates attract excess lithium ions and accommodate them by either dimer formation[3,4] or insertion of lithium enolate that is generated by fragmentation of thf.[5]

With the aim to increase the maximum metal load of phosphazenates we equipped the ligand with additional donor sites. The hexaanionic phosphazenate $\mathbf{A}^{6-}$ presented here carries six *ortho*-anisidyl substituents and features an overall pentadecadentate ligand surface comprising nine N and six O donor functions. The ligand precursor $H_6\mathbf{A}$ (**1**) was synthesised by reaction of excess *ortho*-anisidine with hexachlorocyclotriphosphazene in the presence of triethylamine.† We have reacted **1** with 12 equivalents of Bu^nLi in thf in order to both deprotonate all six NH-functions and incorporate the excess Bu^nLi or lithium enolate into the ligand sphere of $\mathbf{A}^{6-}$. The reaction yields a white precipitate that re-dissolves upon heating. Crystallisation occurs on leaving the solution to cool to room temperature.‡ Spectroscopic data and X-ray structure analysis§ reveal the formation of the monomeric complex $(thf)_6Li_{12}\mathbf{A}(CH_2{=}CHO)_6$ **2** (Fig. 1), which contains six enolate and twelve lithium ions.



$\mathbf{A}^{6-}$

$$\underset{\mathbf{1}}{H_6\mathbf{A}} + 12\,Bu^nLi + 12\,thf \longrightarrow \underset{\mathbf{2}}{(thf)_6Li_{12}\mathbf{A}(CH_2{=}CH\text{-}O)_6} + 12\,C_4H_{10} + 6\,C_2H_4$$

^{31}P NMR spectroscopy shows a single peak at δ 16.4 and the P–N-ring stretching frequency appears as a very strong and broad band with a maximum at 1077 cm^{-1} in the IR spectrum which is considerably red shifted compared to that of **1** (1186 cm^{-1}). The ligand $\mathbf{A}^{6-}$ accommodates a total of twelve lithium ions in bidentate chelation sites. To our knowledge this is the largest number of s-block metal ions being chelated by a single ligand in a molecular complex.

Complex **2** crystallises in space group $R\bar{3}c$ with eight lattice bound thf molecules per formula unit and exhibits D_3 symmetry. The central P_3N_3 ring is arranged around the three-fold axis and each phosphorus along with the opposite ring N atom is located on a two-fold axis. The nine anionic N-centres and six O-donor atoms of the ligand form two large, bowl shaped, nonadentate cavities on either side of the central P_3N_3 ring providing an ideal coordination geometry for the accommodation of twelve lithium ions: six lithium ions (Li1) reside at 'inner' coordination sites represented by six N_{exo}–P–N_{endo} chelates. The other six lithium ions (Li2) occupy the 'outer' sites, which are the N_{exo}–O chelates of the anisidyl groups. The negative charge of the hexaanion is distributed over all nine N-atoms, each binds two lithium ions, the N_{endo} atom (N1) two 'inner' lithium ions and the N_{exo} atom (N2) one 'inner' and one 'outer' lithium ion, respectively. In addition, each 'inner' lithium is coordinated by one thf molecule (O3) and one enolate ion (O1); each 'outer' lithium by the O-donor function of the ligand (O2) and two enolate ions. All lithium ions are coordinated in a tetrahedral fashion. The ^7Li NMR spectrum of **2** recorded in thf at room temperature exhibits two signals at δ 2.15 and 2.81. This suggests that the presence of two non-equivalent lithium ions is retained in solution.

Bond lengths and angles of the P_3N_9 core in **2** are in agreement with those we found in other lithium phosphaze-

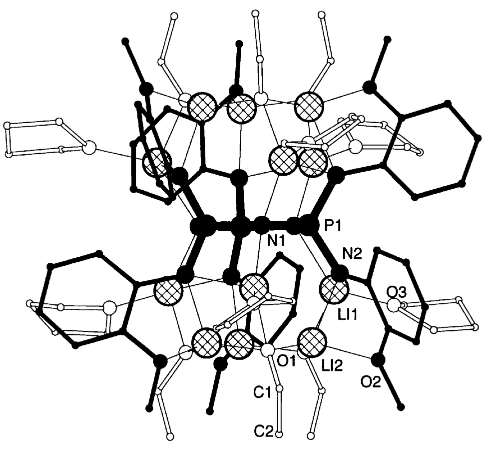


Fig. 1 X-Ray crystal structure of **2**. The $\mathbf{A}^{6-}$ ligand is drawn in black, thf and enolate moieties in white and lithium ions hatched.

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nates.[3,4] P–N$_{endo}$ and P–N$_{exo}$ bonds are of similar length [1.638(2) and 1.637(3) Å, respectively], and the N$_{exo}$–P–N$_{exo}$ angle [115.0(2)°] is similar to the N$_{endo}$–P–N$_{endo}$ angle [113.4(3)°], showing equal P–N$_{endo}$ and P–N$_{exo}$ bond orders and distribution of negative charge over all nine N-atoms. In contrast, the neutral precursor **1** exhibits long P–N$_{exo}$ bonds (av. 1.65 Å) and short P–N$_{endo}$ bonds (av. 1.59 Å); and *endo* angles (av. 115°) are wider than *exo* angles (av. 104°) indicating a higher bond order in the P_3N_3 ring of **1**.§ Surprisingly, the central P_3N_3 ring in **2** is planar, which is in contrast to all other lithiated cyclotriphosphazenates we have investigated so far. All contain highly puckered central P_3N_3 rings of chair conformation. The P–N–P angle of **2** is 126.6(3)° and thus considerably wider than those observed in hexaanionic $[(CyN)_6P_3N_3]^{6-}$,[3] trianionic $[(CyNH)_3(CyN)_3P_3N_3]^{3-}$, $[(PhNH)_3(PhN)_3P_3N_3]^{3-}$,[4] and neutral H$_6$**A**, which are all around 120°. This shows that the P–N–P angle is rather flexible allowing a planar configuration of the central P_3N_3 ring in hexaanionic **2**.

We monitored the reaction of **1** with Bu^{n}Li in thf using ^{31}P NMR spectroscopy. Addition of 3 equivalents of Bu^{n}Li exclusively gives trianionic H$_3$**A**$^{3-}$ as indicated by a single peak at δ 8.7. Addition of 6 equivalents of Bu^{n}Li leads to three broad peaks at δ 13.1, 19.1 and 22.2 suggesting that the fully deprotonated species **A**$^{6-}$ is not present so far. However, **A**$^{6-}$ begins to form after addition of around 8 equivalents of Bu^{n}Li, as shown by the appearance of a sharp single peak at δ 16.4 amongst a pattern of broader signals. Finally there is only one single peak at δ 16.4 after addition of 12 equivalents Bu^{n}Li. This implies that both deprotonation of NH functions and enolate formation occur simultaneously once 3 equivalents of Bu^{n}Li are added.

The fragmentation of thf by Bu^{n}Li, which produces lithium ethenolate and ethylene, is well known[6] and also adduct formation of LiO–CH=CH$_2$ was observed in solid state structures of lithium complexes containing tetraanionic ligands.[5,7] However, the inclusion of six lithium enolate moieties into a molecular complex is unprecedented. We assume, once the ligand acquires a certain charge it acts as a 'Li$^+$ sponge': Bu^{n}Li is dragged into an 'outer' *N,O*-chelation site, which contains an already deprotonated *N*-function, and fragments a thf molecule, which is coordinated to a neighbouring 'inner' lithium ion. The resulting enolate ions are not sufficiently basic to deprotonate H_xA^{x-6} (x = 1, 2) any further, but remain within the complex by forming μ_3-bridges between one 'inner' and two 'outer' lithium ions.

Summarising, the generation of a ligand system with high metal loading capacity has been accomplished by combining the features of a multianionic ligand core with a multidentate ligand surface. The hexaanionic pentadecadentate phosphazenate ligand **A**$^{6-}$ accommodates twelve lithium ions in bidentate chelation sites. Currently, we are investigating self-assembly properties of this new ligand system in the presence of LiX, where X represents a monodentate monoanion (*e.g.* halide, alkoxide, amide, carbanion), potentially leading to complexes $Li_{12}A_6X_6$. Such systems promise interesting template effects, due to the potentially well-defined array of both lithium ions and counter ions X. In addition, the straightforward introduction of a variety of substituents into phosphazenes[8,9] might facilitate the generation of a wide range of other high metal loading ligands based on multidentate phosphazenates.

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Notes and references

† *Preparation* of **1**: to a solution of 10 g hexachlorocyclotriphosphazene in 100 ml of toluene was added 40 ml of *ortho*-anisidine and 100 ml of triethylamine. The mixture was refluxed for several days (^{31}P NMR control). The solution was allowed to cool to room temperature, separated by filtration from the precipitate, which was washed with toluene. All volatile components of combined filtrates were removed *in vacuo*. The resulting residue was washed with hot hexane to give a white powder, which was re-crystallised from thf–hexane. Yield: 19.7 g (79%), mp 175 °C, ^{1}H NMR (300 MHz, d$_8$-thf) δ 3.55 (s, 18H, OCH$_3$), 5.72 (m, 6H, NH), 6.55 (m, 6H, aryl-H), 7.42 (m, 18H, aryl-H); ^{13}C{^{1}H} NMR (75.46 MHz, d$_8$-thf) δ 56.4 (OCH$_3$), 111.29, 119.10, 121.44, 121.90, 132.59, 149.72 (aromatic C); ^{31}P NMR (101.25 MHz, d$_8$-thf, 85% H$_3$PO$_4$ in D$_2$O ext.) δ 5.1; IR (Nujol) ν/cm^{-1} 3385 (N–H), 1596, 1247, 1186 (P–N-ring), 1111, 1026, 870, 734.

‡ *Preparation* of **2**: to a solution of **1** (300 mg, 0.345 mmol) in 20 ml of thf was added Bu^{n}Li (2.6 ml, 1.6 M in hexane, 4.14 mmol). The solution was stirred overnight at room temperature forming a white precipitate, which was re-dissolved by gentle heating. On cooling to room temperature colourless crystals formed, which disintegrated in the absence of mother-liquor by losing lattice bound thf to give a white powder. Yield: 340 mg (88%), decomp. > 180 °C; ^{1}H NMR (300 MHz, d$_8$-thf) δ 3.79 (s, 18H, OCH$_3$), 3.41 (d, 6H, $^3J_{cis}$ 5.4 Hz, HC=), 3.96 (d, 6H, $^3J_{trans}$ 13.9 Hz, HC=), 6.05–6.47 (m, 18H, aryl-H), 6.51 (dd, 6H, $^3J_{cis}$ 5.4, $^3J_{trans}$ 13.9, =CHO), 7.55 (dd, 6H, aryl-H); ^{13}C{^{1}H} NMR (75.46 MHz, d$_8$-thf) δ 56.3 (OCH$_3$), 86.1 (=CH$_2$), 109.5, 114.2, 120.0, 123.1, 144.3, 150.9 (aromatic C), 159.2 (OCH=); ^{31}P NMR (101.25 MHz, thf, 85% H$_3$PO$_4$ in D$_2$O ext.) δ 16.43; ^{7}Li NMR (97.16 MHz, thf, LiCl in D$_2$O ext) δ 2.15, 2.81; IR (Nujol) ν/cm^{-1} 1621, 1590, 1377, 1316, 1282, 1258, 1216, 1178, 1077 (P–N-ring), 1056, 1030, 826, 781, 736, 634.

§ Crystallographic data were recorded on a Stoe-IPDS using Mo-Kα radiation (λ = 0.71073 Å), T = 200 K, structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELX-97).

Crystal data: for **1**·0.5thf: M = 903.96, triclinic, $P\bar{1}$, a = 11.570(2), b = 12.059(2), c = 18.076(3) Å, α = 77.42(2), β = 79.85(2), γ = 67.35(2)°, U = 2259.4(5) Å^3, Z = 2, D_c = 1.329, μ(Mo-Kα) = 0.148, 6717 unique reflections. R_1 [$I > 2\sigma(I)$] = 0.037, wR_2 (all data) = 0.068.

For **2**·8thf: M = 2212.76, rhombohedral, $R\bar{3}c$, a = 14.506(8), c = 100.883(11) Å, U = 18384(2) Å^3, Z = 6, D_c = 1.199, μ(Mo-Kα) = 0.119, 2647 unique reflections, R_1 [$I > 2\sigma(I)$] = 0.069, wR_2 (all data) = 0.205. C-positions of coordinated thf are disordered and were split in two positions. There are 1⅓ lattice bound thf molecules per asymmetric unit: thf on general site is disordered and its C and O atoms were split in two positions, thf on 3 is disordered around the 3-axis generating three positions per atom. Disordered groups were refined using similar distance and similar U restraints and site occupancy factors. All non-H atoms were refined anisotropically, except lattice bound thf molecules, which were treated isotropically. H atoms were fixed in calculated positions on the parent C atoms.

CCDC 152011–152012. See http://www.rsc.org/suppdata/cc/b1/b104124j/ for crystallographic data in CIF or other electronic format.

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