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# Lanthanide nitrate complexes of diphenylmethylphosphine oxide: synthesis and spectroscopic studies. Crystal structures of [La(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>], [La(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>]·*x*Me<sub>2</sub>CO and [Yb(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>

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#### Abstract

The reaction of  $Ln(NO_3)_3$ · $^6H_2O$  (Ln = lanthanide except Pm) with Ph<sub>2</sub>MePO in a 1:3 or 1:4 ratio in acetone or ethanol produces  $[Ln(Ph_2MePO)_3(NO_3)_3]$  which have been characterised by analysis, IR, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and conductance measurements. The  $[Ln'(Ph_2MePO)_3(NO_3)_3]$  (Ln' = Pr–Tb) exist only as tris complexes in solution and are unaffected by the presence of excess Ph\_2MePO. In contrast the  $[Ln'(Ph_2MePO)_3(NO_3)_3]$  (Ln" = Ho–Lu) partially decompose in CH<sub>2</sub>Cl<sub>2</sub> solution into  $[Ln''(Ph_2MePO)_4(NO_3)_2]^+$ , and  $[Ln''(Ph_2MePO)_4(NO_3)_2]PF_6$  are readily isolated from  $Ln''(NO_3)_3$ , Ph<sub>2</sub>MePO and NH<sub>4</sub>PF<sub>6</sub> in acetone. For lanthanum only, a neutral 1:4 complex  $[La(Ph_2MePO)_4(NO_3)_3]$ · $xMe_2CO$  contains a ten-coordinate metal centre. The structure of  $[Yb(Ph_2MePO)_4(NO_3)_2]PF_6$  reveals an eight-coordinate cation and all complexes contain bidentate nitrato-groups. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Lanthanide; Phosphine oxide; X-ray structure

#### 1. Introduction

Phosphine oxides have proved popular ligands for complexing with oxophilic metals like the lanthanides and actinides, and they have been widely used in solvent extraction and separation processes. The overwhelming majority of complexes isolated with the lanthanides have involved Ph<sub>3</sub>PO, with very limited data on complexes of other R<sub>3</sub>PO ligands [1]. We have recently reported [2] a detailed study of the reactions of Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = lanthanide except Pm) with Ph<sub>3</sub>PO, and found subtle variations with the lanthanide concerned and the reaction conditions. Whilst nine-coordinate [Ln(Ph<sub>3</sub>PO)<sub>3</sub>( $\eta^2$ -NO<sub>3</sub>)<sub>3</sub>] are known for all the metals, nine-coordinate [Ln'(Ph<sub>3</sub>PO)<sub>4</sub>( $\eta^2$ -NO<sub>3</sub>)<sub>2</sub>( $\eta^1$ -  $NO_3$ ] form only with Ln' = La, Ce, Pr or Nd, whilst for the elements Tb-Lu eight-coordinate  $[Ln(Ph_3PO)_4(\eta^2-NO_3)_2]NO_3$  were isolated as solids. Solution speciation also varies with Ln. In related studies with Sc and Y [3], the complexes characterised included  $[Sc(Ph_3PO)_2(\eta^2-NO_3)_3],$  $[Y(Ph_3PO)_3(\eta^2-NO_3)_3]$ and  $[Y(Ph_3PO)_4(\eta^2-NO_3)_2]NO_3$ . Here we report the complexes formed between Ln(NO<sub>3</sub>)<sub>3</sub> and Ph<sub>2</sub>MePO, which is expected to be a stronger donor and sterically less demanding than Ph<sub>3</sub>PO. The synthesis and crystal structures  $[Sc(Ph_2MePO)_4(NO_3)_2]NO_3$ of and  $[Y(Ph_2MePO)_3(NO_3)_3]$  have been described [3].

#### 2. Experimental

Lanthanide nitrates were obtained as before [2] and Ph<sub>2</sub>MePO (Aldrich) was used as received. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker DPX400 at

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161.9 MHz and referenced to external 85% H<sub>3</sub>PO<sub>4</sub>. Other physical measurements were carried out as described previously [2,3].

# 2.1. Synthesis

The complexes were prepared by similar methods, representative examples of which are described. For others only the physical data are noted.

## 2.1.1. $[La(Ph_2MePO)_3(NO_3)_3]$

A solution of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.43 g, 1.0 mmol) in acetone (10 cm<sup>3</sup>) was added to a solution of Ph<sub>2</sub>MePO (0.54 g, 2.5 mmol) in acetone (10 cm<sup>3</sup>), and the mixture heated to boiling. After concentration to 5 cm<sup>3</sup> the solution was refrigerated for 24 h. The white solid was filtered off and dried in vacuo. Yield: 0.46 g (47%). *Anal.* Found: C, 47.9; H, 4.0; N, 4.3. Calc. for C<sub>39</sub>H<sub>39</sub>LaN<sub>3</sub>O<sub>12</sub>P<sub>3</sub>: C, 48.1; H, 4.0; N, 4.3%. IR (CsI, cm<sup>-1</sup>) 3084w, 3005w, 1489br, 1474s, 1438m, 1361s, 1292s, 1165sh, 1144s, 1127m, 1097m, 1072m, 1029s, 998m, 895s, 854s, 819m, 782s, 732s, 718m, 698s, 503s, 397s. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  1.95 (d, <sup>2</sup>*J* = 16 Hz), 7.3–7.8 (m).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 1.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.2. [Ce(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]

Colourless solid. Yield: 59%. *Anal.* Found: C, 48.0; H, 3.7; N, 4.1. Calc. for  $C_{39}H_{39}CeN_3O_{12}P_3$ : C, 48.1; H, 4.0; N, 4.3%. IR (CsI, cm<sup>-1</sup>) 3057w, 3005w, 2918w, 1594w, 1473br, 1438m, 1357s, 1340s, 1299s, 1165sh, 1149s, 1124s, 1096s, 1070m, 1029s, 997m, 895s, 888s, 820m, 782m, 748s, 717m, 695s, 511s, 445m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  4.1 (d, <sup>2</sup>*J* = 16 Hz), 7.5–7.8 (m), 8.7 (m).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 1  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.3. $[Pr(Ph_2MePO)_3(NO_3)_3]$

Green powder. Yield: 49%. *Anal.* Found: C, 47.8; H, 3.3; N, 4.1. Calc. for  $C_{39}H_{39}N_3O_{12}P_3Pr$ : C, 48.0; H, 4.0; N, 4.3%. IR (CsI, cm<sup>-1</sup>) 3056w, 3006w, 2920w, 1484br, 1456s, 1438m, 1300s, 1284s, 1165m, 1142s, 1123m, 1090m, 1069m, 1028s, 994m, 892s, 880s, 817m, 780m, 742s, 715m, 695s, 509s, 438m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  7.2 (br), 8.3 (br), 11.3 (br).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 1  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.4. $[Nd(Ph_2MePO)_3(NO_3)_3]$

Pale blue crystals. Yield: 50%. Anal. Found: C, 47.7; H, 4.0; N, 4.1. Calc. for  $C_{39}H_{39}N_3NdO_{12}P_3$ : C, 47.9; H, 4.0; N, 4.3%. IR (CsI, cm<sup>-1</sup>) 3058w, 3006w, 2916w, 1475br, 1437s, 1338m, 1289s, 1167m, 1142s, 1126m, 1090m, 1071w, 1023m, 994w, 896s, 880s, 818m, 781m, 743s, 709m, 690s, 509s, 443m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  4.7 (d, <sup>2</sup>*J* = 15 Hz), 7.9 (m), 9.4 (m).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 1  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

## 2.1.5. $[Sm(Ph_2MePO)_3(NO_3)_3]$

White crystals. Yield: 59%. *Anal.* Found: C, 47.2; H, 4.0; N, 4.3. Calc. for  $C_{39}H_{39}N_3O_{12}P_3Sm$ : C, 47.6; H, 4.0; N, 4.3%. IR (CsI, cm<sup>-1</sup>) 3057w, 3006w, 2918w, 1484br, 1460m, 1438m, 1292s, 1169s, 1147s, 1126m, 1097m, 1071m, 1031m, 996w, 894s, 883s, 817m, 782m, 746s, 716m, 697s, 510s, 447m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  5.5 (br), 6.7 (m), 7.1 (m).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 3  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.6. [Eu(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]

White powder. Yield: 50%. *Anal.* Found: C, 47.0; H, 4.1; N, 4.2. Calc. for  $C_{39}H_{39}EuN_3O_{12}P_3$ : C, 47.5; H, 4.0; N, 4.3%. IR (CsI, cm<sup>-1</sup>) 3031w, 2920w, 1497br, 1484s, 1438m, 1359s, 1302s, 1170m, 1148s, 1127m, 1099m, 1072w, 1033m, 996w, 895m, 885s, 818m, 783m, 746s, 694s, 508s, 450m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  3.3 (br), 4.7–5.6 (br).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.7. [Gd(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]

White powder. Yield 48%. *Anal.* Found: C, 47.5; H, 3.8; N, 4.2. Calc. for  $C_{39}H_{39}GdN_3O_{12}P_3$ : C, 47.2; H, 4.0; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3096w, 3058w, 2913w, 1487br, 1438m, 1357s, 1304m, 1172m, 1154s, 1125m, 1106m, 1077w, 1033m, 995w, 896m, 888s, 818m, 779m, 743s, 695s, 511s, 449m.  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 3  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.8. [Tb(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]

White powder. Yield: 66%. *Anal.* Found: C, 47.0; H, 3.8; N, 4.5. Calc. for  $C_{39}H_{39}N_3O_{12}P_3Tb$ : C, 47.2; H, 4.0; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3053w, 3010w, 2918w, 1492br, 1438m, 1359s, 1304s, 1174m, 1149s, 1127m, 1099m, 1073w, 1035m, 999w, 896m, 884s, 818m, 784m, 746s, 717m, 697s, 511s, 450m.  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 4  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.9. $[Dy(Ph_2MePO)_3(NO_3)_3]$

White powder. Yield: 65%. *Anal.* Found: C, 46.1; H, 3.8; N, 4.4. Calc. for  $C_{39}H_{39}DyN_3O_{12}P_3$ : C, 46.8; H, 3.9; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3058w, 3006w, 2920w, 1475br, 1437m, 1318s, 1299s, 1171m, 1151s, 1123m, 1099m, 1071w, 1033m, 994w, 895m, 885s, 814m, 780m, 743s, 716m, 690s, 509s, 504s, 447w.  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 7  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.10. [Ho(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>]

Pink crystals. Yield: 43%. *Anal.* Found: C, 45.9; H, 4.2; N, 3.7. Calc. for  $C_{39}H_{39}HoN_3O_{12}P_3$ : C, 46.8; H, 3.9; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3054w, 3007w, 2920w, 1474br, 1437m, 1325s, 1294s, 1175m, 1151s, 1123m, 1099m, 1071w, 1033m, 994w, 892s, 885s, 814m, 776m, 747s, 714m, 695s, 504s, 448m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K): δ 3.5 (br), 11.2–12.5 (m).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 11  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 2.1.11. $[Er(Ph_2MePO)_3(NO_3)_3]$

Pink crystals. Yield: 44%. *Anal.* Found: C, 46.8; H, 4.3; N, 3.8. Calc. for  $C_{39}H_{39}ErN_3O_{12}P_3$ : C, 46.7; H, 3.9; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3058w, 3006w, 1480s, 1438m, 1304s, 1294s, 1171s, 1147s, 1127m, 1099m, 1066w, 1033m, 994w, 895m, 885s, 814m, 776m, 743s, 714m, 695s, 512s, 505s, 443m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  2.4 (d) 7.4 (m), 7.9 (m).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 10  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

### 2.1.12. $[Tm(Ph_2MePO)_3(NO_3)_3]$

White powder. Yield: 45%. *Anal.* Found: C, 46.7; H, 3.9; N, 3.7. Calc. for  $C_{39}H_{39}N_3O_{12}P_3Tm$ : C, 46.7; H, 3.9; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3067w, 2963w, 1484br, 1438m, 1384s, 1304s, 1185s, 1150s, 1126m, 1098m, 1034m, 996w, 894m, 880s, 815m, 802m, 746s, 735m, 690s, 514s, 499s, 450m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  3.4 (d), 7.2 (br,m).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 11  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 2.1.13. $[Yb(Ph_2MePO)_3(NO_3)_3]$

White powder. Yield: 63%. Anal. Found: C, 46.7; H, 3.9; N, 4.2. Calc. for  $C_{39}H_{39}N_3O_{12}P_3Yb$ : C, 46.5; H, 3.9; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3057w, 3013w, 1471br, 1342s, 1309s, 1161br, 1127m, 1098m, 1068w, 1030m, 994w, 886m, 875s, 816m, 781m, 749s, 716m, 698s, 512s, 503s, 440w. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  4.3–6.0 (br).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 13  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 2.1.14. $[Lu(Ph_2MePO)_3(NO_3)_3]$

White powder. Yield: 55%. *Anal.* Found: C, 46.3; H, 3.8; N, 4.2. Calc. for  $C_{39}H_{39}LuN_3O_{12}P_3$ : C, 46.4; H, 3.9; N, 4.2%. IR (CsI, cm<sup>-1</sup>) 3062w, 2963w, 1478m, 1439m, 1325s, 1262m, 1165s, 1150s, 1126m, 1100s, 1032m, 891m, 876w, 815m, 802m, 781w, 749s, 717m, 690s, 500s, 392m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  1.9 (d, <sup>2</sup>*J* = 16 Hz), 7.3–7.6 (m).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 12  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

## 2.1.15. $[Ho(Ph_2MePO)_4(NO_3)_2]PF_6$

Ammonium hexafluorophosphate (0.08 g, 0.5 mmol) and holmium nitrate hydrate (0.22 g, 0.5 mmol) were dissolved separately in acetone (5 cm<sup>3</sup>) and the solutions mixed and stirred for 5 min. The solution was filtered and a solution of Ph<sub>2</sub>MePO (0.55 g, 2.5 mmol) in acetone (15 cm<sup>3</sup>) added, and the mixture boiled. The solution was cooled, concentrated in vacuo until it became cloudy and refrigerated for 48 h. The pink crystals produced were filtered off, rinsed with diethyl ether (10 cm<sup>3</sup>) and dried in vacuo. The solid was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>. Yield: 0.55 g (43%). Anal. Found: C, 48.1; H, 4.3; N, 2.2. Calc. for  $C_{52}H_{52}F_{6}HoN_{2}O_{10}P_{5}$ ; C, 48.1; H, 4.0; N, 2.2%. IR (CsI, cm<sup>-1</sup>) 3054w, 3007w, 1511s, 1485m, 1441m, 1362m, 1294m, 1186sh, 1152vs, 1129m, 1110w, 1076w, 1033m, 999m, 898m, 839vs, 779s, 754s, 747s, 717m, 696s, 559s,

510s. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  15.4 (br), 10.6–10.1, 7.4.  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 23  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

## 2.1.16. $[Er(Ph_2MePO)_4(NO_3)_2]PF_6$

Pink crystals. Yield: 48%. *Anal.* Found: C, 47.6; H, 4.3; N, 2.2. Calc. for  $C_{52}H_{52}ErF_6N_2O_{10}P_5$ : C, 48.1; H, 4.0; N, 2.2%. IR (CsI, cm<sup>-1</sup>) 3058w, 3006w, 1506s, 1440m, 1358s, 1298s, 1188sh, 1153vs, 1127m, 1102m, 1074w, 1033m, 999w, 897m, 839vs, 779m, 755s, 746s, 719m, 696s, 559s, 510s, 443m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  4.5–5.5, 6.5–7.2.  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 22 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

# 2.1.17. [Tm(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>

White powder. Yield: 55%. *Anal.* Found: C, 47.7; H, 4.3; N, 2.0. Calc. for  $C_{52}H_{52}F_6N_2O_{10}P_5Tm$ : C, 47.9; H, 4.0; N, 2.2%. IR (CsI, cm<sup>-1</sup>) 3067w, 2963w, 1505br, 1440m, 1362s, 1298s, 1185sh, 1153vs, 1127m, 1110m, 1074w, 1034m, 999w, 897m, 839vs, 780m, 777s, 719m, 697s, 559s, 510s. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  2.5 (br) 4.0–4.8.  $A_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 25  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 2.1.18. $[Yb(Ph_2MePO)_4(NO_3)_2]PF_6$

White powder. Yield: 60%. *Anal.* Found: C, 48.3; H, 4.4; N, 2.3. Calc. for  $C_{52}H_{52}F_6N_2O_{10}P_5Yb$ : C, 47.8; H, 4.0; N, 2.1%. IR (CsI, cm<sup>-1</sup>) 3057w, 3013w, 1484br, 1440m, 1357s, 1299s, 1154vs, 1127m, 1100m, 1074w, 1034m, 999w, 887m, 839vs, 782m, 749s, 719m, 679s, 559m, 510s, 474m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  3.0–3.5, 5.8–6.4.  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 24  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 2.1.19. $[Lu(Ph_2MePO)_4(NO_3)_2]PF_6$

White powder. Yield: 65%. *Anal.* Found: C, 48.2; H, 4.4; N, 2.4. Calc. for  $C_{52}H_{52}F_6LuN_2O_{10}P_5$ : C, 47.7; H, 4.0; N, 2.1%. IR (CsI, cm<sup>-1</sup>) 3062w, 2963w, 1482br, 1440m, 1365s, 1300s, 1155vs, 1127m, 1110m, 1074w, 1035m, 999w, 888m, 839vs, 783m, 749s, 719m, 697s, 559s, 514s, 475m. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  1.75 (d, <sup>2</sup>*J* = 16 Hz), 7.3–7.6 (m).  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) 24  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

## 2.1.20. $[La(Ph_2MePO)_4(NO_3)_3]$

Ph<sub>2</sub>MePO (0.11 g, 0.50 mmol) was added to a solution of  $[La(Ph_2MePO)_3(NO_3)_3]$  (0.098 g, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) and the mixture heated to reflux, then cooled. A <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this solution at  $-80^{\circ}$ C showed the tetrakis complex and free ligand as the only major species. The solvent was removed in vacuo, and the product dried, and then ground to a fine powder. The white powder was stirred with diethyl ether (50 cm<sup>3</sup>) for 48 h, the residual solid filtered off and dried in vacuo. Yield: 0.11 g (90%). *Anal.* Found: C, 52.0; H, 3.4; N, 4.0. Calc. for C<sub>52</sub>H<sub>52</sub>LaN<sub>3</sub>O<sub>13</sub>P<sub>4</sub>: C, 52.5; H, 3.5; N, 4.4%. IR (CsI, cm<sup>-1</sup>) 3066w, 3005w,

#### Table 1 Crystallographic data <sup>a</sup>

Compound	$[La(Ph_2MePO)_3(NO_3)_3]$	$[La(Ph_2MePO)_4(NO_3)_3]$ ·xMe <sub>2</sub> CO	[Yb(Ph <sub>2</sub> MePO) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>
Empirical formula	$C_{39}H_{39}LaN_3O_{12}P_3$	$C_{52}H_{52}LaN_{3}O_{13}P_{4} + xC_{3}H_{6}O$	$C_{52}H_{52}F_6N_2O_{10}P_5Yb$
M <sub>r</sub>	973.55	1247.83 (x = 1)	1306.85
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>P</i> 1 (no. 2)	C2/c (no. 15)	$P\overline{1}$ (no. 2)
Unit cell dimensions			
a (Å)	10.1697(2)	22.896(3)	13.1163(2)
b (Å)	10.2766(2)	25.231(4)	14.9535(2)
<i>c</i> (Å)	21.6636(3)	12.784(4)	15.7817(2)
α (°)	98.879(1)	90.0	103.064(1)
β (°)	99.412(1)	119.97(1)	101.265(1)
γ (°)	103.229(1)	90.0	106.621(1)
$V(Å^3)$	2130.52(7)	6397(2)	2774.9(1)
$D_{\text{calc}} (\text{g cm}^{-3})$	1.518	1.296	1.564
Ζ	2	4	2
Total number of observations	24884	5792	37259
Number of unique observations	9398 ( $R_{\rm int} = 0.0604$ )	5646 ( $R_{\rm int} = 0.0397$ )	9661 ( $R_{\rm int} = 0.096$ )
Absorption correction	sortav	psi-scan	sortav
Number of data in refinement	9398	5646	9661
Number of parameters/restraints	524/0	272/0	623/18
$\mu  (\rm cm^{-1})$	11.78	8.27	19.07
S	1.04	1.14	0.96
$R (F_{o} > 2\sigma(F_{o}))$	0.0393 (7817 refls)	0.0962 (4675 refls)	0.0552 (8714 refls)
$wR_2$ (all data)	0.0915	0.2785	0.1598

<sup>a</sup> In common, T = 150 K,  $\lambda$  (Mo K $\alpha$ ) = 0.71073 Å.  $R = \Sigma ||F_o| - |F_c|| / \Sigma ||F_o|; wR_2 = \left[ \Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^4 \right]^{1/2}$ .

1484br, 1474s, 1438m, 1360s, 1288s, 1166sh, 1143s, 1127m, 1097m, 1072m, 1030s, 998m, 895s, 819m, 783s, 747s, 718m, 697s, 512s, 397s. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 K):  $\delta$  1.95 (d, <sup>2</sup>*J* = 16 Hz), 7.3 – 7.8 (m).

#### 2.2. Crystal structure determinations

#### 2.2.1. $[La(Ph_2MePO)_3(NO_3)_3]$

Very thin small platy crystals were obtained from the NMR sample in CH<sub>2</sub>Cl<sub>2</sub> by slow evaporation over several weeks. Data were collected on a Nonius CCD diffractometer at 150 K and corrected for absorption using the SORTAV procedure [4]. The default PATT and TREF calculations in SHELXS-86 [5] failed to give a solution and the La position was obtained by hand calculation from the Patterson map. Repeated structure factor and electron density calculations revealed the remaining non-H atoms. At a later stage most of the H atoms appeared and were added to the model in calculated positions. Full-matrix least-squares refinement on  $F^2$  [6] converged to the final solution (see Table 1).

## 2.2.2. $[La(Ph_2MePO)_4(NO_3)_3]$ ·xMe<sub>2</sub>CO

Repeated attempts to grow suitable crystals failed, but a few modest quality needle crystals were obtained directly from one synthesis with very dilute solutions over several weeks and used to collect data at 150 K on a Rigaku AFC7S diffractometer. The diffraction peaks were broad, and the systematic absences gave the space group as Cc or C2/c of which the latter was finally used for the solution. The trial solution came from SHELXS-86 (TREF) [5] with La(1), N(2) and O(6) located on a twofold axis. Refinement as in Section 2.2.1 [6] with geometrically fixed rings (AFIX 66), disorder in one phenyl ring with two images observed in the electrondensity map and a partially modelled, disordered acetone solvate molecule. No H atoms were included in the model (see Table 1).

## 2.2.3. $[Yb(Ph_2MePO)_4(NO_3)_2]PF_6$

Crystals were obtained by vapour diffusion of  $Et_2O$ into a  $CH_2Cl_2$  solution on the compound with the sealed container held in the refrigerator. Data were collected as in Section 2.2.1 and corrected for absorption using the SORTAV procedure [4]. Structural solution and refinement are as given in Section 2.2.2. The  $PF_6$  anion was disordered and although six F atoms were identified there were a number of potential F atom peaks in the electron-density map that were not modelled. Restraints (DFIX) were used on P–F and F…F distances and in the final cycle the  $PF_6$  group was kept fixed. There was also evidence of disorder in one of the phenyl groups on P(4).

## 3. Results and discussion

## 3.1. $[Ln(Ph_2MePO)_3(NO_3)_3]$

The reaction of  $Ln(NO_3)_3 \cdot 6H_2O$  with  $Ph_2MePO$  in a 1:2–1:4 molar ratio in hot acetone produced good

yields of  $[Ln(Ph_2MePO)_3(NO_3)_3]$ , which in contrast to  $[Ln(Ph_3PO)_3(NO_3)_3]$ ·2Me<sub>2</sub>CO are not solvated. The Xray structure of  $[La(Ph_2MePO)_3(NO_3)_3]$  shows a ninecoordinate lanthanum centre coordinated to three phosphine oxides and three bidentate nitrate groups (below), and the very similar IR spectra indicate this



Fig. 1. Structure of  $[La(Ph_2MePO)_3(NO_3)_3]$  showing the atom numbering scheme. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

Table 2					
Selected bond	lengths (Å	) and	angles (°)	for	[La(Ph2MePO)3(NO3)3]

Bond lengths			
La(1) - O(1)	2.418(2)	La(1)–O(8)	2.584(2)
La(1)–O(2)	2.407(2)	La(1)-O(9)	2.641(2)
La(1)–O(3)	2.436(2)	La(1)–O(11)	2.630(2)
La(1)–O(5)	2.634(2)	La(1)–O(12)	2.589(2)
La(1)–O(6)	2.629(2)		
P(1)–O(1)	1.507(2)	P(1)-C(1)	1.779(3)
P(2)–O(2)	1.503(2)	P(1)–C(2)	1.795(3)
P(3)-O(3)	1.505(2)	P(1)–C(8)	1.800(3)
P(2)-C(14)	1.785(3)	P(3)-C(27)	1.778(3)
P(2)-C(15)	1.794(3)	P(3)-C(28)	1.795(3)
P(2)-C(21)	1.798(3)	P(3)-C(34)	1.797(3)
N(1)-O(4)	1.223(3)	N(1)–O <sub>c</sub> <sup>a</sup>	1.273(3),
			1.263(3)
N(2)–O(7)	1.227(3)	$N(2)-O_c$	1.279(3),
			1.256(3)
N(3)-O(10)	1.217(3)	$N(3)-O_c$	1.261(3),
			1.281(3)
Bond angles			
O(1)-La(1)-O(2)	82.03(7)	O(5)-La(1)-O(6)	48.50(6)
O(1)-La(1)-O(3)	85.60(7)	O(8)-La(1)-O(9)	48.84(6)
O(2)-La(1)-O(3)	88.84(7)	O(11)-La(1)-O(12)	48.96(6)
La(1)-O(1)-P(1)	144.8(1)	La(1)–O(2)–P(2)	165.1(1)
La(1)–O(3)–P(3)	147.0(1)		
O-P-C	110.0(1)-	C-P-C	106.3(1)-
	113.2(1)		108.9(1)

<sup>a</sup> O<sub>c</sub> are coordinated O atoms of the nitrate ligand.

structure is present in the other complexes. IR spectra were obtained in both Nujol mulls and in CsI discs, generally the CsI disc spectra were better resolved and the data quoted in the Section 2 refers to the latter.<sup>1</sup> Very strong features 1165-1140 cm<sup>-1</sup> are associated with v(PO) (compare 1172 cm<sup>-1</sup> in the 'free' ligand) and features at approximately 1475, 1325, 1030 and 815  $cm^{-1}$  are attributable to the bidentate nitrate groups. The structure of [La(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] reveals a ninecoordinate La centre (Fig. 1, Table 2) with coordination from three phosphine oxide ligands and three symmetrically bonded bidentate nitrate groups. The three (P)O-La-O(P) angles (ca. 86°) shows that this complex may be described as *fac*-octahedral where the nitrate ligands have been replaced conceptually by monoatomic species. The nitrate groups are symmetrically bonded and show clearly the changes in geometry (bond lengths and angles) noted before [3]. The triphenylphosphine oxide analogue  $[La(Ph_3PO)_3(NO_3)_3]$ has been reported [7] as the mer isomer but the La-O(P) (2.373-2.427) and La-O(N) (2.583-2.681 Å) are similar to the present compound.

As observed for Ph<sub>3</sub>PO complexes [2], the solution behaviour varies along the Ln series, although that with Ph<sub>2</sub>MePO differs in detail from that previously observed with Ph<sub>3</sub>PO. The complexes [Ln'(Ph<sub>2</sub>MePO)<sub>3</sub>- $(NO_3)_3$  (Ln' = Pr, Nd, Sm, Eu, Gd and Tb) are nonconductors in  $10^{-3}$  mol dm<sup>-1</sup> CH<sub>2</sub>Cl<sub>2</sub><sup>2</sup> and the conductances do not increase upon addition of a fivefold molar excess of Ph<sub>2</sub>MePO. The La and Ce complexes behave differently and are discussed in Section 3.2. The complexes  $[Ln''(Ph_2MePO)_3(NO_3)_3]$  (Ln'' = Dy, Ho, Er,Tm, Yb or Lu) have small but significant conductances although mostly less than half those expected for 1:1 electrolytes, and these conductances increase upon addition of excess Ph<sub>2</sub>MePO. We were unable to observe <sup>31</sup>P NMR spectra for the Gd or Tb complexes no doubt due to extreme line broadening. Solutions of the complexes  $[Ln''(Ph_2MePO)_3(NO_3)_3]$  (Ln'' = Ho, Er, Tm, Yb)or Lu) showed two  ${}^{31}P{}^{1}H$  NMR resonances usually (Table 3) one significantly broader than the other. Addition of Ph<sub>2</sub>MePO to these solutions produced (in addition to a free ligand resonance) a diminution in the broader resonance and an increased intensity in the sharper one. From our previous studies of  $[Ln'(Ph_3PO)_3(NO_3)_3]$  [2], these data are readily interpreted as due to a mixture of [Ln'(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] (broader resonance) and  $[Ln'(Ph_2MePO)_4(NO_3)_2]^+$ 

<sup>&</sup>lt;sup>1</sup> In some cases KBr disc spectra showed weak features due to the presence of ionic nitrate ions, which appear to arise from reaction during the die pressing, particularly if the KBr is not thoroughly dry. These problems were not experienced using dry CsI.

 $<sup>^{2}</sup>$  Although CH<sub>2</sub>Cl<sub>2</sub> is not commonly used for conductivity measurements it was used here so that correlation could be made with the NMR data obtained from chlorocarbon solutions.

Table 3 <sup>31</sup>P{<sup>1</sup>H} NMR spectra <sup>a</sup>

Compound	$\delta$ (295 K)
[La(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	39.2(25)
[Ce(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	79(190) <sup>b</sup>
$[Pr(Ph_2MePO)_3(NO_3)_3]$	138(250) <sup>b</sup>
[Nd(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	133(500) <sup>b</sup>
[Sm(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	38.5(40)
$[Eu(Ph_2MePO)_3(NO_3)_3]$	-95(150)
$[Gd(Ph_2MePO)_3(NO_3)_3]$	not observed
[Tb(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	not observed
[Dy(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	-166(2000)
[Ho(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	$-65(1200), -97(275)^{\circ}$
$[Er(Ph_2MePO)_3(NO_3)_3]$	-120(600) °, -165(1000)
[Tm(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	-72(200) °, -135(1500)
[Yb(Ph <sub>2</sub> MePO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]	14.5(220) °, -19.5(380)
$[Lu(Ph_2MePO)_3(NO_3)_3]$	42.1(30) °, 40.3(35)
[Ho(Ph <sub>2</sub> MePO) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	$-98(250), -145(quintet)^{d}$
[Er(Ph <sub>2</sub> MePO) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	$-120(500), -145(quintet)^{d}$
[Tm(Ph <sub>2</sub> MePO) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	$-72(200), -145(quintet)^{d}$
[Yb(Ph <sub>2</sub> MePO) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	14.5(190), $-145$ (quintet) <sup>d</sup>
[Lu(Ph <sub>2</sub> MePO) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	42.1(30), $-145$ (quintet) <sup>d</sup>

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>-10%CDCl<sub>3</sub>; approximate line-widths at half-height in parentheses.

<sup>b</sup> At 273 K.

- <sup>c</sup> Resonance assigned to [Ln(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation.
- <sup>d</sup> [PF<sub>6</sub>]<sup>-</sup> anion.



Fig. 2. Structure of the La residue in  $[La(Ph_2MePO)_4(NO_3)_3]$ xMe<sub>2</sub>CO showing the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. The molecule has crystallographic twofold symmetry.

(sharper resonance), which also correlates with the conductance data. Although  $[Dy(Ph_2MePO)_3(NO_3)_3]$  shows a small conductance, only one very broad <sup>31</sup>P{<sup>1</sup>H} resonance was observed; if two species are present either the resonances are within the same broad envelope or one resonance is too broad to observe.

## 3.2. $[La(Ph_2MePO)_4(NO_3)_3]$

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [La(Ph<sub>2</sub>MePO)<sub>3</sub>- $(NO_3)_3$ ] in CH<sub>2</sub>Cl<sub>2</sub> solution at ambient temperatures is a sharp line at  $\delta$  39.2 (Table 3), and on addition of Ph<sub>2</sub>MePO ( $\delta$  29.0) an averaged signal is observed consistent with fast intramolecular exchange. Cooling the solution slows the exchange and at 195 K two resonances are present at  $\delta$  39.7 (tris) and 38.1 and the latter increases in relative intensity with more added Ph<sub>2</sub>MePO. The second resonance is assigned to  $[La(Ph_2MePO)_4(NO_3)_3]$  and notably the solution shows no significant increase in conductance at this stage. Many attempts to crystallise  $[La(Ph_2MePO)_4(NO_3)_3]$ from these solutions resulted in isolation of only  $[La(Ph_2MePO)_3(NO_3)_3]$ . Serendipitously, from one such attempt using a very dilute acetone solution a very small number of crystals formed over about six weeks and one was submitted to X-ray crystallographic study. Although a poor quality crystal, the structure is clearly established as  $[La(Ph_2MePO)_4(\eta^2-NO_3)_3]$  with ten-coordinate La (Fig. 2, Table 4). The structure is molecular and has crystallographic twofold symmetry with La(1), N(2) and O(6) positioned on the  $C_2$  axis. Although the data are not of good quality, the La-O(P) distances (Table 4) are longer than in  $[La(Ph_2MePO)_3(NO_3)_3]$ (Table 2). The corresponding triphenylphosphine oxide complex  $[La(Ph_3PO)_4(NO_3)_3]$  is again molecular but has a nine-coordinate La due to the presence of one monodentate  $\eta^1$ -NO<sub>3</sub> ligand [2]. A bulk (powdered) sample of  $[La(Ph_2MePO)_4(\eta^2-NO_3)_3]$  was eventually obtained by rapidly evaporating to dryness a mixture of [La(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] and excess Ph<sub>2</sub>MePO in CH<sub>2</sub>Cl<sub>2</sub> (shown by low temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy to be predominently the tetrakis complex), and removing the excess Ph<sub>2</sub>MePO by prolonged extraction with diethyl ether. The IR spectrum has only small differences to that of  $[La(Ph_2MePO)_3(\eta^2-NO_3)_3]$ , whilst the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 195 K shows, as expected, almost complete decomposition into the tris(complex) and Ph<sub>2</sub>MePO. On further addition of  $Ph_2MePO$  to the ' $[La(Ph_2MePO)_4(NO_3)_3]$ ' in  $CH_2Cl_2$ , the resonance at 39.7 diminishes further, a new resonance at 36.8 appears, and the solution now shows a significant conductance which we tentatively suggest is  $[La(Ph_2MePO)_5(NO_3)_2]^+$ . At very high due to  $Ph_2MePO:La ratios (>15:1)$  the  ${}^{31}P{}^{1}H{}$  NMR spectrum at 195 K contains the  $\delta$  36.8 resonance and free ligand as the major features, and has a molar conductance of approximately 20  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup> typical of a 1:1 electrolyte. However all attempts to isolate this complex as a solid have failed. A large excess (> 15:1)molar ratio) of Ph<sub>2</sub>MePO added to [Ce(Ph<sub>2</sub>MePO)<sub>3</sub>-(NO<sub>3</sub>)<sub>3</sub>] solution also produces a significant conductance (limiting value ca. 10  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>). Studies of the cerium system are complicated by the effects of paramagnetism ( $f^1$ ) where the  ${}^{31}P{}^{1}H{}$  NMR resonance

is both contact shifted and broadened, and both effects vary markedly with temperature [8]. At 300 K fast exchange occurs with added Ph<sub>2</sub>MePO, but on cooling to 220 K, the exchange is slow and the resonance of [Ce(Ph<sub>2</sub>MePO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>] is found at  $\delta$  115 ( $W_{1/2} = 1500$ Hz). A large excess of added ligand produces a new sharper resonance  $\delta$  92 ( $W_{1/2} = 800$  Hz) which we tentatively attribute to [Ce(Ph<sub>2</sub>MePO)<sub>x</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, although the reaction does not go to completion. Similar effects were not observed for Pr, Nd, Sm or Eu for which only a single broad (contact shifted) <sup>31</sup>P resonance was observed, and this was unaffected by added ligand, exchange being slow even at near ambient temperatures.

## 3.3. $[Ln'(Ph_2MePO)_4(NO_3)_2]PF_6 (Ln' = Ho-Lu)$

The  ${}^{31}P{}^{1}H$  NMR studies of  $[Ln'(Ph_2MePO)_3-$ 

Table 4

Selected bond lengths (Å) and angles (°) for  $[La(Ph_2MePO)_4-(NO_3)_3]\cdot xMe_2CO$  and  $[Yb(Ph_2MePO)_4(NO_3)_2]PF_6$ 

[La(Ph <sub>2</sub> MePO) <sub>4</sub> (N	$VO_3)_3] \cdot x Me_2CC$	)	
Bond lengths	5/54 2		
La(1) - O(1)	2.462(7)	La(1)–O(7)	2.650(7)
La(1) - O(2)	2.513(7)	P(1) - O(1)	1.480(8)
La(1)–O(4)	2.649(8)	P(2)–O(2)	1.502(7)
La(1)–O(5)	2.708(8)		
P–C	1.74(1)-	N–O	1.23(1)-
	1.89(1)		1.26(1)
Bond angles			
O(1)-La(1)-O(2)	74.9(2)	O(1)-La(1)-O(1') <sup>a</sup>	73.2(4)
O(1)-La(1)-O(4)	73.9(3)	O(2)-La(1)-O(4)	70.6(2)
O(4)-La(1)-O(5)	46.8(2)	O(7)–La(1)–O(7') <sup>a</sup>	47.9(3)
La(1)-O(1)-P(1)	154.9(5)	La(1)-O(2)-P(2)	149.3(4)
O–P–C	108.2(6)-	C-P-C	94.6(8)-
	114.4(6)		117.4(8)
[Yb(Ph2MePO)4(I	$NO_3)_2$ ]PF <sub>6</sub>		
Bond lengths	5,24 0		
Yb(1)-O(1)	2.221(4)	Yb(1)–O(6)	2.421(5)
Yb(1)-O(2)	2.186(5)	Yb(1)–O(7)	2.452(5)
Yb(1)–O(3)	2.193(4)	Yb(1)-O(9)	2.423(5)
Yb(1)–O(4)	2.222(4)	Yb(1)-O(10)	2.410(5)
P(n)-O(n)	1.490(5)-	P-C	1.792(7)-
	1.508(5)		1.809(9)
N–O <sub>t</sub> <sup>b</sup>	1.221(8),	N–O <sub>c</sub> <sup>b</sup>	1.256(8)-
	1.221(9)		1.280(7)
Bond angles			
O(1)-Yb(1)-O(2)	155.9(2)	O(2)-Yb(1)-O(3)	96.0(2)
O(1)-Yb(1)-O(3)	89.9(2)	O(2)-Yb(1)-O(4)	92.4(2)
O(1)-Yb(1)-O(4)	91.9(2)	O(3)-Yb(1)-O(4)	154.9(2)
O(6)-Yb(1)-O(7)	52.5(2)	O(9)-Yb(1)-O(10)	52.6(2)
Yb(1)-O(1)-P(1)	159.1(3)	Yb(1)-O(3)-P(3)	161.4(3)
Yb(1)–O(2)–P(2)	167.6(4)	Yb(1)-O(4)-P(4)	150.0(3)
O-P-C	108.6(3)-	C-P-C	106.3(3)-
	113.7(3)		111.0(3)
O(6)-N(1)-O(7)	116.5(5)	O(9)-N(2)-O(10)	115.9(6)

<sup>a</sup> Symmetry operation: prime (') -x, y, 1/2-z.

 $^{\rm b}$  O<sub>t</sub> and O<sub>c</sub> are terminal and coordinated O atoms of the nitrate ligand, respectively.

 $(NO_3)_3$ ] described in Section 3.1 show two species in solution, the species producing the sharper resonance in each system is proposed as  $[Ln'(Ph_2MePO)_4(NO_3)_2]^+$ . However, in contrast to the Ln'(NO<sub>3</sub>)<sub>3</sub>-Ph<sub>3</sub>PO systems, where the [Ln'(Ph<sub>3</sub>PO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> are readily isolated from ethanol solutions of 1:6 Ln'(NO<sub>3</sub>)<sub>3</sub>-Ph<sub>3</sub>PO molar ratio [2], in the present case attempts to crystallise or precipitate solids from such solutions only produced  $[Ln'(Ph_2MePO)_3(NO_3)_3]$ , confirmed by a combination of IR spectroscopy and analysis. The [Y(Ph<sub>2</sub>MePO)<sub>4</sub>-(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> (Y is of similar radius to the later lanthanides) behaves similarly [3]. Rather than attempt to find a solvent and Ln'-Ph2MePO ratio from which the tetrakis complexes could be isolated, we adopted an alternative approach. This involved the reaction of  $Ln'(NO_3)_3$ ,  $NH_4PF_6$  and  $Ph_2MePO$  in acetone in a 1:1:5 molar ratio, which deposited [Ln'(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]- $PF_6$  (Ln' = Ho-Lu) on concentration, and these were recrystallised without decomposition from CH<sub>2</sub>Cl<sub>2</sub>. The IR spectra of these complexes show single broad v(PO)approximately 1150 cm<sup>-1</sup> and strong PF<sub>6</sub><sup>-</sup> vibrations at 840 and 560 cm<sup>-1</sup> [9]. The 10<sup>-3</sup> mol dm<sup>-3</sup> solutions in CH<sub>2</sub>Cl<sub>2</sub> are 1:1 electrolytes and the <sup>31</sup>P{<sup>1</sup>H} NMR spectra show the characteristic septet of  $[PF_{\delta}]^{-}$  at  $\delta$ -145, and a second broader resonance attributable to  $[Ln'(Ph_2MePO)_4(NO_3)_2]^+$  (Table 3). The crystal structure of [Yb(Ph<sub>2</sub>MePO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> showed an eight-coordinate Yb with approximately a planar YbO<sub>4</sub> group formed by the phosphine oxide ligands with bidentate nitrates above and below this plane (Fig. 3, Table 4). On our previous formalism this is a *trans*-octahedral geometry. The two nitrate groups are approximately perpendicular to each other.



Fig. 3. Structure of the cation in  $[Yb(Ph_2MePO)_4(NO_3)_2]PF_6$  showing the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

## 4. Conclusions

The results combined with our previous study of Ph<sub>3</sub>PO complexes [2] show the subtle variations along the lanthanide series. Whilst nine-coordination is favoured early in the lanthanide series (as in  $[Ln(R_3PO)_3 (NO_3)_3$  and nine or eight (as in  $[Ln(R_3PO)_4(NO_3)_2]^+$ ) coordination later which correlates with the reducing  $Ln^{3+}$  radius along the series, the fine detail is less easily rationalised. For example the formation of eight-coordinate Ln as  $[Ln(R_3PO)_4(\eta^2-NO_3)_2]^+$  rather than  $[Ln(R_3PO)_2(\eta^2-NO_3)_3]$  shows a preference for  $R_3PO$ over NO<sub>3</sub> later in the series, whereas for La itself, the solid  $[La(R_3PO)_4(NO_3)_3]$  lose one  $R_3PO$  in solution. Our assumption that Ph<sub>2</sub>MePO should be a better donor than Ph<sub>3</sub>PO (based upon the usual inductive effects between Me and Ph) may be supported by the somewhat shorter La-O(P) distances in the Ph<sub>2</sub>MePO complexes compared with those of Ph<sub>3</sub>PO. However the proposal that Ph<sub>2</sub>MePO is sterically less demanding is uncertain in practice, since the Ln-O-P angles are highly variable ranging from approximately 145-170°. It should also be remembered that the solid and solution speciation may be different, several cases are described above where the major solution form is not the form which separates as a solid, obviously a consequence of solubility differences and fast equilibria interconverting the forms in solution.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 158449, 158448, and 158450 for compounds ( $[La(Ph_2MePO)_3(NO_3)_3]$ ), ( $[La(Ph_2-MePO)_4(NO_3)_3]$ ·xMe<sub>2</sub>CO), and (Yb), respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http:// www.ccdc.cam.ac.uk).

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## References

- T.S. Lobana, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, vol. 2, Wiley, New York, 1992, p. 409.
- [2] W. Levason, E.H. Newman, M. Webster, Polyhedron 19 (2000) 2697.
- [3] L. Deakin, W. Levason, M.C. Popham, G. Reid, M. Webster, J. Chem. Soc., Dalton Trans. (2000) 2439.
- [4] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
- [5] G.M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, 1985.
- [6] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, 1997.
- [7] C. Huang, R. Xu, Y. Zhou, G. Xu, F. Guo, N. Zhu, Acta Phys.-Chim. Sin. 3 (1987) 491 (Chem. Abs. 108 (1988) 123246r).
- [8] G.N. LaMar, W.D. Horrocks Jr., R.H. Holm (Eds.), NMR of Paramagnetic Molecules, Academic Press, NY, 1973 (chaps 12 and 13).
- [9] G.M. Begun, A.C. Rutenberg, Inorg. Chem. 6 (1967) 2213.