# First lanthanide complexes and unusual coordination behavior of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene

**Bo Hwan Koo, Younghun Byun, Eunkee Hong, Youngjo Kim and Youngkyu Do*†**

*Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea*

**Reaction of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene (L) with $LnCl_3$ (Ln = La, Ce, Nd, Sm) affords new mononuclear lanthanophosphazenes [L·$LnCl_3$] with hendecahedral coordination polyhedron in which the ligand L employs an unprecedented κ$^5$N binding core consisting of one cyclotriphosphazene ring nitrogen atom and four pyridinic nitrogen atoms of two sets of geminal pyrazolyl groups.**

The use[1–6] of exocyclic donor groups attached to phosphazene skeletal phosphorus appears to be the most versatile method of preparing metallophosphazene complexes, the chemistry of which has been the subject of increasing research interest in conjunction with the potential opportunities for discovering new materials.[7] Successful applications of exocyclic donors such as pyrazolyl[1–4] and cyclopentadienyl[5] groups are cases in point. However, the scope of the coordination chemistry of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene (L), a potential multidentate ligand due to its multiple chelate sites,[8] has only been examined with $d^{10}$ metal halides[1] and $d^9$ $Cu^{II}$ ion,[2] revealing the limited coordination behavior with the binding cores of (κ$^3$N) for mononuclear species and (κ$^3$N–κ$^2$N) and (κ$^3$N–κ$^3$N) for dinuclear complexes. Here, we present the first examples of lanthanophosphazenes [L·$LnCl_3$] (Ln = La, Ce, Nd, Sm) where the ligand L acts as an unprecedented κ$^5$N binding core donor for a metal center to form a hendecahedral coordination sphere.

A solid mixture of anhydrous $LnCl_3$ (0.3–0.6 mmol) and L (0.2 mmol) was allowed to react in 20 ml of $CH_2Cl_2$ under $N_2$ atmosphere. After being stirred at room temperature for 12 h, the reaction mixture was filtered. The volume of the filtrate was reduced *in vacuo*, and *ca.* 30 ml of $Et_2O$ added. The resulting crystalline solid‡ was collected and recrystallized from $CH_2Cl_2$–$Et_2O$, affording the extremely air sensitive analytically pure§ product [L·$LnCl_3$] (Ln = La **1**, Ce **2**, Nd **3**, Sm **4**) in a yield of 50–55%.

In contrast to the single phosphazene ring P–N stretching band at 1226 $cm^{-1}$ for free L, the appearance of two $\nu_{PN}$ peaks at *ca.* 1235 and 1210 $cm^{-1}$ for [L·$LnCl_3$] indicates that the phosphazene ring nitrogen atom is involved in coordination to the metal center. In addition, the comparison of the IR spectra suggests that all four lanthanophosphazenes have the same structural core. Single crystal X-ray analysis,¶ performed on **4**, revealed unprecedented κ$^5$N pentadentate coordination behavior of L as displayed in Fig. 1. One cyclophosphazene ring nitrogen atom N(1) and four pyridinic nitrogen atoms N(12), N(22), N(32) and N(42) from two sets of geminal pyrazole substituents on P(1) and P(2) constitute the κ$^5$N binding core to coordinate $SmCl_3$, forming an eight-coordinate complex. The analysis of the shape parameters[11] indicates that the coordination sphere of **4** can be best described as a distorted hendecahedron illustrated in Fig. 2. The complexation caused $P_3N_3$ ring puckering the extent of which can be measured from the displacement of the N(1) atom (0.305 Å) from the plane defined by P(1), P(2), P(3), N(2) and N(3) and the dihedral angle of 22.1° between the P(1)N(1)P(2) plane and the P(1)N(3)P(3)N(2)P(2) plane. The overall molecular symmetry approaches *pseudo*-$C_s$. The Sm atom interacts more strongly with L *via* the phosphazene ring nitrogen atom N(1) than *via* the pyridinic nitrogen atoms: the Sm–$N_{ring}$ bond distance of 2.499 Å is shorter than the average Sm–$N_{pyz}$ distance of 2.832 Å. It is noteworthy that the reversed pattern in interaction between metal centers and the ligand L was observed in previously reported transition metal phosphazene complexes.[1,2]

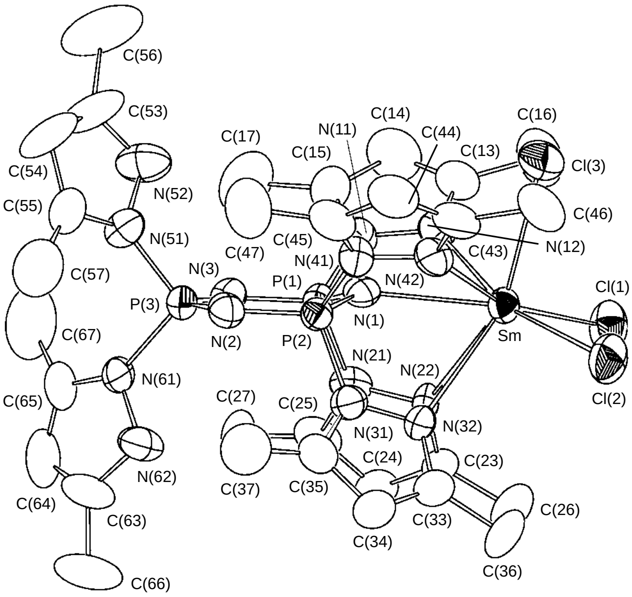

**Fig. 1** Molecular structure of **4** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Sm–Cl(1) 2.659(3), Sm–Cl(2) 2.632(3), Sm–Cl(3) 2.628(2), Sm–N(1) 2.499(8), Sm–N(12) 2.859(10), Sm–N(22) 2.771(8), Sm–N(32) 2.860(8), Sm–N(42) 2.839(10), P(1)–N(1) 1.592(9), P(1)–N(3) 1.564(10), P(2)–N(1) 1.593(9), P(2)–N(2) 1.574(9), P(3)–N(2) 1.577(9); Cl(1)–Sm–N(1) 135.1(2), Cl(1)–Sm–N(12) 78.3(2), Cl(1)–Sm–N(22) 79.8(2), Cl(1)–Sm–N(32) 126.1(2), Cl(1)–Sm–N(42) 160.2(2), Cl(3)–Sm–N(32) 140.2(2).

In solution at room temperature, the compounds [L·$LnCl_3$] lose their solid state symmetry and undergo a new type of fluxional motion (Fig. 3) not seen in $d^{10}$ metal complexes of L.[1]

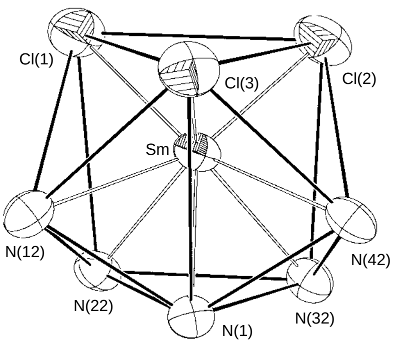

**Fig. 2** Hendecahedral coordination geometry of **4**

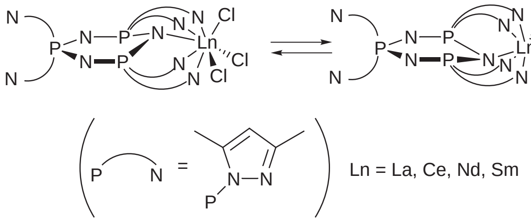

**Fig. 3** Solution fluxional motion of [L·LnCl$_3$] in CDCl$_3$

The $^{31}$P{$^1$H} NMR spectra§ of [L·LnCl$_3$] complexes are of $A_2X$ type, invoking only the rotational motion of geminal pyrazolyl groups at P(3) around P–N bonds. However $^1$H-NMR spectra§ in CDCl$_3$ show two pyrazolyl ring proton signals of ratio 2 : 4 and four methyl peaks with 12 : 6 : 6 : 12 ratio and thus indicate the presence of two types of magnetically different pyrazolyl rings in 1 : 2 ratio. Two pyrazolyl rings at P(3) and four pyrazolyl rings involved in coordination are respectively magnetically identical, requiring the presence of a fluxional motion such as the movement of the N(1)–LnCl$_3$ unit as illustrated in Fig. 3. The assignment of the most upfield peak as 3-methyl protons of pyrazolyl groups coordinated to metal was made based on the observation of the upfield shift and simultaneous broadening of the peak upon cooling to 218 K for **4**.

The use of 3,5-dimethyl substituted pyrazole seems critical in preparing compounds of the type [L·LnCl$_3$] since analogous reactions with cyclotriphosphazene ligand containing unsubstituted or mono 3-methyl substituted pyrazoles do not proceed as monitored by *in situ* NMR spectroscopy. Efforts to establish the reactivity scope of [L·LnCl$_3$] toward various reagents including d$^{10}$ metal halides are in progress.

We gratefully acknowledge financial support provided by the Korea Science and Engineering Foundation.

## Notes and References

† E-mail: ykdo@single.kaist.ac.kr

‡ Color of products: white for **1**, **2**, **4** and sky blue for **3**.

§ *Selected data*: **1**, IR (Nujol), $\nu_{PN}$/cm$^{-1}$ 1237, 1210; $^{31}$P{$^1$H} NMR (CDCl$_3$), $\delta$ 0.8 (1 P, t, *J* 45 Hz) and −1.3 (2 P, d, *J* 48 Hz); $^1$H NMR (CDCl$_3$), $\delta$ 6.07 (2 H, d, $^4J_{PH}$ 3.5 Hz), 5.84 (4 H, s), 2.63 (12 H, s), 2.41 (12 H, s), 2.19 (6 H, s), 2.00 (6 H, s). **2**, IR, $\nu_{PN}$/cm$^{-1}$ 1235, 1210; $^{31}$P{$^1$H} NMR, $\delta$ 7.8 (1 P, t, *J* 45 Hz) and 1.3 (2 P, d, *J* 37 Hz); $^1$H NMR, $\delta$ 7.04 (2 H, s), 4.95 (4 H, s), 3.89 (12 H, s), 3.57 (6 H, s), 2.80 (6 H, s), −4.23 (12 H, s). **3**, IR, $\nu_{PN}$/cm$^{-1}$ 1236, 1213; $^{31}$P{$^1$H} NMR, $\delta$ 13.0 (1 P, t, *J* 44 Hz) and −39.7 (2 P, d, *J* 47 Hz); $^1$H NMR, $\delta$ 6.75 (2 H, s), 5.57 (4 H, s), 3.39 (12 H, s), 3.22 (6 H, s), 2.61 (6 H, s), −3.42 (12 H, s). **4**, IR, $\nu_{PN}$/cm$^{-1}$ 1233, 1209; $^{31}$P{$^1$H} NMR, $\delta$ 5.4 (2 P, d, *J* 48 Hz) and 1.0 (1 P, t, *J* 49 Hz); $^1$H NMR, $\delta$ 6.14 (2 H, d, $^4J_{PH}$ 3.7 Hz), 5.67 (4 H, s), 2.56 (12 H, s), 2.25 (6 H, s), 2.19 (6 H, s), 1.73 (12 H, s). Satisfactory elemental analyses were obtained for all four compounds by Oneida Research Services, USA.

¶ *Crystallographic data* for **4**·2CH$_2$Cl$_2$: $C_{32}H_{46}Cl_7N_{15}P_3Sm$, $M_r$ = 1132.25, monoclinic, space group $P2_1/c$, $a$ = 16.860(3), $b$ = 17.330(12), $c$ = 18.289(5) Å, $\beta$ = 113.669(14)°, $U$ = 4894.2(16) Å$^3$, $Z$ = 4, $D_c$ = 1.537 g cm$^{-3}$, $F$(000) = 2276, $\mu$(Mo-K$\alpha$) = 1.722 mm$^{-1}$, $R_1$ = 0.0552, $wR_2$ = 0.1412 for 3899 observed reflections [$|F_o| > 4.0\sigma(F_o)$]. Reflection data were collected on an Enraf-Nonius CAD4TSB diffractometer with graphite-monochromated Mo-K$\alpha$ radiation at 293 K. A total of 4926 data were collected in the range $4° < 2\theta < 50°$. Two oil-coated crystals were used to collect reflection data due to their rapid decaying nature. All data were collected with the $\omega$–$2\theta$ scan mode and corrected for $L_p$ effects. The decay correction of each crystal was applied to the data set. The structure was solved by Patterson's heavy atom methods (SHELXS-86).[9] Non-hydrogen atoms except solvate atoms were refined by full-matrix least-squares techniques (SHELXL-93)[10] with anisotropic displacement parameters. The solvate CH$_2$Cl$_2$ molecules exhibited positional disorder and the Cl atoms were each assigned an occupancy factor of 0.4 and 0.6. All hydrogens except disordered CH$_2$Cl$_2$ hydrogens were placed at their geometrically calculated positions [$d_{C-H}$ = 0.93(pyrazolyl), $d_{C-H}$ = 0.96(methyl)] and refined riding on the corresponding carbon atoms with isotropic thermal parameters [(1.2*U*(pyrazolyl), 1.5*U*(methyl)]. CCDC 182/858.

1 Y. Byun, D. Min, J. Do, H. Yun and Y. Do, *Inorg. Chem.*, 1996, **35**, 3981; D. Min and Y. Do, *Chem. Lett.*, 1994, 1989.

2 K. R. J. Thomas, V. Chandrasekhar, P. Pal, S. R. Scott, R. Hallford and A. W. Cordes, *Inorg. Chem.*, 1993, **32**, 606; K. R. J. Thomas, V. Chandrasekhar, S. R. Scott, R. Hallford and A. W. Cordes, *J. Chem. Soc., Dalton Trans.*, 1993, 2589.

3 K. R. J. Thomas, P. Tharmaraj, V. Chandrasekhar, C. D. Bryan and A. W. Cordes, *Inorg. Chem.*, 1994, **33**, 5382; K. R. J. Thomas, P. Tharmaraj, V. Chandrasekhar and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1994, 1301.

4 A. Chandrasekaran, S. S. Krishnamurthy and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, 1994, 63; A. Chandrasekaran, S. S. Krishnamurthy and M. Nethaji, *Inorg. Chem.*, 1994, **33**, 3085; 1993, **32**, 6102.

5 H. R. Allcock and M. L. Turner, *Macromolecules*, 1993, **26**, 3; H. R. Allcock, J. A. Dodge, I. Manners, M. Parvez, G. H. Riding and K. B. Visscher, *Organometallics*, 1991, **10**, 3098; H. R. Allcock, J. A. Dodge, I. Manners and G. H. Riding, *J. Am. Chem. Soc.*, 1991, **113**, 9596; I. Manners, G. H. Riding, J. A. Dodge and H. R. Allcock, *J. Am. Chem. Soc.*, 1989, **111**, 3067; I. Manners, W. D. Coggio, M. N. Mang, M. Parvez and H. R. Allcock, *J. Am. Chem. Soc.*, 1989, **111**, 3481.

6 H. R. Allcock, R. A. Nissan, P. J. Harris and R. R. Whittle, *Organometallics*, 1984, **3**, 432; H. R. Allcock, K. D. Lavin, N. M. Tollefson and T. L. Evans, *Organometallics*, 1983, **2**, 432; H. R. Allcock, A. G. Scopelianos, R. R. Whittle and N. M. Tollefson, *J. Am. Chem. Soc.*, 1983, **105**, 1316.

7 J. E. Mark, H. R. Allcock and R. West, *Inorganic Polymers*, Prentice-Hall Inc., New York, 1992, ch. 3; V. Chandrasekhar and K. R. J. Thomas, *Appl. Organomet. Chem.*, 1993, **7**, 1.

8 K. D. Gallicano, N. L. Paddock, S. J. Rettig and J. Trotter, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 417; K. D. Gallicano and N. L. Paddock, *Can. J. Chem.*, 1982, **60**, 521.

9 G. M. Sheldrick, SHELXS-86 User Guides, Crystallographic Department, University of Göttingen, Germany, 1985.

10 G. M. Sheldrick, SHELXL-93 User Guides, Crystallographic Department, University of Göttingen, Germany, 1993.

11 C. W. Haigh, *Polyhedron*, 1996, **15**, 605; S. J. Lippard, *Prog. Inorg. Chem.*, 1967, **8**, 109.

*Received in Cambridge, UK, 11th March 1998; 8/01988F*