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

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Reaction of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene (L) with LnCl₃ (Ln = La, Ce, Nd, Sm) affords new mononuclear lanthanophosphazenes [L·LnCl₃] with hendecahedral coordination polyhedron in which the ligand L employs an unprecedented κ⁵N binding core consisting of one cyclophosphazene ring nitrogen atom and four pyridinic nitrogen atoms of two sets of geminal pyrazolyl groups.

The use 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. Successful applications of exocyclic donors such as pyrazolyl and cyclopentadienyl 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, has only been examined with d¹⁰ metal halides and d⁹ Cu II ion, revealing the limited coordination behavior with the binding cores of (κ⁵N) for mononuclear species and (κ⁵N–κ²N) and (κ⁵N–κ⁵N) for dinuclear complexes. Here, we present the first examples of lanthanophosphazenes [L·LnCl₃] (Ln = La, Ce, Nd, Sm) where the ligand L acts as an unprecedented κ⁵N binding core donor for a metal center to form a hendecahedral coordination sphere.

A solid mixture of anhydrous LnCl₃ (0.3–0.6 mmol) and L (0.2 mmol) was allowed to react in 20 ml of CH₂Cl₂ under N₂ 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 Et₂O added. The resulting crystalline solid was collected and recrystallized from CH₂Cl₂–Et₂O, affording the extremely air sensitive analytically pure product [L·LnCl₃] (Ln = La, Ce, Nd, Sm, Sm) 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 νPN peaks at ca. 1235 and 1210 cm⁻¹ for [L·LnCl₃] 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 κ⁵N 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 κ⁵N binding core to coordinate SmCl₃, forming an eight-coordinate complex. The analysis of the shape parameters indicates that the coordination sphere of 4 can be best described as a distorted hendecahedron illustrated in Fig. 2. The complexation caused P₃N₃ 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-C₅. 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. In solution at room temperature, the compounds [L·LnCl₃] lose their solid state symmetry and undergo a new type of fluxional motion (Fig. 3) not seen in d¹⁰ metal complexes of L.

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(9), 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).

Fig. 2 Hendecahedral coordination geometry of 4
motion such as the movement of the N(1)–LnCl₃ unit as pyrazolyl rings involved in coordination are respectively rings in 1:2 ratio. Two pyrazolyl rings at P(3) 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)–LnCl₃ 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·LnCl₃] since analogous reactions with cyclopentadienylphosphane 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·LnCl₃] complexes are of A₂X₄ type, invoking only the rotational motion of geminal pyrazolyl groups at P(3) around P–N bonds. However ¹H-NMR spectra in CDCl₃ 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)–LnCl₃ 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.

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Notes and References

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‡ Color of products: white for 1, 2, 4 and sky blue for 3.
§ Selected data: 1, IR (Nujol), νₚₒₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑэкономia.
¶ Crystallographic data for 4·CH₂Cl₂: C₂H₆Cl₂N₃P·Sm, Mᵣ = 1132.25, monoclinic, space group P₂₁/c, α = 16.860(3), b = 17.330(12),
c = 18.289(5) Å, β = 113.669(14)°, V = 4894.2(16) Å³, Z = 4, Dₓ = 1.537 g cm⁻³, F(000) = 2276, μ(Mo-Kα) = 1.722 mm⁻¹, R₁ = 0.0552, wR₂ = 0.1412 for 3899 observed reflections ([F₀ > 4σ(F₀)]. Reflection data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation at 293 K. A total of 4926 data were collected in the range 4° < 2θ < 50°. Two oil-coated crystals were used to collect reflection data due to their rapid decaying nature. All data were collected with the α-2θ scan mode and corrected for Lα 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). Non-hydrogen atoms except solvate atoms were refined by full-matrix least-squares techniques (SHELXL-93) with anisotropic displacement parameters. The solvate CH₂Cl₂ molecules exhibited positional disorder and the Cl atoms were each assigned an occupancy factor of 0.4 and 0.6. All hydrogens except disordered CH₂Cl₂ 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 182/8588.

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

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