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A new phase of the complex trinitratotris (triphenylphosphineoxide)neodymium(III)

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The crystal structure of the complex $[\text{Nd}(\text{NO}_3)_3(\text{OPPh}_3)_3]$ (**1**) was obtained by single-crystal X-ray diffraction. The central neodymium(III) ion is nine coordinate arranged in a tricapped trigonal prism geometry. Crystallization of **1** occurs in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with $a = 14.6496(9)$, $b = 18.4506(11)$, $c = 20.5491(11)$; $\beta = 102.925(3)^\circ$; and $Z = 4$.

KEY WORDS: Synthesis; crystal structure; neodymium(III); nitrate; triphenylphosphine oxide.

Introduction

There has been considerable interest in the complexes formed by the lanthanides with various monodentate neutral ligands with O as the donor atom. Phosphine oxides, in particular, have proven useful in complexing to lanthanide metal ions and have found practical application in the solvent extraction and separation of lanthanides.¹ Several lanthanide(III) nitrate complexes with triphenylphosphine oxide (OPPh₃) have been prepared resulting in complexes having as few as two and as many as four OPPh₃ groups per lanthanide center.^{2–4} An earlier study by Cousins and Hart⁵ identified the complex $[\text{Nd}(\text{OPPh}_3)_3(\text{NO}_3)_3]$. Two crystal phases of this same complex were briefly reported later by Mascarenhas *et al.*,⁶ but no structural data was given. A complete struc-

tural analysis of a third phase of the complex $[\text{Nd}(\text{OPPh}_3)_3(\text{NO}_3)_3]$ is reported below.

Experimental

General considerations

All reactions were carried out under ambient conditions. Reagents were used as received from the vendor. An NMR spectrum was recorded on a Bruker DPX 300 NMR spectrometer at the following frequency (MHz): ³¹P{¹H}, 121.5. IR (KBr disc) and UV–Vis (dilute, CH₂Cl₂ solution) spectra were obtained on Nicolet FT-IR and Shimadzu UV-2101PC spectrophotometers, respectively.

Synthesis

Neodymium oxide (0.083 g, 0.25 mmol) was reacted with ca. 2 mL of concentrated nitric acid and heated to dryness to form pale-purple crystals. The crystals and OPPh₃ (0.28 g, 1.0 mmol) were dissolved separately in room-temperature ethanol and mixed to form an approximate 25 mL solution. The reaction mixture was stirred, heated for 1 h, and evaporated to dryness to form pale-purple

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crystals. Recrystallization was performed by slow diffusion of a dichloromethane solution into petroleum ether. Pale-purple crystals of X-ray diffraction quality were formed after several days.

Single-crystal analysis

Low-temperature X-ray measurements were carried out on a Bruker X8 APEX diffractometer using Mo K_{α} X-radiation ($\lambda_{\text{mean}} = 0.71073 \text{ \AA}$). Intensity data frames were processed with SAINT⁷ and corrected for absorption with SADABS.⁸ The structure was solved using SHELXTL vs. 6.10⁹ and refined against all F^2 data using SHELXL-97.¹⁰ All hydrogens were included in calculated positions (C–H = 0.950 \AA) and allowed to ride on their parent carbon atoms with fixed isotropic thermal parameters [$U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{iso}}(\text{C})$]. Final difference Fourier maps indicated insignificant residual electron density near the positions of the neodymium ion, see Table 1.

Table 1. Crystal Data and Structure Refinement

Compound	[Nd(OPPh ₃) ₃ (NO ₃) ₃] 1/2 CH ₂ Cl ₂
CCDC deposit no.	CCDC 233312
Color/shape	Pale-purple prisms
Empirical formula	C _{54.5} H ₄₅ ClN ₃ NdO ₁₂ P ₃
Formula weight	1206.53
Temperature, K	110(2)
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	$a = 14.6496(9) \text{ \AA}$ $b = 18.4506(11) \text{ \AA}$ $c = 20.5491(11) \text{ \AA}$ $\beta = 102.925(3)^\circ$
Volume, \AA^3	5413.6(5)
Z	4
Density (calculated), g/cm^3	1.480
Absorption coefficient, mm^{-1}	1.161
θ range for data collection, $^\circ$	1.50–30.81
Reflections measured	173457
Independent/observed reflections	16732
Data/restraints/parameter	16732/1/676
Goodness of fit on F^2	1.039
Max/min transmission	0.8113/0.7531
Final R indices [$I > 2s(I)$]	$R1 = 0.0238$, $wR2 = 0.0615$
R indices (all data)	$R1 = 0.0312$, $wR2 = 0.0651$
Largest diff. peak/hole, $\text{e} \times \text{\AA}^{-3}$	0.899/–1.372

Results and discussion

Taking into account the presence of three triphenylphosphine oxide ligands along with three bidentate nitrate groups, the structure of **1** has the stoichiometry [Nd(OPPh₃)₃(NO₃)₃]. In addition, the compound crystallizes with one-half molecule of CH₂Cl₂ per formula unit disordered over an inversion center located at Wyckoff site $2d(1/2, 1/2, 0)$. All other atoms are located in general sites ($4e$). Atomic coordinates are tabulated in Table 2. Figure 1 is a representation of the molecular structure of **1**. When considering the presence of

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**

Atom	x	y	z	U_{eq}^a
Nd	2460(1)	1133(1)	7602(1)	13(1)
C(1)	5694(1)	1878(1)	8604(1)	24(1)
C(2)	6329(1)	2365(1)	8989(1)	34(1)
C(3)	6989(1)	2111(1)	9541(1)	37(1)
C(4)	7013(1)	1385(1)	9714(1)	31(1)
C(5)	6390(1)	899(1)	9328(1)	31(1)
C(6)	5733(1)	1143(1)	8777(1)	27(1)
C(7)	5283(1)	2116(1)	7164(1)	26(1)
C(8)	6233(1)	2263(1)	7196(1)	37(1)
C(9)	6554(2)	2300(1)	6611(1)	47(1)
C(10)	5949(2)	2184(1)	6004(1)	47(1)
C(11)	5014(2)	2025(1)	5970(1)	43(1)
C(12)	4677(1)	1993(1)	6551(1)	30(1)
C(13)	4610(1)	3121(1)	8016(1)	28(1)
C(14)	5097(1)	3664(1)	7762(1)	35(1)
C(15)	4943(2)	4389(1)	7885(1)	45(1)
C(16)	4320(2)	4572(1)	8254(2)	63(1)
C(17)	3808(3)	4042(2)	8491(2)	78(1)
C(18)	3948(2)	3313(1)	8370(2)	54(1)
C(19)	3067(1)	1421(1)	9983(1)	20(1)
C(20)	3936(1)	1259(1)	9841(1)	26(1)
C(21)	4667(1)	1014(1)	10351(1)	30(1)
C(22)	4541(1)	940(1)	10994(1)	28(1)
C(23)	3675(1)	1098(1)	11137(1)	30(1)
C(24)	2935(1)	1334(1)	10628(1)	26(1)
C(25)	1049(1)	1449(1)	9441(1)	23(1)
C(26)	742(1)	769(1)	9181(1)	26(1)
C(27)	–116(1)	499(1)	9257(1)	34(1)
C(28)	–669(1)	903(1)	9587(1)	41(1)
C(29)	–364(1)	1580(1)	9848(1)	43(1)
C(30)	495(1)	1856(1)	9777(1)	33(1)
C(31)	2131(1)	2746(1)	9423(1)	23(1)
C(32)	1660(2)	3160(1)	8883(1)	36(1)
C(33)	1591(2)	3905(1)	8957(1)	51(1)
C(34)	1991(2)	4236(1)	9557(1)	48(1)
C(35)	2449(2)	3830(1)	10090(1)	44(1)

Table 2. Continued

Atom	x	y	z	U_{eq}^a
C(36)	2521(2)	3083(1)	10027(1)	32(1)
C(37)	-616(1)	1177(1)	6192(1)	21(1)
C(38)	46(1)	1081(1)	5811(1)	36(1)
C(39)	-234(2)	1027(2)	5117(1)	51(1)
C(40)	-1178(2)	1065(1)	4805(1)	42(1)
C(41)	-1840(2)	1165(1)	5178(1)	35(1)
C(42)	-1569(1)	1222(1)	5871(1)	29(1)
C(43)	-627(1)	2090(1)	7340(1)	22(1)
C(44)	-718(1)	2177(1)	7997(1)	34(1)
C(45)	-1022(2)	2839(1)	8201(1)	44(1)
C(46)	-1245(1)	3408(1)	7750(1)	41(1)
C(47)	-1146(1)	3324(1)	7103(1)	36(1)
C(48)	-831(1)	2668(1)	6894(1)	28(1)
C(49)	-868(1)	544(1)	7434(1)	19(1)
C(50)	-1773(1)	655(1)	7532(1)	32(1)
C(51)	-2235(1)	97(1)	7782(1)	40(1)
C(52)	-1810(1)	-574(1)	7918(1)	35(1)
C(53)	-916(1)	-688(1)	7823(1)	28(1)
C(54)	-438(1)	-132(1)	7584(1)	22(1)
Cl(1)	5773(1)	4506(1)	10174(1)	95(1)
C(55)	5370(3)	5286(3)	9762(4)	76(2)
N(1)	2819(1)	77(1)	6581(1)	22(1)
N(2)	2899(1)	-193(1)	8446(1)	24(1)
N(3)	1780(1)	2393(1)	6739(1)	19(1)
O(1)	3929(1)	1736(1)	7833(1)	23(1)
O(2)	2326(1)	1576(1)	8651(1)	21(1)
O(3)	797(1)	1106(1)	7304(1)	19(1)
O(4)	3388(1)	591(1)	6793(1)	24(1)
O(5)	2065(1)	66(1)	6796(1)	25(1)
O(6)	2981(1)	-378(1)	6190(1)	37(1)
O(7)	3531(1)	175(1)	8256(1)	27(1)
O(8)	3094(1)	-720(1)	8811(1)	47(1)
O(9)	2058(1)	12(1)	8233(1)	20(1)
O(10)	2140(1)	1833(1)	6526(1)	21(1)
O(11)	1895(1)	2453(1)	7366(1)	23(1)
O(12)	1338(1)	2840(1)	6352(1)	31(1)
P(1)	4809(1)	2175(1)	7897(1)	21(1)
P(2)	2158(1)	1780(1)	9324(1)	18(1)
P(3)	-242(1)	1228(1)	7087(1)	16(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

mixed monodentate and polydentate ligands, as exemplified in this work, the choice of an appropriate geometric polyhedron can be subtle. If the coordinated nitrate groups are conceptually reduced to monoatomic ligands, the molecule can be described as *mer*-(pseudo)-octahedral, similar to the results found in the yttrium analog described by Deakin *et al.*⁴ However, it cannot be ignored that each nitrate group actually occupies two coordination sites on the central metal atom,

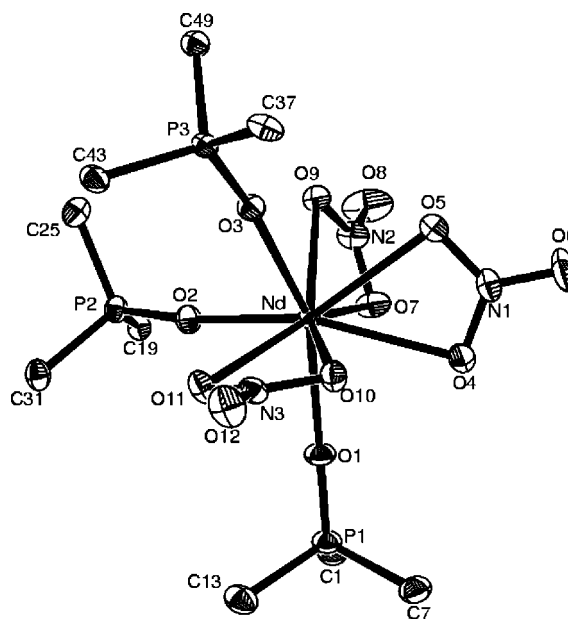


Fig. 1. An ORTEP drawing of the complex [Nd(NO₃)₃(OPPh₃)₃] illustrating the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Only the *ipso*-carbons of the phosphine are shown for clarity.

and thus, the coordination environment around the Nd(III) ions is perhaps better described as a distorted tricapped trigonal prism (TTP), see Fig. 2. As such, the capping oxygens, one from each

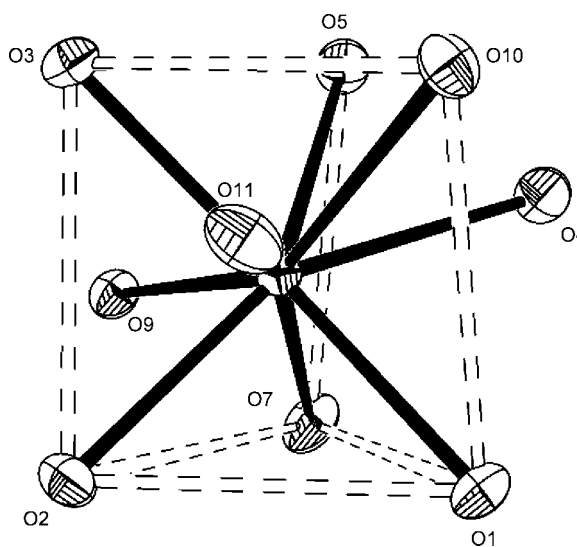


Fig. 2. The distorted tricapped trigonal prism coordination environment of the Nd(III) ion in 1.

Table 3. Select Geometric Parameters for **1** in (Å) and (°)

Nd—O(2)	2.3530(11)	Nd—O(9)	2.5774(11)	N(1)—O(5)	1.2784(18)
Nd—O(1)	2.3736(11)	Nd—O(11)	2.5827(11)	N(2)—O(8)	1.2224(18)
Nd—O(3)	2.3766(11)	O(1)—P(1)	1.5038(11)	N(2)—O(9)	1.2691(17)
Nd—O(10)	2.5131(11)	O(2)—P(2)	1.5071(12)	N(2)—O(7)	1.2774(18)
Nd—O(7)	2.5400(11)	O(3)—P(3)	1.5035(11)	N(3)—O(12)	1.2249(17)
Nd—O(5)	2.5543(12)	N(1)—O(6)	1.2220(18)	N(3)—O(11)	1.2664(18)
Nd—O(4)	2.5742(12)	N(1)—O(4)	1.2734(17)	N(3)—O(10)	1.2815(16)
O(6)—N(1)—O(4)	121.83(14)	O(1)—Nd—O(7)	78.17(4)	O(5)—Nd—O(9)	70.32(4)
O(6)—N(1)—O(5)	121.79(14)	O(3)—Nd—O(7)	126.76(4)	O(4)—Nd—O(9)	103.07(4)
O(4)—N(1)—O(5)	116.38(12)	O(10)—Nd—O(7)	142.68(4)	O(2)—Nd—O(11)	75.84(4)
O(8)—N(2)—O(9)	121.61(14)	O(2)—Nd—O(5)	143.90(4)	O(1)—Nd—O(11)	80.47(4)
O(8)—N(2)—O(7)	121.64(14)	O(1)—Nd—O(5)	123.67(4)	O(3)—Nd—O(11)	72.76(4)
O(9)—N(2)—O(7)	116.75(13)	O(3)—Nd—O(5)	75.33(4)	O(10)—Nd—O(11)	50.31(4)
O(12)—N(3)—O(11)	122.28(13)	O(10)—Nd—O(5)	81.68(4)	O(7)—Nd—O(11)	152.84(4)
O(12)—N(3)—O(10)	121.18(14)	O(7)—Nd—O(5)	80.22(4)	O(5)—Nd—O(11)	126.05(4)
O(11)—N(3)—O(10)	116.54(12)	O(2)—Nd—O(4)	152.95(4)	O(4)—Nd—O(11)	116.03(4)
O(12)—N(3)—Nd	167.51(11)	O(1)—Nd—O(4)	74.04(4)	O(9)—Nd—O(11)	138.67(4)
O(11)—N(3)—Nd	60.53(7)	O(3)—Nd—O(4)	119.02(4)	P(1)—O(1)—Nd	172.38(8)
O(10)—N(3)—Nd	57.45(7)	O(10)—Nd—O(4)	69.69(4)	P(2)—O(2)—Nd	172.75(7)
O(2)—Nd—O(1)	84.93(4)	O(7)—Nd—O(4)	73.65(4)	P(3)—O(3)—Nd	169.96(7)
O(2)—Nd—O(3)	87.26(4)	O(5)—Nd—O(4)	50.03(4)	N(1)—O(4)—Nd	96.30(9)
O(1)—Nd—O(3)	153.20(4)	O(2)—Nd—O(9)	75.12(4)	N(1)—O(5)—Nd	97.11(8)
O(2)—Nd—O(10)	126.14(4)	O(1)—Nd—O(9)	125.03(4)	N(2)—O(7)—Nd	97.29(8)
O(1)—Nd—O(10)	85.28(4)	O(3)—Nd—O(9)	77.09(4)	N(2)—O(9)—Nd	95.73(8)
O(3)—Nd—O(10)	78.77(4)	O(10)—Nd—O(9)	146.74(4)	N(3)—O(10)—Nd	97.09(9)
O(2)—Nd—O(7)	85.71(4)	O(7)—Nd—O(9)	50.14(3)	N(3)—O(11)—Nd	94.20(8)

nitrate group, have an average Nd—O_{NO₃} distance of 2.578(3) Å and are the longest metal–ligand internuclear separations in the complex—as expected for a TTP. The remaining Nd—O_{NO₃} distances range from 2.5131(11) to 2.5543(12) Å; the average Nd—O_{OPPh₃} separation is 2.368(10) Å. The two triangular faces of the trigonal prism (O1, O2, O7 and O3, O5, O10) are essentially parallel with a dihedral angle of 0.87(8)° between them. The bite of the nitrate group, corresponding to the O—Nd—O angle, averages 50.16(12)° for the three nitrate groups in **1** and is in agreement with those found in similar complexes. Selected geometric parameters are presented in Table 3.

The ³¹P{¹H} NMR spectrum of **1** at 300 K (CDCl₃) indicates the presence of a singlet at δ 144. Infrared assignments are as expected and include the following peaks: 3056.16 m, 1972.52 w, 1896.81 w, 1818.56 w, 1762.36 w, 1730.18 w, 1629.65 m, 1591.57 m, (NO₃) 1465.23 s, 1439.00 s, 1384.23 m, (NO₃) 1302.27 s, (PO) 1159.55 s, (PO) 1146.77 s, 1120.42 s, 1089.46 s,

1071.28 m, 1037.46 m, 1027.30 s, 998.12 m, 871.81 m, 851.34 w, 815.74 m, 754.06 m, 749.51 m, 734.77 m, 725.12 s, 691.62 s, 617.18 w, 538.44 s, 517.04 m, 460.75 m, 442.35 w, 411.90 w. A dilute solution of compound **1** in dichloromethane gave the following UV–Vis absorptions (nm): 260.5, 266.5, 273.5, 356.0, 512.5, 525.0, 585.0, 745.00, and 800.0.

In the past, there has been significant discussion about the nature of the P—O bond order in phosphine oxides (X₃PO). Much of this work has been reviewed.¹¹ The P—O bond in phosphine oxides has been described as a formal triple bond¹² to roughly a single bond.¹³ There are several methods available for the estimation of bond order including the bond distance–bond order relationship, first described by Pauling¹⁴ and later modified as the Bond Valence Model,^{15–18} along with an analysis of IR force constants. See *et al.*¹⁹ recently published an analysis of the P—O bond in triarylphosphine oxides using these methods and including the compounds (*p*-CIPh)₃PO and

Table 4. Potential C—H···O interactions for **1**

Donor—H···acceptor	D—H	H···A	D···A	D—H···A
C15—H15···O4 ^a	0.950	2.520	3.257(3)	134.4
C46—H46···O5 ^b	0.950	2.540	3.490(2)	177.5
C24—H24···O12 ^c	0.950	2.543	3.399(2)	150.0

Note. Symmetry transformations used to generate equivalent atoms: ^a 1-x, y-0.5, 1.5-z; ^b -x, y-0.5, 1.5-z; ^c x, 0.5-y, 0.5+z.

(*p*-OMePh)₃PO. Similar calculations for the P—O bond in **1** yield an average bond order of 1.69(1) for the bond distance—bond order relationship and 1.67 when considering IR force constants (based on the peak at 1159.55 cm⁻¹). These are slightly lower than those predicted for the discrete triphenylphosphines discussed by See—an expected observation after considering coordination of the triphenylphosphine oxide ligand to the Nd(III) metal center via the oxygen atom.

Several oxygen atoms from the various nitrate groups are involved in multiple close contacts with surrounding hydrogen atoms and thus, crystal packing appears to be stabilized by C—H···O interactions; details are included in Table 4. According to the somewhat liberal definition ascribed by Desiraju and Steiner,²⁰ these contacts may be classified as weak to very weak C—H···O hydrogen bonds.

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Supplementary material CCDC-233312 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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