Synthesis of the First Lanthanide Complexes of Dialkyl α-Hydroxyiminophosphonates; Ambivalent Ligand Bonding in the Pr^{III} and Nd^{III} Complexes of Diisopropyl α-Hydroxyiminopropylphosphonate (L^1), $[PrL^1_3Cl_3]$ and $[NdL^1_2(NO_3)_3(H_2O)]$

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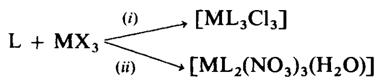
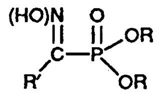
Lanthanide complexes of dialkyl α-hydroxyiminophosphonates $(RO)_2P(O)C(R')N(OH)$ (L^1–L^3), where R = Et or Pr^i and R′ = Me or Et, have been prepared for the first time; the crystal structures of two complexes of L^1 (R = Pr^i, R′ = Et) have been determined, showing nine-co-ordination geometry in both cases with asymmetric bidentate ligands in $[PrL^1_3Cl_3]$ and monodentate bonding in $[NdL^1_2(NO_3)_3(H_2O)]$ demonstrating that the ambivalent nature of the new ligands allow formation of neutral complexes.

The study of new lanthanide(III) complexes is an area of considerable current activity, mainly because of their important chemical and biomedical applications, for example as luminescent probes,[1] relaxation agents in NMR imaging,[2] and shift reagents in NMR spectroscopy.[3] There is great interest in the design of new ligands capable of selectively binding lanthanide(III) metal ions and allowing their isolation. Dialkyl α-hydroxyiminophosphonates are well known as useful intermediates for conversion to aminophosphonates,[4,5] and their chemistry has also been intensively studied because of the interest in their biological activity.[6–8] We have demonstrated for the first time that these readily available non-ionic compounds are versatile bifunctional ligands, not only for transition metals,[9] but also for lanthanide(III) ions. They show unusual co-ordination ambivalence, changing from symmetrically to asymmetrically bidentate and then to monodentate bonding modes, to accommodate the different steric requirements of mono- and bi-dentate anions in facilitating neutral-complex formation.

All the dialkyl α-hydroxyiminophosphonate compounds L^1–L^4 were prepared by a modification[9] of a literature method,[10] and the preparation of the lanthanide complexes was carried out by reaction of the ligands and lanthanide metal salts in methanolic solution (Scheme 1), the formulation of the products being verified by elemental analysis, mass spectrometry, NMR and IR spectroscopy. All six complexes obtained are neutral and each has three anions co-ordinated, but two different formulations are observed. When X = Cl three phosphorus ligands are co-ordinated giving the complexes $[ML_3Cl_3]$, but when three nitrate anions are present in the co-ordination sphere, only two α-hydroxyiminophosphonate ligands are co-ordinated giving $[ML_2(NO_3)_3(H_2O)]$. Crystal structure analysis of one complex of each type confirms the formulations and shows marked differences in ligand-bonding mode.*



Scheme 1 (*i*) X = Cl, M = Pr, L = L^1 or L^3. (*ii*) X = NO_3, M = La or Gd, L = L^2; X = NO_3, M = Nd, L = L^1; X = NO_3, M = Dy, L = L^3



L	R	R′
L^1	Pr^i	Et
L^2	Et	Me
L^3	Et	Et
L^4	Pr^i	Ph

The praseodymium complex $[PrL^1_3Cl_3]$ (Fig. 1) has exact crystallographic C_3 symmetry with a nine-co-ordinate geometry at the Pr^{III} ion that may be envisaged as a tricapped-trigonal prism. One triangular face of the prism is defined by the three chloro ligands [Pr–Cl 2.783(4) Å]; the opposite triangular face

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* For both compounds data collected on a Philip PW1100 four-circle diffractometer, Mo-Kα radiation (λ = 0.710 69 Å), θ range 3–25°, coordinates of P, Nd and Cl atoms found from Patterson vector maps, with subsequent Fourier-difference syntheses used for detection of remaining non-hydrogen atoms. Structure solved using SHELX 76.[11]

Crystal data: $[PrL^1_3Cl_3]$, $C_{27}H_{60}Cl_3N_3O_{12}P_3Pr$, $M = 958.975$, hexagonal, space group $P6_3$, $a = 13.784(3)$, $c = 14.356(3)$ Å, $U = 2362.19$ Å^3, $Z = 2$, $F(000) = 988$, $D_c = 1.348$ g cm^{-3}, μ(Mo-Kα) = 13.0 cm^{-1}, λ = 0.710 69 Å, pale blue crystal with dimensions 0.25 × 0.30 × 0.15 mm. Full-matrix least-squares refinement with $w = 1/\sigma^2(F)$ applied to all reflections converged at $R = 0.0462$ ($R' = 0.0409$) for 993 absorption corrected data[12] with $I/\sigma(I) > 3.0$. All carbon-bonded hydrogen atoms given idealized geometry (C–H 1.08 Å) with $U = 0.1$ Å^2. Anisotropic thermal parameters applied to Pr, Cl, P, O, N and some terminal carbon atoms. The metal atom is on the three-fold axis at $\frac{1}{3}, \frac{2}{3}, 0$, with $\frac{1}{3}$ site occupancy.

$[NdL^1_2(NO_3)_3(H_2O)]$, $C_{18}H_{42}N_5NdO_{18}P_2$, $M = 822.7$, monoclinic, space group $P2_1/c$, $a = 14.323(3)$, $b = 17.258(3)$, $c = 14.250(3)$ Å, β = 97.82(2)°, $U = 3489.68$ Å^3, $Z = 4$, $F(000) = 1676$, $D_c = 1.566$ g cm^{-3}, μ(Mo-Kα) = 15.7 cm^{-1}, $R = 0.0374$ ($R' = 0.0387$) for 4002 absorption corrected data[12] with $I/\sigma(I) > 3.0$. Carbon-bonded H-atoms treated as above with $U = 0.08$ Å^2, all non-hydrogen atoms assigned anisotropic thermal parameters.

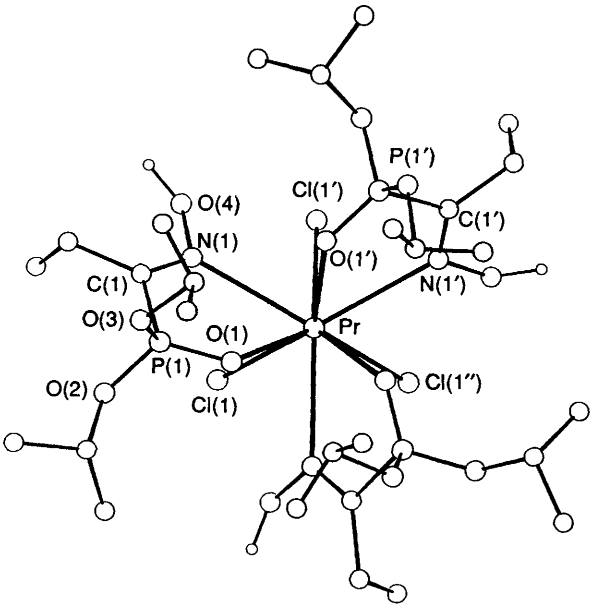

Fig. 1 The tricapped-prismatic co-ordination geometry of $\mathrm{Pr^{III}}$ in $[\mathrm{PrL^1_3Cl_3}]$ showing the asymmetrically bidentate bonding mode of $\mathrm{L^1}$. Selected bond lengths (Å): Pr–O(1) 2.464(9), Pr–N(1) 2.796(8), Pr–Cl(1) 2.783(4), P(1)–O(1) 1.461(9), P(1)–O(3) 1.549(8), P(1)–O(2) 1.530(8), C(1)–N(1) 1.257(13) and N(1)–O(4) 1.388(12)

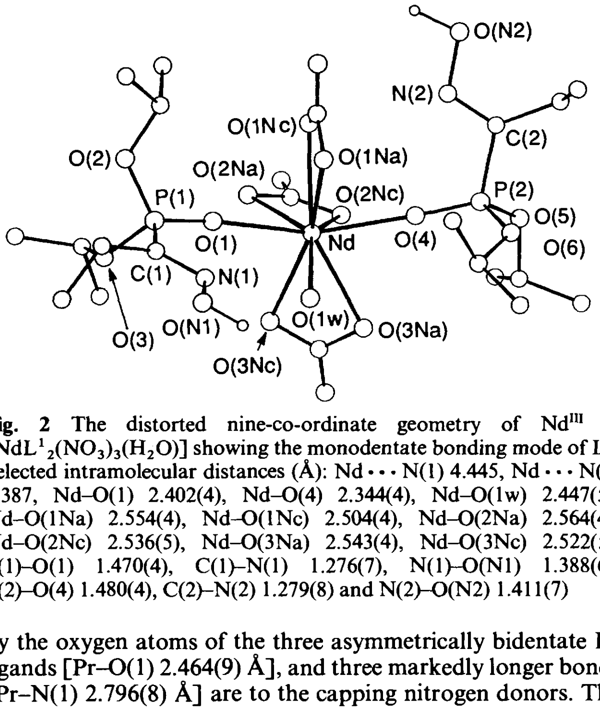

Fig. 2 The distorted nine-co-ordinate geometry of $\mathrm{Nd^{III}}$ in $[\mathrm{NdL^1_2(NO_3)_3(H_2O)}]$ showing the monodentate bonding mode of $\mathrm{L^1}$. Selected intramolecular distances (Å): Nd ··· N(1) 4.445, Nd ··· N(2) 4.387, Nd–O(1) 2.402(4), Nd–O(4) 2.344(4), Nd–O(1w) 2.447(5), Nd–O(1Na) 2.554(4), Nd–O(1Nc) 2.504(4), Nd–O(2Na) 2.564(4), Nd–O(2Nc) 2.536(5), Nd–O(3Na) 2.543(4), Nd–O(3Nc) 2.522(5), P(1)–O(1) 1.470(4), C(1)–N(1) 1.276(7), N(1)–O(N1) 1.388(6), P(2)–O(4) 1.480(4), C(2)–N(2) 1.279(8) and N(2)–O(N2) 1.411(7)

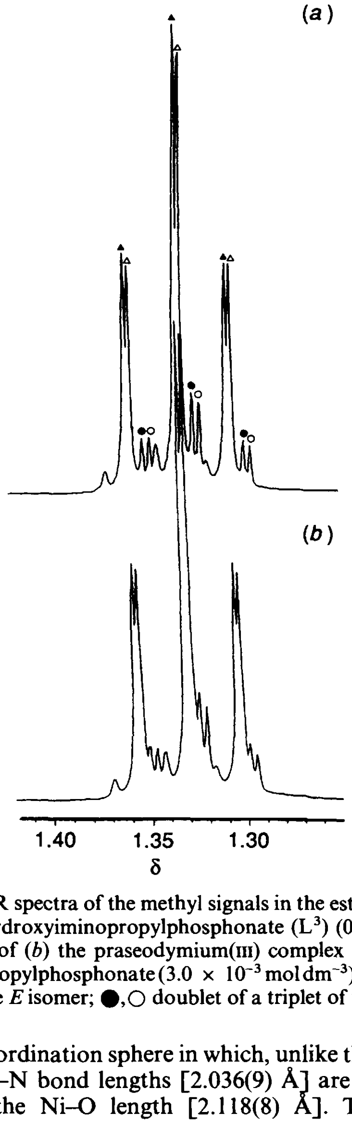

Fig. 3 ^{1}H NMR spectra of the methyl signals in the ester region of (*a*) *E*,*Z*-diethyl α-hydroxyiminopropylphosphonate ($\mathrm{L^3}$) (0.17 mol dm^{-3}), in the presence of (*b*) the praseodymium(III) complex of *E*-diethyl α-hydroxyiminopropylphosphonate (3.0 × 10^{-3} mol dm^{-3}) [▲,△ doublet of a triplet of the *E* isomer; ●,○ doublet of a triplet of the *Z* isomer]

by the oxygen atoms of the three asymmetrically bidentate $\mathrm{L^1}$ ligands [Pr–O(1) 2.464(9) Å], and three markedly longer bonds [Pr–N(1) 2.796(8) Å] are to the capping nitrogen donors. The structure of the neodymium complex $[\mathrm{NdL^1_2(NO_3)_3(H_2O)}]$ (Fig. 2) is very different, although it also has nine-co-ordination of the metal atom. The three nitrate anions are bidentate, occupying six-co-ordination sites and, together with the water ligand, form an irregular 'girdle' round the metal. Two oxygen donors of two monodentate $\mathrm{L^1}$ ligands occupy opposite bonding sites [Nd–O(1) 2.402(4), Nd–O(4) 2.344(4) Å] in an extended approximately linear arrangement [Nd–O(1)–P(1) 172.5(3), O(1)–Nd–O(4) 148.5(1), Nd–O(4)–P(2) 176.4(3)°], with the potential nitrogen donors of $\mathrm{L^1}$ at non-bonding distances [Nd ··· N(1) 4.445, Nd ··· N(2) 4.387 Å].

A comparison of the metal–ligand bond lengths in these complexes to those of the only other complex reported for this class of ligand, *trans*-$[\mathrm{NiL^3_2Cl_2}]$,[9] demonstrates the range of bonding modes available to these new ligands. In the $\mathrm{Ni^{II}}$ complex $\mathrm{L^3}$ adopts a symmetric bidentate bonding mode in an octahedral co-ordination sphere in which, unlike the lanthanide complexes, Ni–N bond lengths [2.036(9) Å] are considerably *shorter* than the Ni–O length [2.118(8) Å]. The range of different bonding modes observed so far for the α-hydroxyiminophosphonate ligands (bidentate, asymmetric bidentate and monodentate), are related to differences in the hard/soft character of the metals and to the nature of the other ligands present. The hard $\mathrm{Nd^{III}}$ cation co-ordinates three hard anionic bidentate nitrate ligands, although this is at the expense of the normally favourable bidentate mode for the α-hydroxyiminophosphonates, and from the consistent formulation $[\mathrm{LnL_2(NO_3)_3(H_2O)}]$ it may be deduced that this is also true for the related nitrate complexes of the other lanthanide(III) ions.

Proton NMR spectra of the ligands show overlapping signals in the ester region attributed to the presence of *E* and *Z* isomers. The *E* isomer of $\mathrm{L^4}$ has been characterized by X-ray crystallography and this, together with ^{31}P NMR, allowed the ratio of the *E* and *Z* isomers to be estimated for each ligand.[9] These results provided suitable data for an initial assessment of the efficacy of the complexes as shift reagents for isomer resolution in ^{1}H NMR spectroscopy. For $\mathrm{L^3}$, in the presence of $[\mathrm{PrL^3_3Cl_3}]$, the overlapping signals in the ^{1}H NMR spectrum are clearly separated (Fig. 3), allowing full assignment* of the

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* ^{1}H NMR (270 MHz, $\mathrm{CD_3OD}$, $\mathrm{SiMe_4}$) data for (*i*) *E*-diethyl α-hydroxyiminopropylphosphonate: δ 1.12 (3 H, t, ^3J 7.53, γ-$\mathrm{CH_3}$), 1.33 (6 H, dt, $^4J_{\mathrm{PH}}$ 0.59, ^3J 7.04, ester $\mathrm{CH_3}$), 2.48 (2 H, dq, $^3J_{\mathrm{PH}}$ 14.32, ^3J 7.56, β-$\mathrm{CH_2}$), 4.13 (4 H, dq, $^3J_{\mathrm{PH}}$ 7.56, ^3J 7.04, ester $\mathrm{CH_2}$) and (*ii*) *Z*-diethyl α-hydroxyiminopropylphosphonate: δ 1.12 (3 H, t, ^3J 7.53, γ-$\mathrm{CH_3}$), 1.32 (6 H, dt, $^4J_{\mathrm{PH}}$ 0.98, ^3J 6.55, ester $\mathrm{CH_3}$), 2.48 (2 H, dq, $^3J_{\mathrm{PH}}$ 14.32, ^3J 7.56, β-$\mathrm{CH_2}$), 4.10 (4 H, dq, $^3J_{\mathrm{PH}}$ 8.10, ^3J 7.02, ester $\mathrm{CH_2}$)

complex multiplets to be made. More importantly, the ratio of the *E* and *Z* isomers can also be evaluated in this ^1H NMR spectrum (with the shift reagent present), and it gives a ratio close to the one deduced from ^{31}P NMR.

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