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Synthesis and structural properties of metal complexes of dialkyl α-hydroxyiminophosphonates

S. W. Annie Bligh,* Nick Choi, Catherine M. McGrath, Mary McPartlin and Thomas M. Woodroffe

Division of Chemical Sciences, School of Biological and Applied Sciences, Holloway Road, London, UK N7 8DB

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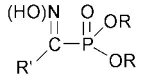
A range of dialky α-hydroxyiminophosphonates $R'C{=}N(OH)P(O)(OR)_2$, with substituents of varying bulk (R = Et, R′ = Me L^1, Et L^2, ^{c}Pr L^3, 3-heptyl L^4; R = ^{i}Pr, R′ = Et L^5, 3-heptyl L^6; R = ^{n}Bu, R′ = Pr L^7) have been used to synthesise neutral metal complexes with nickel(II) $[Ni(L^{1-3,5})Cl_2]$, cobalt(II) $[Co(L^{1-3,5})Cl_2]$ and lanthanides (La^{III} with $L^{1,2,5}$, Pr^{III} with $L^{1,2,4-7}$, Nd^{III} with L^5, Gd^{III} with $L^{2,5}$ and Dy^{III} with $L^{2,5}$) the charge being balanced by anionic ligands chloride or nitrate. Included in this range are two 3-heptyl derivatives which have not previously been reported. All the metal complexes have been fully characterised by elemental analysis, IR, electronic and NMR spectroscopy and mass spectrometry. X-Ray crystallography has been used to establish the structure of six key metal complexes and one of the free ligands (L^3). Three different bonding modes have been established. The d-block metal chlorides consistently show symmetrical bidentate coordination in $[ML_2Cl_2]$, the lanthanide chlorides $[ML_3Cl_3]$ are all asymmetrically bidentate and monodentate coordination was observed in the neodymium nitrate complex $[NdL^5_2(NO_3)_3(H_2O)]$.

Introduction

α-Hydroxyiminophosphonates are most widely known as intermediates in the synthesis of the industrially important α-aminophosphonic acids,[1] and were first prepared by Berlin *et al.* as a route to this type of compound.[2] The initial synthetic method involved oximation of α-oxophosphonates to yield α-hydroxyimino*aryl*phosphonate diesters. The same procedure was used by Asano and co-workers to prepare a series of α-hydroxyimino*alkane*phosphonates.[3] More recently the oxime of *tert*-butyl diethoxyphosphorylacetate was obtained from the reaction of diethoxyphosphorylacetic ester anion and ethyl nitrite.[4]

α-Hydroxyiminophosphonates have a range of potential applications including their use as fungicidal agents,[5] as a source of iminoxy radicals as possible spin probes in enzymic centres,[6] and as generators, in physiological conditions, of monomeric metaphosphates,[7] which are implicated in phosphoryl transfer *in vivo*.[8] Despite the fact that much of this interest in α-hydroxyiminophosphonates arises from their marked affinity for calcified tissues and bone metastases,[9] very little is known about their metal complexing abilities.

The interests in investigating new transition metal and lanthanide compounds, based on their chemical and biomedical applications,[10,11] have led us to study the preparation and structural properties of this class of organophosphorus ligands. Although combination of adjacent oxime and phosphoryl groups can produce a 5-membered ring upon chelation with a metal ion, so far very few examples of metal complexes of dialkyl α-hydroxyiminoalkanephosphonate derivatives have been reported.[12–16] Both *E*- and *Z*-isomers are, in general, present in the product of the preparation of the dialkyl α-hydroxyiminophosphonates. Our initial studies have shown that the selection of the *E*-isomers as ligands, occurs in preference to the *Z*-isomers.[15,16] This work describes the synthesis and characterisation of a range of new transition metal and lanthanide complexes of dialkyl α-hydroxyiminoalkanephosphonates (L^1–L^7). Two of the ligands, L^4 and L^6, are new and have been designed to have enhanced lipophilic characteristics.



	R	R'
L^1	Et	Me
L^2	Et	Et
L^3	Et	^{c}Pr
L^4	Et	3-Heptyl
L^5	^{i}Pr	Et
L^6	^{i}Pr	3-Heptyl
L^7	^{n}Bu	Pr

Results and discussion

Synthesis

The α-hydroxyiminophosphonates (L^1–L^7) were prepared by oximation of the α-oxophosphonate diester precursors by an adaptation of the method of Berlin *et al.*[17] The products obtained are odourless pale yellow oils or crystalline solids which melt below 100 °C, and were characterised by elemental analysis, NMR and IR spectroscopy and LSI mass spectrometry. They are soluble in most common organic solvents, none of the examples reported here is soluble in water.[18] The solid α-hydroxyiminophosphonate diesters are stable over long periods of time but those isolated as oils show signs of slow decomposition (1–2 y) to give phosphate ($\delta_P < 0$) products.

Alcoholic solutions of the ligands with lanthanide and transition metal nitrates and chlorides were mixed at room temperature and allowed to stand. In general the chlorides are crystalline or amorphous solids, and the nitrates tend to be viscous oils. These crude products were obtained in a matter of days. After isolation and washing with chilled solvent, the solids were air-dried. Isolated yields varied from 10–90%, depending on the anion used, lower yields were obtained using metal

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Table 1 Elemental analyses, IR and mass spectrometry data of the metal complexes (^{a} not enough sample for measurements)

Complex	Colour	Yield (%)	μ/μ_B	Calc., Found (%)			IR ν/cm^{-1}				LSI ms (m/z)
				C	H	N	C=N	P–O	P=O	NO_3	
$[Co(L^1)_2Cl_2]$	Purple	86	4.65	27.7 28.0	5.43 5.46	5.38 5.35	1647w	1030s, 1000s	1200vs		484(12), 448(8), 391(23), 196(100) $[L + H]^+$, 168(8), 140(22)
$[Ni(L^1)_2Cl_2]$	Green	72	3.44	27.7 27.7	5.43 5.46	5.38 5.29	1654sh,	1047s, 1016s	1191s		613(5), 577(7), 541(32), 485(5), 447(100) $[M + H + \text{glycerol} - 2HCl - 4CH_2{=}CH_2 - H_2O]^+$, 196(10), 178(5), 168(5), 140(13)
$[La(L^1)_2]Cl_3$-$(H_2O)_2]$	White	86	—	21.5 21.6	4.80 4.69	4.17 4.09	1634m	1019vs	1223m, 1187vs		600(100) $[M + H - 2H_2O - HCl]^+$, 563(78), 527(13), 140(15)
$[La(L^1)_2(H_2O)$-$(NO_3)_3]$	White	25	—	19.7 19.5	4.12 4.04	9.55 9.56	1636m	1026vs	1230m, 1188vs	1464, 1385, 1322vs	653 (100) $[M + H - HNO_3]^+$, 590(95), 527(7), 196(6), 140(10)
$[Pr(L^1)_2Cl_3$-$(H_2O)_2]$	Green	78	3.28	21.4 21.8	4.78 4.70	4.16 4.15	1636m	1005vs	1222s		601(90), 565(100) $[M + H - 2H_2O - 2HCl]^+$, 529(23), 473(5)
$[Co(L^2)_2Cl_2]$	Purple	44	4.65	30.7 30.6	5.85 5.83	5.11 5.02	1639w	1020s, 1014s	1219, 1184s		641(11), 605(7), 569(66), 512(37), 476(100) $[M + H - 2HCl]^+$, 303(33), 275(12), 247(29)
$[Ni(L^2)_2Cl_2]$	Green	67	3.12	30.7 30.7	5.89 5.91	5.24 5.24	1645w	1019s	1214vs, 1189s		605(7), 569(60), 475(100) $[M + H - 2HCl]^+$, 302(15), 266(10), 248(13)
$[La(L^2)_3Cl_3]$	White	36	—	28.9 28.9	5.54 5.55	4.81 4.78	1630m	1047m, 1015vs	1215s, 1201s, 1180s		837(8), 801(28), 629(93), 593(46), 557(12), 420(6), 384(16)
$[Pr(L^2)_3Cl_3]\cdot 4H_2O$	Green	40	3.66	26.6 26.8	5.96 5.39	4.44 4.37	1633m	1047s, 1018s	1210s, 1178s		838(6), 802(10), 629(100) $[M + H - 4H_2O - L - HCl]^+$, 593(13), 384(17)
$[Gd(L^2)_4Cl_3]\cdot 2H_2O$	White	46	7.54	29.6 29.6	6.03 5.87	4.93 4.91	1623m	1049s, 1024s	1218s, 1178s		819(6), 646(100) $[M + H - 2H_2O - 2L - HCl]^+$, 610(43)
$[Gd(L^2)_2Cl_3$-$(H_2O)_2]$	White	53	7.62	23.4 23.5	5.07 5.00	3.91 3.92	1627m	1048s, 1025s	1218s, 1178s		646(62), 611(50), 584(100) $[M + H - 2H_2O - 2HCl - CH_2{=}CH_2]^+$, 192(19)
$[Dy(L^2)_2(H_2O)$-$(NO_3)_3]$	White	13	10.71	21.4 21.6	4.36 4.40	8.92 9.09	1663m, 1618m	1025s	1215s, 1176s	1386w, 1294s	706(100) $[M + H - H_2O - HNO_3]^+$, 643(56), 192(39)
$[Co(L^3)_2Cl_2]$	Purple	44	4.68	33.6 33.7	5.64 5.66	4.90 4.81	1630vw	1046s, 1019s	1192vs		850(6), 665(16), 629(6), 593(52), 536(86), 500(100) $[M + H - 2HCl]^+$, 222(51), 194(7)
$[Ni(L^3)_2Cl_2]$	Green	80	3.18	33.6 33.6	5.65 5.64	4.78 4.90	1663w	1049vs, 1013	1195vs		812(9), 778(6), 593(22), 535(15), 499(100) $[M + H - 2HCl]^+$, 222(13)
$[Pr(L^4)_3Cl_3]$	Green	70	3.68	39.8 39.9	7.24 7.34	3.87 3.82	1629, 1618m	1054m, 1018vs	1198m		771(66), 734(35), 698(10), 418(10)
$[Co(L^5)_2Cl_2]$	Purple	41	4.62	35.8 35.6	6.67 6.68	4.64 4.77	1647w	994vs	1203vs, 1184s		898(6), 862(9), 826(11), 697(19), 661(9), 625(61), 568(100) $[M + H - HCl]^+$, 532(94), 490(74), 448(22), 406(20), 364(31), 331(12), 247(95), 211(34), 193(39)
$[Ni(L^5)_2Cl_2]$	Green	60	3.15	35.8 35.8	6.68 6.61	4.64 4.60	1651w	997vs	1207, 1185m		862(18), 826(7), 697(10), 661(6), 625(48), 532(75), 489(21), 447(6), 364(18), 331(12), 246(100) $[M + H - L - 2CH_3\text{-}CH_2{=}CH_2 - HCl]^+$, 211(34), 193(39)
$[La(L^5)_3Cl_3]$	White	37	—	34.0 34.0	6.32 6.40	4.39 4.33	1633m	1001vs	1204m, 1180s		1063(7), 685(28), 607(5)
$[Pr(L^5)_3Cl_3]$	Green	40	3.52	33.8 33.7	6.31 6.35	4.38 4.32	1635m	1005s	1207s, 1180s		1067(17), 685(81), 649(17), 613(6)
$[Nd(L^5)_2(H_2O)$-$(NO_3)_3]$	Lilac	10	^{a}	26.3 26.8	5.15 5.43	8.51 8.63	1656m, 1629m	1010s	1209s, 1173s	1385w, 1294s	740(100) $[M + H - H_2O - HNO_3]^+$, 677(18), 635(11), 238(74), 196(27)
$[Gd(L^5)_2(H_2O)$-$(NO_3)_3]$	White	90	7.74	25.9 25.9	5.07 5.01	8.38 8.27	1655br, 1608sh	1029s, 1010s	1213s, 1174s	1385w, 1291	756(100) $[M + H - H_2O - HNO_3]^+$, 693(64), 651(12)
$[Dy(L^5)_2(H_2O)$-$(NO_3)_3]$	White	22	10.67	25.7 25.7	5.00 5.00	8.33 8.30	1658m, 1618w	1011s	1213s, 1174s	1385w, 1294s	761(98) $[M + H - H_2O - HNO_3]^+$, 697(54), 634(14)
$[Pr(L^6)_3Cl_3]$	Green	55	3.58	43.2 42.8	7.76 7.74	3.59 3.62	1628m	1002vs	1196m		826(56), 789(44), 753(9), 445(12)
$[Pr(L^7)_3Cl_3]$	Green	55		39.8 39.9	7.24 7.34	3.87 3.82	1630m	1064s, 1010vs	1196m, 1175s		769(66), 733(54), 697(6), 454(10)

nitrates. The crystalline nitrate and chloride complexes were stable in air and lost solvent only on prolonged drying under vacuum.

The colours of the metal complexes varied according to the metal ions they contained (Table 1). In all cases with Co(II) and Ni(II) chlorides, the elemental and infrared analyses showed that adducts of the form $[ML_2Cl_2]$ were isolated with no trace of solvent. Attempts to prepare similar Cu(II) complexes failed and the uncomplexed copper(II) salt was re-deposited. For the corresponding divalent metal nitrates, an apparent mixture of complexed and uncomplexed species was established from examination of their IR spectra.

With lanthanide chlorides and nitrates the resulting metal : ligand ratio depended on the ligand, the anion and the metal cation used (Table 1). Generally the trivalent lanthanide nitrates obtained were M : L = 1 : 2 complexes and in contrast to the transition metal complexes all were solvated with one water molecule, resulting in the formulation $[ML_2(NO_3)_3(H_2O)]$. For the chlorides a greater range of stoichiometries were observed in the lanthanides, for example in La(III) and Pr(III) complexes M : L 1 : 2 was obtained with L^1, but M : L 1 : 3 with L^2 and L^5. With Gd(III) two stoichiometries were obtained with the same ligand, M : L^2 1 : 2 and 1 : 4 (Table 1), depending on the pH of the solution after mixing.

Table 2 Comparison of mean bond distances (Å) in examples of free ligand and metal complexes of α-hydroximinophosphonate derivatives

			“Bite”				
Species	M–N	M–O	N···O	C=N	C–P	P=O	Ref.
L^{1a}	—	—	—	1.284(7)	1.828(4)	1.462(4)	22
L^3	—	—	(3.660)	1.286(7)	1.801(6)	1.477(4)	This work
[Ni(L^2)$_2$Cl$_2$]	2.037(9)	2.116(7)	2.698(10)	1.298(13)	1.783(12)	1.479(7)	This work
[Co(L^3)$_2$Cl$_2$]	2.150(7)	2.150(6)	2.725(6)	1.292(10)	1.800(9)	1.479(6)	This work
[Ni(L^3)$_2$Cl$_2$]	2.065(4)	2.121(4)	2.719(1)	1.282(8)	1.808(5)	1.478(4)	This work
[La(L^2)$_3$Cl$_3$]	2.851(9)	2.512(9)	2.797(7)	1.29(2)	1.762(15)	1.484(10)	This work
[Pr(L^5)$_3$Cl$_3$]	2.798(7)	2.461(9)	2.746(1)	1.26(1)	1.76(1)	1.461(9)	This work
[Nd(L^5)$_2$(NO$_3$)$_3$(H$_2$O)]^b	4.45	2.402(4)	2.970(5)	1.276(7)	1.801(6)	1.470(4)	This work
	4.39	2.344(4)	2.880(6)	1.279(8)	1.783(6)	1.480(4)	

^{a} *E*-isomer only. ^{b} Two non-equivalent monodentate ligands.

IR spectra

Analysis by IR spectroscopy provides initial evidence of coordination by transition or lanthanide metal ions. A number of characteristic features may be noted in the main IR bands of these complexes.[15,19] Typically the broad, weak band at *ca.* 1600 cm^{-1} associated with ν(C=N) in the free ligand, shifts to higher energy by 20–60 cm^{-1} on complexation and becomes more intense and significantly sharper. In the nitrate complexes the band attributed to ν(C=N) is broader and in the lanthanide complexes subdivided into two bands. This feature may suggest differences in the nature of individual imine bonds in these nitrate complexes.

The phosphoryl band, ν(P=O), occurs in the free ligand as two bands at *ca.* 1230 cm^{-1} and 1180 cm^{-1}. On complexation the higher energy band shifts down by about 20 cm^{-1}. The second band does not move as significantly and shifts in either direction ±5 cm^{-1}. This is noted in both transition and lanthanide complexes over all the ligands studied (Table 1).

The appearance of the nitrate bands in the series of lanthanide complexes poses some interesting questions as to the mode of nitrate coordination present. A number of literature sources identify series of bands characterising the mode of nitrate coordination (relevant to bands in the region 1000–1600 cm^{-1});[19–21] intense bands *ca.* 1380–1385 cm^{-1} are attributed to ionic nitrates, bands at 1540 and 1300 cm^{-1} for coordinated bidentate nitrates and bands at 1430 and 1300 cm^{-1} for coordinated monodentate nitrates. In the latter cases the magnitude of splitting ($\Delta\nu$) between these two sets of bands is used to identify coordinated monodentate from bidentate (generally Δ_{mono} (*ca.* 120 cm^{-1}) < Δ_{bi} (*ca.* 210 cm^{-1}). A mixture of nitrate coordination modes is represented by more than one set of bands.

In all the reported nitrate complexes of this work, bands at 1385 cm^{-1} were assigned to free ionic nitrates. In addition other nitrate coordination modes were also identified. Specifically for those nitrate complexes isolated mainly as intractable oils or as solids in some cases, a series of bands at 1440 and 1300 cm^{-1} ($\Delta = 140$ cm^{-1}) as well as a band for the ionic nitrates was observed. Where crystallization was successfully induced for the oils, the band at 1440 cm^{-1} has shifted to higher energy (*ca.* 1540 cm^{-1}) indicating a change to a bidentate coordination mode for the nitrate group with $\Delta = 220$ cm^{-1}.

The appearance of bands believed to be due to both intramolecular (*Z*-isomer only) and intermolecular (both *E*- and *Z*-isomers) hydrogen bonding was a distinctive feature in the IR spectra of the free ligands at *ca.* 3100–3200 cm^{-1}. Since the complexation appears to be specific for the *E*-isomer, the intramolecular hydrogen bonding mode is expected to be lost. Weak bands at around 3100 cm^{-1} are assigned to intermolecular hydrogen bonding modes in the metal complexes. Solid-state structural characterisation of selected complexes appears to support this assignment.

Mass spectra

The LSI mass spectra obtained showed some differences between the transition and lanthanide complexes (Table 1). The transition metal complexes (Co(II), Ni(II), L$^{1-3}$ and L^5) tended to give two sets of peaks; one results from fragmentation of a pseudo-molecular ion formed by addition of glycerol molecules to the parent ion and the second series of peaks arising from fragmentation of the parent ion. The base peak for the transition metal chloride complexes is associated with loss of either one or two anions as HCl. In a few cases the base peak is associated with loss of one anion followed by one ligand and two of the phosphorus alkoxy groups as neutral alkenes. The loss of these alkoxy groups was previously noted with the free ligands themselves and that the dealkylation of phosphonate diesters may be facilitated by the presence of chloride ions.

The parent ion is similarly not observed in the lanthanide nitrate and lanthanide chloride complexes. The base peak of the nitrate complexes is generally associated with loss of the water molecules and one HNO$_3$ molecule from the parent ion.

The treatment of the LSI mass spectral data for the complexes of the diesters allows a number of conclusions about the nature of the metal complexes formed to be made. The exact metal : ligand ratio is not apparent due to the facile loss of the coordinated ligands but it is true that for each complex the number of ligands identified is equal to or less than that determined from elemental analysis. The anions, coordinated water molecules and a certain number of the coordinated ligands are lost rapidly from the complexes, however a certain ‘core’ structure invariably remains suggesting that these ligands do coordinate moderately strongly to the metal ions. The fact that the free ligand appears is some proof that the ligands remain intact in these species.

Single crystal X-ray structural characterisation

The structure determination of the ligand L^3 allows comparison between the bond lengths in a free ligand with those observed in the coordinated ligands; the mean values for the principal bond lengths in L^3 and the six metal complexes are listed in Table 2. The structure of L^3 in the crystal (Fig. 1) shows strong intermolecular hydrogen bonding between phosphoryl oxygen atoms and oximic hydrogen atoms of molecules related by unit cell translations in the *a*-axis direction [O(1)···H(4A) 1.83, O(1)···O(4A) 2.696 Å], which are consistent with the IR evidence (*vide supra*).

Three distinct modes of co-ordination have been identified for α-hydroxyiminoalkanephosphonate ligands in the metal compounds. The Ni(II) complex of L^2,[15] and the Co(II) and Ni(II) complexes of L^3, all formulated [M(L)$_2$Cl$_2$], each show a *symmetric* bidentate mode of coordination *via* the oxime nitrogen and the phosphoryl oxygen; these are illustrated in Fig. 2 which shows a view of the [Co(II)(L^3)$_2$Cl$_2$] molecule. In contrast, in both the Pr(III) complex of L^5, [Pr(L^5)$_3$Cl$_3$], and the La(III)

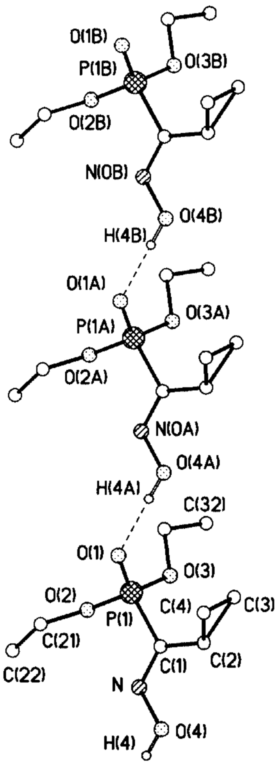

Fig. 1 The structure of the free ligand L^3 in the crystal showing the linear polymeric chain formed by hydrogen bonding between molecules in adjacent unit cells [O(1) · · · H(4A) 1.83, O(1) · · · O(4A) 2.696 Å, the final letters denote translations A: $1+x, y, z$ and B: $2+x, y, z$].

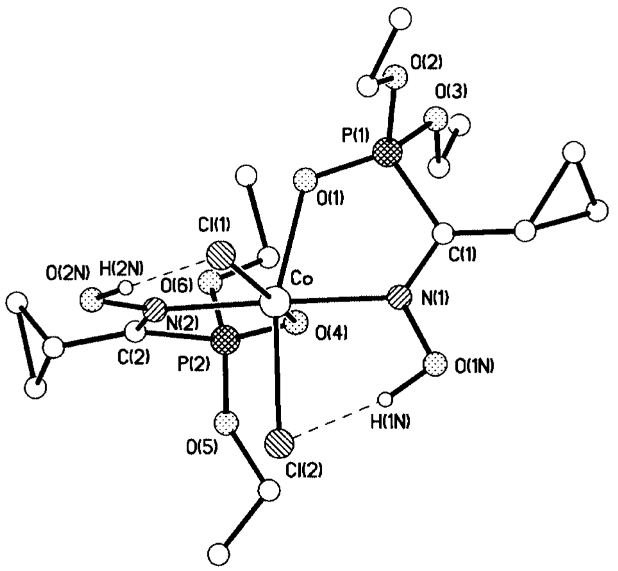

Fig. 2 The molecular structure of $[M(L^3)_2Cl_2]$ M = Co and Ni, illustrated by the Co(II) complex, showing the symmetric bidentate bonding mode of L^3; the structure of the $[Ni(L^2)_2Cl_2]$ is very similar but has exact C_2 symmetry (ref. 22).

complex of L^2, $[La(L^2)_3Cl_3]$, although the ligand also coordinates *via* the oxime nitrogen and the phosphoryl oxygen, it is in an *asymmetric* bidentate coordination mode, illustrated for $[La(L^2)_3Cl_3]$ in Fig. 3. In the only nitrate metal complex to have been structurally characterised, $[Nd(L^5)_2(NO_3)_3(H_2O)]$, a third bonding mode is adopted, with both ligands coordinated in *monodentate* mode, *via* the phosphoryl oxygen only as illustrated in Fig. 4.

In the isomorphous $[Co(L^3)_2Cl_2]$ and $[Ni(L^3)_2Cl_2]$ crystals, the molecules have distorted octahedral co-ordination at the metal atom (see Fig. 2), with *cis* configurations for the two chloro ligands [mean M–Cl 2.404(3) Co, 2.388(2) Å Ni] and the phosphoryl oxygen atoms [mean M–O 2.150(6) Co, 2.121(4) Å Ni]; the co-ordination is completed by two *trans* oximic nitrogen atoms [mean M–N 2.150(7) Co, 2.065(4) Å Ni]. The structure of $[Ni(L^2)_2Cl_2]$ is very similar, but the molecule has exact crystallographic C_2 symmetry and slightly shorter bond lengths [Ni–Cl 2.346(4), Ni–O 2.116(7) and Ni–N 2.037(9) Å]. All three compounds show hydrogen-bonding between the oxime hydrogen atom and the chloro ligand [mean H · · · Cl 2.07, mean O(ox) · · · Cl 2.974 Å], effectively forming pseudo 5-membered chelate rings.

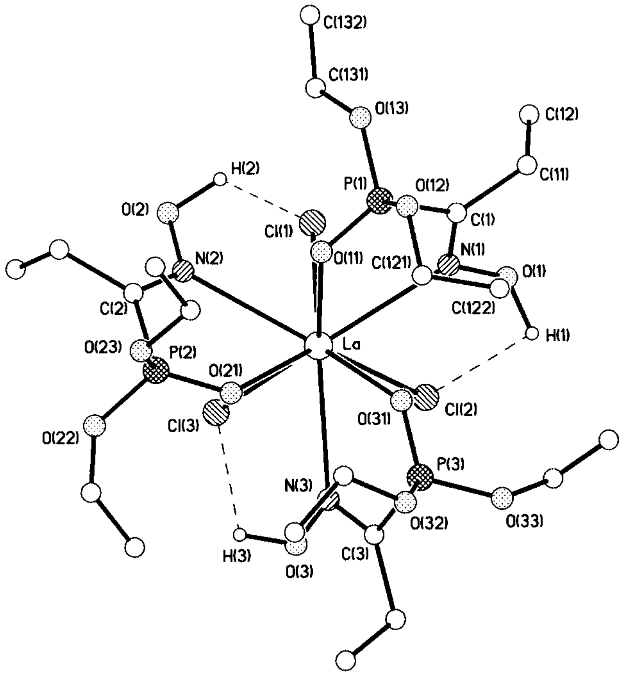

Fig. 3 The tricapped-prismatic co-ordination geometry in the molecule $[La(L^2)_3Cl_3]$, showing the asymmetric bidentate bonding mode of L^5. The structure of $[Pr(L^5)_3Cl_3]$ is very similar but has crystallographic C_3 symmetry.

The complex $[Pr(L^5)_3Cl_3]$ has exact C_3 symmetry in the solid state,[16] and $[La(L^2)_3Cl_3]$ complex has the very similar structure of virtual C_3 symmetry illustrated in Fig. 3. Both compounds have similar nine-coordinate geometry at the M(III) ion, which may be envisaged as tricapped-trigonal prismatic (Fig. 3),[16] with the three capping positions occupied by imine nitrogen atoms, with relatively long bonds [mean La–N 2.851(9) and Pr–N 2.798(7) Å]; the oxygen donors form one end of the trigonal prism [mean La–O 2.512(9) and Pr–O 2.461(9) Å] and the three chloro ligands form the other end [mean La–Cl 2.860(5) and Pr–Cl 2.784(4) Å]. Both complexes show evidence of a similar type of hydrogen bonded 'chelate ring' to that observed in the transition metal chloro complexes. Although the oximic hydrogen atoms were directly located in both structures, their contact distances are rather unreliable. However supporting evidence of hydrogen bonding may be deduced from the O(H) · · · Cl distances [mean 2.983 (La) and 2.916 (Pr) Å] which are within the sum of the van der Waals radii (Cl 1.75, O 1.4 Å).

The ligand L^5 adopts a monodentate bonding mode in the structure of $[Nd(L^5)_2(NO_3)_3(H_2O)]$ [Fig. 4(a)], and the metal atom is also nine-coordinate, but with an irregular coordination polyhedron. In this case three symmetrically bidentate nitrate ions [Nd–O(nitrate) range 2.504(4)–2.554(4) Å], occupy six coordination sites and, together with the water ligand [Nd–O(1w) 2.447(5) Å], form an irregular 'girdle' around the metal. The oxygen atoms of two monodentate L^5 ligands occupy approximately *trans* bonding sites [O(1)–Nd–O(4) 148.5(1)°] with almost linear bonding at the donor oxygen atoms [Nd–

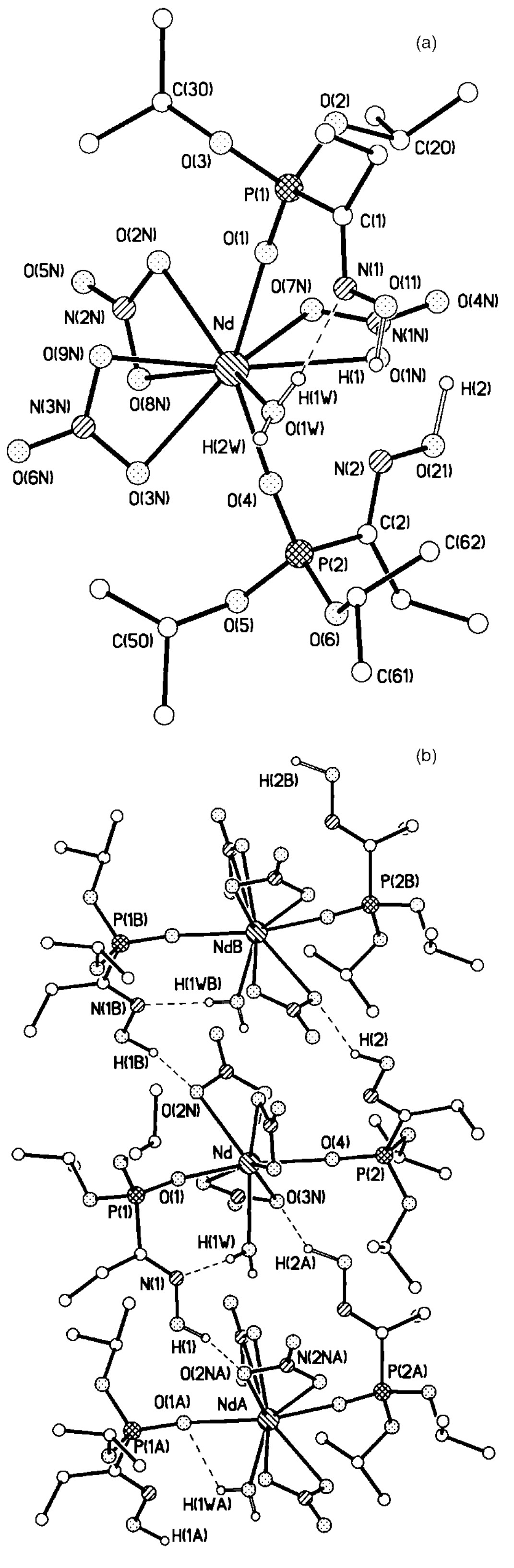

Fig. 4 Views of the complex $[Nd(L^5)_2(NO_3)_3(H_2O)]$ showing: (a) the distorted nine-coordinate geometry at Nd(III), and the monodentate bonding mode of L^5; (b) the polymeric chain formed in the solid state by hydrogen bonding between adjacent molecules related by the *c*-glide [H(1)···O(2NA) 1.71, O(11)···O(2NA) 2.717, H(2)···O(3NB), 1.96, O(21)···O(3NB) 2.897 Å, final letters denote symmetry operations A: $x, \frac{1}{2} - y, \frac{1}{2} - z$, B: $x, \frac{1}{2} - y, \frac{1}{2} - z$].

O(1)–P(1) 172.5(3), Nd–O(4)–P(2) 176.4(3)°]. The two bonds from the oxygen donors are significantly different in length, Nd–O(1) 2.402(4) and Nd–O(4) 2.344(4) Å; the potential nitrogen donors of L^5 are remote from the metal, Nd···N(1) 4.445 and Nd···N(2) 4.387 Å, and are clearly non-bonding. The preference of the neodymium ion for the oxygen donor of the ligand over the potential imine nitrogen donor; is consistent with the 'hard' nature of the f-element ions. One of the uncoordinated oximic nitrogen atoms is involved in hydrogen-bonding to a proton of the coordinated water molecule [(N(1)···H(1W) 2.121, N(1)···O(1W) 2.909 Å], effectively forming a seven-membered 'chelate ring' with the metal. Both oximic protons, and the second hydrogen atom of the water ligand, form hydrogen-bonds to nitrate oxygen atoms of adjacent molecules, related by the crystallographic *c*-glide, on either side of complex [Fig. 4(a)], resulting in hydrogen-bonded chains of molecules which run throughout the crystal parallel to the *c*-axis.

Table 3 Comparison of $^{31}P-\{^1H\}$ NMR data for a series of La(III) complexes

Ligand	δ_P	Complex	δ_P	$\Delta(\delta_P$(ligand − complex))/ppm
L^1	11.84	$[La(L^1)_2Cl_3(H_2O)_2]$	12.95	−1.11
L^1	11.84	$[La(L^1)_2(NO_3)_3(H_2O)]$	12.37	−0.53
L^2	11.80	$[La(L^2)_3Cl_3]$	13.29	−1.49
L^5	9.90	$[La(L^5)_3Cl_3]$	11.36	−1.46

On complexation there appears to be no significant change in the length of the phosphoryl bond (P=O) length in the metal complexes studied, which range from 1.461(9) to 1.484(10) Å, similar to the value 1.477(4) Å observed in the free ligand L^3 and of 1.462(4) Å previously reported for L^1 (Table 2). The 'bite' distances (N···O) range from 2.698(10) to 2.725(6) Å for the transition metal complexes and are slightly longer in the asymmetric bidentate lanthanide complexes [2.746(1) and 2.797(7) Å for the Pr(III) and La(III) complexes respectively]. Interestingly, for the monodentate ligand in the Nd(III) complex, the corresponding N···O distances [N(1)···O(1) 2.970(5) and N(2)–O(4) 2.880(6) Å] are only slightly longer than in the complexes where the ligands are bidentate, and are considerably shorter than the corresponding length of 3.660 Å in the free ligand L^3.

NMR spectra

The ^1H, $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectra for the diamagnetic La(III) complexes were recorded in CD_3OD and the nitrate complex of L^1 in D_2O. In general the ^1H NMR spectra for these complexes are very similar to the parent ligands with minor adjustments of the position, δ_H and the J_{HH} and J_{HP} coupling constants.

In the $^{13}C-\{^1H\}$ NMR spectra the signals for methyl and methylene carbons are largely unchanged. The doublet at *ca.* 155 ppm for the α-carbon has $^1J_{PC}$ of >200 Hz which is indicative of complexation by a ligand of *E*-isomer composition.[15,16]

The single sharp peak observed in the $^{31}P-\{^1H\}$ NMR spectrum is shifted *ca.* 0.5–1.5 ppm upfield from the free ligand. It may be noted that in the lanthanum nitrate species ($[La(L^1)_2(NO_3)_3(H_2O)]$ in D_2O) the shift is only 0.5 ppm while in the tris-chloro complexes and especially those with a third ligand $\Delta\delta$ increases to 1.5 ppm (in CD_3OD). The smaller magnitude of shift with the nitrate complex may reflect the change in coordination mode in these nitrate complexes (Table 3).

Evidence for the presence of two α-hydroxyiminophosphonate isomers in the ^1H NMR spectrum is often difficult to establish due to overlap in the δ_H = 1–4 region caused by the presence of the isomers and the complex nature of coupling to the phosphorus. Breuer *et al.* suggest that the P–O–Me proton signal of the *E*-isomer always appears at lower fields by *ca.* 0.05–0.08 ppm than that of the corresponding *Z*-isomer,[22] however assignment of these resonances to the *E*- and *Z*-isomers is fairly arbitrary and not easily quantified.

Table 4 Electron absorption spectra data, λ/nm (ε/dm^3 mol^{-1} cm^{-1}), for transition and lanthanide metal complexes

Assignment	$[Ni(H_2O)_6Cl_2]$	$[Ni(L^2)_2Cl_2]$	$[Ni(L^3)_2Cl_2]$
$^3A_{2g}$–$^3T_{1g}(F)$	743 (2.7)	758 (3.4)	753 (4.1)
$^3A_{2g}$–$^3T_{1g}(P)$	392 (6.4)	410 (8.4)	411 (9.9)
Assignment	$[Co(H_2O)_6Cl_2]$	$[Co(L^2)_2Cl_2]$	$[Co(L^3)_2Cl_2]$
$^4T_{1g}$–$^4T_{2g}$	527 (7.9)	529 (15.1)	529 (12.9)
Assignment	$[Pr(H_2O)_7Cl_3]$	$[Pr(L^2)_3Cl_2]$	$[Pr(L^5)_3Cl_3]$
$^3H_4$–$^3P_2$	446 (7.4)	446 (9.7)	446 (8.1)
$^3H_4$–$^3P_1$	470 (3.6)	471 (5.2)	471 (4.1)
$^3H_4$–$^3P_0$	483 (4.6)	485 (6.2)	483 (5.0)
$^3H_4$–$^1D_2$	594 (2.1)	595 (2.9)	594 (2.3)

In an attempt to explore this problem a series of NMR experiments, using the α-hydroxyiminophosphonate free ligands treated with the lanthanide complexes of the α-hydroxyiminophosphonates, were conducted in order to examine the complexes as shift reagents for isomer resolution in ^{1}H NMR spectroscopy.[16,23] The methyl signals in the ester region of a mixture of *E*,*Z*-dialkyl-α-hydroxyiminoalkanephosphonate isomers can be resolved in the presence of the Pr(III) complex (3 mmol dm^{-3}) or at a lower concentration of the Dy(III) complex (1 mmol dm^{-3}). For L^2, for example, in the presence of the corresponding complexes, $[Pr(L^2)_3Cl_3]$, and $[Dy(L^2)_3(NO_3)_3(H_2O)]$, these overlapping signals in the ^{1}H NMR spectrum are clearly separated, allowing full assignment of the complex multiplets to be made. Consequently the ratio of *E*- and *Z*-isomers can also be examined in this ^{1}H NMR spectrum and this gives a ratio close to that deduced from ^{31}P NMR.

Electronic spectra

The electronic spectra of the Co(II) and Ni(II) chloride complexes of L^2 were recorded in methanol in the region 300–900 nm. Both transition metal complexes gave bands with low ε assigned to forbidden d–d transitions and indicative of octahedral coordination.[24] The 10*Dq* value is similar to that for the hexaaqua divalent ion. The bands are assigned on the basis of the Tanabe–Sugano diagram in octahedral symmetry (Table 4). For the Ni(II) complexes the band assigned to $^3A_{2g}$–$^3T_{1g}(F)$ has a small shoulder, this is attributed to spin–orbit coupling which mixes the $^3T_{1g}(F)$ and ^1E_g states.[25] The electronic spectra of the Pr(III) chloride complexes of L^2 and L^5 were also recorded in methanol (Table 4). In contrast to the broad bands in the spectra for the d-block transition elements, those for the Pr(III) complexes show sharp f–f transition bands arising from a well-defined ground state ($^3H_4$). Information about the metal environment is obtained mainly from effects on the hypersensitive bands.[26] In these examples, no information could be extracted from such bands, suggesting that the f-electrons are not directly involved in complex formation.

Effect of anions

In general metal chloride salts appear to readily form well-defined transition and lanthanide metal complexes with these α-hydroxyiminophosphonates. With lanthanide nitrates, complexes are formed although isolation of solid materials was not always effected, for the oils a mixture of ionic and coordinated monodentate nitrate modes were observed. Changing the solution pH after mixing appeared to help in recovery of the lanthanide complexes, although this appeared to modify the resulting relative intensities of the two assigned oxime bands at *ca.* 1660 and 1630 cm^{-1}. With transition metal nitrates, (Fe(III), Ni(II) and Cu(II)), the IR spectra of the resultant oils did not reveal successful complexation and in general the use of base did not aid in complex formation with these metal salts.

A preliminary investigation was also undertaken of the coordination of lanthanide thiocyanates with these ligands. Solutions containing freshly prepared thiocyanate metal salts were used and on mixing with the ligands the metal solutions changed colour rapidly and deposited solid in a matter of minutes. The products were insoluble in most solvents except DMSO and decomposed above 200 °C. IR analysis of the species shows the ν(P=O) band at slightly lower wavenumbers compared to the nitrate and chloride complexes (1180 cm^{-1}). A strong, very intense thiocyanate peak at *ca.* 2078 cm^{-1} is attributed to thiocyanate bonding (*via* the nitrogen);[27,28] however disconcertingly most of the complexes also had peaks assigned to ionic thiocyanates.

Conclusions

A series of late transition metal (Co(II) and Ni(II)) and trivalent lanthanide complexes have been prepared and characterised for a number of dialkyl α-hydroxyiminoalkanephosphonates. Three modes of ligand coordination have to-date been identified in these metal complexes, one monodentate and two bidentate modes with the monodentate mode exemplified by a sole lanthanide nitrate complex. A single example of a mixed coordination mode has been reported for a Ca(II) complex of methyl α-hydroxyiminobenzylphosphonate monoester.[29] Although no lanthanide species with mixed monodentate and bidentate coordination modes for the diesters has so far been identified, it seems possible, in view of the predicted similarity of Ca(II) and Ln(III) coordination modes, that further structural types may be anticipated for these metals.

Experimental

General procedures for the preparation of dialkyl α-oxophosphonate precursors

Trialkyl phosphite (0.25 mol) was added dropwise, under dry nitrogen, to a stirring, cooled (0–2 °C) solution of the acyl chloride (0.25 mol). The solution was allowed to stir at rt overnight ($CaCl_2$ drying tube or under N_2), the following day volatile materials were removed with gentle heating *in vacuo* and used immediately or else the remaining viscous material was distilled under high vacuum to give colourless or pale yellow fractions of the dialkyl α-oxophosphonate. Characterizing data for the two new ligand precursors L^4 and L^6 are listed below.

Diethyl α-oxo-2-ethylhexanephosphonate. From 2-ethylhexanoyl chloride and triethyl phosphite. Colourless liquid (yield 77%). NMR: ^{1}H ($CDCl_3$) δ_H 0.88 (t, 3H, CH_3, $^3J_{HCCH}$ = 7.20 Hz), 1.37 (t, 6H, ester CH_3, $^3J_{HCCH}$ = 6.7 Hz), 2.05–2.16 (m, 6H, CH_2), 3.11 (m, 1H, CH), 4.21 (dqnt, 4H, ester CH_2, $^3J_{HCCH}$ = 7.1 Hz), ^{31}P-{^{1}H} ($CDCl_3$) δ_P −3.46 (s).

Diisopropyl α-oxo-2-ethylhexanephosphonate. From 2-ethylhexanoyl chloride and triisopropyl phosphite. Colourless liquid (yield 78%); NMR: ^{31}P-{^{1}H} ($CDCl_3$) δ_P −4.64 (s). IR (KBr disk): ν/cm^{-1} ν(C=O) 1691 s, ν(P=O) 1254 s, ν(P-O) 992 s.

General procedure for the preparation of dialkyl α-hydroxyiminophosphonates (L^1–L^7)

The dialkyl α-oxophosphonate (0.14 mol) was slowly added, under dry nitrogen, to a mixture of hydroxylamine hydrochloride (0.15 mol) and pyridine (0.15 mol) dissolved in methanol, in an ice-salt bath at −10 °C, during a period of 20 min. The solution was left to stand overnight under nitrogen. The following day, any volatile material was removed *in vacuo*. The resulting solution was treated with hydrochloric acid (10% w/v, 50 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The organic layers were combined and washed with aqueous sodium hydrogen carbonate (10%, 2 × 50 cm^3) and dried over anhydrous magnesium sulfate. The solution was filtered to remove the drying agent and the dichloromethane removed *in vacuo* leaving the dialkyl α-hydroxyiminophosphonate as

Table 5 Crystal data and structure refinement for L^3, $[Ni(L^2)_2Cl_2]$, $[Co(L^3)_2Cl_2]$, $[Ni(L^3)_2Cl_2]$, $[La(L^2)_3Cl_3]$, $[Pr(L^5)_3Cl_3]$, and $[Nd(L^5)_2(NO_3)_3(H_2O)]$

	L^3	$[Ni(L^2)_2Cl_2]$	$[Co(L^3)_2Cl_2]$	$[Ni(L^3)_2Cl_2]$	$[La(L^2)_3Cl_3]$	$[Pr(L^5)_{3Cl_3})]$	$[Nd(L^5)_2(NO_3)_3$-$(H_2O)]$
Formula	$C_8H_{18}NO_4P$	$C_{14}H_{32}Cl_2N_2O_8$-P_2Ni	$C_{16}H_{36}Cl_2N_2O_8$-P_2Co	$C_{16}H_{36}Cl_2N_2O_8$-P_2Ni	$C_{21}H_{40}Cl_3N_3O_{12}$-$P_3La$	$C_{27}H_{60}Cl_3N_3O_{12}$-$P_3Pr$	$C_{18}H_{42}N_5O_{18}$-P_2Nd
M	223.21	547.97	576.24	576.02	872.79	958.95	822.75
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Tetragonal	Hexagonal	Monoclinic
Space group	$P2_1/n$ (Alt. no. 14)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P4_2/n$ (no. 86)	$P6_3$ (no. 173)	$P2_1/c$ (no. 14)
Unit cell dimensions							
a/Å	6.9912(2)	8.980(2)	10.599(2)	10.008(2)	29.432(6)	13.784(3)	14.323(3)
b/Å	15.254(3)	13.345(3)	14.754(3)	15.478(3)	29.432(6)	13.784(3)	17.258(3)
c/Å	10.902(2)	21.218(14)	9.822(2)	9.982(2)	9.280(2)	14.356(3)	14.250(3)
α/°	—	—	99.93(2)	95.54(2)	—	—	—
β/°	97.43(2)	94.86(2)	116.85(2)	118.63(2)	—	—	97.82(2)
γ/°	—	—	71.053(2)	72.42(2)	—	—	—
V/Å^3	1152.8(5)	2551(1)	1296(1)	1292(1)	8038(2)	2362(1)	3490(1)
Z	4	4	2	2	8	2	4
μ/mm^{-1}	0.230	1.130	0.962	1.120	1.430	1.350	1.650
Reflections collected	1306	2874	4850	5253	—	4488	6639
Independent reflections (R_{int})	1227 (0.0492)	876 [$I > 3\sigma(I)$]	2223 [$I > 3\sigma(I)$]	2727	2308 [$I > 3\sigma(I)$]	993 [$I > 3\sigma(I)$]	4002 [$I > 3\sigma(I)$]
Final R indices^a							
[$I > 2\sigma(I)$]	$R_1 = 0.0490$, $wR_2 = 0.1037$	$R = 0.0709$, $R' = 0.0663^b$	$R = 0.0639$, $R' = 0.0667^b$	$R = 0.0555$, $R' = 0.0550^b$	$R = 0.0645$, $R' = 0.0627^b$	$R = 0.0460$, $R' = 0.0406^b$	$R = 0.0374$, $R' = 0.0387^b$
(all data)	$R_1 = 0.1079$, $wR_2 = 0.1381$	—	—	—	—	—	—
Weights a, b^a	0, 2.8023	^{b}	^{b}	^{b}	^{b}	^{b}	^{b}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$. [b] Data collected in a skipping mode; weights of $1/\sigma^2(F)$ were applied; $[I/\sigma(I) > 3]$; $R = \Sigma(\Delta F)/\Sigma(F_o)$; $R' = [\Sigma(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.

colourless or yellow viscous oils, which may solidify on standing. The solid materials were recrystallized from the appropriate solvents. Characterizing data for the two new ligands L^4 and L^6 are listed below.

Diethyl α-hydroxyimino-2-ethylhexanephosphonate (L^4). Orange liquid, (yield 73%). (Found: C, 51.5; H, 9.31; N, 5.12. Calculated for $C_{12}H_{26}NO_4P$; C, 51.6; H, 9.38; N, 5.01%). NMR: ^1H ($CDCl_3$) δ_H 0.88 (t, 6H, CH_3, $^3J_{HCCH} = 7.32$ Hz), 1.34 (t, 6H, ester CH_3, $^3J_{HCCH} = 7.08$ Hz), 2.48 (m, 2H, CH_2), 2.50 (m, CH_2), 4.21 (m, 4H, ester CH_3, $^3J_{HCCH} = 7.10$ Hz), 15.5 (br, OH), ^{31}P-{^1H} ($CDCl_3$) δ_P 10.03 (*E*) (14%), (*Z*) (86%), after isomerization δ_P 10.43 (*E*) (95%), (*Z*) (5%). IR (KBr disk): ν/cm^{-1} ν(OH) 3172 br, s, ν(C=N) 1656 w, ν(P=O) 1228 s, ν(P–O) 1027 vs, 976 m.

Diisopropyl α-hydroxyimino-2-ethylhexanephosphonate (L^6). Yellow liquid, (yield 74%). (Found: C, 54.7; H, 9.77; N, 4.91. Calculated for $C_{14}H_{30}NO_4P$; C, 54.7; H, 9.86; N, 4.56%). NMR: ^1H ($CDCl_3$) δ_H (*E*,*Z*)-isomers: 0.88 (m, 3H, CH_3 of β-CH), 1.0–2.0 (m, 11H, all CH_2), 1.87 (m, β-CH (*Z*)), 3.12 (m, β-CH, (*E*)), 4.84 (m, 2H, CH), 5.32 (H_2O, broad singlet), 11.09 (br, OH (*E*)), 11.30 (br, OH, (*Z*), OH protons disappear after D_2O shake), ^{13}C-{^1H} (*E*-isomer) ($CDCl_3$) δ_C 11–72, alkyl region unassigned, 154.58 (d, α-C, (*Z*-isomer, 46%), $^1J_{PC} = 147.87$ Hz), 157.72 (d, α-C, (*E*-isomer, 54%), $^1J_{PC} = 209.19$ Hz), ^{31}P-{^1H} ($CDCl_3$) δ_P 9.34 (*E*) (55%), 4.34 (*Z*) (45). IR (KBr plates): ν/cm^{-1} ν(OH) 3166 br, m, ν(C=N) 1666 w, ν(P=O) 1226 s, ν(P–O) 996 vs.

General procedure for the preparation of metal complexes of dialkyl α-hydroxyiminophosphonates (L^1–L^7)

To the metal salt (2 mmol) in methanol (2 cm^3) was added a methanolic solution of the dialkyl α-hydroxyiminophosphonate (4 mmol). After mixing the solution was left to stand and after several days the resulting solid was filtered off, washed with chilled methanol, diethyl ether and air-dried. Elemental analyses, IR and mass spectrometry data of the metal complexes studied in this work are presented in Table 1. The NMR data of the lanthanum complexes of L^1 and L^2 are given below.

$[La(L^1)_2Cl_3(H_2O)_2]$. From lanthanum(III) chloride heptahydrate (5.1 mmol) and L^1 (2.6 mmol). NMR: ^1H (CD_3OD) δ_H 1.36 (dt, 6H, ester CH_3, $^3J_{HCCH} = 7.01$ Hz, $J = 0.63$ Hz), 2.03 (d, 3H, CH_3, $^3J_{HCCP} = 11.23$ Hz), 4.24 (qt, 4H, ester CH_2, $^3J_{HCCH} = 7.4$ Hz), ^{13}C-{^1H} (CD_3OD) δ_C 11.94 (d, CH_3, $^2J_{PCC} = 16.86$ Hz), 16.58 (d, ester CH_3, $^3J_{POCC} = 6.48$ Hz), 65.42 (d, ester CH_2, $^2J_{POC} = 6.16$ Hz), 150.72 (d, α-C, $^1J_{PC} = 219.38$ Hz), ^{31}P-{^1H} (CD_3OD) δ_P 12.95 (s).

$[La(L^1)_2(NO_3)_3(H_2O)]$. NMR: ^1H (CD_3OD) δ_H 1.35 (dt, 6H, ester CH_3, $^3J_{HCCH} = 6.88$ Hz), 2.05 (d, 3H, CH_3, $^3J_{HCCP} = 11.54$ Hz), 4.18 (dqnt, 4H, ester CH_2, $^3J_{HCCH} = 7.12$ Hz), ^{13}C-{^1H} (CD_3OD) δ_C 14.08 (d, CH_3, $^2J_{PCC} = 16.23$ Hz), 18.21 (d, ester CH_3, $^3J_{POCC} = 5.84$ Hz), 67.40 (d, ester CH_2, $^2J_{POC} = 5.91$ Hz), 154.26 (d, α-C, $^1J_{PC} = 201.15$ Hz), ^{31}P-{^1H} (CD_3OD) δ_P 12.37 (s).

$[La(L^2)_3Cl_3]$. From lanthanum(III) chloride heptahydrate (1.6 mmol) and L^2 (4.8 mmol). NMR: ^1H (CD_3OD) δ_H 1.13 (t, 3H, CH_3, $^3J_{HCCH} = 7.57$ Hz), 1.30 (t, 6H, ester CH_3, $^3J_{HCCH} = 7.08$ Hz), 2.57 (m, 2H, CH_2, $^3J_{HCCH} = 7.31$ Hz), 4.61 (qnt, 4H, ester CH_2, $^3J_{HCCH} = 7.08$ Hz), ^{13}C-{^1H} (CD_3OD) δ_C 10.42 (d, CH_3, $^4J_{POCC} = 1.64$ Hz), 16.59 (d, ester CH_3, $^4J_{POCC} = 6.23$ Hz), 20.84 (d, CH_2, $^2J_{PCC} = 15.85$ Hz), 65.12 (d, ester CH_2, $^2J_{POC} = 6.35$ Hz), 155.47 (d, α-C, $^1J_{PC} = 214.16$ Hz), ^{31}P-{^1H} (CD_3OD) δ_P 13.29 (s).

X-Ray crystallography

X-Ray intensity data for L^3, $[Ni(L^2)_2Cl_2]$, $[Co(L^3)_2Cl_2]$, $[Ni(L^3)_2Cl_2]$, $[La(L^2)_3Cl_3]$, $[Pr(L^5)_3Cl_3]$, and $[Nd(L^5)_2(NO_3)_3$-$(H_2O)]$ were collected with graphite-monochromated radiation on a Philips PW1100 four-circle diffractometer at 298 K. Details of refinement and crystal data are listed in Table 5. Absorption corrections (ψ-scans) were applied to the data of all the metal complexes.

In $[Co(L^3)_2Cl_2]$ relatively high thermal displacement parameters indicated some disorder of the terminal methyl groups and three of the methyl carbon atoms were resolved into two components of 50:50 occupancy and similarly in $[Ni(L^3)_2Cl_2]$ one methyl group was resolved. For the metal complexes refinement was based on F,[30] and for L^3 on F^2.[31] For all compounds the hydrogen atoms bonded to oxygen atoms were directly located, and were included in structure factor calculations but were allowed to refine only in L^3, $[Ni(L^2)_2Cl_2]$, $[Pr(L^5)_3Cl_3]$, $[Nd(L^5)(NO_3)_3(H_2O)]$; all other hydrogen atoms were placed in calculated positions. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters (except the components of the disordered methyl carbon atoms in $[Co(L^3)_2Cl_2]$ and $[Ni(L^3)_2Cl_2]$, and the non-methyl carbon atoms in $[Pr(L^5)_3Cl_3]$).

CCDC reference number 186/2056.

Other measurements

Melting points were recorded on an Electrothermal Digital Melting Points Apparatus and are uncorrected. Elemental analyses (C, H, N) were performed by the Scientific Analysis and Consultancy Service at the University of North London using a Carlo Erba 1106 Microanalyser. IR spectra were recorded on a Digilab FTS-40 Infrared Spectrometer as KBr microdisks and UV/VIS solution spectra on a Shimadzu UV-2100 UV/VIS recording spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were obtained using a Bruker-Spectrospin AM 250 FT-NMR spectrometer.

Magnetic susceptibility measurements were carried out on a Johnson Matthey Chemicals magnetic susceptibility balance. Corrections for the diamagnetism of the complexes were estimated from Pascals constants. Low resolution electron impact mass spectra were obtained on a Kratos 'Profile' HV3 spectrometer operating at 70 eV ionizing energy. LSI mass spectra were obtained using a Vacuum Generator (VG) Kratos 'Profile' Double Focusing mass spectrometer, equipped with a Cs fast ion gun operating at 10 kV. Samples were inserted immediately after mixing with the matrix, generally glycerol or 3-nitrobenzylalcohol. The intensities of the ions were expressed in percent relative to the intensity of the most abundant peak.

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