Tertiary phosphine oxide complexes of lanthanide diiodides and dibromides

Robert D. Bannister, William Levason *, Mark E. Light, Gillian Reid

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

ABSTRACT

The reaction of OPR_3 (R = Me, Ph) with YbI_2, EuI_2 and $EuBr_2$ in rigorously anhydrous MeCN under N_2 produces the divalent lanthanide complexes $[LnX_2(OPR_3)_4]$ (Ln = Yb, Eu, X = I; Ln = Eu, X = Br) in moderate to good yield, whilst $[SmI_2(OPR_3)_4]$ were obtained from SmI_2 and OPR_3 in dry, degassed thf. These are the first examples involving divalent lanthanide ions and the complexes have been characterised by micro-analysis, IR, UV–Vis and $^{31}P\{^1H\}$ NMR spectroscopy. The X-ray crystal structure of $[EuI_2(OPPh_3)_4]\cdot MeCN$ confirmed the six-coordinate Eu(II) species with a *cis*-octahedral geometry, which IR spectroscopy suggests is present in all of the $OPPh_3$ complexes. In contrast the $[LnX_2(OPMe_3)_4]$ complexes appear to be *trans* isomers. The $OPPh_3$ complexes are readily oxidised by dry O_2 or I_2, yielding the corresponding trivalent cations, $[LnX_2(OPPh_3)_4]^+$; a crystal structure of the product formed by oxidation of $[EuI_2(OPPh_3)_4]$ in MeCN solution confirms this to be $[EuI_2(OPPh_3)_4]I_3\cdot 1.5MeCN$, containing a *trans*-octahedral cation.

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1. Introduction

While the overwhelming majority of lanthanide coordination chemistry involves the Ln(III) state [1–3], the last twenty five years have seen a steady growth of complexes of divalent lanthanides, mostly based upon Eu, Yb and Sm, but with a small number of complexes of Dy, Nd and Tm also characterised [4,5]. In parallel, an organometallic chemistry containing low valent lanthanide centres has been developed, and EuI_2 and SmI_2 are valuable one electron reductants and cross-coupling reagents in organic chemistry [6–8]. Tertiary phosphine oxides (OPR_3) have proved to be popular ligands for trivalent lanthanides, and many examples with a range of R groups are known as oxo-anion salts (nitrate, triflate, etc.), diketonates and halides, as described in a very recent comprehensive review [9]. Taking $OPPh_3$ (the most thoroughly investigated ligand) as an example, all the $LnCl_3$ complexes are six-coordinate, with both *mer*-$[LnCl_3(OPR_3)_3]$ and *trans*-$[LnCl_2(OPR_3)_4]Cl$ characterised for all (except Pm). The former type is preferred for the early lanthanides, with the cations becoming more favoured later in the series [10], whilst the $[LnX_2(OPPh_3)_4]X$ (X = Br, I) are favoured for the heavier halides [11,12]. There are also some $[LnCl(OPPh_3)_5]^{2+}$ cations formed using halide abstractors and one series of homoleptic cations in the form $[Ln(OPMe_3)_6][PF_6]_3$ [13]. No examples of divalent lanthanide phosphine oxide complexes have been reported [9], although hexamethylphosphoramide

$((Me_3N)_3PO$, HMPA) complexes, $[Yb(HMPA)_4(thf)_2]I_2$, $[Sm(HMPA)_6]I_2$ and $[SmI_2(HMPA)_4]$ have been isolated from reaction of the appropriate LnI_2 with HMPA in thf solution [14].

Here we report the preparations and properties of complexes of $OPPh_3$ and $OPMe_3$ with the divalent LnI_2 (Ln = Yb, Eu and Sm) and $EuBr_2$.

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. UV–Vis spectra were recorded from sealed PTFE cell with silica window on neat samples, using the diffuse reflectance attachment, in a Perkin Elmer 750S spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker AV 400 spectrometer and are referenced to external 85% H_3PO_4. Microanalyses were undertaken by London Metropolitan University. Lanthanide dihalides, solvents and other reagents were obtained from Sigma–Aldrich and used as received. Trimethylphosphine oxide was dried by sublimation *in vacuo*, and triphenylphosphine oxide melted under vacuum before use. MeCN was dried by distillation from CaH_2 and thf from sodium benzophenone-ketyl. Syntheses were routinely carried out under a dry dinitrogen atmosphere, and all solids and spectroscopic samples were handled in a dry dinitrogen filled glove box. Since the complexes have limited stability in dilute solution, all NMR samples were freshly prepared immediately before recording data.

2.1. [YbI₂(OPPh₃)₄]

YbI₂ (0.05 g, 0.12 mmol) was dissolved in anhydrous MeCN (10 mL), a solution of OPPh₃ (0.13 g, 0.47 mmol) in MeCN (5 mL) added, and the mixture stirred from 20 min. during which the orange colour of the solution deepened. The solution was concentrated to a small volume when a bright yellow precipitate formed. This was filtered off, and dried *in vacuo* to yield a bright yellow powder. Yield 0.14 g, 79%. Required for $C_{72}H_{60}I_2O_4P_4Yb$ (1539.2): C, 56.13; H, 3.93. Found: C, 55.89; H, 3.77%. IR spectrum (Nujol mull/cm⁻¹): 1140 br s, 1085 m (PO). UV–Vis (diffuse reflectance/cm⁻¹): 27 320. $^{31}P\{^1H\}$ NMR (CD₃CN): δ = +36.1.

The MeCN solution of [YbI₂(OPPh₃)₄] exposed to air or O₂ resulted in rapid diminution of the $^{31}P\{^1H\}$ NMR resonance and development of a new resonance at δ = −39.0, assigned as a Yb (III) species, often with a weak feature at +29.6 ppm (OPPh₃). The same species was generated by addition of I₂ to an MeCN solution of the divalent complex.

2.2. [YbI₂(OPMe₃)₄]

Was made similarly from YbI₂ (0.05 g, 0.12 mmol) and OPMe₃ (0.043 g, 0.47 mmol) in MeCN. The product was a pale yellow powder. Yield 0.02 g, 21%. Required for $C_{12}H_{36}I_2O_4P_4Yb$ (795.0): C, 18.11; H, 4.56. Found: C, 18.05; H, 4.56%. IR spectrum (Nujol mull/cm⁻¹): 1112 br s (PO). $^{31}P\{^1H\}$ NMR (CD₃CN): δ = +50.9. Treatment of the CD₃CN solution with I₂ produced an orange-brown solution with δ ($^{31}P\{^1H\}$) = −13.9 and −25.0.

2.3. [EuI₂(OPPh₃)₄]

EuI₂ (0.05 g, 0.12 mmol) was dissolved in anhydrous MeCN (10 mL), a solution of OPPh₃ (0.14 g, 0.49 mmol) in MeCN (5 mL) added, and the pale yellow solution stirred from 20 min. The solution was concentrated to small volume when a yellow precipitate formed. This was filtered off and dried *in vacuo* to yield a yellow powder. Yield 0.12 g, 64%. Required for $C_{72}H_{60}EuI_2O_4P_4$ (1598.1): C, 56.91; H, 3.98. Found: C, 56.63; H, 4.11%. IR spectrum (Nujol mull/cm⁻¹): 1135 br s, 1082 m (PO). UV–Vis (diffuse reflectance/cm⁻¹): 26 900. $^{31}P\{^1H\}$ NMR (CD₃CN): not observed. An I₂ (or air) oxidised solution had $^{31}P\{^1H\}$ NMR (CD₃CN): δ = −125.0. Crystals were obtained from cooling an MeCN solution of the complex.

2.4. [EuI₂(OPMe₃)₄]

Was made similarly from EuI₂ (0.05 g, 0.12 mmol) and OPMe₃ (0.045 g, 0.49 mmol) in MeCN. The product was a pale yellow powder. Yield 0.06 g, 66%. Required for $C_{12}H_{36}EuI_2O_4P_4$ (773.9): C, 18.61; H, 4.69. Found: C, 18.41; H, 4.53%. IR spectrum (Nujol mull/cm⁻¹): 1142 (sh), 1104 br, s, (PO). UV–Vis (diffuse reflectance / cm⁻¹): 27 470(sh), 26 455. $^{31}P\{^1H\}$ NMR (CD₃CN): δ = not observed. $^{31}P\{^1H\}$ NMR spectrum of [EuI₂(OPMe₃)₄] after exposure to air (CD₃CN, 298 K): −8.0.

2.5. [EuBr₂(OPPh₃)₄]

EuBr₂ (0.05 g, 0.16 mmol) was dissolved in MeCN (10 mL) and a solution of OPPh₃ (0.18 g, 0.64 mmol) in MeCN (10 mL) added, and the mixture stirred overnight. On standing a yellow precipitate formed, and the solution was concentrated to small volume, and the precipitate filtered off and dried *in vacuo*. Yield 0.14 g, 62%. Required for $C_{72}H_{60}Br_2EuO_4P_4$ (1424.1): C, 60.67; H, 4.25. Found: C, 60.55; H, 4.43%. IR spectrum (Nujol mull/cm⁻¹): 1141 br s, 1084 m (PO). UV–Vis (diffuse reflectance/cm⁻¹): 26 040. $^{31}P\{^1H\}$ NMR (CD₃CN): not observed. An air-oxidised solution had $^{31}P\{^1H\}$ NMR (CD₃CN): δ = −97.0.

2.6. [EuBr₂(OPMe₃)₄]

Was made similarly from EuBr₂ (0.05 g, 0.16 mmol) and OPMe₃ (0.059 g, 0.64 mmol). The product was a pale yellow powder. Yield 0.07 g, 64%. Required for $C_{12}H_{36}Br_2EuO_4P_4$ (680.1): C, 21.19; H, 5.34. Found: C, 21.31; H, 5.45%. IR spectrum (Nujol mull/cm⁻¹): 1108 br s (PO). UV–Vis (diffuse reflectance / cm⁻¹): 25 840. $^{31}P\{^1H\}$ NMR (CD₃CN): not observed. $^{31}P\{^1H\}$ NMR spectrum of [EuBr₂(OPMe₃)₄] after addition of Br₂ (CD₃CN, 298 K): −7.7.

2.7. [SmI₂(OPPh₃)₄]

SmI₂ (0.05 g, 0.12 mmol) was dissolved in thf (10 mL) to form a dark blue solution. A solution of OPPh₃ (0.14 g, 0.49 mmol) in thf (5 mL) was then added. On stirring, the solution became dark purple and on concentration a dark blue solid was deposited, which was filtered off and dried *in vacuo*. Yield: 0.13 g, 71%. Required for $C_{72}H_{60}I_2O_4P_4Sm$ (1516.5): C, 56.97; H, 3.99. Found: C, 56.59; H, 4.24%. IR spectrum (Nujol mull/cm⁻¹): 1167 br s, 1071 s (PO). UV–Vis (diffuse reflectance/cm⁻¹): 26 730, 17 300. $^{31}P\{^1H\}$ NMR (d₈-thf): δ = +18.5. Treatment of the d₈-thf solution with I₂ produced a red brown solution with new resonances at δ = +35.6, +25.7 (Ph₃PO), together with a red-brown precipitate.

2.8. [SmI₂(OPMe₃)₄]

Was made similarly from SmI₂ (0.05 g, 0.12 mmol) and OPMe₃ (0.046 g, 0.49 mmol) in thf. The product was a pale blue powder. Yield 0.08 g, 84%. Required for $C_{12}H_{36}I_2O_4P_4Sm$ (772.3): C, 18.64; H, 4.70. Found: C, 18.53; H, 4.70%. IR spectrum (Nujol mull/cm⁻¹): 1103 br s, (PO). $^{31}P\{^1H\}$ NMR: insoluble in d₈-thf and CD₂Cl₂, decomposed by CD₃CN.

2.9. X-ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+detector mounted at the window of

Table 1
Crystallographic data.[a]

Compound	[EuI₂(OPPh₃)₄]· MeCN	[EuI₂(OPPh₃)₄] I₃·1.5MeCN
Formula	$C_{74}H_{63}EuI_2NO_4P_4$	$C_{150}H_{129}Eu_2I_{10}N_3O_8P_8$
M	2329.40	3922.23
Crystal system	monoclinic	triclinic
Space group (no.)	Pn (7)	$P\bar{1}$ (2)
a (Å)	13.6401(4)	13.6846(3)
b (Å)	17.5450(4)	20.1433(4)
c (Å)	14.0307(4)	28.4990(4)
α (°)	90	91.6050(10)
β (°)	95.185(3)	91.558(2)
γ (°)	90	109.605(2)
U (Å³)	3344.03(16)	7391.9(3)
Z	2	2
μ(Mo Kα) (mm⁻¹)	2.006	3.071
F(0 0 0)	1550	3780
Total number reflections	63 559	94 005
R_{int}	0.125	0.040
Unique reflections	13 995	28 933
No. of parameters, restraints	776, 710	1609, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.045, 0.100	0.050, 0.112
R_1, wR_2 (all data)	0.053, 0.103	0.063, 0.116

[a] Common data: T = 293 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°.
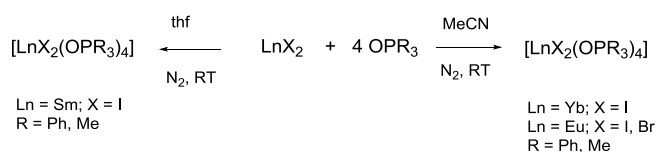[b] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma wFo^4]^{1/2}$.

an FR-E+SuperBright molybdenum ($\lambda = 0.71073$ Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinements were performed with either SHELX(S/L)97 or SHELX(S/L)2013 [15]. H atoms bonded to C were placed in calculated positions using the default C—H distance and refined using a riding model. The crystallographic data in cif format have been deposited as CCDC numbers 1853203 ([EuI$_2$(OPPh$_3$)$_4$]·MeCN) and 1853204 ([EuI$_2$(OPPh$_3$)$_4$] I$_3$·1.5MeCN).

3. Results and discussion

The reaction of YbI$_2$ with OPR$_3$ (R = Ph or Me) in anhydrous and deoxygenated MeCN produced yellow complexes [YbI$_2$(OPR$_3$)$_4$], while the corresponding reactions of EuI$_2$ gave pale yellow [EuI$_2$(OPR$_3$)$_4$] (Scheme 1). The [EuBr$_2$(OPR$_3$)$_4$] complexes were made similarly, although the reactions needed overnight stirring due to the poorer solubility of the EuBr$_2$ in MeCN. Attempts to isolate [EuCl$_2$(OPR$_3$)$_4$] were unsuccessful. The deep blue samarium complexes [SmI$_2$(OPR$_3$)$_4$] were made from thf solutions, since SmI$_2$ reacts with MeCN [8]. However, attempts to make analogous complexes of TmI$_2$ failed, the green solution of the diiodide in thf was immediately decolourised on addition of OPR$_3$. The isolated solid complexes decompose quite rapidly in air and samples were manipulated and stored under dinitrogen. Even in the glove box solid samples deteriorate over time and therefore all spectroscopic measurements were made on freshly prepared samples. There was no evidence for any other complexes in these systems even in the presence of excess phosphine oxide.

The solid [SmI$_2$(OPMe$_3$)$_4$] proved to be insoluble in thf and decomposed by MeCN, but the other complexes could be dissolved in MeCN ([EuX$_2$(OPR$_3$)$_4$], [YbI$_2$(OPR$_3$)$_4$]) or thf ([SmI$_2$(OPPh$_3$)$_4$]), although the solutions decomposed on standing either from adventitious ingress of air or internal redox chemistry. This low stability made collection of solution spectroscopic data challenging and growth of crystals suitable for X-ray analysis problematic. Many attempts to obtain crystals for X-ray crystallographic studies, either by slow evaporation of solutions of the pre-formed complexes or layering solutions of LnI$_2$ and OPR$_3$, failed or gave poor quality crystals, sometimes of Ln(III) products. However, crystals of [EuI$_2$(OPPh$_3$)$_4$]·MeCN were obtained from MeCN solution and the structure, which contains a *cis* octahedral molecule, is shown in Fig. 1. The *cis* geometry was unexpected – all trivalent lanthanide [LnX$_2$(OPR$_3$)$_4$]$^+$ cations are *trans* isomers [9–11]. The energy differences between *cis* and *trans* isomers may be small and adoption of a *cis* geometry may reflect solid state packing, or crystallisation of the least soluble form from an exchanging solution mixture. Generally, the solution NMR data obtained from LnX$_3$-OPR$_3$ systems show separate resonances for different complexes present, but do not distinguish inequivalent ligands within a single complex, suggesting dynamic processes in solution [9,10,16,17]. Examples of isomers with bent or linear MX$_2$ units have been observed in lanthanide chemistry with higher coordinated metal centres, for example co-crystallised in [SmI$_2$(MeOCH$_2$CH$_2$OMe)$_3$] [18] or [YCl$_2$(18-crown-6)]$_3$[Y$_2$Cl$_9$] [19].

The IR spectra of the [LnI$_2$(OPPh$_3$)$_4$] and [EuBr$_2$(OPPh$_3$)$_4$] show two bands at ∼1170–1140 and ∼1085–1060 cm^{-1}, assigned as

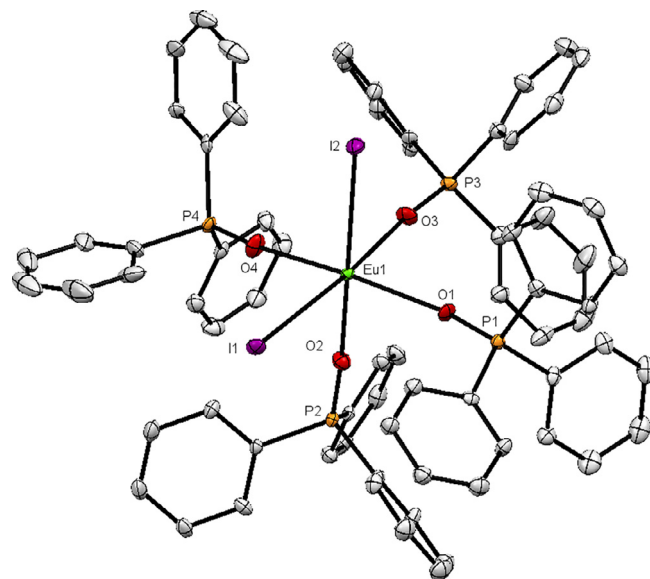**Fig. 1.** View of the structure of [EuI$_2$(OPPh$_3$)$_4$]·MeCN with atom numbering scheme. H atoms and the lattice MeCN are omitted for clarity and ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Eu1—I1 = 3.3250(6), Eu1—I2 = 3.3787(6), Eu1—O1 = 2.475(6), Eu1—O2 = 2.476(6), Eu1—O3 = 2.451(6), Eu1—O4 = 2.445(7), P—O = 1.491(6)–1.502(6); I1—Eu1—I2 = 95.970(17), Eu—O—P = 165.3(4)–173.9(5).

v(PO), which compare with the value of 1196 cm^{-1} in OPPh$_3$ and suggest that all may be *cis* isomers in the solid state. In contrast, the IR spectra of [LnI$_2$(OPMe$_3$)$_4$] and [EuBr$_2$(OPMe$_3$)$_4$] each contain only a single broad v(PO) vibration at ∼1100–1115 cm^{-1} consistent with *trans* isomers; compare OPMe$_3$ v(PO) = 1141 cm^{-1}. The UV–Vis spectra of the solid complexes were also obtained. The UV–Vis spectra of LnI$_2$ complexes mainly consist of broad bands assigned as $4f^n \rightarrow 4f^{n-1}$ $5d^1$ transitions [20–23] and are quite different to the f-f spectra seen in the Ln(III) complexes. For phosphine oxide complexes, the near UV region is dominated by the $\pi \rightarrow \pi^*$ transitions of the P=O unit [24] (and for OPPh$_3$ $\pi \rightarrow \pi^*$ transitions of the aryl groups), but at lower energy the expected Ln(II)-centred transitions are seen (Section 2) and support the attribution as divalent metal centres.

Although most lanthanide ions are paramagnetic, ^{31}P{^{1}H} NMR spectra for Ln(III) phosphine oxide complexes are mostly obtainable and show characteristic shifts correlating with the $4f^n$ configuration present [10,13]. For the diamagnetic divalent complexes, [YbI$_2$(OPR$_3$)$_4$], the complexes show sharp singlets at +36.1 (R = Ph) and +50.9 (R = Me) shifted from the values in the parent phosphine oxides of +29 and +36 respectively [10,16]. In contrast, the [EuX$_2$(OPR$_3$)$_4$] failed to exhibit any ^{31}P resonance, presumably due to the effect of the f^7 Eu(II) centre. Gadolinium(III) complexes, which are also f^7, were the only Ln(III) complexes that did not exhibit a ^{31}P NMR resonance from their [GdCl$_3$(OPPh$_3$)$_3$] and [GdCl$_2$(OPPh$_3$)$_4$]Cl complexes [10]. The blue solution of [SmI$_2$(OPPh$_3$)$_4$] in d^8-thf showed a broad resonance at +18.8 ppm, but [SmI$_2$(OPMe$_3$)$_4$] was not sufficiently soluble to observe a spectrum. On exposure to air or addition of I$_2$, the resonances of the [LnI$_2$(OPR$_3$)$_4$] complexes were lost, and new resonances appeared (Section 2), attributed to Yb(III) or Sm(III) species, [LnI$_2$(OPR$_3$)$_4$]$^+$, and resonances were now present from the solutions of the Eu complexes due to Eu(III) species.

Crystals of the oxidised product, [EuI$_2$(OPPh$_3$)$_4$]I$_3$·MeCN were obtained by exposing an MeCN solution of the divalent complex to air, followed by cooling the solution in a freezer. The crystal structure shows (Fig. 2) the distorted octahedral Eu(III) cation
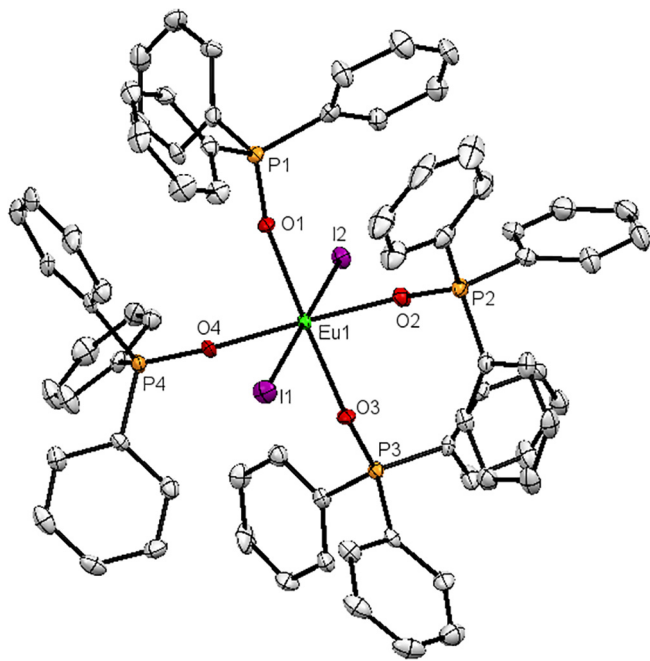
$$[LnX_2(OPR_3)_4] \xleftarrow[N_2, \; RT]{thf} LnX_2 + 4 \; OPR_3 \xrightarrow[N_2, \; RT]{MeCN} [LnX_2(OPR_3)_4]$$

Ln = Sm; X = I
R = Ph, Me

Ln = Yb; X = I
Ln = Eu; X = I, Br
R = Ph, Me

Scheme 1. Synthesis of LnX$_2$ phosphine oxide complexes.

Fig. 2. View of the structure of the cation in $[EuI_2(OPPh_3)_4]I_3\cdot1.5MeCN$ with atom numbering scheme. Note that the asymmetric unit contains a second, crystallographically independent cation and I_3^- anion. H atoms are omitted for clarity and ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Eu1—I1 = 3.0866(6), Eu1—I2 = 3.0481(6), Eu1—O1 = 2.254(5), Eu1—O2 = 2.253(5), Eu1—O3 = 2.273(5), Eu1—O4 = 2.254(5), Eu2—I3 = 3.0305(6), Eu2—I4 = 3.0766(6), Eu2 = O5 = 2.247(5), Eu2—O6 = 2.249(5), Eu2—O7 = 2.269(5), Eu2—O8 = 2.275(5), P—O = 1.497(5)–1.510(5); I1—Eu1—I2 = 177.024(18), I3—Eu2—I4 = 175.371(19).

bearing four equatorial $OPPh_3$ ligands and two mutually *trans* iodides. The Eu—I bond distances in the divalent $[EuI_2(OPPh_3)_4]$ complex (3.3250(6), 3.3787(6) Å) are significantly longer than in the trivalent $[EuI_2(OPPh_3)_4]^+$ cation (3.0481(6), 3.0866(6); 3.0305(6), 3.0766(6) Å) – mostly likely a consequence of the larger ionic radius of Eu(II). Similarly the Eu—O bond lengths (Eu(II): 2.451(6)–2.476(6) Å) are all ca. 0.2 Å longer than in the Eu(III) complex.

4. Conclusions

The first examples of divalent lanthanide halide complexes bearing phosphine oxide ligands have been isolated and characterised. Unexpectedly, spectroscopic and crystallographic data confirm that with $OPPh_3$ these six-coordinate species adopt a *cis*-octahedral geometry, $[LnX_2(OPPh_3)_4]$, in the solid state, while the $OPMe_3$ complexes appear to be the *trans* isomers. As might be expected, the divalent species are very readily oxidised to form $[LnX_2(OPR_3)_4]^+$ and crystallographic analysis shows that for Eu(III), the $[EuI_2(OPPh_3)_4]^+$ cation is the *trans* isomer, similar to other known trivalent analogues. The extension of the ligand types known to form Ln(II) species to OPR_3, indicates that Ln(II) complexes with other ligand types merit investigation, including $OAsR_3$, O_2SR_2 and possibly PR_3. Although not observed in the present work, it seems possible that under appropriate (different) conditions, SmI_2 especially, may be able to reduce P=O bonds since it can reduce OSR_2 or O_2SR_2 to SR_2 [8].

Appendix A. Supplementary data

CCDC 1853203 and 1853204 contains the supplementary crystallographic data for paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2018.07.057.

References

[1] S.A. Cotton, Lanthanide and Actinide Chemistry, John Wiley, Chichester, 2006.
[2] S.A. Cotton, in: Comprehensive Coordination Chemistry II, Elsevier, Oxford, 2004, p. 93.
[3] S.A. Cotton, P.R. Raithby, Coord. Chem. Rev. 340 (2017) 220.
[4] M.N. Bochkarev, Coord. Chem. Rev. 248 (2004) 835.
[5] W.J. Evans, Coord. Chem. Rev. 206–207 (2000) 263.
[6] W.J. Evans, J. Organometal. Chem. 647 (2002) 2.
[7] W.J. Evans, Polyhedron 6 (1987) 803.
[8] M. Szostak, N.J. Fazakerley, D. Parmar, D.J. Procter, Chem. Rev. 114 (2014) 5959.
[9] A.W.G. Platt, Coord. Chem. Rev. 340 (2017) 62.
[10] M.J. Glazier, W. Levason, M.L. Matthews, P.L. Thornton, M. Webster, Inorg. Chim. Acta 357 (2004) 1083.
[11] A. Bowden, A.W.G. Platt, K. Singh, R. Townsend, Polyhedron 363 (2010) 243.
[12] J.-C. Berthet, M. Nierlich, M. Epritikhine, Polyhedron 22 (2003) 3475.
[13] N.J. Hill, L.S. Leung, W. Levason, M. Webster, Inorg. Chim. Acta 343 (2003) 169.
[14] Z. Hou, Y. Zhang, Y. Wakatsuki, Bull. Chem. Soc. Japan 70 (1997) 149.
[15] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.
[16] N.J. Hill, W. Levason, M.C. Popham, G. Reid, M. Webster, Polyhedron 21 (2002) 445.
[17] W. Levason, E.H. Newman, M. Webster, Polyhedron 19 (2000) 2697.
[18] W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, Polyhedron 17 (1998) 3361.
[19] M.J.D. Champion, P. Farina, W. Levason, G. Reid, Dalton Trans. 42 (2013) 13179.
[20] N.B. Mikheev, S.A. Kulyukhin, A.N. Kamenskaya, I.A. Rumer, N.A. Konovalova, Radiochemistry 46 (2004) 521.
[21] E. Rogers, P. Dorenbos, J.T.M. de Haas, E. van der Kolk, Phys. Condens. Matter 24 (2012) 275502.
[22] Y. Okaue, Y. Isobe, Inorg. Chim. Acta 144 (1988) 143.
[23] A.N. Kamenskaya, S.A. Kulyukhin, E.S. Levchenko, V.N. Kalinin, Koord. Khim. 16 (1990) 1141.
[24] H. Schindlbauer, Monatsch. Chem. 94 (1963) 99.