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## Nitrite complexes of the rare earth elements†

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Jacky Pouessel, Pierre Thuéry, Jean-Claude Berthet and Thibault Cantat\*

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The coordination chemistry of the nitrite anion has been investigated with rare earth elements, and the resulting complexes were structurally characterized. Among them, the first homoleptic examples of nitrite complexes of samarium, ytterbium and yttrium are described. The coordination behavior of the nitrite ion is directly controlled by the ionic radius of the metal cation. While the nitrito ligand is stable in the coordination sphere of cerium(III), it is readily reduced by SmI<sub>2</sub>.

Nitrogen oxides are privileged ligands in the inorganic chemistry of the actinides and the rare earth elements (REEs), with nitric media being utilized at both ends of the life cycle of these strategic metal ions. In fact, the extraction of uranium or the REEs relies on the dissolution of f-element oxides and hydroxides in nitric acid.<sup>1</sup> Similarly, most technologies aimed at reprocessing nuclear waste or recycling the REEs involve the formation of nitrate complexes, prior to the separation of the effluent constituents.<sup>1,2</sup> Importantly, the nitrate anion (NO<sub>3</sub><sup>-</sup>) exhibits a very rich redox chemistry and its problematic reduction to nitrite (NO<sub>2</sub><sup>-</sup>) in natural groundwater and nuclear wastes motivated our preliminary interest in actinide nitrite complexes.<sup>3,4</sup> To overcome the absence of molecular models of thorium and uranium nitrite complexes, we reported, earlier this year, the synthesis of [PPh<sub>4</sub>]<sub>2</sub>[Th(NO<sub>2</sub>)<sub>6</sub>] and [PPh<sub>4</sub>]<sub>2</sub>[UO<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>].<sup>4</sup> These complexes represent the first homoleptic complexes of uranyl and thorium with nitrite ligands. Beyond the nuclear fuel cycle context, lanthanide nitrites are desirable complexes both from structural and synthetic perspectives. Examples of nitrite complexes remain scarce within the REEs series. Early efforts focused on hexanitritolanthanide salts Cs<sub>2</sub>NaLn(NO<sub>2</sub>)<sub>6</sub> (Ln = La to Gd), which are obtained as solids from multi-step salt metathesis reactions in water.<sup>5</sup> This series was completed in 2004 with the isolation of La(NO<sub>2</sub>)<sub>3</sub>, as a coordination polymer.<sup>6</sup> Only six molecular nitrite complexes have been reported with REEs, namely [(Tp<sup>Me<sub>2</sub>,4-Et</sup>)<sub>2</sub>Sm(NO<sub>2</sub>)],<sup>7</sup> [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb(NO<sub>2</sub>)(THF)],<sup>8</sup> [Ln(L)(NO<sub>2</sub>)(H<sub>2</sub>O)] (Ln = Sm, Eu, L = 2,2'-(biphenyl-4,4'-diylbis(oxy))diacetate),<sup>9</sup> [La(NO<sub>2</sub>)(SO<sub>4</sub>)(H<sub>2</sub>O)]<sup>10</sup> and [{Fe(bipy)(CN)<sub>4</sub>}-{Sm(phen)(NO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>}]<sup>11</sup>. Importantly, [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb(NO<sub>2</sub>)(THF)] is the only complex obtained using a nitrite anion (NaNO<sub>2</sub>) as a

source of the nitrito ligand and the remaining examples resulted from redox disproportionation of nitrate or NO.<sup>8</sup> [(Tp<sup>Me<sub>2</sub>,4-Et</sup>)<sub>2</sub>Sm<sup>III</sup>(NO<sub>2</sub>)] was formed by reduction of NO to NO<sub>2</sub><sup>-</sup> and N<sub>2</sub>O, promoted by [(Tp<sup>Me<sub>2</sub>,4-Et</sup>)<sub>2</sub>Sm<sup>II</sup>].<sup>7</sup> Reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> was proposed as the source of the nitrito ligand in [La(NO<sub>2</sub>)(SO<sub>4</sub>)(H<sub>2</sub>O)].<sup>10</sup> From a structural point of view, the rational synthesis and the characterization of well-defined REEs nitrite complexes would therefore afford molecular models to better apprehend the redox chemistry of nitrogen oxides in lanthanide chemistry. Additionally, it has been recently shown that the nitrite anion NO<sub>2</sub><sup>-</sup> behaves as an attractive one electron oxidant in the coordination sphere of uranium(III) and uranium(IV), to access uranium-oxo functionalities.<sup>4,12</sup> The transposition of this chemical behavior to the lanthanide series could in principle offer an attractive route to Ln=O complexes or oxide clusters. Because the nitrite anion NO<sub>2</sub><sup>-</sup> possesses three donor atoms, it exhibits a variety of coordination behaviors and electron rich metal ions tend to form nitro complexes (κ<sup>1</sup>-(N)-NO<sub>2</sub>) while hard Lewis acids adopt the κ<sup>1</sup>-(O)-NO<sub>2</sub> and κ<sup>2</sup>-(O,O)-NO<sub>2</sub> coordination modes (nitrito ligand).<sup>13</sup> This coordination versatility has been recently utilized to prepare Ru/Ln heterometallic clusters, in the search for bifunctional materials combining photochromic and magnetic properties.<sup>14</sup> In the absence of isolated anionic nitritolanthanide complexes, the synthesis of such molecules is however limited to the formation of {Ln[Ru(NO)(μ-NO<sub>2</sub>)<sub>4</sub>-(μ<sub>3</sub>-OH)<sub>2</sub>Ln]} motifs, obtained from Na<sub>2</sub>[Ru(NO)(NO<sub>2</sub>)<sub>4</sub>OH] as a nitrite source.<sup>14</sup> From a synthetic viewpoint, the availability of well-defined REEs anionic nitrite complexes will allow the rapid construction of a wide range of heterometallic coordination polymers. In this contribution, we report novel nitrite compounds of the REEs (La, Ce, Pr, Nd, Sm, Yb, Y), including the first homoleptic examples of nitrite complexes of samarium, ytterbium and yttrium, from simple salt metathesis reactions between rare earth iodide and triflate salts with the nitrite anion. Importantly, all the nitrite compounds presented thereafter were characterized by X-ray diffraction.

CEA, IRAMIS, SIS2M, CNRS UMR 3299, CEA/Saclay, 91191 Gif-sur-Yvette, France.

E-mail: thibault.cantat@cea.fr; Fax: +33 1 6908 6640; Tel: +33 1 6908 4338

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Table 1 Selected bond lengths (Å) and angles (°)<sup>a</sup>

	[PPh <sub>4</sub> ] <sub>2</sub> [1] La	[PPh <sub>4</sub> ] <sub>2</sub> [2] Ce	[PPh <sub>4</sub> ] <sub>2</sub> [3] Ce	[PPh <sub>4</sub> ] <sub>2</sub> [4] Pr	[PPh <sub>4</sub> ] <sub>2</sub> [5][NO <sub>2</sub> ] Nd	[PPh <sub>4</sub> ] <sub>2</sub> [6] Nd	[PPh <sub>4</sub> ] <sub>2</sub> [7] Nd
M-O(κ <sup>1</sup> )	2.556(7)–2.727(11)	2.545(8)–2.664(7)	2.526(4)	2.524(9)–2.659(6)	2.499(3)–2.606(3)	2.530(3)–2.646(3)	2.3896(16)
M-O(κ <sup>2</sup> )	[2.64(5)]	[2.60(4)]	[2.65(3)]	[2.59(4)]	[2.55(4)]	[2.58(3)]	2.5421(15)–2.6480(14)
M-N(py)	2.796(6)	2.781(6)	1.251(5), 1.244(6)	2.764(5)	2.6547(17), 2.6373(16)	2.743(3)	2.7081(15)
O-N(κ <sup>1</sup> )							1.064(11)–1.290(14)
O-N(κ <sup>2</sup> )	1.152(10)–1.266(9)	1.161(9)–1.268(7)	1.209(8)–1.316(8)	1.178(9)–1.276(9)	1.214(5)–1.282(6)	1.210(4)–1.333(6)	[1.19(8)]
O-M-O(κ <sup>2</sup> )	[1.23(3)]	[1.23(3)]	[1.25(2)]	[1.24(3)]	[1.25(2)]	[1.25(3)]	1.256(2)–1.273(2)
O-N-O(κ <sup>1</sup> )	43.2(2)–47.17(19)	44.2(2)–47.5(2)	42.67(18)–46.80(13)	45.3(2)–48.98(19)	47.06(8)–48.81(10)	43.72(15)–50.73(10)	1.262(6)
O-N-O(κ <sup>2</sup> )	[45.2(14)]	[46.1(13)]	[45.8(16)]	[46.9(13)]	[48.1(7)]	[47(2)]	47.47(4)–48.79(5)
O-N-O(κ <sup>2</sup> )	105.1(9)–113.0(6)	106.3(8)–114.0(10)	105.4(8)–114.0(4)	108.4(7)–114.6(9)	109.6(4)–116.2(4)	99.3(7)–114.9(5)	[48.2(6)]
O-N-O(κ <sup>2</sup> )	[111(3)]	[112(3)]	[111(3)]	[112(2)]	[113(2)]	[111(5)]	121.6(4), 124.9(13)
							112.67(17)–113.05(18)
							[112.9(2)]
	[PPh <sub>4</sub> ] <sub>2</sub> [8] Pr	[PPh <sub>4</sub> ] <sub>2</sub> [9] Nd	[PPh <sub>4</sub> ] <sub>2</sub> [10] py Sm	[PPh <sub>4</sub> ] <sub>2</sub> [11] py Yb	[PPh <sub>4</sub> ] <sub>2</sub> [12] py Y	[PPh <sub>4</sub> ] <sub>2</sub> [13] Sm	[PPh <sub>4</sub> ] <sub>2</sub> [14] Y
M-O(κ <sup>1</sup> )	2.435(4), 2.438(4)	2.425(3), 2.431(3)	2.480(2)–2.558(2)	2.3741(14)–2.5104(14)	2.4191(14)–2.5226(14)	2.3569(18)–2.4040(17)	2.3005(15)–2.3410(15)
M-O(κ <sup>2</sup> )	[2.60(4)]	[2.58(4)]	[2.51(2)]	[2.42(4)]	[2.45(3)]	[2.38(2)]	[2.32(2)]
M-N(py)	1.133(4), 1.185(4)	1.130(4), 1.183(3)	1.245(4)–1.274(3)	1.246(3)–1.273(2)	1.249(2)–1.273(2)	1.247(3)–1.261(2)	1.251(2)–1.270(2)
O-N(κ <sup>1</sup> )			[1.261(9)]	[1.262(8)]	[1.262(7)]	[1.255(6)]	[1.259(7)]
O-N(κ <sup>2</sup> )	1.239(5)–1.280(5)	1.242(5)–1.283(4)	48.89(9)–50.18(7)	50.76(5)–52.02(5)	50.28(5)–51.37(5)	48.30(5)–49.08(5)	49.53(5)–50.44(5)
O-M-O(κ <sup>2</sup> )	[1.26(2)]	[1.257(14)]	[49.4(5)]	[51.2(5)]	[50.7(4)]	[48.7(4)]	[50.0(5)]
O-N-O(κ <sup>1</sup> )	46.50(13)–48.85(13)	46.92(12)–49.35(12)	152.6(5), 151.1(4)			114.58(18)–138.4(4)	114.39(15)–134.2(3)
O-N-O(κ <sup>1</sup> )	[47.7(9)]	[48.1(9)]				[123(13)]	[121(9)]
O-N-O(κ <sup>2</sup> )	111.5(3)–115.2(3)	111.6(3)–115.7(3)	112.3(2)–113.7(2)	111.68(17)–112.58(17)	112.34(16)–113.01(17)	112.81(18)–113.61(19)	112.30(16)–112.58(15)
	[113.7(14)]	[113.9(15)]	[112.9(6)]	[112.3(4)]	[112.7(3)]	[113.1(4)]	[112.46(12)]

<sup>a</sup> Individual values or ranges are given, with average values in brackets in the last case.





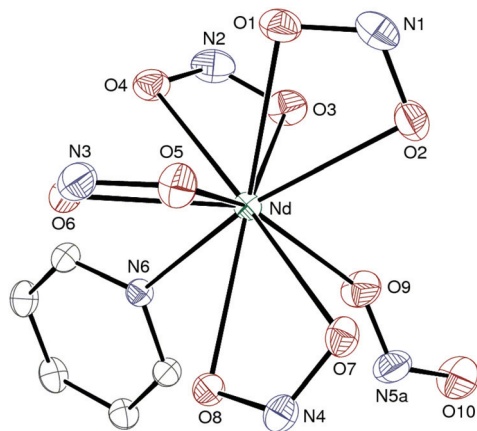


Fig. 4 Molecular structure of anion  $7^{2-}$  with displacement ellipsoids drawn at the 30% probability level. Only one position of the disordered atom is represented.

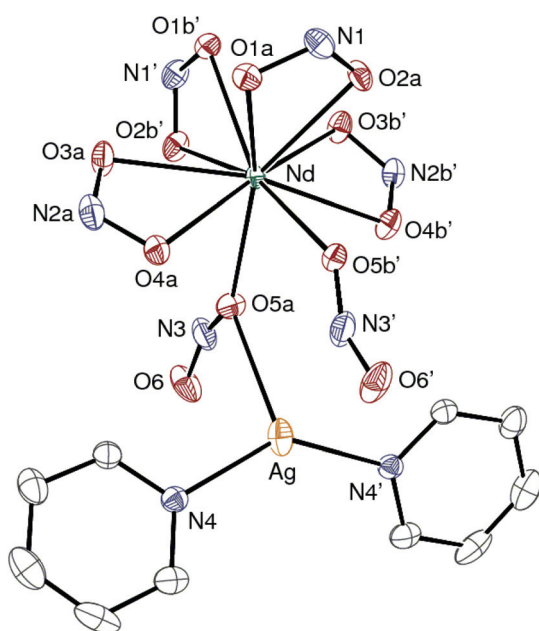
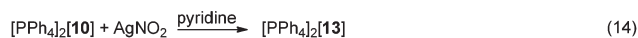
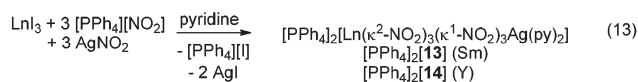
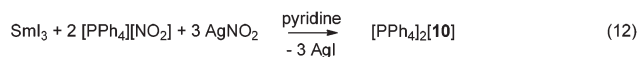
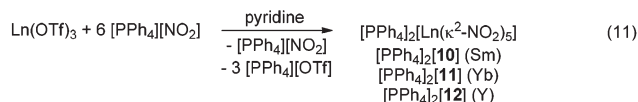


Fig. 5 Molecular structure of anion  $9^{2-}$  with displacement ellipsoids drawn at the 20% probability level. Only one set of positions of the disordered atoms is represented. Symmetry code: ' =  $-x, y, 1/2 - z$ .

Fig. 6,  $10^{2-}$  is a pentanitrito complex of samarium(III) and the five nitrite ligands adopt the  $\kappa^2-(O,O)$ -NO<sub>2</sub> coordination mode. The distorted bicapped square antiprism in  $10^{2-}$  is better described by the distorted trigonal bipyramid defined by the SmN<sub>5</sub> backbone (Fig. 6) where N1, N2 and N3 form the equatorial plane. As such, [PPh<sub>4</sub>]<sub>2</sub>[10], [PPh<sub>4</sub>]<sub>2</sub>[11] and [PPh<sub>4</sub>]<sub>2</sub>[12] represent the first homoleptic nitrito complexes of the REEs. As discussed above, analytically pure samples of the complexes can be prepared in high yield using a combination of [PPh<sub>4</sub>][NO<sub>2</sub>] and silver nitrite, as exemplified with the synthesis of [PPh<sub>4</sub>]<sub>2</sub>[10], from SmI<sub>3</sub>, in eqn (12). Noticeably, utilization of AgNO<sub>2</sub> enables the formation of the hexanitrito complexes



Scheme 3 Syntheses of [PPh<sub>4</sub>]<sub>2</sub>[10], [PPh<sub>4</sub>]<sub>2</sub>[11] and [PPh<sub>4</sub>]<sub>2</sub>[12] by salt metathesis reactions, carried out at RT in pyridine solvent.

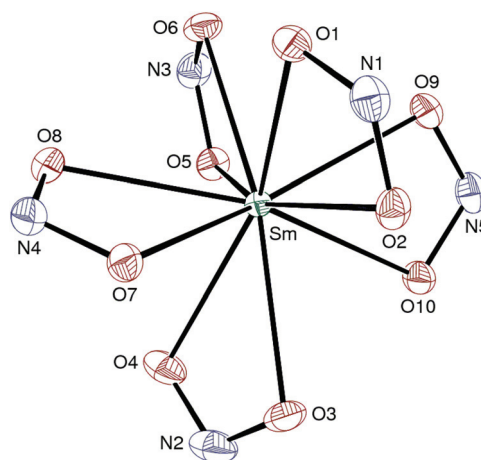


Fig. 6 Molecular structure of anion  $10^{2-}$  with displacement ellipsoids drawn at the 20% probability level.

of samarium(III) and yttrium(III). In fact, LnI<sub>3</sub> (Ln = Sm, Y) reacts with a 3:3 mixture [PPh<sub>4</sub>][NO<sub>2</sub>] and AgNO<sub>2</sub> to yield [PPh<sub>4</sub>]<sub>2</sub>[Ln(κ<sup>2</sup>-NO<sub>2</sub>)<sub>3</sub>(κ<sup>1</sup>-NO<sub>2</sub>)<sub>3</sub>Ag(py)<sub>2</sub>] (Ln = Sm ([PPh<sub>4</sub>]<sub>2</sub>[13]), Y ([PPh<sub>4</sub>]<sub>2</sub>[14])), at room temperature, and the purity of [PPh<sub>4</sub>]<sub>2</sub>[13] was confirmed by H, C, N elemental analyses (see the Experimental section). As shown in Fig. 7, anion  $13^{2-}$  results from the coordination of three κ<sup>2</sup>-(O,O) and three κ<sup>1</sup>-(O) NO<sub>2</sub><sup>-</sup> ligands to the Sm<sup>3+</sup> cation, in agreement with the smaller ionic radius of samarium (and yttrium), compared to neodymium. Interestingly, [PPh<sub>4</sub>]<sub>2</sub>[13] is obtained as a coordination polymer with the [Ag(py)<sub>2</sub>]<sup>+</sup> cation bridging two [Ln(κ<sup>2</sup>-NO<sub>2</sub>)<sub>3</sub>(κ<sup>1</sup>-NO<sub>2</sub>)<sub>3</sub>]<sup>3-</sup> units *via* coordination to two κ<sup>1</sup>-(O)-NO<sub>2</sub> ligands (Fig. 7). Overall, the formation of REEs/Ag complexes [PPh<sub>4</sub>]<sub>2</sub>[X] (X = 3, 8, 9, 13, 14) demonstrates the potential of anionic Ln nitrito compounds to serve as building blocks for the synthesis of novel heterometallic coordination polymers.

As outlined in the introduction, the nitrite anion behaves as a one electron oxidant towards uranium(III) and uranium(IV) to yield a U=O functional group, with the concomitant release of NO.<sup>4,12</sup> Interestingly, cerium(III) complex [PPh<sub>4</sub>]<sub>2</sub>[2] is thermally stable and no oxidation of the metal ion to Ce<sup>4+</sup> was

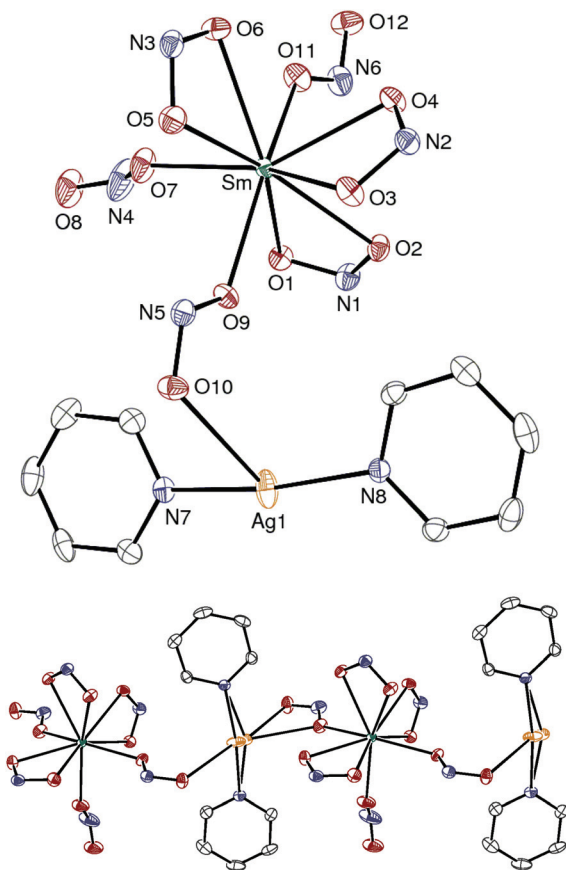


Fig. 7 Molecular structure of anion  $13^{2-}$  (top) and its polymeric organization (bottom) with displacement ellipsoids drawn at the 20% probability level. Only one position of the disordered silver atom is represented in the upper view.

observed upon heating a pyridine solution of the complex at 120 °C for 7 days. This stability likely originates from the rather high oxidation potential of  $Ce^{3+}$ .<sup>19</sup> In contrast,  $Sm^{II}I_2$  is readily oxidized to  $Sm^{III}$  in the presence of  $[PPh_4][NO_2]$ . In fact, the salt metathesis reaction between  $SmI_2$  and 6 equiv.  $[PPh_4][NO_2]$  results in slow gas evolution and the formation of crystals of  $[PPh_4]_2[10]$  and a white solid (eqn (15) in Scheme 3). Given the absence of the oxo group in  $[PPh_4]_2[10]$ , the latter solid likely features an “ $Sm_2O_3$ ” fragment.

Having in hand a series of 14 novel nitrito complexes of the rare earth elements, general trends can be deduced from their X-ray structures. First, in the absence of a Lewis acidic counter-cation, pentanitrito REEs complexes ( $[PPh_4]_2[X]$ ,  $X = 1, 2, 4, 6, 10, 11, 12$ ) are formed selectively across the series. The formation of hexanitrito complexes is available for all the elements and it requires the presence of  $Ag^+$  as a cation, presumably to balance the electrostatic inter-ligand repulsion through coordination (as shown in  $[PPh_4]_2[X]$ ,  $X = 3, 7, 8, 9, 13, 14$ ). Nonetheless, the coordination of the REE cation varies and it is directly controlled by the metal ionic radius. Following the lanthanide contraction, the pentanitrito complexes exhibit a coordination number of 11 for La–Nd and a coordination number of 10 for Nd–Y.  $Nd^{3+}$  is the pivot in this series

of complexes and four distinct structures were obtained with this single cation. The coordination sphere of the hexanitrito complexes is even more sensitive to the lanthanide contraction and, while  $[PPh_4]_2[3]$  ( $Ln = Ce$ ) is undeca-coordinated, complexes  $[PPh_4]_2[X]$  ( $X = 8$  (Pr), 9 (Nd)) are deca-coordinated and  $[PPh_4]_2[13]$  ( $Ln = Sm$ ) and  $[PPh_4]_2[14]$  ( $Ln = Y$ ) are nona-coordinated, resulting in a progressive increase in the number of  $\kappa^1$ -(O)- $NO_2$  ligands. The contraction is also observable in the linear decrease of the mean M–O bond distance measured for the  $M[\kappa^2$ -(O,O)- $NO_2]$  interactions (Table 1). In complexes  $[PPh_4]_2[X]$  ( $X = 3, 6, 8, 9, 13, 14$ ), the nitrito ligands adopt two different coordination modes, namely  $\kappa^2$ -(O,O) and  $\kappa^1$ -(O), and we found that the M–O bond distance is  $\sim 0.16$  Å shorter for the  $\kappa^1$ -(O)-bound nitrito ligand, regardless of the nature of the REE or the coordination of  $Ag^+$ . This finding is in agreement with the 0.15 Å bond difference observed in  $[PPh_4]_2[UO_2(\kappa^2-NO_2)_2(\kappa^1-NO_2)_2]$ .<sup>4</sup> However, all the nitrito complexes reported herein present a single set of two NO stretching frequencies in their IR spectra (1212–1229 and 1305–1307  $cm^{-1}$ ), including for complexes with two different nitrite coordination modes. In comparison, the nitrite anion is characterized by frequencies at 1240 and 1311  $cm^{-1}$  in  $[PPh_4][NO_2]$  and at 1212 and 1304  $cm^{-1}$  in  $[PPh_4]_2[Th(\kappa^2-NO_2)_6]$ .<sup>4</sup>

In summary, the coordination chemistry of the nitrite anion has been investigated with rare earth elements, and the resulting complexes were structurally characterized. Among them, the first homoleptic examples of nitrite complexes of samarium, ytterbium and yttrium are described. The coordination behavior of the nitrite ion is directly controlled by the ionic radius of the metal cation. While the nitrito ligand is stable in the coordination sphere of cerium(III), it is readily reduced by  $SmI_2$ .

## Experimental section

### General considerations

The complexes described herein are all moisture sensitive. Syntheses and manipulations of the compounds were conducted under a ultra-high purity argon atmosphere with rigorous exclusion of air and water, using Schlenk-vessel and vacuum-line techniques or recirculating mBraun LabMaster glove boxes. Glassware was dried overnight at 120 °C before use. IR samples were prepared as Nujol mulls between KBr round cell windows and the spectra recorded on a Perkin-Elmer FT-IR 1725X spectrometer. Elemental analyses were performed at Medac Ltd at Chobham, Surrey (United Kingdom). Celite (Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use.  $PPh_4I$ ,  $AgNO_2$  and the lanthanide precursors  $SmI_2$ ,  $Ln(OTf)_3$  ( $Ln = La, Ce, Pr, Nd, Sm, Yb, Y$ ) and  $LnI_3$  ( $Ln = Ce, Pr, Nd, Sm, Yb, Y$ ) were purchased from commercial suppliers (Aldrich and Acros) and directly used without purification.  $[PPh_4][NO_2]$  was synthesized as previously described.<sup>4</sup> Pyridine was dried over sodium and distilled before use. Tetrahydrofuran (THF), tetrahydrofuran- $d_8$  (THF- $d_8$ ), pentane, diethyl ether and benzene- $d_6$

were dried over a sodium(0)–benzophenone mixture and distilled before use. Acetonitrile, acetonitrile-*d*<sub>3</sub>, dichloromethane and dichloromethane-*d*<sub>2</sub> were dried over CaH<sub>2</sub> and distilled before use.

**General procedure for the formation of crystals [PPh<sub>4</sub>]<sub>2</sub>[1], [PPh<sub>4</sub>]<sub>2</sub>[2], [PPh<sub>4</sub>]<sub>2</sub>[4], [PPh<sub>4</sub>]<sub>2</sub>[5], [PPh<sub>4</sub>]<sub>2</sub>[10], [PPh<sub>4</sub>]<sub>2</sub>[11] and [PPh<sub>4</sub>]<sub>2</sub>[12]**

An NMR tube was charged with Ln(OTf)<sub>3</sub>, 6 equiv. [PPh<sub>4</sub>][NO<sub>2</sub>] and freshly distilled pyridine (~0.5 mL). After complete dissolution of the solids, the solution was sonicated in an ultrasonic bath for 1 h. Crystals were grown for days by slow diffusion of a blank of pure pyridine (0.1 mL) and then diethyl ether (1.5 mL) onto the initial mixture in pyridine. The quantities for the preparation of [PPh<sub>4</sub>]<sub>2</sub>[1], [PPh<sub>4</sub>]<sub>2</sub>[2], [PPh<sub>4</sub>]<sub>2</sub>[4], [PPh<sub>4</sub>]<sub>2</sub>[5], [PPh<sub>4</sub>]<sub>2</sub>[10], [PPh<sub>4</sub>]<sub>2</sub>[11] and [PPh<sub>4</sub>]<sub>2</sub>[12] were as follows:

- [PPh<sub>4</sub>]<sub>2</sub>[La(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>(py)] ([PPh<sub>4</sub>]<sub>2</sub>[1]): La(OTf)<sub>3</sub> (22.2 mg, 0.038 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (87.6 mg, 0.227 mmol). Translucent light yellow crystals were formed after 2 days.

- [PPh<sub>4</sub>]<sub>2</sub>[Ce(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>(py)] ([PPh<sub>4</sub>]<sub>2</sub>[2]): Ce(OTf)<sub>3</sub> (29.4 mg, 0.050 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (115.6 mg, 0.30 mmol). Translucent light yellow crystals were obtained after 1 day.

- [PPh<sub>4</sub>]<sub>2</sub>[Pr(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>(py)] ([PPh<sub>4</sub>]<sub>2</sub>[4]): Pr(OTf)<sub>3</sub> (15.2 mg, 0.026 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (59.8 mg, 0.155 mmol). Translucent light yellow crystals were obtained after 2 days.

- [PPh<sub>4</sub>]<sub>2</sub>[Nd(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>(py)]<sub>2</sub>(NO<sub>2</sub>) ([PPh<sub>4</sub>]<sub>2</sub>[5]): Nd(OTf)<sub>3</sub> (23.5 mg, 0.040 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (91.9 mg, 0.239 mmol). Colourless crystals were obtained after 5 days.

- [PPh<sub>4</sub>]<sub>2</sub>[Sm(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>] ([PPh<sub>4</sub>]<sub>2</sub>[10]): Sm(OTf)<sub>3</sub> (13.3 mg, 0.022 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (51.6 mg, 0.134 mmol). Colourless crystals were obtained after 2 days.

- [PPh<sub>4</sub>]<sub>2</sub>[Yb(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>] ([PPh<sub>4</sub>]<sub>2</sub>[11]): Yb(OTf)<sub>3</sub> (20.3 mg, 0.033 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (75.7 mg, 0.196 mmol). Colourless crystals were obtained after 2 days.

- [PPh<sub>4</sub>]<sub>2</sub>[Y(κ<sup>2</sup>-NO<sub>2</sub>)<sub>5</sub>] ([PPh<sub>4</sub>]<sub>2</sub>[12]): Y(OTf)<sub>3</sub> (15.3 mg, 0.029 mmol) and [PPh<sub>4</sub>][NO<sub>2</sub>] (66.0 mg, 0.171 mmol). Colourless crystals were obtained after two 2 days.

The synthesis, purification and elemental analyses for complexes [PPh<sub>4</sub>]<sub>2</sub>[2], [PPh<sub>4</sub>]<sub>2</sub>[6], [PPh<sub>4</sub>]<sub>2</sub>[7], [PPh<sub>4</sub>]<sub>2</sub>[10] are given thereafter, as representative examples. Data were not collected for compounds [PPh<sub>4</sub>]<sub>2</sub>[1], [PPh<sub>4</sub>]<sub>2</sub>[4], [PPh<sub>4</sub>]<sub>2</sub>[5], [PPh<sub>4</sub>]<sub>2</sub>[11] and [PPh<sub>4</sub>]<sub>2</sub>[12].

**Synthesis of [PPh<sub>4</sub>]<sub>2</sub>[Ce(NO<sub>2</sub>)<sub>5</sub>(py)] ([PPh<sub>4</sub>]<sub>2</sub>[2])**

A 25 mL round bottom flask was charged with CeI<sub>3</sub> (72.0 mg, 0.138 mmol), 2 equiv. [PPh<sub>4</sub>][NO<sub>2</sub>] (106.6 mg, 0.276 mmol), 3 equiv. AgNO<sub>2</sub> (63.8 mg, 0.415 mmol) and freshly distilled pyridine (10 mL). After complete dissolution of the solids, the clear yellow solution, sheltered from light, was vigorously stirred at room temperature for 1 h. The solvent was then evaporated off and after 15 h drying under vacuum, acetonitrile (10 mL) was condensed onto the yellow residue. Rapidly, a pale-yellow precipitate of AgI deposited which was filtered off from the yellow solution. The solvent was then evaporated off and the residue was dried under vacuum (15 h, rt) to afford

pure [PPh<sub>4</sub>]<sub>2</sub>[2] as a yellow powder (143.9 mg, 92%). Yellow crystals of [PPh<sub>4</sub>]<sub>2</sub>[2] were formed by slow diffusion of diethyl ether (1.5 mL) on a pyridine solution (0.5 mL) of the product (*ca.* 10 mg).

Anal. calcd for C<sub>53</sub>H<sub>45</sub>CeN<sub>6</sub>O<sub>10</sub>P<sub>2</sub> (1128.03): C, 56.43; H, 4.02; N, 7.45; Found: C, 56.12; H, 4.24; N, 7.54; IR (cm<sup>-1</sup>): 525, 616, 688, 722, 754, 821, 850, 994, 1033, 1104, 1157, 1215 (N–O), 1305 (N–O), 1584, 2671, 2726.

**Synthesis of [PPh<sub>4</sub>]<sub>2</sub>[Nd(NO<sub>2</sub>)<sub>5</sub>(py)] ([PPh<sub>4</sub>]<sub>2</sub>[6] and [PPh<sub>4</sub>]<sub>2</sub>[7])**

A 25 mL round bottom flask was charged with NdI<sub>3</sub> (83.7 mg, 0.159 mmol), 2 equiv. [PPh<sub>4</sub>][NO<sub>2</sub>] (122.9 mg, 0.319 mmol), 3 AgNO<sub>2</sub> (73.6 mg, 0.478 mmol) and freshly distilled pyridine (10 mL). After complete dissolution of the solids, the solution, sheltered from light, was vigorously stirred at room temperature for 1 h. The solvent was then evaporated off and after 15 h drying under vacuum, the product was separated from the insoluble AgI by extraction in acetonitrile (10 mL). The solvent was then evaporated off and the residue dried under vacuum (15 h, rt) to afford pure [PPh<sub>4</sub>]<sub>2</sub>[Nd(NO<sub>2</sub>)<sub>5</sub>(py)] as an off-white powder (169.2 mg, 94%). Colourless crystals of [PPh<sub>4</sub>]<sub>2</sub>[6] were formed by slow diffusion of diethyl ether (1.5 mL) on a pyridine solution (0.5 mL) of the product (*ca.* 10 mg). Colourless crystals of [PPh<sub>4</sub>]<sub>2</sub>[7] were obtained similarly but with diffusion of pentane instead of Et<sub>2</sub>O.

Anal. calcd for C<sub>53</sub>H<sub>45</sub>N<sub>6</sub>NdO<sub>10</sub>P<sub>2</sub> (1132.15): C, 56.23; H, 4.01; N, 7.42; Found: C, 55.77; H, 3.84; N, 7.46. IR (cm<sup>-1</sup>): 524, 617, 688, 722, 754, 823, 994, 1021, 1101, 1156, 1221 (N–O), 1305 (N–O), 1584, 2671, 2726.

**Synthesis of [PPh<sub>4</sub>]<sub>2</sub>[Sm(NO<sub>2</sub>)<sub>5</sub>] ([PPh<sub>4</sub>]<sub>2</sub>[10])**

A 25 mL round bottom flask was charged with SmI<sub>3</sub> (78.7 mg, 0.148 mmol), 2 equiv. [PPh<sub>4</sub>][NO<sub>2</sub>] (114.2 mg, 0.296 mmol), 3 equiv. AgNO<sub>2</sub> (68.4 mg, 0.444 mmol) and freshly distilled pyridine (10 mL). After complete dissolution of the solids, the solution, sheltered from light, was vigorously stirred at room temperature for 1 h. The solvent was then evaporated off and after 15 h drying under vacuum, the product was separated from the insoluble AgI by extraction in acetonitrile (10 mL). The solvent was then evaporated off and the leaving off-white powder was dried under vacuum for 15 h to afford [PPh<sub>4</sub>]<sub>2</sub>[10] in almost quantitative yield (156.1 mg). Colourless crystals of [PPh<sub>4</sub>]<sub>2</sub>[10] were grown by slow diffusion of diethyl ether (1.5 mL) on a pyridine solution (0.5 mL) of the product (*ca.* 10 mg).

Anal. calcd for C<sub>48</sub>H<sub>40</sub>N<sub>5</sub>O<sub>10</sub>P<sub>2</sub>Sm (1059.17): C, 54.43; H, 3.81; N, 6.61; found: C, 55.16; H, 3.78; N, 6.87; the analysis suggests that the compound is not completely desolvated and would contain 0.4 pyridine (required C, 55.05; H, 3.88; N, 6.93). IR (cm<sup>-1</sup>): 527, 617, 688, 722, 751, 826, 850, 891, 968, 996, 1025, 1104, 1158, 1229 (N–O), 1305 (N–O), 1584, 2671, 2726.

**General procedure for the preparation of the crystals of [PPh<sub>4</sub>]<sub>2</sub>[3], [PPh<sub>4</sub>]<sub>2</sub>[8], [PPh<sub>4</sub>]<sub>2</sub>[9], [PPh<sub>4</sub>]<sub>2</sub>[13] and [PPh<sub>4</sub>]<sub>2</sub>[14] containing silver salt**

An NMR tube was charged with LnI<sub>3</sub>, 3.0 equiv. [PPh<sub>4</sub>][NO<sub>2</sub>], 3.0 equiv. AgNO<sub>2</sub> and freshly distilled pyridine (~0.5 mL). After



complete dissolution, the solution sheltered from light was sonicated in an ultrasonic bath for 1 h. Crystals were grown for days by slow diffusion of pyridine (0.1 mL) and then diethyl ether (1.5 mL) on the initial pyridine mixture. The quantities for the preparation of  $[\text{PPh}_4]_2[\mathbf{3}]$ ,  $[\text{PPh}_4]_2[\mathbf{8}]$ ,  $[\text{PPh}_4]_2[\mathbf{9}]$ ,  $[\text{PPh}_4]_2[\mathbf{13}]$  and  $[\text{PPh}_4]_2[\mathbf{14}]$  were as follow:

-  $[\text{PPh}_4]_2[\text{Ce}(\kappa^2\text{-NO}_2)_5(\kappa^1\text{-NO}_2)\text{Ag}(\text{py})_2]$  ( $[\text{PPh}_4]_2[\mathbf{3}]$ ):  $\text{CeI}_3$  (12.1 mg, 0.023 mmol),  $[\text{PPh}_4][\text{NO}_2]$  (27.0 mg, 0.07 mmol) and  $\text{AgNO}_2$  (11.0 mg, 0.07 mmol). Translucent light yellow crystals were obtained after 3 days.

-  $[\text{PPh}_4]_2[\text{Pr}(\kappa^2\text{-NO}_2)_5(\kappa^1\text{-NO}_2)\text{Ag}(\text{py})_2]$  ( $[\text{PPh}_4]_2[\mathbf{8}]$ ):  $\text{PrI}_3$  (16.5 mg, 0.032 mmol),  $[\text{PPh}_4][\text{NO}_2]$  (36.6 mg, 0.095 mmol) and  $\text{AgNO}_2$  (14.6 mg, 0.095 mmol). Translucent light yellow crystals were obtained after 2 days.

-  $[\text{PPh}_4]_2[\text{Nd}(\kappa^2\text{-NO}_2)_4(\kappa^1\text{-NO}_2)_2\text{Ag}(\text{py})_2]$  ( $[\text{PPh}_4]_2[\mathbf{9}]$ ):  $\text{NdI}_3$  (17.8 mg, 0.034 mmol),  $[\text{PPh}_4][\text{NO}_2]$  (39.3 mg, 0.10 mmol) and  $\text{AgNO}_2$  (15.7 mg, 0.102 mmol). Colourless crystals were obtained after 3 days.

-  $[\text{PPh}_4]_2[\text{Sm}(\kappa^2\text{-NO}_2)_3(\kappa^1\text{-NO}_2)_3\text{Ag}(\text{py})_2]$  ( $[\text{PPh}_4]_2[\mathbf{13}]$ ):  $\text{SmI}_3$  (16.2 mg, 0.03 mmol),  $[\text{PPh}_4][\text{NO}_2]$  (35.2 mg, 0.091 mmol) and  $\text{AgNO}_2$  (14.1 mg, 0.091 mmol). Colourless crystals were obtained after 3 days.

-  $[\text{PPh}_4]_2[\text{Y}(\kappa^2\text{-NO}_2)_3(\kappa^1\text{-NO}_2)_3\text{Ag}(\text{py})_2]$  ( $[\text{PPh}_4]_2[\mathbf{14}]$ ):  $\text{YI}_3$  (15.9 mg, 0.034 mmol),  $[\text{PPh}_4][\text{NO}_2]$  (39.3 mg, 0.102 mmol) and  $\text{AgNO}_2$  (15.7 mg, 0.10 mmol). Colourless crystals were obtained after 3 days.

The synthesis, purification and elemental analyses for complexes  $[\text{PPh}_4]_2[\mathbf{3}]$  and  $[\text{PPh}_4]_2[\mathbf{13}]$  are given thereafter, as representative examples. Data were not collected for compounds  $[\text{PPh}_4]_2[\mathbf{8}]$ ,  $[\text{PPh}_4]_2[\mathbf{9}]$  and  $[\text{PPh}_4]_2[\mathbf{14}]$ .

#### Synthesis of $[\text{PPh}_4]_2[\text{Ce}(\text{NO}_2)_6\text{Ag}(\text{py})_{1.5}]$ and crystals of $[\text{PPh}_4]_2[\mathbf{3}]$

A 25 mL round bottom flask was charged with  $[\text{PPh}_4]_2[\mathbf{2}]$  (35.8 mg, 0.032 mmol), 1 equiv.  $\text{AgNO}_2$  (4.9 mg, 0.003 mmol) and freshly distilled pyridine (5 mL). After complete dissolution of the solids, the yellow solution, sheltered from light, was vigorously stirred at room temperature for 1 h. The solvent was then evaporated off and after 15 h under vacuum, a yellow brown powder of a product  $[\text{PPh}_4]_2[\text{Ce}(\text{NO}_2)_6\text{Ag}(\text{py})_{1.5}]$  was isolated (40.8 mg, 97%). Translucent light yellow crystals of  $[\text{PPh}_4]_2[\mathbf{3}]$  were grown by slow diffusion of diethyl ether (1.5 mL) in a pyridine solution (0.5 mL) of the analyzed product (*ca.* 10 mg).

Anal. calcd for  $\text{C}_{55.5}\text{H}_{47.5}\text{AgCeN}_{7.5}\text{O}_{12}\text{P}_2$  (1321.45): C, 50.44; H, 3.62; N, 7.95; Found: C, 49.73; H, 3.64; N, 8.35; IR ( $\text{cm}^{-1}$ ): 524, 689, 705, 722, 757, 800, 824, 891, 995, 1106, 1156, 1212 (N–O), 1305 (N–O), 1584, 1599, 2671, 2726.

#### Synthesis of $[\text{PPh}_4]_2[\text{Sm}(\text{NO}_2)_6\text{Ag}(\text{py})_2]$ ( $[\text{PPh}_4]_2[\mathbf{13}]$ )

A 25 mL round bottom flask was charged with  $[\text{PPh}_4]_2[\mathbf{10}]$  (52.3 mg, 0.049 mmol), 3 equiv.  $\text{AgNO}_2$  (7.6 mg, 0.005 mmol) and freshly distilled pyridine (5 mL). After complete dissolution of the solids, the solution, sheltered from light, was vigorously stirred at room temperature for 1 h. The solvent was then evaporated off and after 15 h under vacuum,  $[\text{PPh}_4]_2[\mathbf{13}]$

was isolated pure as a pale brown powder (65.1 mg, 96%). Colourless crystals of  $[\text{PPh}_4]_2[\mathbf{13}]$  were grown by slow diffusion of diethyl ether (1.5 mL) on a pyridine solution (0.5 mL) of the product (*ca.* 10 mg).

Anal. calcd for  $\text{C}_{58}\text{H}_{50}\text{AgN}_8\text{O}_{12}\text{P}_2\text{Sm}$  (1371.24): C, 50.80; H, 3.68; N, 8.17; found: C, 50.86; H, 3.79; N, 8.38; IR ( $\text{cm}^{-1}$ ): 523, 687, 722, 756, 803, 826, 1020, 1100, 1156, 1212 (N–O), 1261, 1307 (N–O), 1583, 1599, 2671, 2727.

#### Oxidation of $\text{Sm}^{\text{II}}$ to $\text{Sm}^{\text{III}}$ by $[\text{PPh}_4][\text{NO}_2]$

An NMR tube was charged with  $\text{SmI}_2$  (17.8 mg, 0.04 mmol) and a solution of 6 equiv.  $[\text{PPh}_4][\text{NO}_2]$  (101.8 mg, 0.26 mmol) and freshly distilled pyridine (~0.5 mL). The mixture was then sonicated for 1 h, a time during which the black insoluble  $\text{SmI}_2$  was transformed into a white precipitate with a few but visible release of gas. The solution was then filtered-off and crystals were grown by slow diffusion of diethyl ether (1.5 mL) on the pyridine filtrate. Colourless crystals of  $[\text{PPh}_4]_2[\text{Sm}(\text{NO}_2)_5]$  ( $[\text{PPh}_4]_2[\mathbf{10}]$ ) were obtained after 3 days.

#### Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer<sup>20</sup> using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of  $\phi$ - and  $\omega$ -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.<sup>21</sup> Absorption effects were corrected empirically with the program SCALEPACK.<sup>21</sup> The structures were solved by direct methods with SHELXS-97, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-97.<sup>22</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Special details are as follows.

In the series of isomorphous complexes  $[\text{PPh}_4]_2[\mathbf{1}]$ ,  $[\text{PPh}_4]_2[\mathbf{2}]$ ,  $[\text{PPh}_4]_2[\mathbf{4}]$  and  $[\text{PPh}_4]_2[\mathbf{6}]$ , two nitrite ions (containing N1 and N5) are badly resolved. In all cases, one of them (N5) was found to be disordered over two positions sharing the oxygen atom O10, which were refined with occupancy parameters constrained to sum to unity. In complex  $[\text{PPh}_4]_2[\mathbf{6}]$  only, the nitrite containing N1 could also be modeled with two positions; the position A of the nitrite containing N1 and B of that containing N5 are incompatible, and the occupancy parameters, constrained to sum to unity, have been assigned accordingly. Restraints on bond lengths, angles and displacement parameters had to be applied for several nitrite ions in all these compounds.

In complexes  $[\text{PPh}_4]_2[\mathbf{3}]$ ,  $[\text{PPh}_4]_2[\mathbf{13}]$  and  $[\text{PPh}_4]_2[\mathbf{14}]$ , the Ag atom is disordered over two positions which were refined with occupancy parameters constrained to sum to unity.

Table 2 Crystal data and structure refinement details

	[PPh <sub>4</sub> ] <sub>2</sub> [1]	[PPh <sub>4</sub> ] <sub>2</sub> [2]	[PPh <sub>4</sub> ] <sub>2</sub> [3]	[PPh <sub>4</sub> ] <sub>2</sub> [4]	[PPh <sub>4</sub> ] <sub>2</sub> [5][NO <sub>2</sub> ]	[PPh <sub>4</sub> ] <sub>2</sub> [6]	[PPh <sub>4</sub> ] <sub>2</sub> [7]
Chemical formula	C <sub>53</sub> H <sub>45</sub> LaN <sub>6</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>53</sub> H <sub>45</sub> CeN <sub>6</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>58</sub> H <sub>50</sub> AgCeN <sub>8</sub> O <sub>12</sub> P <sub>2</sub>	C <sub>53</sub> H <sub>45</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Pr	C <sub>58</sub> H <sub>50</sub> N <sub>7</sub> NdO <sub>10</sub> P <sub>2</sub>	C <sub>53</sub> H <sub>45</sub> N <sub>6</sub> NdO <sub>10</sub> P <sub>2</sub>	C <sub>53</sub> H <sub>45</sub> N <sub>6</sub> NdO <sub>10</sub> P <sub>2</sub>
<i>M</i> /g mol <sup>-1</sup>	1126.80	1128.01	1360.99	1128.80	1211.23	1132.13	1132.13
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1
<i>a</i> /Å	13.2741(4)	13.2645(5)	10.3567(5)	13.2497(4)	9.4292(2)	13.2408(2)	10.0031(4)
<i>b</i> /Å	17.9504(8)	17.9358(7)	16.1781(9)	17.9467(6)	9.6856(3)	17.9735(4)	12.8890(7)
<i>c</i> /Å	21.7777(8)	21.7448(7)	17.3706(6)	21.7355(3)	15.8367(6)	21.7067(3)	21.3346(11)
<i>α</i> /°	90	90	97.503(4)	90	76.145(2)	90	87.813(2)
<i>β</i> /°	96.307(3)	96.433(2)	97.694(4)	96.6330(18)	75.304(2)	96.8113(12)	77.576(3)
<i>γ</i> /°	90	90	98.777(3)	90	81.595(2)	90	68.306(3)
<i>V</i> /Å <sup>3</sup>	5157.7(3)	5140.7(3)	2816.4(2)	5133.9(2)	1352.68(7)	5129.38(16)	2493.4(2)
<i>Z</i>	4	4	2	4	1	4	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.451	1.457	1.605	1.460	1.487	1.466	1.508
<i>μ</i> (Mokα)/mm <sup>-1</sup>	0.954	1.012	1.273	1.075	1.085	1.139	1.171
<i>F</i> (000)	2288	2292	1370	2296	617	2300	1150
Reflections collected	17 4882	17 769	141 359	193 839	80 560	191 378	159 280
Independent reflections	9781	9748	10 682	9732	8246	15 604	15 217
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	7431	7415	7439	8308	7975	13 465	12 029
<i>R</i> <sub>int</sub>	0.045	0.049	0.072	0.025	0.037	0.018	0.051
Parameters refined	668	668	749	668	436	695	659
<i>R</i> <sub>1</sub>	0.057	0.058	0.049	0.057	0.028	0.040	0.033
<i>wR</i> <sub>2</sub>	0.161	0.160	0.129	0.165	0.076	0.112	0.069
<i>S</i>	1.129	1.127	1.011	1.046	1.050	1.124	1.003
Δρ <sub>min</sub> /e Å <sup>-3</sup>	-2.05	-1.51	-1.01	-1.66	-1.03	-1.19	-1.05
Δρ <sub>max</sub> /e Å <sup>-3</sup>	1.76	2.17	1.39	3.31	0.77	2.11	0.56

	[PPh <sub>4</sub> ] <sub>2</sub> [8]	[PPh <sub>4</sub> ] <sub>2</sub> [9]	[PPh <sub>4</sub> ] <sub>2</sub> [10]ppy	[PPh <sub>4</sub> ] <sub>2</sub> [11]ppy	[PPh <sub>4</sub> ] <sub>2</sub> [12]py	[PPh <sub>4</sub> ] <sub>2</sub> [13]	[PPh <sub>4</sub> ] <sub>2</sub> [14]
Chemical formula	C <sub>58</sub> H <sub>50</sub> AgN <sub>8</sub> O <sub>12</sub> P <sub>2</sub> Pr	C <sub>58</sub> H <sub>50</sub> AgN <sub>8</sub> NdO <sub>12</sub> P <sub>2</sub>	C <sub>53</sub> H <sub>45</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Sm	C <sub>53</sub> H <sub>45</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Yb	C <sub>53</sub> H <sub>45</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Y	C <sub>58</sub> H <sub>50</sub> AgN <sub>8</sub> O <sub>12</sub> P <sub>2</sub> Sm	C <sub>58</sub> H <sub>50</sub> AgN <sub>8</sub> O <sub>12</sub> P <sub>2</sub> Y
<i>M</i> /g mol <sup>-1</sup>	1361.78	1365.11	1138.24	1160.93	1076.80	1371.22	1309.78
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 1
<i>a</i> /Å	31.9249(10)	31.8726(10)	17.8243(8)	17.7881(5)	17.8054(7)	10.1729(5)	10.1741(3)
<i>b</i> /Å	10.8245(5)	10.8359(3)	13.6518(3)	13.6149(4)	13.6258(6)	11.6627(5)	11.6470(5)
<i>c</i> /Å	20.8700(8)	20.8434(7)	22.0678(10)	21.9841(5)	22.0104(5)	24.7799(9)	24.6852(12)
<i>α</i> /°	90	90	90	90	90	95.368(3)	95.277(2)
<i>β</i> /°	127.881(2)	127.829(2)	109.511(2)	109.6818(17)	109.628(2)	93.817(3)	94.020(3)
<i>γ</i> /°	90	90	90	90	90	103.994(2)	103.847(3)
<i>V</i> /Å <sup>3</sup>	5692.4(4)	5685.8(3)	5061.5(3)	5013.1(2)	5029.7(3)	2828.1(2)	2815.2(2)
<i>Z</i>	4	4	4	4	4	2	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.589	1.595	1.494	1.538	1.422	1.610	1.545
<i>μ</i> (Mokα)/mm <sup>-1</sup>	1.316	1.374	1.288	1.995	1.288	1.501	1.501
<i>F</i> (000)	2744	2744	2340	2340	2216	1378	1332
Reflections collected	100 289	64 608	175 865	172 017	164 062	155 212	163 001
Independent reflections	8682	8658	13 075	15 284	12 979	17 283	17 198
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	6727	7081	8465	11 714	8570	12 818	11 391
<i>R</i> <sub>int</sub>	0.035	0.032	0.083	0.036	0.052	0.053	0.054
Parameters refined	425	425	649	649	649	749	749
<i>R</i> <sub>1</sub>	0.038	0.035	0.038	0.028	0.040	0.035	0.038
<i>wR</i> <sub>2</sub>	0.096	0.090	0.070	0.062	0.084	0.078	0.089
<i>S</i>	1.135	1.168	0.911	0.955	0.961	1.002	1.002
Δρ <sub>min</sub> /e Å <sup>-3</sup>	-1.74	-1.95	-0.88	-1.03	-0.46	-1.08	-0.56
Δρ <sub>max</sub> /e Å <sup>-3</sup>	1.94	1.62	0.66	0.50	0.35	1.08	0.92

In complex  $[\text{PPh}_4]_2[\text{5}][\text{NO}_2]$ , all the nitrite ions, both coordinated and free, and the pyridine ligand, are disordered over two positions (sharing one nitrogen atom for one nitrite ion and one oxygen atom for another one), which have been refined with occupancy parameters constrained to sum to unity (fixed to 0.5 for the free nitrite which is disordered around an inversion centre). Restraints on bond lengths and displacement parameters had to be applied for the free nitrite anion, and the two positions of the pyridine molecule, close to one another, were refined as idealized hexagons.

In complex  $[\text{PPh}_4]_2[\text{7}]$ , atom N5 is disordered over two positions which were refined with occupancy parameters constrained to sum to unity and with restraints on displacement parameters.

In the two isomorphous complexes  $[\text{PPh}_4]_2[\text{8}]$  and  $[\text{PPh}_4]_2[\text{9}]$ , the three nitrite ions are disordered: two of them (containing N1 and N2) have two components nearly orthogonal to one another while only one oxygen atom is disordered over two positions in the third (N3). The occupancy parameters of all these positions have been refined to values very close to 0.5, then fixed to this value to allow for the mixing of the different positions and their symmetry equivalents (some positions being mutually incompatible). Restraints have been applied for some bond lengths and displacement parameters in the disordered parts.

Crystal data and structure refinement parameters are given in Table 2 and selected bond lengths and angles in Table 1. The molecular plots were drawn with ORTEP-3.<sup>23</sup>

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