Synthesis, spectroscopic studies and structural systematics of phosphine oxide complexes with Group II metal (beryllium–barium) nitrates

Martin F. Davis,[a] William Levason,*[a] Raju Ratnani,*[b] Gillian Reid*[a] and Michael Webster[a]

Received (in Durham, UK) 10th January 2006, Accepted 23rd February 2006
First published as an Advance Article on the web 21st March 2006
DOI: 10.1039/b600301j

Complexes of the nitrates of beryllium, magnesium, calcium, strontium and barium with the phosphine oxides $OPPh_3$, $Ph_2P(O)CH_2P(O)Ph_2$, and $o\text{-}C_6H_4(P(O)Ph_2)_2$ have been prepared and characterised by analysis and IR spectroscopy and the structures of $[Be(OPPh_3)_2(NO_3)_2]$, $[Mg(OPPh_3)_2(NO_3)_2]$, $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ and $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$ have been determined. The solution speciation has been probed by a combination of ^1H, $^{31}P\{^1H\}$ and ^9Be NMR spectroscopy and conductance measurements. The variation in speciation and stability from Be–Ba is interpreted in terms of changes in the charge/radius ratio of the cations—thus whilst Be and Mg interact strongly with the phosphinoyl ligands, strontium and especially barium have very limited affinity for these ligands, and the complexes are extensively dissociated in solution.

Introduction

The coordination chemistry of the heavier alkaline earth metal cations Ca^{2+}, Sr^{2+} and Ba^{2+} remains relatively little explored, and the complexes with neutral ligands are mostly with crown ethers, cryptands and podands,[1–4] whilst there has been recent interest in charged bi- and poly-dentates such as diketonates and poly-ether-alkoxides as CVD (chemical vapour deposition) precursors.[2] Magnesium has attracted rather more attention, with particular emphasis on complexes with nitrogen polydentates as chlorophyll models.[1,2] Beryllium, although forming the bonds with the highest covalent character in this group, also attracts little work, probably due to its perceived high toxicity. As with related closed shell metal ions such as those of Groups I and III and the lanthanides, the chemistries in Group II are largely influenced by the charge/radius ratios and the balance between maximising M–L interaction whilst minimising inter-ligand repulsions. Often the most informative studies result from examining how these factors influence the chemistry down the group whilst the ligands are kept constant. We recently reported studies of a series of homoleptic cations with phosphine oxides and diphosphine dioxides,[5] including the four-coordinate $[M(OPPh_3)_4]^{2+}$(M = Mg, Ca, Sr or Ba), five-coordinate $[Mg\{Ph_2P(O)CH_2P(O)Ph_2\}_2(H_2O)]^{2+}$, six-coordinate $[M\{Ph_2P(O)CH_2P(O)Ph_2\}_3]^{2+}$ (M = Ca or Sr) and $[M\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_3]^{2+}$ (M = Ca, Sr or Ba) and seven-coordinate $[Sr\{Ph_2P(O)CH_2P(O)Ph_2\}_3(EtOH)]^{2+}$. Only three beryllium complexes, $[Be(OPPh_3)_4]Y$ (Y = BF_4 or ClO_4) and $[Be(OPPh_3)_2(NO_3)_2]$ have been reported with limited characterisation.[6,7] In the present paper we extend these studies to the complexes of the three phosphine oxides $OPPh_3$, $Ph_2P(O)CH_2P(O)Ph_2$, and $o\text{-}C_6H_4(P(O)Ph_2)_2$ with the nitrates of Be–Ba. Nitrate coordinates readily to hard metal ions and a rich chemistry of Sc, Y and lanthanide nitrates with phosphine oxides has been described[8–11] which also provide comparison data for the present study.

Results and discussion

Beryllium complexes

Beryllium (Be^{2+} r = 34 pm) is much smaller even than Mg (Mg^{2+} r = 78 pm) and usually has a coordination number of ≤4. It is also the only metal in this group suited to NMR studies with ^9Be ($I = 3/2$, 100%, Ξ = 14.05 MHz, $Q = 5.2 \times 10^{-30}$ m^2, D_c = 78) readily observed.[12] The reaction of aqueous $Be(NO_3)_2$ with $OPPh_3$ in a 1 : 2–4 ratio in methanol in the presence of 2,2-dimethoxypropane as dehydrating agent, followed by recrystallisation from acetone afforded colourless crystals of $[Be(OPPh_3)_2(NO_3)_2]$. The complex was previously described by de Bolster,[6] although only analytical and IR/Raman data were reported. The structure consists of discrete molecules with Be in a four-coordinate environment formed from two phosphine oxides and two monodentate nitrate ligands (Table 1 and Fig. 1). The molecule has no crystallographic symmetry. The angles at Be1 (103–117°) are close to tetrahedral and the NO_3 ligands are clearly monodentate (Be–O–N 122°) with the $N\text{–}O_{bridging}$ distances *ca.* 0.08 Å longer than the $N\text{–}O_{terminal}$. The Be–O–P angles (174, 157°) are both large and different, presumably reflecting packing requirements around the Be. The complex has a small molar conductance Λ_M = 7 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} CH_2Cl_2 solution† and the $^{31}P\{^1H\}$ NMR spectrum shows two species present both 1 : 1 : 1 : 1 quartets at δ = 38.2 (major) and 39.5 (minor) ($^2J_{BeP}$ = 4 Hz) (Fig. 2b). The

---

[a] *School of Chemistry, University of Southampton, Southampton, UK SO17 1BJ*
[b] *Department of Pure and Applied Chemistry, M. D. S. University, Ajmer, 305009, India*

† 1 : 1 Electrolytes in CH_2Cl_2 have Λ_M = 20–25 Ω^{-1} cm^2 mol^{-1} and 2 : 1 electrolyes Λ_M = *ca.* 35–45 Ω^{-1} cm^2 mol^{-1} although lower values are found with very large ions.

Table 1 Selected bond lengths (Å) and angles (°) for $[Be(OPPh_3)_2(NO_3)_2]$

Be1–O1	1.644(6)	Be1–O7	1.571(6)
Be1–O4	1.648(6)	Be1–O8	1.609(6)
O1–N1	1.298(4)	O7–P1	1.490(3)
O4–N2	1.298(4)	O8–P1	1.495(3)
O2–N1	1.223(4)	O5–N2	1.210(4)
O3–N1	1.215(4)	O6–N2	1.224(4)
P–C	1.774(5)–1.788(5)	C–C	1.341(6)–1.396(7)
O1–Be1–O4	105.7(3)	O4–Be1–O7	110.2(4)
O1–Be1–O7	117.2(3)	O4–Be1–O8	103.4(3)
O1–Be1–O8	107.5(4)	O7–Be1–O8	111.8(4)
Be1–O1–N1	122.3(4)	Be1–O7–P1	173.6(3)
Be1–O4–N2	121.5(3)	Be1–O8–P2	156.8(3)
O1–N1–O2	118.1(5)	O7–P1–C1	110.83(19)
O1–N1–O3	117.7(5)	O7–P1–C7	110.7(2)
O2–N1–O3	124.2(5)	O7–P1–C13	110.5(2)
O4–N2–O5	118.4(4)	O8–P2–C19	112.39(19)
O4–N2–O6	118.8(4)	O8–P2–C25	109.38(18)
O5–N2–O6	122.8(5)	O8–P2–C31	110.6(2)
C–P–C	107.0(2)–109.2(2)		

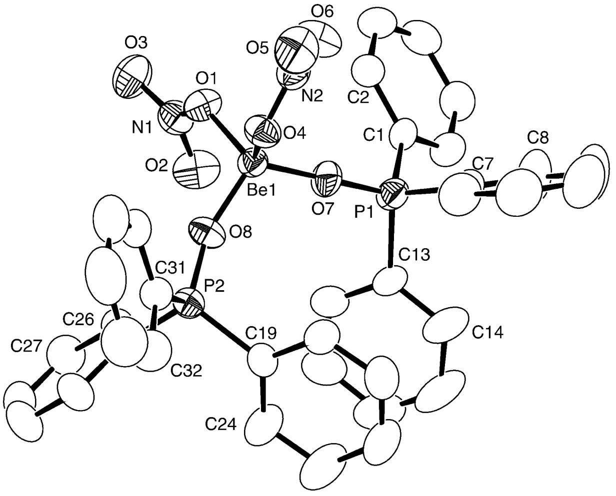

Fig. 1 The structure of $[Be(OPPh_3)_2(NO_3)_2]$ determined at 300 K, showing the atom numbering scheme. Ellipsoids are drawn at the 35% probability level and H atoms omitted for clarity.

corresponding ^9Be NMR spectrum (Fig. 2a) shows a 1 : 2 : 1 triplet at $\delta = +0.68$ and a weaker quartet (1 : 3 : 3 : 1) at +0.34 showing the two species are $[Be(OPPh_3)_2(NO_3)_2]$ and $[Be(OPPh_3)_3(NO_3)]^+$. On addition of excess $OPPh_3$ to this solution, the $^{31}P\{^1H\}$ NMR spectrum shows three resonances with $\delta = 28.0$ ($OPPh_3$), 38.2 ($[Be(OPPh_3)_2(NO_3)_2]$) and 39.5 ($[Be(OPPh_3)_3(NO_3)]^+$), with the last now the major beryllium containing species, and the solution has a significant conductance (Λ_M = *ca.* 18 Ω^{-1} cm^2 mol^{-1}). Mass balance requires another beryllium species, but none was observed in the ^9Be spectrum (Fig. 2a), although given the small chemical-shift range it could be obscured by the resonances of the phosphine oxide complexes. Even with a large excess of $OPPh_3$ some $[Be(OPPh_3)_2(NO_3)_2]$ was still present. Notably, exchange between $OPPh_3$ and the complexes is slow even at room temperature, which contrasts with the behaviour observed for the other metal ions in this study. The known complex[7] $[Be(OPPh_3)_4][ClO_4]_2$ has $\delta(P) = 42.4$ ($^2J_{BeP} = 4$ Hz) and the tetrakis(ligand) cation did not appear to form in the nitrate systems even with a large excess of ligand present. The

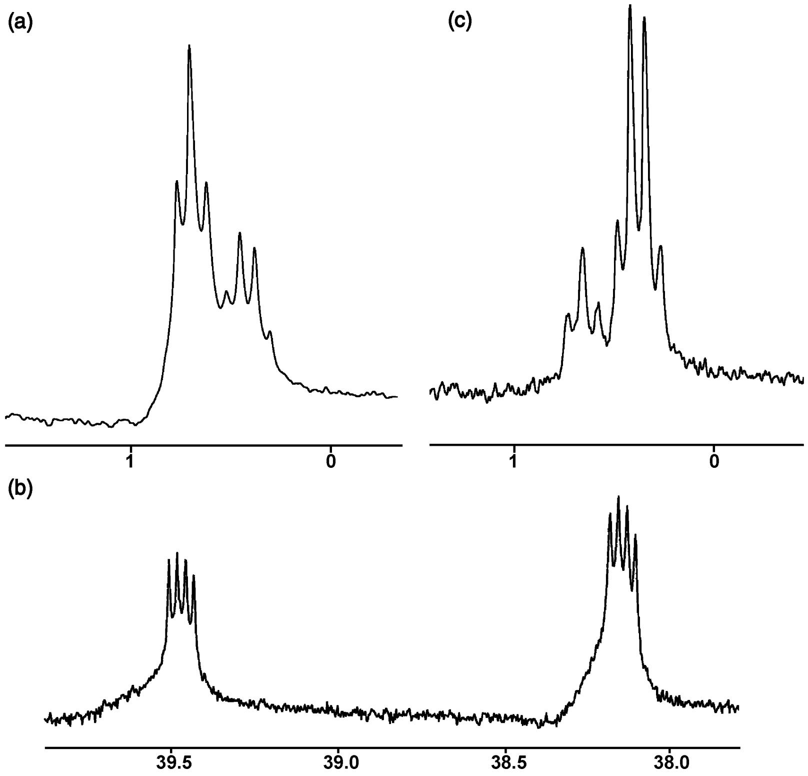

Fig. 2 (a) The ^9Be NMR and (b) $^{31}P\{^1H\}$ NMR spectra of $[Be(OPPh_3)_2(NO_3)_2]$ in CH_2Cl_2 solution at 295 K; (c) ^9Be NMR spectrum of $[Be(OPPh_3)_2(NO_3)_2]$ with excess $OPPh_3$ in CH_2Cl_2 at 295 K.

progressive shift of the ^{31}P NMR resonance to high frequency along the series $[Be(OPPh_3)_2(NO_3)_2]$ < $[Be(OPPh_3)_3(NO_3)]^+$ < $[Be(OPPh_3)_4]^{2+}$ is consistent with increasing O → Be donation as the charge on the beryllium increases.

The two diphosphine dioxide complexes $[Be\{Ph_2P(O)CH_2P(O)Ph_2\}(NO_3)_2]$ and $[Be\{o\text{-}C_6H_4(P(O)Ph_2)_2\}(NO_3)_2]$ were obtained as cream powders from methanol solutions of the constituents. The IR spectra (Experimental section) show only coordinated phosphine oxide groups, and the bands assigned as nitrate modes are generally similar to those in $[Be(OPPh_3)_2(NO_3)_2]$ indicating monodentate nitrato coordination and hence four-coordinate beryllium. In solution both are non-conductors and show broad singlet $^{31}P\{^1H\}$ NMR resonances, with larger coordination shifts than observed for the heavier metals, consistent with the high charge/radius of Be^{2+}. The absence of resolved beryllium coupling is probably attributable to a combination of a very distorted tetrahedral environment produced by these chelates on the very small beryllium centre resulting in faster Be quadrupolar relaxation, and the small coupling constants expected. The ^{9}Be NMR spectra are similarly singlets ($W_{1/2}$ *ca.* 12 Hz) and the spectra do not sharpen on cooling the solutions to 223 K.

Magnesium complexes

In contrast to the tetrakis species formed by the heavier alkaline earth nitrates (below), the reaction of magnesium nitrate and four equivalents of $OPPh_3$ in ethanol yields only $[Mg(OPPh_3)_2(NO_3)_2]$. This species shows features due to coordinated nitrate groups and $OPPh_3$ in its IR spectrum (Experimental section), and is a non-conductor in CH_2Cl_2 solution. Colourless crystals of the complex were obtained from CH_2Cl_2/Et_2O and the structure (Fig. 3 and Table 2) consists of discrete molecules with Mg in a six-coordinate environment formed from two phosphine oxides and two bidentate nitrate ligands. The molecule has 2-fold crystallographic symmetry. The nitrate ligands are symmetrically bonded to a good approximation (*ca.* 5% difference in Mg–O) and the Mg–O(P) agrees well with that found[13] in $[MgCl_2(Ph_3PO)_2]$ (1.9401(8) Å) but is longer than the Mg–O found in the homoleptic cation[5] $[Mg(OPPh_3)_4]^{2+}$ (1.890(2)–1.919(2) Å). The Mg–O–P (167.75(11)°) is some 10° larger than in the chloro-complex $[MgCl_2(Ph_3PO)_2]$ reflecting perhaps the larger steric bulk of the nitrate.

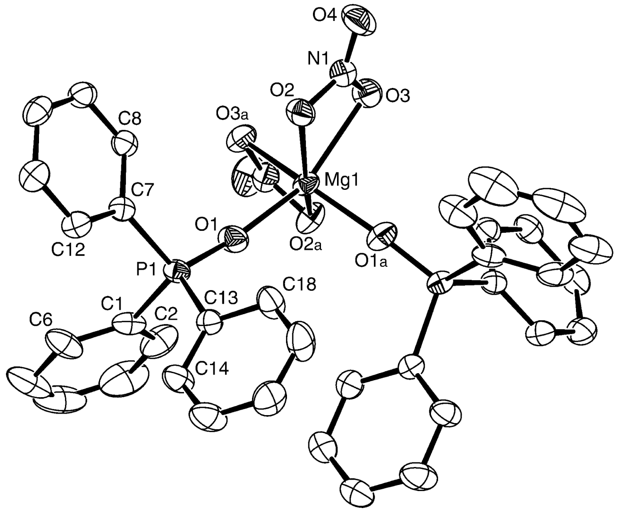

Fig. 3 The structure of $[Mg(OPPh_3)_2(NO_3)_2]$ showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity. Mg1 is located on a 2-fold axis. Symmetry operation: $a = -x, y, \frac{1}{2} - z$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Mg(OPPh_3)_2(NO_3)_2]$

Mg1–O1	1.9397(17)	P1–O1	1.4972(16)
Mg1–O2	2.0863(16)	P1–C1	1.802(2)
Mg1–O3	2.1822(18)	P1–C7	1.795(2)
N1–O2	1.275(2)	P1–C13	1.798(2)
N1–O3	1.268(2)	N1–O4	1.216(3)
O1–Mg1–O1a	99.47(11)	O2–Mg1–O3	60.42(6)
O1–Mg1–O2	95.56(6)	O2–Mg1–O2a	155.98(11)
O1–Mg1–O3	155.05(6)	O3–Mg1–O3a	86.79(10)
Mg1–O1–P1	167.75(11)	O1–P1–C1	109.33(11)
C1–P1–C7	108.68(11)	O1–P1–C7	111.07(10)
C1–P1–C13	108.95(10)	O1–P1–C13	110.00(10)
C7–P1–C13	108.77(10)	O2–N1–O3	115.42(18)
O2–N1–O4	121.6(2)	O3–N1–O4	122.9(2)

Symmetry operation: $a = -x, y, \frac{1}{2} - z$.

In dry CH_2Cl_2 the $^{31}P\{^1H\}$ NMR spectrum at 295 K is a broad singlet at $\delta = 36.0$ which sharpens on cooling and <233 K shows two resonances at δ 36.2 and 33.9 (ratio *ca.* 10 : 1); the values may be compared with the chemical shift observed[5] in $[Mg(OPPh_3)_4]^{2+}$ of 41.6, showing that as expected, coordination of the nitrate anions results in a less electron-poor magnesium centre and a corresponding shielding of the phosphorus. Addition of $OPPh_3$ to the solution at 295 K produces a broad feature whose chemical shift varies with the amount of added phosphine oxide consistent with fast exchange. On cooling to <210 K two resonances are resolved at $\delta = 28.0$ ($OPPh_3$) and 34.0, the effects reversing on warming. The species responsible for the $\delta = 34.0$ resonance is presumably $[Mg(OPPh_3)_x(NO_3)_2]$ ($x = 3$ or 4) since the solution remains non-conducting (six-coordination could still be maintained by switching the nitrate group(s) from bi- to mono-dentate coordination). In spite of this, only $[Mg(OPPh_3)_2(NO_3)_2]$ has been isolated in the solid state. Different speciation between the isolated solids and solutions in non-coordinating solvents is also commonly found in Group 3 and lanthanide nitrate complexes with phosphinoyl ligands.[8–11]

The complex $[Mg\{o\text{-}C_6H_4(P(O)Ph_2)_2\}(NO_3)_2]$ was readily isolated from reaction of either a 1 : 1 or 1 : 2 mol ratio of Mg : ligand in ethanol, and the spectroscopic data (Experimental section) are consistent with a neutral six-coordinate magnesium centre. The $^{31}P\{^1H\}$ NMR spectrum of this complex in CH_2Cl_2 is a singlet at $\delta = 38.5$ and is unchanged on cooling the solution to 190 K. On adding excess $o\text{-}C_6H_4(P(O)Ph_2)_2$ to the solution a new species with $\delta = 35.7$ is formed and the conductivity of the solution increases. The $[Mg\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_3]^{2+}$ has[5] $\delta = 40.1$ and is therefore not the product; and the new species is possibly $[Mg\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)]NO_3$.

The reaction of a 1 : 2 molar ratio of $Mg(NO_3)_2 \cdot 6H_2O$: $Ph_2P(O)CH_2P(O)Ph_2$ in ethanol–CH_2Cl_2 gave a white powder $[Mg\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2] \cdot CH_2Cl_2$. The solid state structure is uncertain since repeated attempts from a variety of solvents failed to produce crystals suitable for an X-ray study. The IR spectrum shows ν(PO) at 1171(vs), 1165(sh) cm^{-1} and hence all PO groups are coordinated ($Ph_2P(O)CH_2P(O)Ph_2$ has ν(PO) at 1187 cm^{-1}), and there is no evidence for 'free' nitrate ions. The IR spectrum differs in detail, particularly in the nitrate regions, from those of $[M\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ (M = Ca–Ba), but it is difficult to draw conclusions due to the very different size and mass of the cations. Eight-coordination as found for the heavier elements can be ruled out due to the small size of the magnesium, and the most probable formulation is $[Mg\{Ph_2P(O)CH_2P(O)Ph_2\}_2(\kappa^1\text{-}NO_3)_2]$. The $^{31}P\{^1H\}$ NMR spectrum of this complex in CH_2Cl_2 is a singlet at δ = 34.1 and is unchanged on cooling the solution to 190 K, and in contrast to most of the complexes in this work, addition of $Ph_2P(O)CH_2P(O)Ph_2$ to the solution produces a spectrum with resonances at δ = 34.1 and 25.0, indicating exchange is slow on the NMR timescale. In 10^{-3} mol dm^{-3} solution in CH_2Cl_2 the complex has a molar conductivity of Λ_M = 6 Ω^{-1} cm^2 mol^{-1} consistent with a non-electrolyte.

Calcium, strontium and barium complexes

The reaction of calcium, strontium or barium nitrate with $OPPh_3$ in ethanol with a $M(NO_3)_2 : OPPh_3$ ratio of 1 : ≥ 4 results, on concentration of the solutions, in white, air-stable powders of composition $[M(OPPh_3)_4(NO_3)_2]$. The IR spectra are very similar, showing broad strong features *ca.* 1180 cm^{-1} assigned as ν(PO) of the coordinated phosphine oxide (compared to 1196 cm^{-1} in $OPPh_3$) and weaker features near 1300 and 815 cm^{-1} attributed to coordinated nitrate groups[9–11] (other expected bands from the nitrates are difficult to identify due to the strong absorptions of the phosphine oxides). There is no evidence for nitrate ions in the IR spectra. The $^{31}P\{^1H\}$ NMR spectra of the complexes in dry‡ CH_2Cl_2 solution show rather broad singlets with only small coordination shifts from $OPPh_3$, and the shifts are markedly less positive than in the homoleptic cations previously reported.[5] Addition of excess $OPPh_3$ to the solutions results in broad singlet resonances indicative of fast exchange and these resonances remain unchanged (apart from a small temperature drift) on cooling to 180 K in the case of M = Sr or Ba. However for M = Ca, two resonances can be resolved <200 K attributed (from their chemical shifts) to $OPPh_3$ and $[Ca(OPPh_3)_4(NO_3)_2]$, showing that the nitrates are not displaced by the phosphine oxide, and that no other complexes form in significant amounts. Consistent with this, the complexes are non-electrolytes in dry CH_2Cl_2 solution and the conductances do not increase on adding $OPPh_3$. Whilst the distinction of mono- and bi-dentate nitrate coordination by IR spectroscopy is uncertain, it seems likely that the three complexes have eight-coordinate geometries with bidentate nitrate (*cf.* the preference for bidentate nitrate in the lanthanides and Y complexes, except where steric factors promote κ^1-NO_3 binding).[9–11]

Table 3 Selected bond lengths (Å) and angles (°) for $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$

Ca1–O1	2.313(7)	Ca1–O5	2.496(10)
Ca1–O2	2.453(8)	Ca1–O6	2.505(11)
Ca1–O3	2.358(8)	Ca1–O8	2.560(10)
Ca1–O4	2.359(7)	Ca1–O9	2.521(9)
P1–O1	1.487(7)	P3–O3	1.483(9)
P2–O2	1.479(8)	P4–O4	1.484(8)
P1–C13	1.814(10)	P3–C38	1.850(13)
P2–C13	1.795(10)	P4–C38	1.798(11)
N1–O5	1.242(15)	N2–O8	1.287(14)
N1–O6	1.211(15)	N2–O9	1.223(14)
N1–O7	1.215(14)	N2–O10	1.189(15)
O1···O2	2.997(10)	O3···O4	3.041(10)
P–C (Ph)	1.757(11)–1.828(11)		
O1–Ca1–O2	77.9(2)	O5–Ca1–O6	47.7(4)
O3–Ca1–O4	80.3(3)	O8–Ca1–O9	49.8(3)
O1–Ca1–O4	156.2(3)	O6–Ca1–O8	75.5(4)
O2–Ca1–O3	78.1(3)	O5–Ca1–O9	110.0(5)
Ca1–O1–P1	139.5(4)	Ca1–O3–P3	136.5(5)
Ca1–O2–P2	135.7(4)	Ca1–O4–P4	138.7(4)
P1–C13–P2	114.0(5)	P3–C38–P4	115.2(7)
O–P–C(H2)	112.6(5)–113.2(5)	O–P–C (Ph)	109.7(5)–112.9(5)

The reaction of $Ca(NO_3)_2\cdot4H_2O$ with bis(diphenylphosphinoyl)methane in a 1 : 2.2 molar ratio in ethanol gave a white powder $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$. The corresponding strontium salt was made similarly except that the metal nitrate was dissolved in the minimum of hot water and then reacted with the diphosphine dioxide in ethanol. The complexes are poorly soluble in alcohols but dissolve easily in CH_2Cl_2 in which they are non-electrolytes. Crystals of $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ were obtained from CH_2Cl_2 layered with diethyl ether. The structure consists of discrete molecules with Ca in an eight-coordinate environment formed from two bidentate chelating phosphine oxides and two bidentate nitrate ligands (Table 3 and Fig. 4). The phosphine oxide ligand's bite is *ca.* 79° in the six-membered chelate ring. Conceptually replacing the nitrates by monodentate ligands, the geometry can be described as a very distorted octahedron with *cis* nitrates: for example the N1···Ca1···N2 is 99.6(4)°. The nitrates are symmetrically bonded to Ca. The

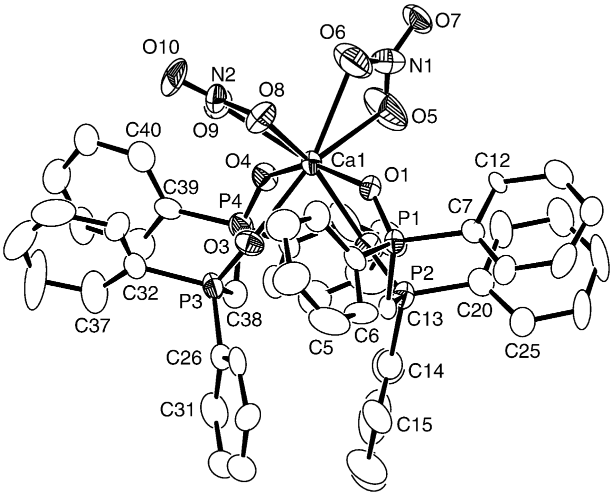

Fig. 4 Structure of $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level. To aid clarity, H atoms are omitted and C atoms are shown as boundary ellipsoids.

---

‡ Addition of oxygen donor solvents including alcohols and water lead to partial displacement of the $OPPh_3$ and the formation of a mixture of species.

IR spectra of the Ca and Sr complexes are very similar and almost certainly both have similar structures. The $^{31}P\{^1H\}$ NMR spectrum of $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ in CH_2Cl_2 solution at 295 K is a singlet at $\delta = 29.9$ (compare $Ph_2P(O)CH_2P(O)Ph_2$, $\delta = 25.0$). The spectrum is unchanged down to 210 K, but below this temperature other features appear and at 190 K, weak peaks at δ 25.0 and 32.4 are present in addition to the major feature at δ 29.9. The minor species are assigned to $Ph_2P(O)CH_2P(O)Ph_2$ and $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_3]^{2+}$ (lit.[5] 32.6 at 295 K), respectively (mass balance also requires some phosphinoyl ligand-free calcium species). Addition of $Ph_2P(O)CH_2P(O)Ph_2$ to the solution results in a very broad resonance δ *ca.* 27 at 295 K, but on cooling to 190 K, the spectrum shows only features at δ 25.0 and 32.4 suggesting that excess ligand converts the sample to $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_3]^{2+}$. The conductance of a solution of $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ in CH_2Cl_2 is $\Lambda_M = 8\ \Omega^{-1}\ cm^2\ mol^{-1}$ and increases on adding excess diphosphine dioxide to *ca.* $28\ \Omega^{-1}\ cm^2\ mol^{-1}$ consistent with the inferences from the NMR study. The $^{31}P\{^1H\}$ NMR spectrum of $[Sr\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ in CH_2Cl_2 solution at 295 K is a singlet at $\delta = 27.6$ and this is little changed on cooling to 190 K. Addition of $Ph_2P(O)CH_2P(O)Ph_2$ to the solution results in a very broad resonance δ *ca.* 26 at 295 K, but on cooling to 190 K broad features at δ 25.0 and 28.0 are present. The resonance[5] of $[Sr\{Ph_2P(O)CH_2P(O)Ph_2\}_3]^{2+}$ is δ 31.5, suggesting that in contrast to calcium, the homoleptic cation does not form.

The $[M\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$ (M = Ca, Sr) were obtained similarly to the $Ph_2P(O)CH_2P(O)Ph_2$ complexes. A crystal structure of $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$ established that the structure consists of discrete molecules with Ca in an eight-coordinate environment formed from two bidentate chelating phosphine oxides and two bidentate nitrate ligands (Table 4 and Fig. 5). There are two chemically similar but crystallographically distinct molecules in the asymmetric unit and each molecule has 2-fold crystallographic symmetry. The bidentate phosphine oxide has a (P)O–Ca–O(P) ligand bite of *ca.* 74°, smaller than in the previous example above, despite the larger seven-membered ring. Conceptually replacing the nitrates by monodentate ligands, the geometry can be described as a very distorted octahedron with *trans* nitrates; for example the N1···Ca1···N1a is 155.10(1)°. The differences between the two diphosphine dioxide structures presumably result from the lack of any geometric preference from the closed shell calcium ion and the different steric requirements of the two ligands. The solution behaviour is similar to that described above for the $Ph_2P(O)CH_2P(O)Ph_2$ complexes, but differs in detail. The calcium complex is a non-electrolyte in CH_2Cl_2 solution ($\Lambda_M = 10\ \Omega^{-1}\ cm^2\ mol^{-1}$ and at 295 K the $^{31}P\{^1H\}$ NMR spectrum is a singlet at δ 35.0. At 190 K the major resonance now at δ 33.3 is accompanied by minor features at δ 36.2, 34.2 and 31.0. Addition of $o\text{-}C_6H_4(P(O)Ph_2)_2$ to the solution shows only a broad resonance, consistent with fast exchange at room temperature, but at 190 K, four resonances are again present, although those with δ 36.2 and 31.0 are relatively much more intense. Comparison with literature data[5] allows assignments of the δ 36.2 and 31.0 resonances as $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_3]^{2+}$ and $o\text{-}C_6H_4(P(O)Ph_2)_2$, respectively, and the resonance at δ 33.3 is probably $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$. The solution shows a marked increase in conductivity in the presence of excess ligand ($\Lambda_M = 30\ \Omega^{-1}\ cm^2\ mol^{-1}$). The $^{31}P\{^1H\}$ NMR data on solutions of $[Sr\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$ show similar behaviour with a room temperature resonance $\delta = 32.9$, splitting at <200 K into four resonances at δ 31.0, 32.2, 33.0, 36.3 in the approximate ratio 1 : 2 : 2 : 4. The first is 'free' ligand and the last the homoleptic cation $[Sr\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_3]^{2+}$, one of the intermediate shifts will be due to $[Sr\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$. Addition of $o\text{-}C_6H_4(P(O)Ph_2)_2$ to the solution results in fast exchange, and even at 190 K, broad lines are still

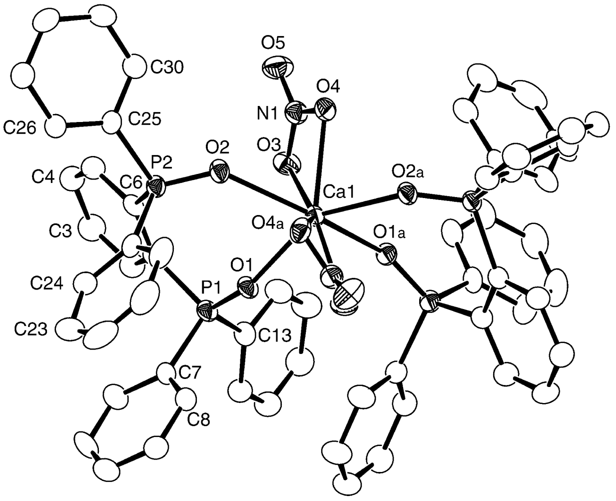

Fig. 5 Structure of the Ca1 centred molecule of $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$ showing the atom numbering scheme. The other (Ca2) molecule has a similar geometry. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity. Ca1 (and Ca2) is positioned on a 2-fold axis. Symmetry operation: $a = 3/2 - x, y, \frac{1}{2} - z$.

Table 4 Selected bond lengths (Å) and angles (°) for $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$

Ca1–O1	2.3208(18)	Ca2–O6	2.3119(19)
Ca1–O2	2.3866(19)	Ca2–O7	2.4079(19)
Ca1–O3	2.580(2)	Ca2–O8	2.563(2)
Ca1–O4	2.493(2)	Ca2–O9	2.460(2)
P1–O1	1.486(2)	P3–O6	1.486(2)
P2–O2	1.485(2)	P4–O7	1.489(2)
N1–O3	1.262(3)	N2–O8	1.254(3)
N1–O4	1.262(3)	N2–O9	1.250(3)
N1–O5	1.226(3)	N2–O10	1.245(4)
P–C	1.791(3)–1.827(3)	P–C	1.795(3)–1.835(3)
O1···O2	2.866(3)	O6···O7	2.819(3)
O1–Ca1–O2	75.00(6)	O6–Ca2–O7	73.32(7)
O1–Ca1–O3	83.82(7)	O6–Ca2–O8	86.08(7)
O1–Ca1–O4	130.26(7)	O6–Ca2–O9	131.97(7)
O2–Ca1–O3	71.67(7)	O7–Ca2–O8	72.07(7)
O2–Ca1–O4	73.11(6)	O7–Ca2–O9	73.81(7)
O3–Ca1–O4	50.31(6)	O8–Ca2–O9	50.73(7)
Ca1–O1–P1	149.88(13)	Ca2–O6–P3	151.64(12)
Ca1–O2–P2	139.02(11)	Ca2–O7–P4	137.77(12)
O3–N1–O4	117.6(3)	O8–N2–O9	118.7(3)
O3–N1–O5	121.7(3)	O8–N2–O10	121.7(3)
O4–N1–O5	120.7(2)	O9–N2–O10	119.5(3)
O–P–C	108.45(12)–116.61(12)	C–P–C	102.75(13)–108.48(13)

present indicating the low temperature limit has not been reached.

The affinity of barium nitrate for the diphosphine dioxides is small. The reaction of $Ba(NO_3)_2$ with ≥ 3 equivalents of $Ph_2P(O)CH_2P(O)Ph_2$ in aqueous ethanol, followed by recrystallisation of the product from methanol/CH_2Cl_2/diethyl ether containing added $Ph_2P(O)CH_2P(O)Ph_2$ (Ba : added ligand *ca.* 1 : 2) gave $[Ba\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$, although it was difficult to obtain an analytically pure sample. Recrystallisation in the absence of excess ligand, gave materials with low and variable C, H content, which appeared to be mixtures of this complex and barium nitrate. The $^{31}P\{^1H\}$ NMR spectrum of $[Ba\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ in CH_2Cl_2 solution at 295 K is a singlet at $\delta = 25.2$, only slightly shifted from that of the diphosphine dioxide and little change occurred on lowering the temperature to 195 K, so that no conclusions about solution speciation can be drawn. Repeated attempts to isolate pure products from reaction of *o*-$C_6H_4(P(O)Ph_2)_2$ with $Ba(NO_3)_2$ in a variety of solvents and using molar ratios of Ba : ligand of up to 1 : 4 failed. The white powders isolated had variable composition, and on dissolution in organic solvents left a residue of $Ba(NO_3)_2$. Barium is substantially larger than the other metals in this group (Ba^{2+} r = 143 pm), and the low charge/radius ratio will be diminished further by coordination of the nitrate ions, leading to little affinity for the neutral phosphinoyl ligands. Complexation with *o*-$C_6H_4(P(O)Ph_2)_2$ clearly occurs since the impure solids show no evidence of uncoordinated diphosphine dioxide in the IR spectra, but in solution the complex appears to be extensively dissociated, for example the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance little shifted from that of the ligand even at 190 K, and under such conditions whether a pure complex can by crystallised from the solution will depend upon the relative solubilities of the constituents.

Conclusions

The greatest variable in this series of compounds is the size of the metal centres—taking the metal ionic radii as illustrating this effect—the values[1] range from 34 pm at Be^{2+} to 143 pm at Ba^{2+}, and hence the charge/radius ratio falls dramatically down the group. The data above show that Be is exclusively four-coordinate, has a high affinity for the neutral ligands, and that ligand exchange is slow on the NMR timescale in solution. The combination of ^{9}Be and ^{31}P NMR with conductance measurements also provided a clear picture of solution speciation. The larger Mg (Mg^{2+} r = 78 pm) prefers six-coordination, but still binds both the neutral ligands and the nitrates strongly, although the $OPPh_3/Mg(NO_3)_2$ system shows fast exchange on the NMR timescale at room temperature. The larger Ca (Ca^{2+} r = 106 pm) and Sr (Sr^{2+} r = 127 pm) produce labile complexes which are undergoing fast exchange in solution except at very low temperatures, and the mixture of species present in solution shows reduced discrimination between the neutral phosphine oxide and charged nitrate ligands. Notably, despite the mixture of species in the solution, only the neutral eight-coordinate complexes have been isolated in the solid state. The very large Ba has little affinity for the phosphine oxides and although some examples were isolated (see also ref. 5), these are extensively dissociated in solution and can only be isolated in the presence of an excess of phosphine oxide in the solutions. Due to greater lability and the unsuitability of the metal nuclei for NMR studies, the solution behaviour of the Mg–Ba compounds is less easily probed than that of beryllium, but the combination of low temperature ^{31}P NMR spectroscopy with molar conductance measurements, and the effects of added excess phosphine oxide, has led to a reasonably clear picture of the behaviour in these systems. The occurrence of a mixture of species in solution and a smaller number isolable as pure solids is also a characteristic of other closed shell metal ions including Sc, Y and the lanthanides.[9–11]

Experimental

The metal nitrates, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ and Ph_3PO were obtained from Aldrich and used as received. Aqueous beryllium nitrate (35 wt%) was also obtained from Aldrich. The *o*-$C_6H_4(P(O)Ph_2)_2$ and $Ph_2P(O)CH_2P(O)Ph_2$ were made by SnI_4 catalysed air-oxidation of the corresponding diphosphines.[14] IR spectra were recorded as Nujol mulls on a Perkin Elmer PE 983G spectrometer, ^{1}H NMR spectra in $CDCl_3$ solutions on a Bruker AV300, $^{31}P\{^1H\}$ and ^{9}Be NMR were obtained from CH_2Cl_2/5%CD_2Cl_2 solutions referenced, respectively to external 85% H_3PO_4 and aqueous $[Be(H_2O)_4]^{2+}$ [15] on a Bruker DPX400. Microanalytical measurements were performed by the microanalysis service of Strathclyde University. Conductance measurements were made as described previously,[9] using CH_2Cl_2 distilled from CaH_2.

CAUTION: Beryllium compounds are carcinogenic and particularly hazardous as dust or aerosols. Appropriate precautions should be observed.

$[Be(OPPh_3)_2(NO_3)_2]$

An aliquot (0.5 mmol) of the commercial $Be(NO_3)_2$ aqueous solution (35 wt%) was diluted with water (2 mL) and added to a solution of $OPPh_3$ (0.28 g, 1.0 mmol) in ethanol (20 mL) and 2,2-dimethoxypropane (5 mL). The clear solution was heated to reflux for 20 min and then the solvent removed *in vacuo*. The viscous oil obtained was dissolved in warm acetone (15 mL), diethyl ether added until turbidity was seen, and then allowed to stand. Crystals separated after a few h and these were filtered off and rinsed with diethyl ether, and dried *in vacuo*. Yield 0.27 g, 78%. Calc. for $C_{36}H_{30}BeN_2O_8P_2$: C, 62.7; H, 4.4; N, 4.1. Found: C, 61.3; H, 4.25; N, 4.4%. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.3–7.7 (m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 300 K): δ 38.2 (1 : 1 : 1 : 1 quartet, ^2J = 4 Hz), 39.5 (1 : 1 : 1 : 1, ^2J = 4 Hz), see text. ^{9}Be NMR (CH_2Cl_2, 300 K): δ 0.68 (t, ^2J = 4 Hz), 0.34 (quartet, ^2J = 4 Hz). IR (Nujol/cm^{-1}): (possible nitrate bands are italicised) *1452*(*vs*,*br*), 1342(sh), *1312*(*s*), 1215(m), 1169(br){P=O}, 1165(m){P=O}, 1121(m), 1076(m), 970(w), 843(w), *811*(*s*), *795*(*s*), 752(m), 691(m), 601(s), 516(vs), 438(m). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 7 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 18 Ω^{-1} cm^2 mol^{-1}.

[Mg(OPPh$_3$)$_2$(NO$_3$)$_2$]

Magnesium nitrate hexahydrate (0.045 g, 0.18 mmol) was dissolved in absolute ethanol (10 mL) and a solution of OPPh$_3$ (0.197 g, 0.74 mmol) in ethanol (10 mL) added and the mixture gently refluxed. The solution was concentrated to *ca.* 5 mL and diethyl ether added dropwise until precipitation occured, when the mixture was left to stand for 12 h. The white solid produced was filtered off, rinsed with diethyl ether (10 mL) and dried *in vacuo*. Yield 0.10 g, 80%. Calc. for $C_{36}H_{30}MgN_2O_8P_2$: C, 61.3; H, 4.3; N, 4.0. Found: C, 61.6; H, 4.1; N, 3.8%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 36.0 (s), (210 K) 36.2, 33.9 (ratio 10 : 1). IR (Nujol/cm^{-1}): 1350(sh), *1299(s)*, 1206(w), 1183(br){P=O}, 1153(s), 1028(m), 997(w), *817(s)*, 744(m), 689(m), 538(vs). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 1.5 Ω^{-1} cm^2 mol^{-1}.

[Ca(OPPh$_3$)$_4$(NO$_3$)$_2$]

This was made similarly from calcium nitrate tetrahydrate and OPPh$_3$ in absolute ethanol. White powder. Yield 65%. Calc. for $C_{72}H_{60}CaN_2O_{10}P_4$: C, 67.2; H, 4.7; N, 2.2. Found: C, 67.3; H, 4.4; N, 2.2%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 31.0 (s). IR (Nujol/cm^{-1}): 1572(w), 1345(sh), *1315(m)*, 1179(s){P=O}, 1171(sh){P=O}, 1120(m), 1033(w), 1032(w), 998(w), 975(m), *822(m)*, 740(s), 693(s), 543(vs). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 1.0 Ω^{-1} cm^2 mol^{-1}.

[Sr(OPPh$_3$)$_4$(NO$_3$)$_2$]

Strontium nitrate (0.034 g, 0.16 mmol) was dissolved in the minimum amount of hot water (*ca.* 2 mL) and the solution added to a stirred solution of OPPh$_3$ (0.17 g, 0.64 mmol) in absolute ethanol (20 mL) which was then heated to reflux. Concentration to *ca.* 5 mL resulted in the precipitation of a white powder, which was filtered off, rinsed with diethyl ether (5 mL) and dried *in vacuo*. Yield 0.12 g, 56%. Calc. for $C_{72}H_{60}N_2O_{10}P_4Sr$: C, 65.2; H, 4.6; N, 2.1%. Found: C, 64.2; H, 4.1; N, 2.2%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 29.0(s). IR (Nujol/cm^{-1}): 1576(w), 1345(sh), *1307(m)*, 1183(br,s){P=O}, 1169(sh), 1120(m), 1070(w), 1035(w), 973(m), 857(w), *814(m)*, 740(s), 697(s), 541(vs). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 0.5 Ω^{-1} cm^2 mol^{-1}.

[Ba(OPPh$_3$)$_4$(NO$_3$)$_2$]

This was made similarly to the strontium complex as a white powder. Yield 65%. Calc. for $C_{72}H_{60}BaN_2O_{10}P_4$: C, 62.9; H, 4.4; N, 2.0. Found: C, 61.4; H, 4.1; N, 2.3%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 30.0 (s). IR (Nujol/cm^{-1}): 1590(w), 1364(sh), 1350(sh), *1307(m)*, 1183(br,s){P=O}, 1120(m), 1093(w), 1072(w), 1028(w), 996(w), 970(m), 864(m), 846(m), *816(m)*, 756(s), 697(s), 540(vs). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 1.0 Ω^{-1} cm^2 mol^{-1}.

[Be{Ph$_2$P(O)CH$_2$P(O)Ph$_2$}(NO$_3$)$_2$]

An aliquot (0.5 mmol) of the commercial 35 wt% Be(NO$_3$)$_2$ aqueous solution was diluted with water (2 mL) and added to a solution of Ph$_2$P(O)CH$_2$P(O)Ph$_2$ (0.21 g, 0.5 mmol) in ethanol (20 mL) and 2,2-dimethoxypropane (5 mL). The clear solution was heated to reflux for 20 min and then the solvent removed *in vacuo* to leave a waxy residue. This was stirred with diethyl ether (10 mL) for 2 h, the diethyl ether syringed off and discarded, and the waxy solid dissolved in dichloromethane (10 mL). The solution was decanted from any insoluble material and taken to dryness *in vacuo* to yield a cream powder. Yield 0.19 g, 69%. Calc. for $C_{25}H_{22}BeN_2O_8P_2 \cdot CH_2Cl_2$: C, 49.2; H, 3.8; N, 4.4. Found: C, 49.2; H, 4.3; N, 4.4%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.9 (m), 5.2 (s) (CH$_2$Cl$_2$), 3.8 (m). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 40.7 (s). ^{9}Be NMR (CH$_2$Cl$_2$, 300 K): δ 0.91 (s). IR (Nujol/cm^{-1}): *1450(s,br)*, 1346(m), *1308(m)*, *1259(m)*, 1168(sh){P=O}, 1156(s){P=O}, 1121(m), 1022(m), 966(w), 890(m), 845(w), *806(sh)*, *792(s)*, 736(s), 670(w), 503(s). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 2 Ω^{-1} cm^2 mol^{-1}.

[Mg{Ph$_2$P(O)CH$_2$P(O)Ph$_2$}$_2$(NO$_3$)$_2$]

Solutions of Mg(NO$_3$)$_2 \cdot$6H$_2$O (0.026 g, 0.11 mmol) in ethanol (10 mL) and Ph$_2$P(O)CH$_2$P(O)Ph$_2$ (0.11 g, 0.26 mmol) in CH$_2$Cl$_2$ (15 mL) were mixed and heated to reflux. The solution was cooled, concentrated *in vacuo* to *ca.* 5 mL and diethyl ether (5 mL) added to precipitate a white powder, which was filtered off, rinsed with diethyl ether and dried. Yield 0.075 g, 64%. Calc. for $C_{50}H_{44}MgN_2O_{10}P_4 \cdot CH_2Cl_2$: C, 57.2; H, 4.3; N, 2.6. Found: C, 56.8; H, 4.6; N, 2.4%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m), 5.4 (s), 3.8 (br). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 34.1 (s); (190 K) 34.6 (s). IR (Nujol/cm^{-1}): 1340(m), *1308(m)*, *1260(m)*, 1172(s){P=O}, 1165(sh){P=O}, 1119(m), 994(w), 843(w), *815(sh)*, *795(s)*, 734(s), 670(s), 543(m), 502(s). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 6 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 9 Ω^{-1} cm^2 mol^{-1}.

[Ca{Ph$_2$P(O)CH$_2$P(O)Ph$_2$}$_2$(NO$_3$)$_2$]

Ca(NO$_3$)$_2 \cdot$4H$_2$O (0.025 g, 0.11 mmol) was dissolved in ethanol (10 mL) and a solution of Ph$_2$P(O)CH$_2$P(O)Ph$_2$ (0.11 g, 0.26 mmol) in CH$_2$Cl$_2$ (5 mL) added and the mixture stirred for 2 h. Concentration to small volume (*ca.* 5 mL) and slow addition of diethyl ether (5 mL) gave a white solid, which was filtered off, rinsed with diethyl ether and dried *in vacuo*. Yield. 0.058 g, 49%. Calc. for $C_{50}H_{44}CaN_2O_{10}P_4 \cdot CH_2Cl_2$: C, 56.6; H, 4.3; N, 2.6. Found: C, 55.1; H, 3.9; N, 2.6%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m), 5.4 (s) (CH$_2$Cl$_2$), 3.8 (t). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 29.9 (s); (190 K) 25.0, 29.9, 32.4; ratio *ca.* 2 : 1 : 10. IR (Nujol/cm^{-1}): 1360(sh), *1303(m)*, 1168(s){P=O}, 1121(m), 967(m), 935(m), 892(m), 846(w), *825(m)*, 774(s), 543(vs), 506(s). Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 8.0 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M (10^{-3} mol dm^{-3} CH$_2$Cl$_2$) = 25.0 Ω^{-1} cm^2 mol^{-1}.

[Sr{Ph$_2$P(O)CH$_2$P(O)Ph$_2$}$_2$(NO$_3$)$_2$]

This was made similarly to [Sr(OPPh$_3$)$_4$(NO$_3$)$_2$] using a 1 : 2.2 mol ratio of Sr(NO$_3$)$_2$: Ph$_2$P(O)CH$_2$P(O)Ph$_2$. Yield 58%. Calc. for $C_{50}H_{44}N_2O_{10}P_4Sr \cdot CH_2Cl_2$: C, 54.2; H, 4.1; N, 2.5. Found: C, 54.0; H, 4.0; N, 2.3%. ^{1}H NMR (CDCl$_3$, 300 K): δ 7.2–7.7 (m), 5.4 (s) (CH$_2$Cl$_2$), 3.8 (t). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 300 K): δ 27.6 (s). IR (Nujol/cm^{-1}): 1360(sh), *1311(m)*, 1260(w), 1192(sh){P=O}, 1168(s,br){P=O}, 1120(m), 1020(w), 935(w), 846(w), 798(m), 775(m), 737(m), 563(vs), 506(s). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 8 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M = 12 Ω^{-1} cm^2 mol^{-1}.

[Ba{$Ph_2P(O)CH_2P(O)Ph_2$}$_2$(NO_3)$_2$]

This was made similarly to the strontium analogue but using a 1 : 3 Ba : ligand ratio. The complex was recrystallised from methanol/CH_2Cl_2/diethyl ether containing excess diphosphine dioxide. Yield 63%. Calc. for $C_{50}H_{44}BaN_2O_{10}P_4 \cdot CH_2Cl_2$: C, 51.9; H, 3.9; N, 2.4. Found: C, 50.8; H, 4.3; N, 2.2%. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.2–7.7 (m), 5.4 (s), 3.8 (br,s). ^{31}P{^{1}H} NMR (CH_2Cl_2, 300 K): δ 25.0 (s). IR (Nujol/cm^{-1}): 1330(sh), *1307*(*m*), 1260(m), 1193(s){P=O}, 1168(s,br){P=O}, 1120(m), 1027(m), 935(w), *812*(*w*), 799(s), 775(m), 737(m), 565(m), 512(s). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 4 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M = 8 Ω^{-1} cm^2 mol^{-1}.

[Be{*o*-$C_6H_4(P(O)Ph_2)_2$}(NO_3)$_2$]

This was made similarly to the $Ph_2P(O)CH_2P(O)Ph_2$ analogue as a cream powder in 65% yield. Calc. for $C_{30}H_{24}BeN_2O_8P_2$.: C, 58.9; H, 4.0. Found: C, 58.9; H, 4.4%. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH_2Cl_2, 300 K): δ 44.2 (s). ^{9}Be NMR (CH_2Cl_2, 300 K): δ 0.98 (s). IR (Nujol/cm^{-1}): *1436*(*vs,br*), 1363(m), *1311*(*m*), *1259*(*m*), 1163(vs,br){P=O}, 1121(s), 1095(m), 1020(m), 990(w), 898(m), *811*(*sh*), *798*(*s*), 735(s), 691(s), 560(sh), 546(s), 531(s). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 3 Ω^{-1} cm^2 mol^{-1}.

[Mg{*o*-$C_6H_4(P(O)Ph_2)_2$}(NO_3)$_2$]

$Mg(NO_3)_2 \cdot 6H_2O$ (0.026 g, 0.11 mmol) was dissolved in ethanol (10 mL) and a solution of *o*-$C_6H_4(P(O)Ph_2)_2$ (0.050 g, 0.11 mmol) in CH_2Cl_2 (5 mL) added and the mixture heated to reflux, cooled and stirred for 1 h. Concentration to 5 mL and dropwise addition of diethyl ether (*ca.* 10 mL) produced a white precipitate, which was filtered off, rinsed with diethyl ether (5 mL) and dried *in vacuo*. Yield 0.055 g, 91%. Calc. for $C_{30}H_{24}MgN_2O_8P_2$.: C, 57.3; H, 4.3; N, 4.1. Found: C, 57.5; H, 3.8; N, 4.5%. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH_2Cl_2, 300 K): δ 38.5 (s), unchanged to 190 K. IR (Nujol/cm^{-1}): 1342(sh), *1306*(*m*), 1165(vs){P=O}, 1115(s), 1100(w), 1030(m), 995(w), 887(m), *816*(*w*), 746(s), 690(s), 563(m), 547(s), 530(s). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 4.5 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 18.0 Ω^{-1} cm^2 mol^{-1}.

[Ca{*o*-$C_6H_4(P(O)Ph_2)_2$}$_2$(NO_3)$_2$]

This was made similarly. Yield 87%. Calc. for $C_{60}H_{48}CaN_2O_{10}P_4$: C, 64.3; H, 4.3: N, 2.5. Found: C, 64.0; H, 4.0; N, 2.7%. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH_2Cl_2, 300 K): δ 35.0; (190 K) 36.2, 34.5, 33.4, 31.0; ratio *ca.* 1 : 3 : 10 : 1. IR (Nujol/cm^{-1}): 1350(sh), *1303*(*m*), 1260(w), 1170(vbr,s){P=O}, 1115(s), 1100(m), 1035(m), 997(w), *820*(*m*), 746(s), 690(m), 559(s), 542(s), 532(s). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 10 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M = 33 Ω^{-1} cm^2 mol^{-1}.

[Sr{*o*-$C_6H_4(P(O)Ph_2)_2$}$_2$(NO_3)$_2$]

This was made similarly. Yield 87%. Calc. for $C_{60}H_{48}N_2O_{10}P_4Sr$: C, 61.7; H, 4.1; N, 2.4. Found: C, 62.2; H, 4.0; N, 2.2%. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.2–7.7 (m). ^{31}P{^{1}H} NMR (CH_2Cl_2, 300 K): δ 32.9; (190 K) 31.0, 32.2, 33.0, 36.3; ratio 1 : 2 : 2 : 4. IR (Nujol/cm^{-1}): 1350(sh), *1306*(*m*), 1258(w), 1178(vbr,s){P=O}, 1115(m), 1077(m), 1035(w), 997(w), *814*(*s*), 746(s), 691(s), 653(w), 557(s), 554(s),

Table 5 Crystal data and structure refinement details[a]

Compound Formula	[Be($OPPh_3$)$_2$(NO_3)$_2$] $C_{36}H_{30}BeN_2O_8P_2$	[Mg($OPPh_3$)$_2$(NO_3)$_2$] $C_{36}H_{30}MgN_2O_8P_2$	[Ca{*o*-$C_6H_4(P(O)Ph_2)_2$}$_2$(NO_3)$_2$] $C_{60}H_{48}CaN_2O_{10}P_4$	[Ca{$Ph_2P(O)CH_2P(O)Ph_2$}$_2$(NO_3)$_2$] $C_{50}H_{44}CaN_2O_{10}P_4$
M	689.57	704.87	1120.96	996.82
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2/n$ (no. 13)	$Pca2_1$ (no. 29)
a/Å	10.272(3)[b]	15.343(3)	21.771(4)	20.4255(16)
b/Å	9.579(2)	13.705(2)	10.6990(10)	11.3207(10)
c/Å	34.807(7)	17.202(3)	24.074(4)	22.2120(15)
α/°	90	90	90	90
β/°	90.868(10)	96.971(4)	104.394(5)	90
γ/°	90	90	90	90
U/Å^3	3424.3(13)	3590.4(11)	5431.6(14)	5136.1(7)
Z	4	4	4	4
T/K	300	120	120	120
μ/mm^{-1}	0.182	0.191	0.296	0.303
F(000)	1432	1464	2328	2072
Total no. of obsns. (R_{int})	31143 (0.113)	14502 (0.044)	60223 (0.098)	15486 (0.120)
Unique obsns.	5996	4116	12261	5673
Min, max transmission	0.841, 1.000	0.819, 1.000	0.932, 0.982	0.897, 1.004
No. of parameters, restraints	442, 0	222, 0	695, 0	604, 1
Goodness-of-fit on F^2	1.01	1.00	0.97	1.04
Resid. electron density/e Å^{-3}	−0.24 to +0.18	−0.28 to +0.37	−0.50 to +0.34	−0.42 to +1.37
$R1$, $wR2$ ($I > 2\sigma(I)$)[c]	0.073, 0.115 (2538 ref.)	0.049, 0.118 (2838 ref.)	0.055, 0.116 (6807 ref.)	0.084, 0.213 (4196 ref.)
$R1$, $wR2$ (all data)	0.211, 0.152	0.084, 0.135	0.128, 0.140	0.116, 0.236

[a] Common items: wavelength (Mo-Kα) = 0.71073 Å. [b] The cell dimensions at 120 K are: a = 10.218(2), b = 9.508(2), c = 34.294(9) Å, β = 91.270(9)°, U = 3330.9(13) Å^3. [c] $R1 = \sum \| F_o| - |F_c\| / \sum |F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

531(s), 450(w). Λ_M (10^{-3} mol dm^{-3} CH_2Cl_2) = 6 Ω^{-1} cm^2 mol^{-1}; with excess ligand Λ_M = 10 Ω^{-1} cm^2 mol^{-1}.

X-Ray crystallography

Brief details of the crystal data and refinement are given in Table 5. Data collections were carried out using a Nonius Kappa CCD diffractometer fitted with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) with the crystals held at 120 K in a gas stream (not Be). Crystals of the complexes were made as follows: $[Mg(OPPh_3)_2(NO_3)_2]$ vapour diffusion of diethyl ether into a CH_2Cl_2 solution; $[Ca\{o\text{-}C_6H_4(P(O)Ph_2)_2\}_2(NO_3)_2]$ and $[Ca\{Ph_2P(O)CH_2P(O)Ph_2\}_2(NO_3)_2]$ from CH_2Cl_2 solutions of the complexes layered with diethyl ether; $[Be(OPPh_3)_2(NO_3)_2]$ crystals were obtained directly from the preparation. Structure solution and refinement were carried out using SHELXS[16] and SHELXL[17], respectively with an empirical absorption correction.[18,19] Hydrogen atoms were introduced into the model in calculated positions. Our usual laboratory setup with 120 K as the data collection temperature was used, offering the low temperature advantages[20] and ease of handling crystals of limited room temperature stability due to loss of solvate molecules or moisture/air sensitivity. For the Be compound this arrangement gave a structure solution with several very elongated C atom adp ellipsoids in three phenyl rings. Repeating the experiment gave the same result but attempts to model the presumed disorder were unsuccessful and the suggestion that the ellipsoids were in some way hinting at a solid phase change on lowering the temperature led to a room temperature (300 K) data collection. Although this was a weak data set (42% reflections with $I > 2\sigma(I)$) the ellipsoids' anisotropy was less marked and this is the data set reported.

CCDC reference numbers 298677–298680. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600301j.

Acknowledgements

We thank the EPSRC for support (MFD), the Royal Society, UK (JEB/1676/India) and DST, India for funding, and R. R. thanks M.D.S University, Ajmer (India) for granting leave of absence.

References

1 D. E. Fenton, in *Comprehensive Coordination Chemistry, I*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, p. 1.
2 T. P. Hanusa, in *Comprehensive Coordination Chemistry, II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2003, vol. 3, p. 1.
3 R. D. Rogers and C. B. Bauer, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Elsevier, Oxford, 1996, vol. 1, p. 315.
4 F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, New York, 6th edn, 1998.
5 M. B. Hursthouse, W. Levason, R. Ratnani, G. Reid, H. Stainer and M. Webster, *Polyhedron*, 2005, **24**, 121.
6 M. W. G. de Bolster, *Z. Anorg. Allg. Chem.*, 1977, **434**, 78.
7 F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orlandini, *Inorg. Chem. Commun.*, 2000, **3**, 350.
8 S. Cotton, in *Comprehensive Coordination Chemistry, II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2003, vol. 3, p. 93.
9 L. Deakin, W. Levason, M. C. Popham, G. Reid and M. Webster, *J. Chem. Soc., Dalton Trans.*, 2000, 2439.
10 M. Bosson, W. Levason, T. Patel, M. C. Popham and M. Webster, *Polyhedron*, 2001, **20**, 2055.
11 W. Levason, E. H. Newman and M. Webster, *Polyhedron*, 2000, **19**, 2697.
12 J. Mason, *Multinuclear NMR*, Plenum, New York, NY, 1987.
13 B. E. Kucera, M. M. Olmstead, R. S. Tanke and S. M. Kauzlarich, *Acta Crystallogr., Sect. E*, 2003, **59**, m359.
14 W. Levason, G. Reid and R. Patel, *J. Organomet. Chem.*, 2003, **688**, 280.
15 R. A. Kovar and G. L. Morgan, *J. Am. Chem. Soc.*, 1970, **92**, 5067.
16 G. M. Sheldrick, *SHELXS-97*, Program for crystal structure solution, University of Göttingen, Germany, 1997.
17 G. M. Sheldrick, *SHELXL-97*, Program for crystal structure refinement, University of Göttingen, Germany, 1997.
18 G. M. Sheldrick, *SADABS*, Bruker-Nonius area detector scaling and absorption correction (V 2.10), Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
19 R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.
20 A. E. Golta and J. A. K. Howard, *Chem. Soc. Rev.*, 2004, **33**, 490.