Zinc oxide clusters encapsulated by organozinc phosphazenate assemblies

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Abstract

Phosphazenes (^{i}BuNH)$_6$P$_3$N$_3$ and (BzNH)$_6$P$_3$N$_3$ were combined with 1.5 equivalents of water and 7.5 equivalents of diethylzinc resulting in the formation of zinc oxide phosphazenate complexes Zn$_3$O$_2$[(^{i}BuN)$_6$P$_3$N$_3$(EtZn)$_5$]$_2$ (**6**) and Zn$_2$O$_2$[(BzN)$_6$P$_3$N$_3$(EtZn)$_6$]$_2$ (**7**), respectively. X-ray structure analysis showed that in both complexes the organozinc phosphazenate moieties encapsulate the zinc oxide clusters, Zn$_3$O$_2$ (in **6**) and Zn$_2$O$_2$ (in **7**), which were generated in situ by hydrolysis of Et$_2$Zn. The geometry and nuclearity of the encapsulated zinc oxide clusters is largely controlled by the steric bulk of the host phosphazenate arrangement, which offers well-defined arrays of Lewis acidic Zn and Lewis basic N sites for coordinating both zinc and oxide ions.
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1. Introduction

Molecular metal oxides of low-oxidation state metal ions have attracted much interest in recent years [1,2]. In particular, zinc oxide complexes have been well studied.[3]. The coordination number of oxide ions can vary from two to four depending on the steric demand of substituents on zinc. A survey of the literature shows that several structural motifs are known (Fig. 1). These include Zn$_2$O (**a**) [4], Zn$_3$O (**b**) [5], Zn$_4$O (**c**) [6], Zn$_4$O$_2$ (**e**) [7], Zn$_6$O$_2$ (**f**) [8] and Zn$_7$O$_2$ (**g**) [9,10]. None of the known complexes bearing zinc oxide clusters contain more than two oxide centres. Only recently our group has discovered high nuclearity zinc oxides of the type Zn$_9$O$_3$ (**d**) and Zn$_{12}$O$_6$ (**h**). These complexes were prepared by a one-pot reaction involving aminophosphazenes (RNH)$_6$P$_3$N$_3$, x equivalents of water and $3 + x$ equivalents of diethylzinc (Scheme 1). The zinc oxide clusters were generated in situ by reaction of x equiv-

alents of Et$_2$Zn with x equivalents of H$_2$O. The tri-anionic cyclophosphazenate ligand (**I**) forms in conjunction with three EtZn units a bowl shaped segment **1**. This features three Lewis acidic zinc sites and three Lewis basic N sites and acts as a C_3 symmetrical template for trimeric and hexameric zinc oxide clusters [11]. The type of zinc oxide cluster (trimeric or hexameric) obtained in these reactions depends on the nature of steric groups present in the molecule. While the use of less bulkier phosphazenes ($R = {^n}$Pr, ^{i}Bu) leads to trimeric clusters **2** and **3**, the presence of a bulky phosphazene ($R =$ Cy) results in the hexameric cluster **4** [11]. In view of this we were interested to study the complexing behaviour of the fully deprotonated hexaanionic cyclophosphazenate ligands (**II**) towards zinc oxide clusters (see Fig. 2).

2. Results and discussion

Extending our studies from previous work [11], we carried out the reactions involving aminophosphazenes (RNH)$_6$P$_3$N$_3$, water and diethylzinc in various stoichiometric ratios in view of utilising the fully deprotonated phosp-

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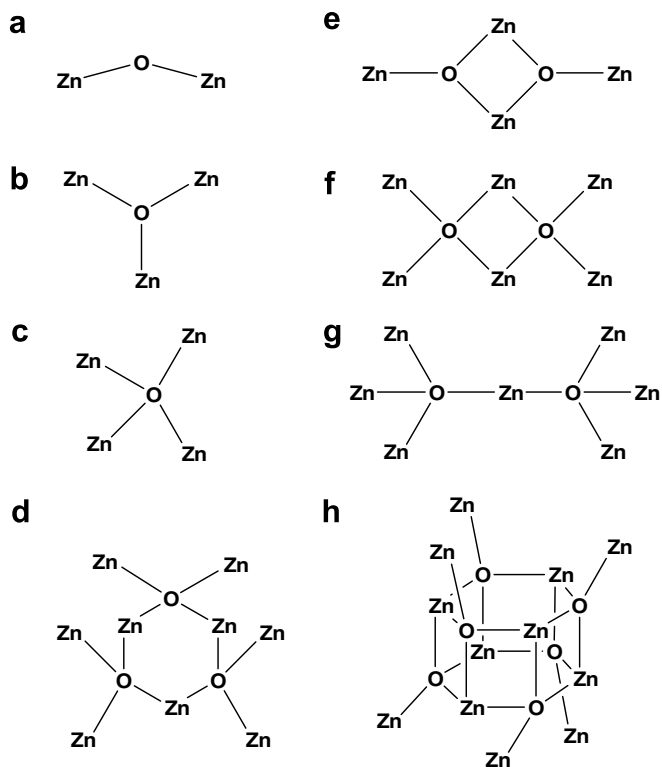 *E-mail addresses:* boomi@liv.ac.uk (R. Boomishankar), a.steiner@liv.ac.uk (A. Steiner).

Fig. 1. Pictorial representation of oxide ions in various molecular Zn–O assemblies.

hazenate ions **II** to encapsulate zinc oxide clusters. We have combined the phosphazene $(RNH)_6P_3N_3$ with 1.5 equivalents of H_2O and 7.5 equivalents of Et_2Zn, which is required for both the full deprotonation of phosphazene and the in situ hydrolysis of the excess Et_2Zn (Scheme 2). Although many of the reactions resulted in indistinct product mixtures, we were able to isolate crystals suitable for X-ray structure analysis from product mixtures in two instances.

In the first instance a hexane solution containing the phosphazene $(^iBuNH)_6P_3N_3$, 1.5 equivalents of water and 7.5 equivalents of diethylzinc was refluxed for 12 h. In the second instance a toluene solution of the phosphazene $(BzNH)_6P_3N_3$, 1.5 equivalents of water and 7.5 equivalents of diethylzinc is refluxed for 12 h. The ^{31}P NMR of both reaction solutions showed a product mixture that contained one major component as indicated by the appearance of a predominant peak at 32.3 and 31.1 ppm, respectively. Storage of the filtered solutions resulted in the formation of single crystals among a white precipitate. Crystal structures of both crystalline products revealed the formation of the complexes $Zn_3O_2[(^iBu)_6P_3N_3(EtZn)_5]_2$ (**6**) and $Zn_2O_2[(BzN)_6P_3N_3(EtZn)_6]_2$ (**7**), respectively (Table 1). Further data could not be obtained for both compounds, since it proved impossible to separate a sufficient amount of pure compound from the precipitate.

Both complexes contain zinc oxide clusters that are encapsulated by two ethylzinc phosphazenate segments. **6** exhibits an acyclic dicationic $[Zn_3O_2]^{2+}$ core, which is part of a Zn_7O_2 assembly of type **g**, whereas **7** displays a neutral

Zn_2O_2 ring that is part of a Zn_6O_2 assembly of type **f**. While in the 14-nuclear zinc complex **7** each hexaanionic ligand hosts six ethylzinc groups to form a $[(EtZn)_6$**II**$]$ segment (Fig. 4), in the 13-nuclear zinc complex **6** each ligand hosts only five ethylzinc groups in a monoanionic $[(EtZn)_5$**II**$]^-$ segment (Fig. 3). However, while **7** contains a neutral Zn_2O_2 unit, the overall charge in **6** is restored by accommodation of the formally dicationic $[Zn_3O_2]^{2+}$ unit. Fig. 5 compares the coordination surfaces of segments $[(EtZn)_3$**I**$]$ (in **2**), $[(EtZn)_5$**II**$]^-$ (in **6**) and $[(EtZn)_6$**II**$]$ (in **7**) that are available for ZnO coordination. While $[(EtZn)_3$**I**$]$ offers three basic N-sites and three acidic EtZn sites, there are only three N-sites and two EtZn sites available at the $[(EtZn)_5$**II**$]^-$ segments in **6** and merely two N-sites and two EtZn sites on offer at the segment $[(EtZn)_6$**II**$]$ in **7**. The restriction of the coordination surfaces in **6** and **7** is due to the uptake of additional EtZn units per ligand. As a result the size of the encapsulated ZnO moieties is reduced to a $[Zn_3O_2]^{2+}$ unit in **6** and a Zn_2O_2 unit in **7**. A closer look at the crystal structure of **6** reveals that the phosphazenate ligands are still 'sandwiching' the zinc oxide cluster, but are puckered into a half-chair conformation. The out-of-plane N atom is bent towards the vacant site of the $[Zn_3O_2]^{2+}$ unit. In **7** the phosphazenate rings are forced into a boat conformation and are bent away from the central Zn_2O_2 unit, leading to a departure from the 'sandwich' mode observed in **2**.

All Zn^{2+} ions in **6** and **7** adopt tetrahedral coordination geometries. The $[Zn_3O_2]^{2+}$ unit of **6** can be regarded as a hexagon missing one vertex. This is reflected by its bond angles which measure 128.44(1)° at Zn and 118.35(2)° at O. Obviously, sharper angles are observed in the planar four-membered Zn_2O_2 ring of **7**, which measure 97.57(1)° at Zn and 84.15(1)° at O. The Zn–O bond lengths involving Zn^{2+} and oxide ions are somewhat shorter in **6** than in **7**. Within the $[Zn_3O_2]^{2+}$ unit of **6**, the central zinc ion is associated with longer Zn–O bond distances (av. 1.98 Å) compared to the two terminal zinc ions (av. 1.928 Å). In contrast, the planar four-membered Zn_2O_2 core of **7** exhibits Zn–O bonds ranging from 2.015(1) to 2.077(1) Å. On the other hand **7** shows on average shorter Zn–O bonds towards EtZn units ranging from 1.917(0) to 1.940(0) Å compared to **6** where the EtZn–O bonds vary from 1.946(5) to 2.007(4) Å. These variations might be a consequence of the different types of chelation of O-coordinating EtZn units in **6** and **7**. In compound **6** these are chelated within a bidentate N(ring)–N(exo) site, while in **7** they are solely coordinated to the ligand via one N(ring) site. EtZn units not engaged in coordination to oxide ions in **6** and **7** are accommodated in either bidentate or tridentate coordination sites resembling those already observed in the previously described hexakis(ethylzinc) phosphazenate complex, which exists as a monomer in the solid state [12]. The variety of coordination modes and the large number of accommodated Zn centres per ligand leads to considerable distortion of the ligand structure. For example the P–N bond lengths in the P_3N_3 rings range by a wide
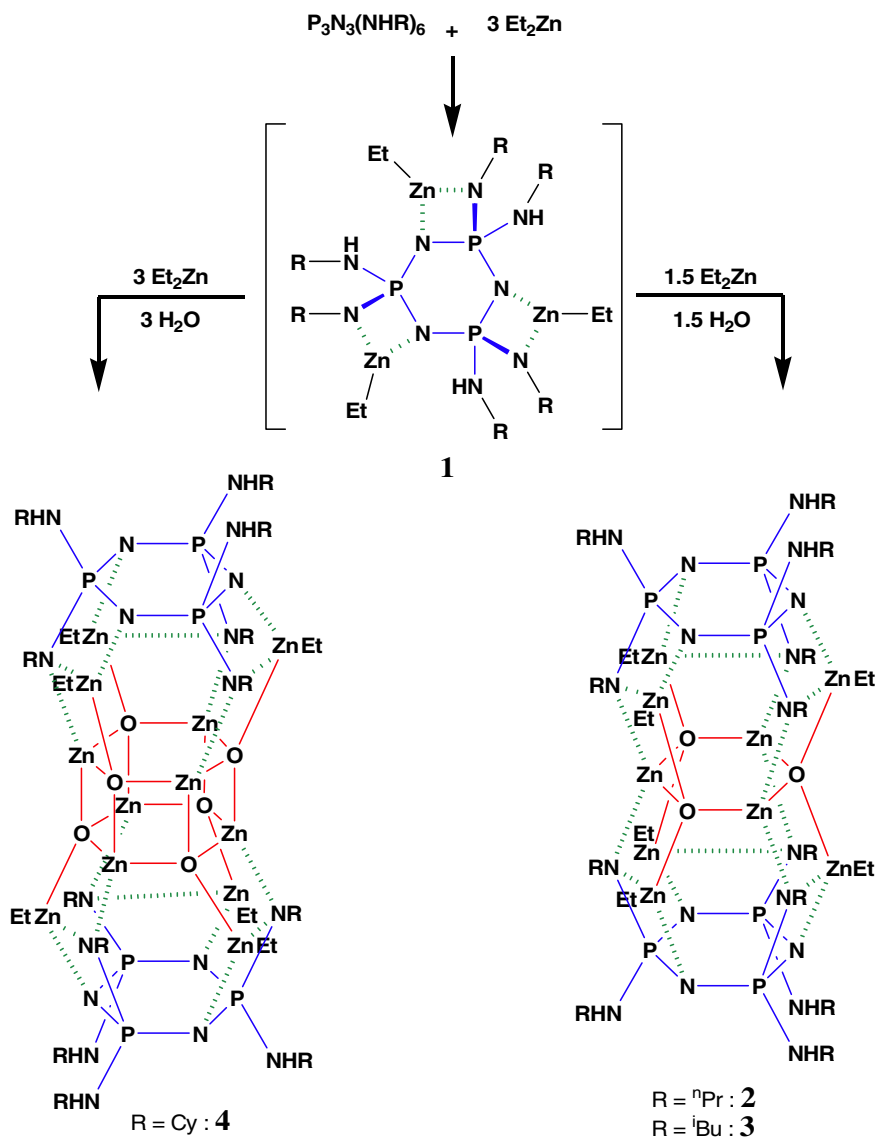
Scheme 1. One-pot syntheses of trimeric and hexameric zinc oxide clusters involving phosphazene, water and diethylzinc in 1:x:3+x ratios.
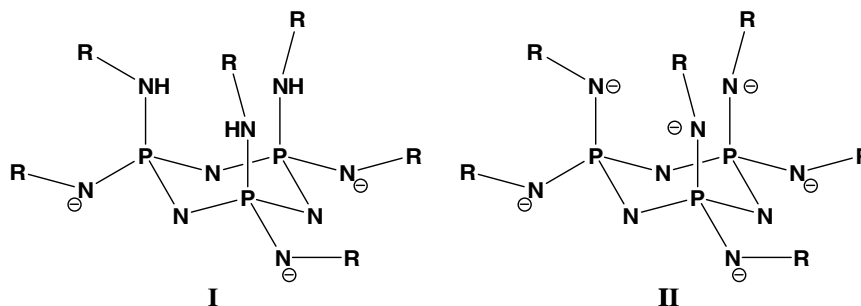

Fig. 2. Schematic drawings of the phosphazenate trianion (**I**) and hexaanion (**II**).

margin from 1.605(4) to 1.667(3) Å in **6** and from 1.618(1) to 1.671(2) Å in **7**. Similarly, the P–N(exo) bond lengths differ from 1.606(3) to 1.666(3) Å in **6** and from 1.586(1) to 1.666(1) Å in **7**. In general, P–N bonds involving N-sites that bind two zinc centres are markedly elongated.

3. Conclusion

We have demonstrated that (ethylzinc) phosphazenate complexes can stabilize various zinc oxide assemblies. While tris(ethylzinc) complexes provide a bowl shaped

$$P_3N_3(NHR)_6 \ + \ 6\,Et_2Zn$$
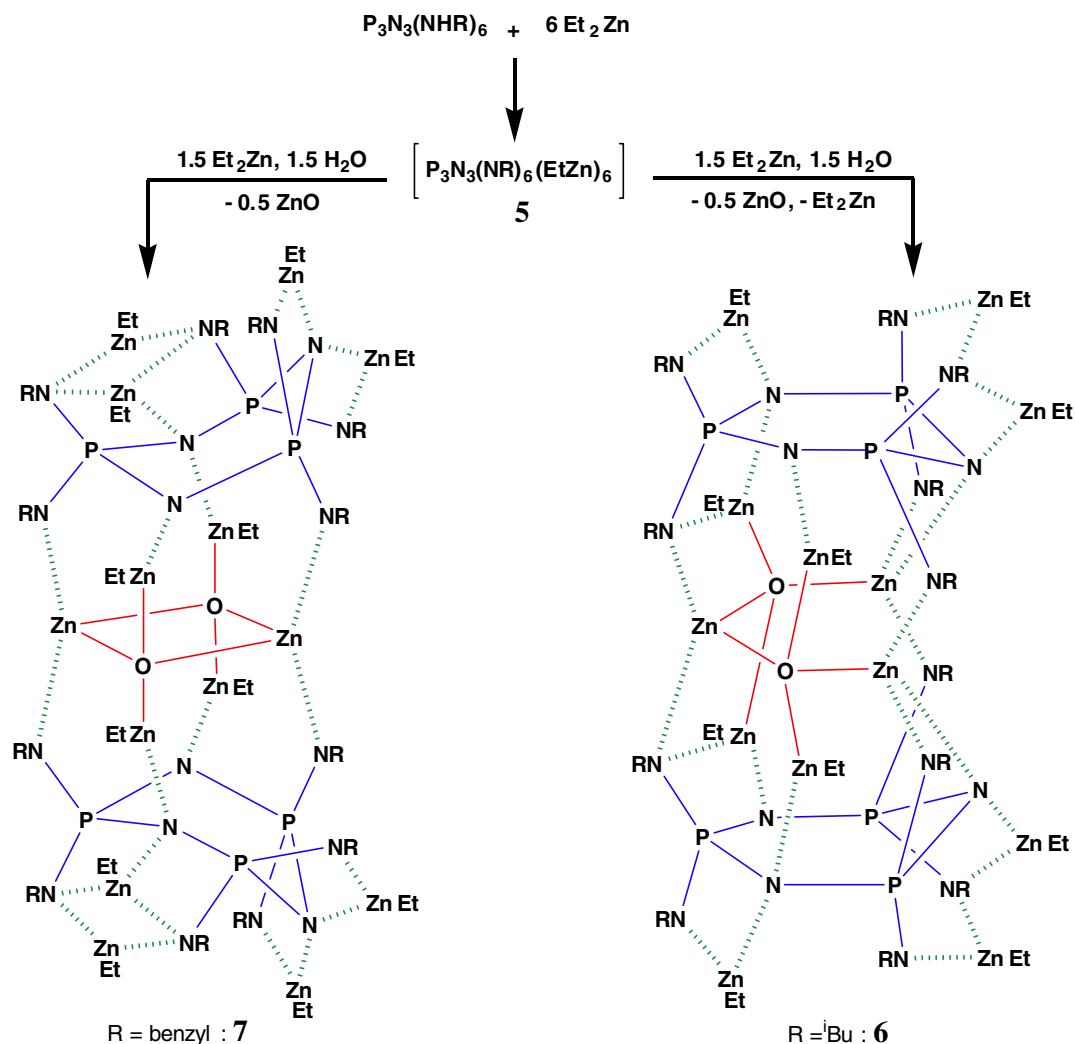
Scheme 2. One-pot syntheses of complexes **6** and **7** involving phosphazene, water and diethylzinc in 1:1.5:7.5 ratios.

Table 1
Crystallographic data for **6** and **7**

Compound	6	7
Chemical formula	$C_{68}H_{158}N_{18}O_2P_6Zn_{13}$	$C_{108}H_{148}N_{18}O_2P_6Zn_{14}$
Formula weight	2295.75	2827.41
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	14.103(4)	18.2874(16)
b (Å)	17.130(5)	24.635(2)
c (Å)	21.683(7)	26.090(2)
α (°)	87.872(5)	90
β (°)	80.793(5)	90.014(2)
γ (°)	72.814(5)	90
V (Å^3)	4940(3)	11760(18)
Z	2	4
μ (Mo Kα) (cm^{-1})	3.237	2.934
ρ_{calc} (g cm^{-1})	1.544	1.597
Reflections, total	13621	17020
Reflections, unique	9628	5846
R_{int}	0.025	0.090
GoF	1.072	1.009
R_1 ($F > 4\sigma(F)$)	0.0428	0.0528
wR_2 (all data)	0.1042	0.1366

coordination surface for trimeric and hexameric Zn–O clusters, the geometries of penta- and hexa(ethylzinc) phosphazenates offer a more restricted coordination surface for zinc oxide clusters. Encapsulation of Zn–O clusters into organozinc phosphazenate assemblies is facilitated by in situ hydrolysis of excess Et$_2$Zn using stoichiometric additions of water. Currently, we are investigating metal oxide inclusion into phosphazenate assemblies using other organometallic reagents.

4. Experimental

4.1. General remarks

All manipulations were performed under dry nitrogen atmosphere in standard Schlenk-glassware or in a glove box. Solvents were dried over sodium (toluene) and potassium (hexane), respectively. Phosphazene precursors (^{i}BuNH)$_6$P$_3$N$_3$ and (BzNH)$_6$P$_3$N$_3$ were prepared according to published procedures [13]. Et$_2$Zn was applied as 1.0 M standard solution in hexane (Aldrich). FT-IR spectra were

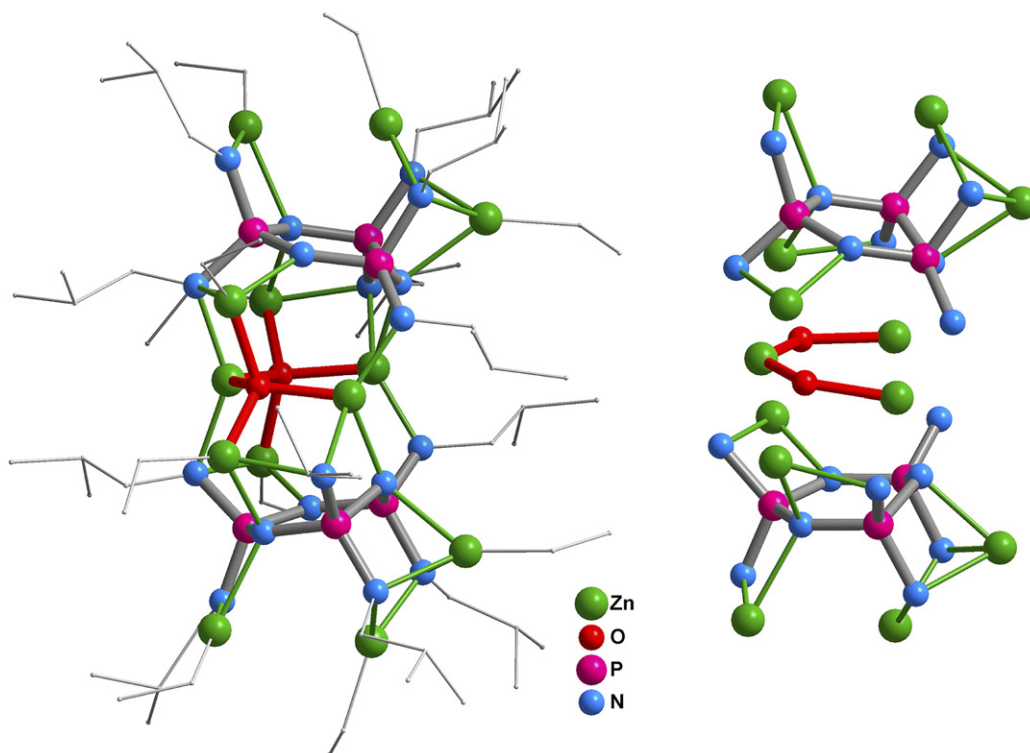Fig. 3. Crystal structure of **6** showing its formal assembly from two [(EtZn)$_5$**II**]$^-$ segments and the centrally accommodated [Zn$_3$O$_2$]$^{2+}$ unit.

recorded on a Perkin–Elmer Paragon 1000 spectrometer in nujol between CsI plates. NMR spectra were recorded on a Bruker AMX 400 Spectrometer.

6: To a mixture of P$_3$N$_3$(NH^{i}Bu)$_6$ (0.25 g, 0.44 mmol) and H$_2$O (0.012 mL, 0.66 mmol) in hexane (15 mL) kept in a Schlenk flask, 3.3 mL of diethylzinc (0.65 g, 3.3 mmol) was added drop wise via a syringe. The reaction mixture was refluxed for 12 h and was filtered through celite. The filtrate was concentrated to 2 ml and kept for crystallization at −20 °C. Colourless block-like crystals were formed after 10 days amongst a white precipitate. ^{31}P NMR taken from reaction solution (162 MHz, hexane, 25 °C, 85% H$_3$PO$_4$ ext.) showed a complex signal pattern amongst which one signal is predominant at δ 32.3 (s). The ^{31}P NMR from the mixture of precipitate and crystals is similar to that taken from the reaction solution. IR spectrum (Nujol, cm^{-1}) taken from the mixture of crystals and precipitate: 1403 (w), 1289 (w), 1259 (s), 1225 (s, sh), 1150 (vs), 1114 (s), 1075 (s).

7: To a mixture of P$_3$N$_3$(NHBz)$_6$ (0.30 g, 0.39 mmol) and H$_2$O (0.011 mL, 0.59 mmol) in toluene (15 mL) kept in a Schlenk flask, 2.95 mL of diethylzinc (0.43 g, 2.95 mmol) was added drop wise via a syringe. The reaction mixture was refluxed for 12 h and was filtered through celite. The filtrate was concentrated to 2 ml and kept for crystallization at −20 °C. Colourless block-like crystals were formed after 15 days accompanied by a white precipitate. ^{31}P NMR taken from reaction solution (162 MHz, toluene, 25 °C, 85% H$_3$PO$_4$ ext.) showed a complex signal pattern amongst which one signal is predominant at δ

31.1 (s). The ^{31}P NMR from the mixture of precipitate and crystals resembles that taken from the reaction solution. IR spectrum (Nujol, cm^{-1}) taken from the mixture of crystals and precipitate: 1401 (w), 1261 (s), 1209 (w), 1095 (w), 1021 (vs).

4.2. Crystallography

Crystallographic data were recorded on a Bruker Smart Apex diffractometer using MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 150 K. Structures were refined by full-matrix least squares against F^2 using all data (SHELXTL) [14]. Two ^{i}butyl and two ethyl groups are disordered in **6**. The structure of **7** contains two disordered ethyl groups. The disordered atoms of the ethylzinc and ^{i}butyl groups were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group. Apart from disordered atoms, all non-hydrogen atoms were refined aniostropically and hydrogen atoms were fixed geometrically.

5. Supplementary material

CCDC 623932 and 623933 contain the supplementary crystallographic data for **6** and **7** in CIF format. These data can be obtained free of charge via http://www.ccdc.cam.a-c.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@-ccdc.cam.ac.uk.
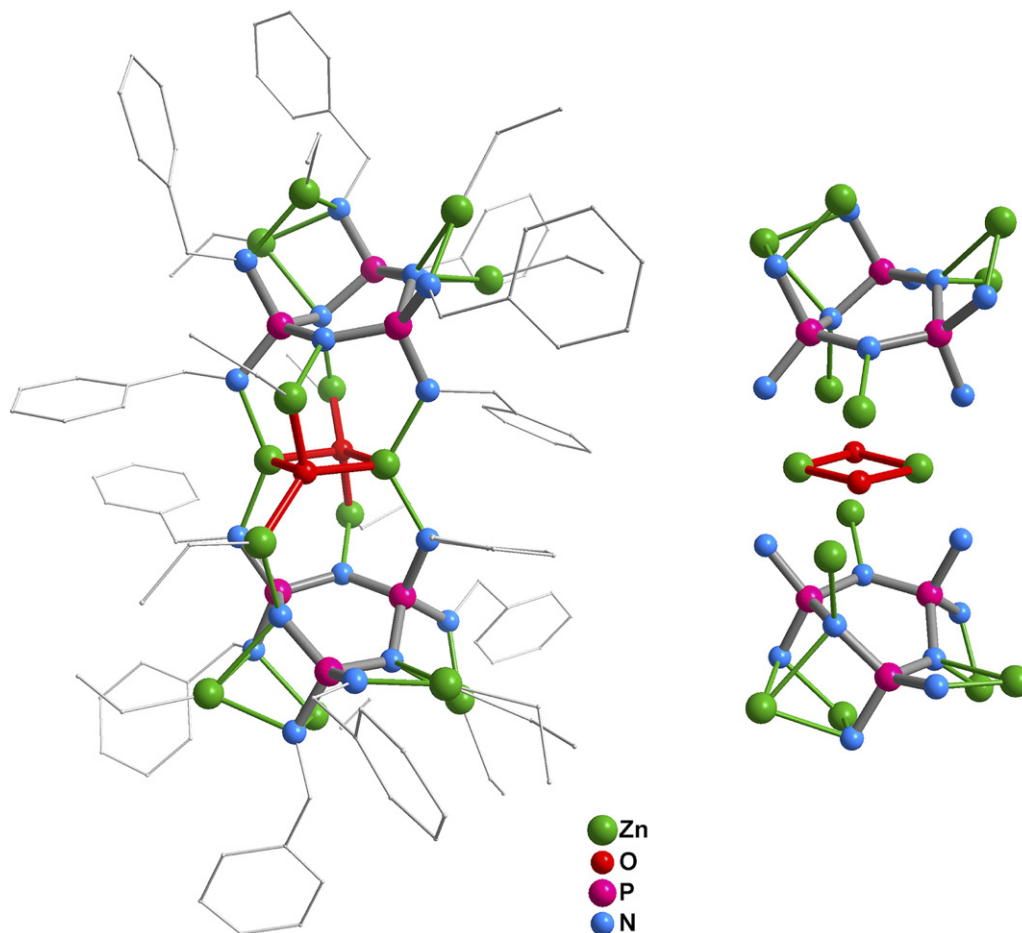
Fig. 4. Crystal structure of **7** showing its formal assembly from two [(EtZn)$_6$**II**] segments and the centrally accommodated Zn$_2$O$_2$ unit.
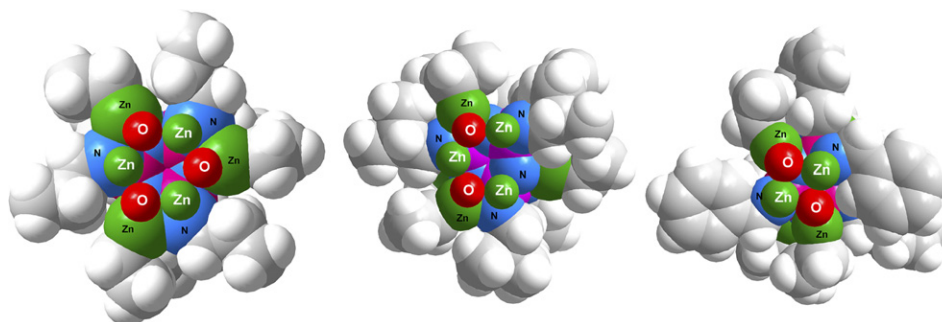

Fig. 5. Coordination surfaces of segments [(EtZn)$_3$**I**] (in **2**), [(EtZn)$_5$**II**]$^-$ (in **6**) and [(EtZn)$_6$**II**] (in **7**) that are available for coordination to ZnO clusters. The smaller spheres represent the encapsulated zinc oxide clusters.

Acknowledgement

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