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Scandium, yttrium and lanthanum nitrate complexes of tertiary arsine oxides: synthesis and multinuclear spectroscopic studies. X-ray structures of $[M(Me_3AsO)_6](NO_3)_3$ (M = Sc or Y), $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$, $[M''(Ph_3AsO)_4(NO_3)_2]NO_3$ (M″ = Y or La) and $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$

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Abstract

The reaction of Ph_3AsO with $Sc(NO_3)_3{\cdot}5H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ or $La(NO_3)_3{\cdot}6H_2O$ in acetone gave $[Sc(Ph_3AsO)_2(NO_3)_3]$, $[Y(Ph_3AsO)_4(NO_3)_2]NO_3$, $[La(Ph_3AsO)_4(NO_3)_2]NO_3$, and $[La(Ph_3AsO)_3(NO_3)_3]$, whilst from ethanol solution $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$, $[Y(Ph_3AsO)_2(EtOH)(NO_3)_3]$ and $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$ were produced. Similar reactions using Me_3AsO produced $[M(Me_3AsO)_6](NO_3)_3$ (M = Sc, Y or La) and $[La(Me_3AsO)_2(H_2O)(NO_3)_3]$. All complexes were characterised by analysis, IR and ^1H, ^{45}Sc or ^{89}Y NMR spectroscopy, and conductance measurements. The solution speciation and interconversions of the Sc and Y complexes have been probed by ^{45}Sc and ^{89}Y NMR spectroscopy. X-Ray crystal structures are reported for the 6-coordinate $[M(Me_3AsO)_6](NO_3)_3$ (M = Sc or Y), seven-coordinate $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$, eight-coordinate $[M''(Ph_3AsO)_4(NO_3)_2]NO_3$ (M″ = Y or La), and nine-coordinate $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Scandium; Yttrium; Lanthanum; NMR spectroscopy; X-ray structures

1. Introduction

Compared to other d-block metals, the coordination chemistries of scandium and yttrium remain little explored. The only accessible oxidation state in solution, the d^0 M(III), form labile complexes and lack both magnetic and d–d UV–Vis spectroscopic probes. However, both metals are suitable for NMR studies, being monoisotopic (^{45}Sc and ^{89}Y) and diamagnetic in the M(III) oxidation state. Scandium-45 is quadrupolar ($I = 7/2$) but with only a moderate quadrupole moment -0.22×10^{-28} m^2, and is one of the most sensitive nuclei in the periodic table (D_c (receptivity relative to ^{13}C) = 1700), whilst ^{89}Y has $I = 1/2$ and moderate sensitivity ($D_c = 0.67$), but has a low absolute frequency ($\Xi = 4.92$ MHz) and very long relaxation times. We have recently described the characterisation of scandium(III) and yttrium(III) nitrate complexes of a range of phosphine oxides, [1] using a combination of multinuclear NMR (^1H, $^{31}P\{^1H\}$, ^{45}Sc or ^{89}Y) and X-ray crystallography. In a related work, the synthesis and structures of $Ln(Ph_3PO)_4(NO_3)_3$ for the lanthanides have been examined [2]. Here, we extend the work to tertiary arsine oxide (Me_3AsO and Ph_3AsO) complexes and demonstrate that ^{45}Sc or ^{89}Y NMR spectroscopy can be used to probe the solution behaviour of these two elements, even without the support of ^{31}P NMR as used for the phosphine oxide analogues. Apart from some early exploratory synthesis of lanthanide nitrate complexes of Ph_3AsO [3], nothing is known about these compounds, and no examples with Sc, Y or La have been structurally characterised.

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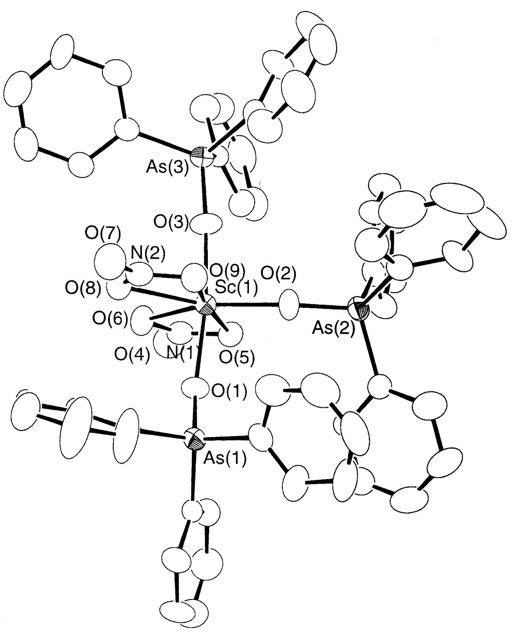

Fig. 1. The structure of the cation in $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3{\cdot}H_2O$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

2. Results and discussion

2.1. Triphenylarsine oxide complexes: scandium

The reaction of $Sc(NO_3)_3{\cdot}5H_2O$ with Ph_3AsO in a 1:3 mol ratio in ethanol produced colourless crystals of $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$. The structure of the cation of $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3{\cdot}H_2O$ is shown in Fig. 1 and selected bond lengths and angles are in Table 1. The Sc is seven-coordinate with two bidentate NO_3 groups and if as commonly done (and used in later descriptions), the coordinated NO_3 are each replaced conceptually with a monodentate group the geometry at Sc is based on a trigonal bipyramid with equatorial NO_3 groups. The IR spectrum shows a very broad ν(AsO) stretch at 899 cm^{-1}, which compares with 880 cm^{-1} in the 'free' ligand. Coordination shifts in arsine oxides are often small (high or low frequency), attributed to a combination of factors including coupling with the M–O vibrations and reduced As=O multiple bond character [4–6]. A weak sharp band at 834 cm^{-1} is attributable to the ν_2 vibration of the ionic nitrate ion [1]. The complex is a 1:1 electrolyte in CH_2Cl_2 solution,[1] and addition of excess Ph_3AsO produced no change in conductance, indicating that displacement of further nitrate groups by Ph_3AsO does not occur. This was confirmed by ^{45}Sc NMR spectroscopy; the $[Sc(Ph_3AsO)_3(NO_3)_2]^+$ shows a broad line at δ 31.9, which is not changed in the presence of excess ligand. The stoichiometry can be compared to that in the corresponding $Ph_3PO/Sc(NO_3)_3$ system where the only complex present [1] is the eight-coordinate $[Sc(Ph_3PO)_2(NO_3)_3]$. A number of reactions of $Sc(NO_3)_3{\cdot}5H_2O$ and Ph_3AsO in ethanol or acetone with lower Ph_3AsO:Sc ratios were carried out, and ^{45}Sc NMR spectroscopy was used to identify any complexes. The $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$ was usually present, but often a second complex with $\delta(^{45}Sc)$ at 14.0 was also identified, which on addition of Ph_3AsO was completely converted into $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$. From the reaction of a 1:1 ratio of $Sc(NO_3)_3{\cdot}5H_2O:Ph_3AsO$ in acetone, followed by recrystallisation from CH_2Cl_2, we obtained an impure sample (contaminated with some $Sc(NO_3)_3{\cdot}nH_2O$) of this second complex, which is identified as $[Sc(Ph_3AsO)_2(NO_3)_3]$.

2.2. Yttrium

The reaction of $Y(NO_3)_3{\cdot}6H_2O$ with Ph_3AsO in ethanol in a 1:1 mol ratio formed $[Y(Ph_3AsO)_2(EtOH)(NO_3)_3]$. The complex exhibits ν(AsO) at 933 and 910 cm^{-1} in the IR spectrum, and the ^1H NMR spectrum confirms the presence of EtOH. In solution in CH_2Cl_2 the complex is a non-electrolyte. The complex has not

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[1] As before (Ref. [1]) the same solvent (CH_2Cl_2) was used for both NMR and conductance studies for consistency.

Table 1
Selected bond lengths (Å) and bond angles (°) for $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3{\cdot}H_2O$

Bond lengths					
Sc(1)–O(1)	2.030(4)	Sc(1)–O(5)	2.250(5)	Sc(1)–O(2)	1.999(4)
Sc(1)–O(6)	2.256(5)	Sc(1)–O(3)	1.996(4)	Sc(1)–O(8)	2.267(5)
Sc(1)–O(9)	2.251(5)	As(1)–O(1)	1.669(4)	As(2)–O(2)	1.665(4)
As(3)–O(3)	1.659(4)	As–C	1.877(7)–1.925(8)	$N–O_c$	1.258(7)–1.287(8) [a]
$N–O_t$	1.222(8), 1.217(8) [a]				
Bond angles					
O(1)–Sc(1)–O(2)	93.4(2)	O(5)–Sc(1)–O(6)	56.2(2)	O(1)–Sc(1)–O(3)	171.4(2)
O(8)–Sc(1)–O(9)	56.8(2)	O(2)–Sc(1)–O(3)	94.2(2)	Sc(1)–O(1)–As(1)	149.2(3)
Sc(1)–O(2)–As(2)	153.1(3)	Sc(1)–O(3)–As(3)	176.4(3)		
O–As–C	106.1(3)–113.1(3)	C–As–C	106.6(3)–112.4(3)		

[a] O_c and O_t refer to coordinated and terminal O atoms of chelated NO_3 groups.

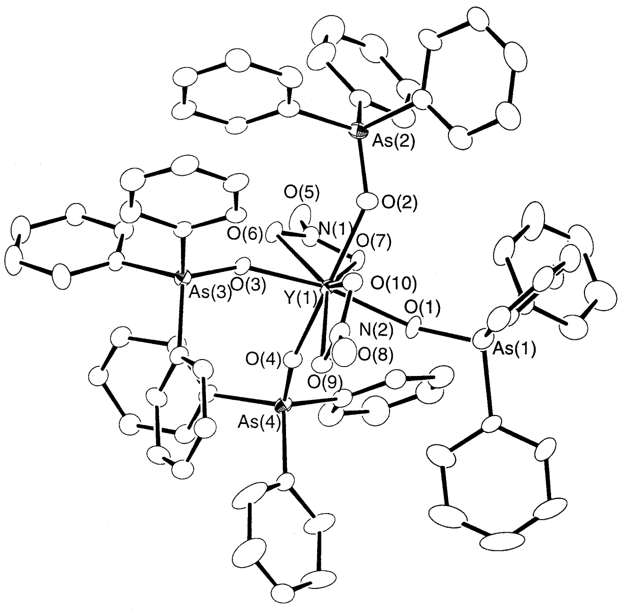

Fig. 2. The structure of the cation in $[Y(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 1/2H_2O$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

been obtained in crystalline form for an X-ray study, but there seems little doubt that it contains a nine-coordinate metal centre like $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$ [1] and the lanthanum analogue (below). The complex was poorly soluble in CH_2Cl_2 which hindered study by ^{89}Y NMR spectroscopy. No ^{89}Y resonance was evident at 300 K, but after long accumulations at 200 K a feature at δ 0.5 was observed along with a sharper feature at δ 21.0, the latter attributable to $[Y(Ph_3AsO)_4(NO_3)_2]NO_3$. Addition of Ph_3AsO to this solution caused immediate loss of the δ 0.5 resonance and enhancement of the δ 21.0, showing ready conversion to the tetrakis complex. From acetone solutions of $Y(NO_3)_3 \cdot 6H_2O$ and Ph_3AsO in mol ratios 1: 3–6 the product was $[Y(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot Me_2CO$. Attempts to grow single crystals yielded $[Y(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 1/2H_2O$ the structure of which has an eight-coordinate Y atom made up from four arsine oxide ligands approximately in the equatorial plane and two bidentate NO_3 groups (Fig. 2, Table 2). The planes of the two NO_3 ligands are approximately perpendicular. A similar coordination geometry is found in $[M(R_3PO)_4(NO_3)_2]^+$ (M = Sc [1] (R_3 = Ph_2Me) or Lu [2] ($R_3 = Ph_3$)).The presence of lattice acetone was confirmed by the IR and ^1H NMR spectra, and the former also showed evidence for an ionic nitrate group ($\nu_2 = 832$ cm^{-1}). The complex shows no ^{89}Y NMR resonance in CH_2Cl_2 solution at 300 K, but on cooling < 250 K a sharp resonance appears at δ 21.0, showing that like the corresponding phosphine oxide systems, the complex is undergoing fast dissociative exchange at ambient temperatures, the exchange rate slowing on cooling. The ^{89}Y NMR spectrum is unchanged by addition of excess Ph_3AsO to the solution, as is the 1:1 electrolyte behaviour, demonstrating that no complexes with a higher Ph_3AsO:Y ratio form. The corresponding $[Y(Ph_3PO)_4(NO_3)_2]NO_3$ is known [1], but in contrast to the present complex is only isolated from ice-cold ethanol solutions containing excess Ph_3PO, and in chlorocarbon solutions is partially decomposed into $[Y(Ph_3PO)_3(NO_3)_3]$, identified by ^{89}Y NMR spectroscopy. In the $Y(NO_3)_3/Ph_3PO$ system it is the tris(Ph_3PO) complex, $[Y(Ph_3PO)_3(NO_3)_3]$ which is easiest to isolate [1], but although $[Y(Ph_3AsO)_3(NO_3)_3]$ has been mentioned previously [3], we have been unable to isolate it. Even from 1:1 ratios of $Y(NO_3)_3 \cdot 6H_2O$: Ph_3AsO in acetone, slow crystallisation produced only the tetrakis(Ph_3AsO) complex. Evaporation to dryness of a 1:1 mixture of the constituents in acetone followed by extraction into CH_2Cl_2 gave a mixture including $Y(NO_3)_3 \cdot nH_2O$ and $[Y(Ph_3AsO)_4(NO_3)_2]NO_3$, and ^{89}Y NMR spectroscopy identified a third species with δ 18 which may be $[Y(Ph_3AsO)_3(NO_3)_3]$, since addition of Ph_3AsO immediately converts this species to the tetrakis complex, but attempted separation results in decomposition.

2.3. Lanthanum

The reaction of $La(NO_3)_3 \cdot 6H_2O$ with Ph_3AsO in boiling ethanol (1:2 mol ratio) and in acetone in 1:1.5 and 1:6 ratios led to $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$, $[La(Ph_3AsO)_3(NO_3)_3]$ and $[La(Ph_3AsO)_4(NO_3)_2]NO_3$, respectively, the first and third of which were identified by single crystal X-ray studies. The $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$ contains nine-coordinate La with three bidentate NO_3 groups and may be described as '*mer*-octahedral' (Fig. 3, Table 3). This complex is isomorphous with the corresponding Sm [7] compound and several triphenylphosphine oxide complexes (Sm [7], Eu, Nd and Ce [8]). In $[La(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 2Me_2CO$ the cation is structurally similar to the yttrium compound above with eight-coordinate La in the '*trans*-octahedral' geometry (Fig. 4, Table 4). There are two acetone molecules in the crystal formula whereas the chemical analysis of the bulk material gives a better fit for one. The corresponding triphenylphosphine oxide cationic species has been reported [9] although with a different counterion. The $[La(Ph_3AsO)_4(NO_3)_2]NO_3$ appears to retain this structure in solution in CH_2Cl_2 where it is a 1:1 electrolyte and the conductance is unchanged by addition of excess Ph_3AsO. In contrast $[La(Ph_3PO)_4(NO_3)_3]$ contains nine-coordinate lanthanum produced by four Ph_3PO, two bidentate and one monodentate NO_3 groups, but is completely decomposed in solution into $[La(Ph_3PO)_3(NO_3)_3]$ and Ph_3PO on the basis of $^{31}P\{^1H\}$ NMR studies [2]. Unfortunately the $La(NO_3)_3/Ph_3AsO$ system is not suited to NMR studies, in that the ^1H and ^{13}C NMR spectra were insensitive to coordination of the Ph_3AsO and attempts to record ^{139}La NMR spectra were unsuccess-

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Y(Ph_3AsO)_4(NO_3)_2]NO_3{\cdot}1/2H_2O$

Bond lengths					
Y(1)–O(1)	2.212(4)	Y(1)–O(6)	2.458(4)	Y(1)–O(2)	2.233(4)
Y(1)–O(7)	2.506(4)	Y(1)–O(3)	2.228(4)	Y(1)–O(9)	2.494(4)
Y(1)–O(4)	2.228(4)	Y(1)–O(10)	2.462(4)	As(1)–O(1)	1.656(4)
As(3)–O(3)	1.660(4)	As(2)–O(2)	1.654(4)	As(4)–O(4)	1.655(4)
As–C	1.901(7)–1.922(6)				
Bond angles					
O(1)–Y(1)–O(4)	88.5(2)	O(1)–Y(1)–O(2)	90.4(2)	O(2)–Y(1)–O(3)	97.1(2)
O(9)–Y(1)–O(10)	51.5(1)	O(6)–Y(1)–O(7)	51.3(1)	Y(1)–O(3)–As(3)	156.1(2)
Y(1)–O(2)–As(2)	147.3(3)	Y(1)–O(1)–As(1)	164.5(3)		
O–As–C	106.8(3)–113.0(2)	Y(1)–O(4)–As(4)	160.6(2)		
C–As–C	107.0(3)–111.9(3)	O(3)–Y(1)–O(4)	93.3(2)		

ful. The combination of labile systems with low symmetry at La, and the quadrupolar ^{139}La nucleus ($I = 7/2$, 99.9%, $\Xi = 14.1$ MHz, $Q = 0.2 \times 10^{-28}$ m^2) produces fast relaxation and unobservably broad resonances.

2.4. Trimethylarsine oxide complexes

The reactions of Me_3AsO with the hydrated nitrates of Sc, Y or La in a $\geq 6{:}1$ mol ratio in cold ethanol produced $[M(Me_3AsO)_6](NO_3)_3$ (M = Sc, Y or La). The complexes are insoluble in chlorocarbons, ethanol or acetone, but dissolve in nitromethane with partial decomposition. The CsI disc IR spectra of all three complexes are very similar and in addition to strong and broad features in the range 930–860 cm^{-1} which can be assigned to methyl rocking modes and the ν(AsO) of the ligand, there are strong features at 1360(br) (ν_3) and 835 (ν_2) cm^{-1} attributable to ionic nitrate groups. The structures of $[M(Me_3AsO)_6](NO_3)_3$ (M = Sc or Y) were established by X-ray studies and the very similar IR spectrum is strong evidence that the La complex also has a six-coordinate metal centre. The $[M(Me_3AsO)_6]^{3+}$ represent the first structurally characterised homoleptic examples in our studies of coordination by arsine or phosphine oxides (Figs. 5 and 6, Table 5). The Y–O distances are similar to the triphenylarsine oxide complexes but the Y–O–As(Me$_3$) angles (130.0(5)–149.1(6)°) are smaller than all but one of the M–O–As(Ph$_3$) angles reported here. The Sc complex conforms to the same pattern. Crystal growing attempts using $[La(Me_3AsO)_6](NO_3)_3$ gave a few crystals identified as the decomposition product $[La(Me_3AsO)_4(NO_3)_3]$ containing nine-coordinate La with two bidentate (η^2) NO_3 and one monodentate (η^1) NO_3 groups but the data were of poor quality and the structure did not refine satisfactorily.[2] In solution in nitromethane the $[M(Me_3AsO)_6](NO_3)_3$ complexes partially decompose having molar conductances (10^{-3} mol dm^{-3} solutions) in the range typical of 2:1 electrolytes, which increase significantly (to values indicative of 3:1 electrolytes) on addition of excess Me_3AsO. The ^{45}Sc NMR spectrum of $[Sc(Me_3AsO)_6](NO_3)_3$ in $MeNO_2$ was a very broad resonance at approximately δ 58 on which was superimposed a sharp feature at δ 56.0. Addition of excess Me_3AsO completely converted the species to that with δ 56.0, the sharp resonance showing the quadrupolar ^{45}Sc nucleus was in a cubic environment, i.e. $[Sc(Me_3AsO)_6]^{3+}$; the broader resonance and lower conductance indicating that $[Sc(Me_3AsO)_{6-n}(NO_3)_n]^{(3-n)+}$ form in the absence of excess Me_3AsO, very similar behaviour to the $Sc(NO_3)_3/Me_3PO$ system [1]. The $[Y(Me_3AsO)_6](NO_3)_3$ behaves similarly with a sharp ^{89}Y NMR resonance (at 200 K in $EtNO_2$ solution)[3] at δ 133 observed in the presence of excess ligand

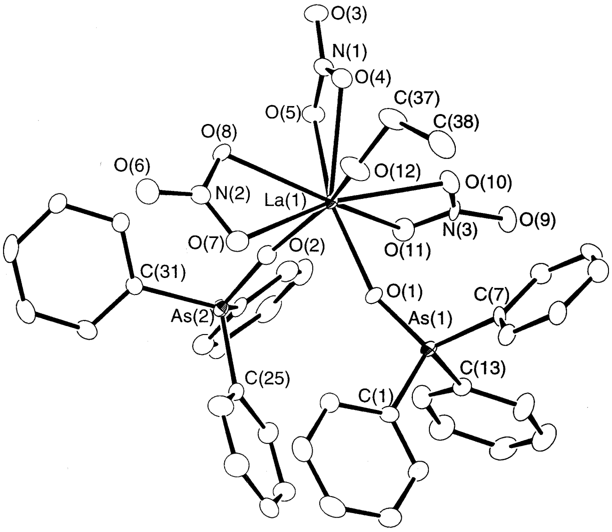

Fig. 3. The structure of $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

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[2] $[La(Me_3AsO)_4(NO_3)_3]$ crystal data: monoclinic, $a = 10.278(3)$, $b = 12.034(4)$, $c = 12.030(2)$ Å, $\beta = 97.42(2)°$, $U = 1475.4(6)$ Å^3. Space group $P2_1$ (no. 4), $Z = 2$, $T = 150$ K. Crystals grown from $La(Me_3AsO)_6(NO_3)_3$ complex by vapour diffusion ($MeNO_2/Et_2O$). $R1 = 0.14$ for 2381 $F_o > 4\sigma(F_o)$ and 237 parameters.

[3] $MeNO_2$ (m.p. −29 °C) is unsuitable for low temperature studies and was replaced by $EtNO_2$ (m.p. −95 °C), which is unlikely to change the chemistry.

Table 3
Selected bond lengths (Å) and bond angles (°) for $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$

Bond lengths					
La(1)–O(1)	2.347(7)	La(1)–O(8)	2.592(7)	La(1)–O(2)	2.324(8)
La(1)–O(10)	2.581(7)	La(1)–O(4)	2.640(7)	La(1)–O(11)	2.615(8)
La(1)–O(5)	2.608(8)	La(1)–O(12)	2.552(7)	La(1)–O(7)	2.664(7)
As–C	1.896(12)–1.932(9)	As(1)–O(1)	1.670(7)	As(2)–O(2)	1.671(7)
Bond angles					
O(1)–La(1)–O(2)	92.0(3)	O(1)–La(1)–O(12)	80.1(3)	O(4)–La(1)–O(5)	48.4(2)
O(10)–La(1)–O(11)	49.5(3)	O(7)–La(1)–O(8)	48.7(2)	O(2)–La(1)–O(12)	149.5(3)
La(1)–O(1)–As(1)	159.2(4)	La(1)–O(2)–As(2)	164.0(5)		
O–As–C	107.5(4)–114.6(4)	C–As–C	106.9(4)–110.6(5)		

and assignable to $[Y(Me_3AsO)_6]^{3+}$, whereas in the absence of added ligand, a broader feature at δ 112 is present probably due to exchanging $[Y(Me_3AsO)_{6-n}(NO_3)_n]^{(3-n)+}$ species. The conductance behaviour of $[La(Me_3AsO)_6](NO_3)_3$ in $MeNO_2$ with added Me_3AsO was similar to that of the lighter analogues, although even in the presence of excess Me_3AsO we were unable to observe a ^{139}La NMR resonance, due either to fast exchange or to the presence of lower symmetry species in solution, either of which would promote fast quadrupolar relaxation. The $[La(Me_3AsO)_4(NO_3)_3]$ complex has not been prepared in bulk, but from $La(NO_3)_3 \cdot 6H_2O$ and Me_3AsO in a 1:2 molar ratio in boiling ethanol, we obtained a species with a 1:2 La:Me_3AsO stoichiometry, which analysis and the IR and ^1H NMR spectra indicated was $[La(Me_3AsO)_2(H_2O)(NO_3)_3]$, presumably containing nine-coordinate lanthanum. The presence of ligated H_2O rather than EtOH was unexpected, but has been seen before in $[Y(Me_3PO)_2(H_2O)(NO_3)_3]$ [1].

2.5. Comparison of R_3PO and R_3AsO

The data in the present paper and that in our previous study [1,2] of R_3PO (R = Me or Ph) complexes of these d^0 metals allow comparison of the ligating properties of the pnictogen oxides. Firstly it is apparent from the stoichiometry of the isolated complexes and from the solution speciation data from NMR studies, that R_3AsO competes with nitrate more successfully for these oxophilic metals than does R_3PO. Consider for example $[Sc(Ph_3PO)_2(NO_3)_3]$ versus $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$ as the preferred complexes, or the great preference for $[Y(Ph_3AsO)_4(NO_3)_2]NO_3$ (and our failure to isolate a tris complex) whereas $[Y(Ph_3PO)_3(NO_3)_3]$ is favoured in the Ph_3PO system and $[Y(Ph_3PO)_4(NO_3)_2]NO_3$ isolated only with a large excess of ligand. Similarly with Me_3AsO, yttrium forms $[Y(Me_3AsO)_6](NO_3)_3$ whereas $[Y(Me_3PO)_4(NO_3)_2]NO_3$ is the species with the highest Me_3PO/Y ratio in the phosphine oxide system. On electronic grounds the higher dipole moments of the arsine oxides compared to the phosphine oxides (Ph_3PO, 4.51; Ph_3AsO, 5.50, Me_3PO, 4.39, Me_3AsO, 5.12 D [10,11]) should result in better donation from the electron richer oxygen atoms of the former. In an attempt to relate these observations to the observed geometry we have examined Ln–O distances in four pairs of compounds where both the phosphine- and arsine oxides are known $[SmL_2(EtOH)(NO_3)_3]$; $[ML_3(NO_3)_3]$ (M = Ce or Eu); $[LaL_4(NO_3)_2]^+$. L = Ph_3XO (X = P or As)] [7,9,12,13]. The species are analogous although not always crystallographically isomorphous. The pair $[La(Ph_3XO)_4(NO_3)_2]^+$ (X = P or As) provides the clearest single example but is supported by the others. In general it appears that the M–O(P) is larger than M–O(As) for M = Sc, Y or Ln species, consistent with stronger binding in the arsine oxide complexes.

The crystal structures of triphenylarsine oxide [14] and a monohydrate [15] have been reported and an electron diffraction study of trimethylarsine oxide is

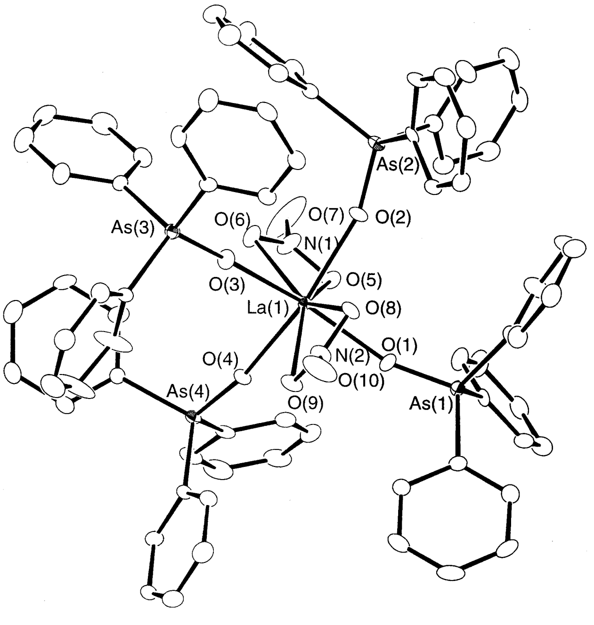

Fig. 4. The structure of the cation in $[La(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 2Me_2CO$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Table 4
Selected bond lengths (Å) and bond angles (°) for $[La(Ph_3AsO)_4(NO_3)_2]NO_3{\cdot}2Me_2CO$

Bond lengths					
La(1)–O(1)	2.361(5)	La(1)–O(5)	2.635(5)	La(1)–O(2)	2.343(4)
La(1)–O(6)	2.641(5)	La(1)–O(3)	2.340(5)	La(1)–O(8)	2.651(5)
La(1)–O(4)	2.347(4)	La(1)–O(9)	2.656(5)	As(1)–O(1)	1.660(5)
As(3)–O(3)	1.658(5)	As(2)–O(2)	1.661(4)	As(4)–O(4)	1.660(4)
As–C	1.907(7)–1.921(7)	$N–O_t$	1.206(8), 1.218(8)	$N–O_c$	1.250(8)–1.270(7)
Bond angles					
O(1)–La(1)–O(2)	94.9(2)	La(1)–O(1)–As(1)	160.0(3)	O(1)–La(1)–O(4)	89.3(2)
La(1)–O(2)–As(2)	162.8(3)	O(2)–La(1)–O(3)	89.8(2)	La(1)–O(3)–As(3)	175.7(3)
O(3)–La(1)–O(4)	92.3(2)	La(1)–O(4)–As(4)	167.5(3)	O(5)–La(1)–O(6)	48.1(2)
O(8)–La(1)–O(9)	48.1(1)	O–As–C	107.0(3)–112.8(3)		

available [16]. As expected there are no major geometry changes on complexation. The steric requirements of the arsine oxide ligands and the phosphorus analogues are complex with considerable variation in the M–O–P/As angle. From our (small) sample it appears that the trimethyl derivatives of both pnictogens have smaller angles (Y–O–As 130–149°; Y–O–P 140–150°) than the triphenyl derivatives (approximately 150° to nearly linear).

3. Conclusions

The results represent the first study of the solution behaviour of the arsine oxide ligands with Sc(III), Y(III) and Ln(III) and including the first series of crystallographic studies. We have shown that R_3AsO has a greater affinity for these metals compared to R_3PO resulting in higher ratio R_3AsO:M species being formed.

4. Experimental

Multinuclear NMR spectra were obtained on a Bruker DPX400 at 97.16 MHz (^{45}Sc), 19.60 MHz (^{89}Y), or 100.6 MHz (^{13}C) using TEMPO as a relaxation agent for the ^{89}Y systems, and referenced as described previously [1]. Other physical measurements were made as before [1]. Ph_3AsO, $Y(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$ (Aldrich) and $Sc(NO_3)_3{\cdot}5H_2O$ (Strem) were used as received. Me_3AsO was made by H_2O_2 oxidation of Me_3As in diethyl ether, and purified by sublimation in vacuo [17]. Me_3AsO ^1H NMR (300 K, $CDCl_3$): δ 1.68(s), $^{13}C\{^1H\}$ NMR (300 K, $CDCl_3$): 16.7(s).

4.1. *[Y(Ph₃AsO)₂(EtOH)(NO₃)₃]*

A solution of $Y(NO_3)_3{\cdot}6H_2O$ (0.38 g, 1.0 mmol) in boiling ethanol (10 cm^3) was added to a solution of Ph_3AsO (0.64 g, 2.0 mmol) in ethanol (15 cm^3), the solution allowed to cool, and then refrigerated for 24 h. The white solid was filtered off and dried in vacuo. Yield 0.34 g, 37%. *Anal.* Found: C, 46.8; H, 3.9; N, 4.3. Calc. for $C_{38}H_{36}As_2N_3O_{12}Y$: C, 47.3; H, 3.8; N, 4.4%. IR (CsI disc, cm^{-1}): 3420br, 3065w, 2989w, 1494s, 1463s, 1441s, 1323s, 1090s, 1045m, 1036m, 999m, 933s, 910s, 877m, 818m, 745s, 691s, 479s, 459m, 373s, 359s. ^1H NMR (300 K, $CDCl_3$): 7.4–7.6(m), 3.7(q, $J=7$ Hz), 1.17(t, $J=7$ Hz). ^{89}Y NMR (300 K, $CH_2Cl_2/CDCl_3$): not observed (200 K) +0.5(br), 21.0(w). Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 2 Ω^{-1} cm^2 mol^{-1}.

4.2. *[Y(Ph₃AsO)₄(NO₃)₂]NO₃·Me₂CO*

A solution of $Y(NO_3)_3{\cdot}6H_2O$ (0.38 g, 1.0 mmol) in acetone (10 cm^3) was added to a solution of Ph_3AsO (0.97 g, 3.0 mmol) in boiling acetone (5 cm^3), the solution was allowed to cool, and then refrigerated for 24 h. The white crystals were filtered off and dried in vacuo. Yield 0.58 g, 35%. *Anal.* Found: C, 54.3; H, 3.8;

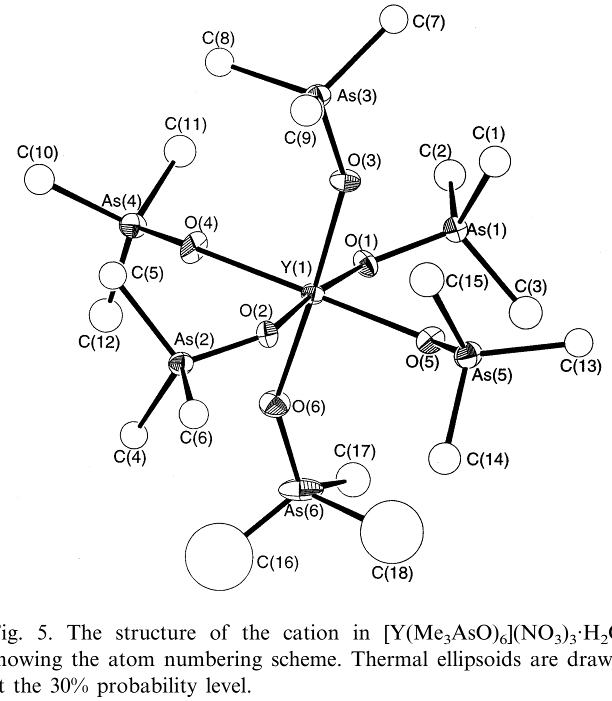

Fig. 5. The structure of the cation in $[Y(Me_3AsO)_6](NO_3)_3{\cdot}H_2O$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

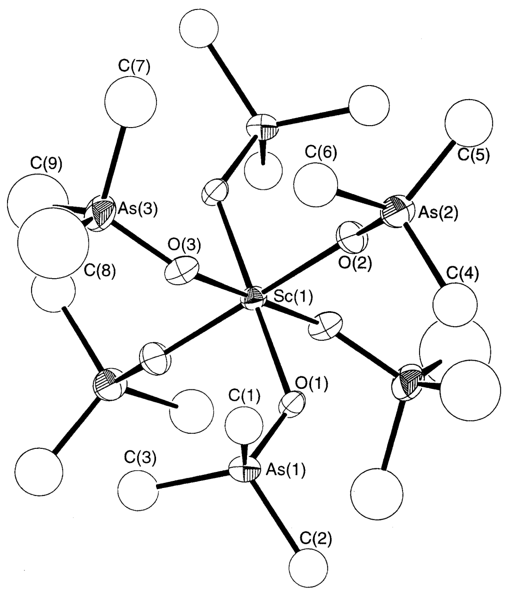

Fig. 6. The structure of the cation in $[Sc(Me_3AsO)_6](NO_3)_3$ showing the atom numbering scheme. The Sc is on a centre of symmetry. Thermal ellipsoids are drawn at the 30% probability level.

N, 2.8. Calc. for $C_{75}H_{66}As_4N_3O_{14}Y$: C, 55.3; H, 4.1; N, 3.0%. IR (CsI disc, cm^{-1}): 3050w, 1706m, 1465s, 1441s, 1362s, 1314s, 1227w, 1186m, 1163w, 1089m, 1038w, 999w, 914br,s, 832m, 821m, 744s, 692s, 479s, 458s, 357s. ^1H NMR (300 K, $CDCl_3$): 7.2–7.7 (m), 2.2(s). ^{89}Y NMR (200 K, $CDCl_3/CH_2Cl_2$): +21. Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 28 Ω^{-1} cm^2 mol^{-1}.

4.3. $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$

A solution of $Sc(NO_3)_3\cdot 5H_2O$ (0.23 g, 1.0 mmol) in boiling ethanol (10 cm^3) was added to a solution of Ph_3AsO (0.97 g, 3.0 mmol) in ethanol (10 cm^3), and stirred for 1 h. The solution was refrigerated for 24 h, and the crystalline solid filtered off, and dried in vacuo. Yield 0.50 g, 42%. *Anal.* Found: C, 53.4; H, 3.7; N, 3.3. Calc. for $C_{54}H_{45}As_3N_3O_{12}Sc$: C, 54.1; H, 3.8; N, 3.5%. IR (CsI disc, cm^{-1}): 3065w, 1521s, 1485m, 1441s, 1362s, 1298m, 1163w, 1089s, 1026m, 999m, 948w, 899br,s, 832w, 812m, 743s, 691s, 478s, 418m, 368s, 357s. ^1H NMR (300 K, $CDCl_3$): 7.4–7.8m. ^{45}Sc NMR (300 K, $CH_2Cl_2/CDCl_3$): 31.9 ($W_{1/2}$, 5200 Hz). Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 27 Ω^{-1} cm^2 mol^{-1}.

4.4. $[Sc(Ph_3AsO)_2(NO_3)_3]$

A solution of $Sc(NO_3)_3\cdot 5H_2O$ (0.23 g, 1.0 mmol) in warm acetone (10 cm^3) was added to a solution of Ph_3AsO (0.32 g, 1.0 mmol) in acetone (10 cm^3), when a white solid formed but redissolved. The solution was evaporated to dryness in vacuo, the residue washed with diethyl ether (20 cm^3), and then extracted with CH_2Cl_2 (10 cm^3) and the solution filtered. The filtrate was evaporated to dryness. Yield: 0.08 g. Not obtained analytically pure, see text. IR (CsI disc, cm^{-1}): 3443br*, 1636m*, 1520m, 1441m, 1357s*, 1186w, 1089m, 1027m, 999m, 898br,s, 834w*, 813m, 743s, 692s, 479m, 413m, 365m, 284m (* attributed to $Sc(NO_3)_3\cdot nH_2O$ impurity). ^1H NMR (300 K, $CDCl_3$): 7.4–7.8m. ^{45}Sc NMR (300 K, $CH_2Cl_2/CDCl_3$): 14.0 ($W_{1/2}$, 3500 Hz). Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 8 Ω^{-1} cm^2 mol^{-1}.

4.5. $[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$

A solution of $La(NO_3)_3\cdot 6H_2O$ (0.43 g, 1.0 mmol) in boiling ethanol (20 cm^3) was added to a solution of

Table 5
Selected bond lengths (Å) and bond angles (°) for $[Y(Me_3AsO)_6](NO_3)_3\cdot H_2O$ and $[Sc(Me_3AsO)_6](NO_3)_3$

(a) $[Y(Me_3AsO)_6](NO_3)_3\cdot H_2O$					
Bond lengths					
Y(1)–O(1)	2.242(10)	Y(1)–O(4)	2.221(9)	Y(1)–O(2)	2.248(10)
Y(1)–O(5)	2.253(9)	Y(1)–O(3)	2.202(10)	Y(1)–O(6)	2.209(11)
As(n)–O(n)	1.65(1)–1.70(1)	As–C	1.82(4)–2.04(4)		
Bond angles					
Y(1)–O(1)–As(1)	131.3(5)	Y(1)–O(4)–As(4)	142.3(6)	Y(1)–O(2)–As(2)	134.0(5)
Y(1)–O(5)–As(5)	130.0(5)	Y(1)–O(3)–As(3)	149.1(6)	Y(1)–O(6)–As(6)	147.1(6)
O–Y(1)–O (approximately 90°)	86.7(4)–96.3(4)	O–As–C	108.0(6)–113.4(7)		
(b) $[Sc(Me_3AsO)_6](NO_3)_3$					
Bond lengths					
Sc(1)–O(1)	2.100(8)	Sc(1)–O(2)	2.064(8)	Sc(1)–O(3)	2.097(8)
As(1)–O(1)	1.662(8)	As(2)–O(2)	1.649(9)	As(3)–O(3)	1.650(8)
As–C	1.86(4)–1.99(2)				
Bond angles					
Sc(1)–O(1)–As(1)	132.6(4)	Sc(1)–O(2)–As(2)	144.3(6)	Sc(1)–O(3)–As(3)	134.3(5)
O–Sc(1)–O (approximately 90°)	88.5(3)–91.5(3)	O–As–C	107.2(6)–112.1(6)		
C–As–C	99(1)–123(2)				

Ph_3AsO (0.64 g, 2.0 mmol) in ethanol (10 cm^3), the solution evaporated to 10 cm^3, and then refrigerated for 24 h. The white solid was filtered off and dried in vacuo. Yield: 0.56 g, 58%. *Anal.* Found: C, 45.6; H, 3.5; N, 3.7. Calc. for $C_{38}H_{36}As_2LaN_3O_{12}$: C, 45.0; H, 3.6; N, 4.1%. IR (CsI disc, cm^{-1}): 3400br, 1477s, 1307s, 1186w, 1089s, 1032m, 999m, 908s, 888s, 820m, 743s, 691s, 478s, 457m, 368s, 361s. ^1H NMR (300 K, $CDCl_3$): 7.3–7.8(m), 3.7(q, $J = 7$ Hz), 1.20(t, $J = 7$ Hz). Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 4 Ω^{-1} cm^2 mol^{-1}.

4.6. $[La(Ph_3AsO)_3(NO_3)_3]\cdot Me_2CO$

A solution of $La(NO_3)_3\cdot 6H_2O$ (0.22 g, 0.50 mmol) in boiling acetone (10 cm^3) was added to a solution of Ph_3AsO (0.48 g, 1.5 mmol) in acetone (10 cm^3), the solution was evaporated to 10 cm^3, then refrigerated for 24 h. The colourless crystals were filtered off and dried in vacuo. Yield: 0.55 g, 85%. *Anal.* Found: C, 50.4; H, 3.7; N, 2.6. Calc. for $C_{57}H_{51}As_3LaN_3O_{13}$: C, 50.7; H, 3.8; N, 3.1%. IR (CsI disc, cm^{-1}): 3054w, 1702w, 1486s, 1454s, 1442s, 1363s, 1304s, 1226w, 1185w, 1163w, 1089m, 1070w, 1033m, 999w, 924w, 890s, 821m, 747s, 693s, 533m, 478s, 359s. ^1H NMR (300 K, $CDCl_3$): 7.2–7.65(m), 2.15(s). Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 4 Ω^{-1} cm^2 mol^{-1}.

4.7. $[La(Ph_3AsO)_4(NO_3)_2]NO_3\cdot Me_2CO$

A solution of $La(NO_3)_3\cdot 6H_2O$ (0.43 g, 1.0 mmol) in boiling acetone (10 cm^3) was added to a solution of Ph_3AsO (1.9 g, 6.0 mmol) in acetone (30 cm^3), and the mixture left at room temperature for 1 d. Colourless crystals formed. Yield: 1.23 g, 73%. *Anal.* Found: C, 53.2; H, 4.2; N, 2.5. Calc. for $C_{75}H_{66}As_4LaN_3O_{14}$: C, 53.6; H, 3.8; N, 2.6%. IR (CsI disc, cm^{-1}): 3059w, 1707m, 1442s, 1361s, 1313s, 1228m, 1189m, 1089s, 1050w, 1036w, 999m, 925sh, 891s, 836w, 820m, 746s, 693s, 614w, 479s, 366s. ^1H NMR (300 K, $CDCl_3$): 7.2–7.7 (m), 2.15(s). Λ_M (CH_2Cl_2, 10^{-3} mol dm^{-3}) 21 Ω^{-1} cm^2 mol^{-1}.

4.8. $[Sc(Me_3AsO)_6](NO_3)_3$

Scandium nitrate hydrate (0.17 g, 0.75 mmol) and Me_3AsO (0.61 g, 4.5 mmol) were dissolved separately in ice-cold ethanol (10 cm^3), the solutions mixed and stirred for 1 h. The solution was concentrated in vacuo to 10 cm^3 and refrigerated overnight. The white solid was filtered off and dried in vacuo. Yield: 0.18 g, 38%. *Anal.* Found: C, 20.3; H, 5.1; N, 4.6. Calc. for $C_{18}H_{54}As_6N_3O_{15}Sc$: C, 20.7; H, 5.2; N, 4.0%. IR (CsI disc, cm^{-1}): 3010w, 1648w, 1364s, 1269m, 1111m, 1048w, 925s, 873vs, 848s, 836sh, 648s, 396s, 303m. ^1H NMR (300 K, CD_3NO_2): 2.3(s). $^{13}C\{^1H\}$ NMR (300 K, $MeNO_2/CD_3NO_2$): 15.0(s). ^{45}Sc NMR (300 K, $MeNO_2/CD_3NO_2$): 58.0 ($W_{1/2}$, 1200 Hz); with excess Me_3AsO 56.0 ($W_{1/2}$, 80 Hz). Λ_M ($MeNO_2$, 10^{-3} mol dm^{-3}) 157 Ω^{-1} cm^2 mol^{-1}; with excess Me_3AsO $\Lambda_M = 220$.

4.9. $[Y(Me_3AsO)_6](NO_3)_3$

Prepared as above from $Y(NO_3)_3\cdot 6H_2O$ (0.19 g, 0.5 mmol) and Me_3AsO (0.408 g, 3.0 mmol). Yield: 0.29 g, 53%. *Anal.* Found: C, 19.6; H, 4.9; N, 3.9. Calc. for $C_{18}H_{54}As_6N_3O_{15}Y$: C, 19.8; H, 5.0; N, 3.9%). IR (CsI disc, cm^{-1}): 3010w, 1642w, 1358s, 1270m, 1095m, 926s, 877vs, 836s, 650s, 353s, 288m. ^1H NMR (300 K, CD_3NO_2): 2.55 (s). $^{13}C\{^1H\}$ NMR (300 K, $MeNO_2/CD_3NO_2$): 15.0(s). ^{89}Y NMR (200 K, $EtNO_2/CDCl_3$): 112(s); with excess Me_3AsO 133(s). Λ_M ($MeNO_2$, 10^{-3} mol dm^{-3}) 180 Ω^{-1} cm^2 mol^{-1}; with excess Me_3AsO $\Lambda_M = 240$.

4.10. $[La(Me_3AsO)_6](NO_3)_3$

A boiling solution of $La(NO_3)_3\cdot 6H_2O$ (0.14 g, 0.33 mmol) in acetone (10 cm^3) was added to a solution of Me_3AsO (0.27 g, 2.0 mmol) in acetone (10 cm^3). The solution was refrigerated overnight and the white solid produced, filtered off and dried in vacuo. Yield: 0.21 g, 55%. *Anal.* Found: C, 19.2; H, 4.9; N, 4.2. Calc. for $C_{18}H_{54}As_6LaN_3O_{15}$: C, 19.0; H, 4.8; N, 3.7%. IR (CsI disc, cm^{-1}): 2936w, 1653w, 1359s, 1269w, 1091m, 987w, 924s, 864vs, 847s, 836sh, 647s, 317s, 279m. ^1H NMR (300 K, CD_3NO_2): 2.3 (s). $^{13}C\{^1H\}$ NMR (200 K, $EtNO_2/CDCl_3$): 15.0 (s). Λ_M ($MeNO_2$, 10^{-3} mol dm^{-3}) 121 Ω^{-1} cm^2 mol^{-1}; with excess Me_3AsO $\Lambda_M = 285$.

4.11. $[La(Me_3AsO)_2(H_2O)(NO_3)_3]$

A solution of $La(NO_3)_3\cdot 6H_2O$ (0.43 g, 1.0 mmol) in boiling ethanol (10 cm^3) was treated with Me_3AsO (0.27 g, 2.0 mmol) in ethanol (10 cm^3). The mixture was refrigerated overnight and the white solid which separated, filtered off and dried in vacuo. Yield: 0.12 g, 20%. *Anal.* Found: C, 12.4; H, 3.6; N, 6.4. Calc. for $C_6H_{20}As_2LaN_3O_{12}$: C, 11.7; H, 3.3; N, 6.8%. IR (CsI disc, cm^{-1}): 3400br, 3095w, 1620m, 1455m, 1407m, 1358m, 1322w, 1287s, 1266w, 1040m, 924m, 875s, 860s, 850m, 822w, 736m, 644m, 595w, 323s, 285sh. ^1H NMR (300 K, CD_3NO_2): 2.2 (s), 2.6 (s).

4.12. X-ray crystallographic studies

Selected crystallographic details of the six compounds studied are given in Table 6. Crystals which were either small or of modest quality were obtained by vapour diffusion using the liquids CH_2Cl_2/Et_2O or $MeNO_2/Et_2O$ (Me_3AsO complexes) with the sealed containers being held in the refrigerator. Data were

Table 6
Crystallographic data [a]

	$[Sc(Ph_3AsO)_3(NO_3)_2]NO_3 \cdot H_2O$	$[Y(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 1/2H_2O$	$[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$	$[La(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 2Me_2CO$	$[Y(Me_3AsO)_6](NO_3)_3 \cdot H_2O$	$[Sc(Me_3AsO)_6](NO_3)_3$
Formula	$C_{54}H_{47}As_3N_3O_{13}Sc$	$C_{72}H_{61}As_4N_3O_{13.5}Y$	$C_{38}H_{36}As_2LaN_3O_{12}$	$C_{78}H_{72}As_4LaN_3O_{15}$	$C_{18}H_{56}As_6N_3O_{16}Y$	$C_{18}H_{54}As_6N_3O_{15}Sc$
Formula weight	1215.67	1572.83	1015.45	1730.03	1109.10	1047.12
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	Pn (no. 7)	$P2_1/n$ (no. 14)
Unit cell dimensions						
a (Å)	10.9069(2)	13.2731(2)	17.239(3)	14.8068(1)	11.1136(5)	10.9800(4)
b (Å)	12.7505(4)	14.4205(2)	10.904(2)	15.6295(1)	11.4594(5)	11.2665(4)
c (Å)	22.2281(7)	20.1717(5)	21.907(4)	18.3401(1)	15.9320(9)	15.7688(7)
α (°)	84.792(2)	104.293(7)	90	65.9821(6)	90	90
β (°)	81.577(2)	96.302(9)	104.32(2)	80.3764(5)	91.088(2)	90.833(2)
γ (°)	73.000(1)	112.06(1)	90	86.7683(4)	90	90
U (Å^3)	2920.5(1)	3378.2(1)	3990.0(12)	3821.96(5)	2028.7(2)	1950.5(1)
Z	2	2	4	2	2	2
μ(Mo Kα) (cm^{-1})	18.73	28.74	27.82	23.41	63.45	52.98
Unique reflections	10 179 ($R_{int} = 0.038$)	11 685 ($R_{int} = 0.064$)	6940 ($R_{int} = 0.099$)	17165 ($R_{int} = 0.079$)	6448 ($R_{int} = 0.088$)	3421 ($R_{int} = 0.085$)
No. of parameters/restraints	642/0	832/6	506/0	910/0	244/14	126/13
R [b] ($I > n\sigma(I)$)	0.066 ($n = 2$, 6562 refls)	0.057 ($n = 2$, 9012 refls)	0.081 ($n = 2$, 5347 refls)	0.056 ($n = 3$, 10440 refls)	0.064 ($n = 2$, 4413 refls)	0.091 ($n = 2$, 2040 refls)
wR_2 [b] (all data)	0.220	0.158	0.271		0.161	0.275

[a] $\lambda = 0.71073$ Å, $T = 150$ K.

[b] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

recorded on either a Rigaku AFC7S or Nonius CCD diffractometer, the latter usually used with the smaller crystals. Psi-scan (Rigaku) or SORTAV [18] (Nonius) absorption corrections were used. Structure solution was routine [19,20] with refinement being carried out using SHELXL-97 [21] or the TEXSAN package [22]. The compound $[Y(Me_3AsO)_6](NO_3)_3 \cdot H_2O$ is described in the space group *Pn* rather than the centrosymmetric space group *P*2/*n*. The intensity statistics favoured *Pn* and more importantly attempts to solve the structure in *P*2/*n* or transform the coordinates of *Pn* into *P*2/*n* did not yield a satisfactory structure. Refinement was as a racemic twin and restraints (N–O,O···O) on two nitrate anions were used. $La(Ph_3AsO)_4(NO_3)_2]NO_3$ was isolated as the acetone solvate from the synthesis. The anions in $[Y(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 1/2H_2O$ are described as one disordered group with the N located on a centre of symmetry and a second general (two-fold) NO_3 with a site occupation of 0.5. E.s.d. values of the cell dimensions are taken from the diffractometer software recognising that for the CCD data the values are unrealistically small [23].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 160950 ($[La(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 2Me_2CO$), 160951 ($[La(Ph_3AsO)_2(EtOH)(NO_3)_3]$), 160952 ($[Sc(Me_3AsO)_6](NO_3)_3$), 160953 ($[Sc(Ph_3AsO)_3(NO_3)_2]NO_3 \cdot H_2O$), 160954 ($[Y(Ph_3AsO)_4(NO_3)_2]NO_3 \cdot 1/2H_2O$) and 160955 ($[Y(Me_3AsO)_6](NO_3)_3 \cdot H_2O$). 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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