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Triisothiocyanatotetrakis(triphenylphosphine oxide)neodymium(III)

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In the neodymium(III) complex, $[Nd(NCS)_3\{OP(C_6H_5)_3\}_4]$, the coordination about the central neodymium(III) ion is sevenfold with a slightly distorted capped trigonal prismatic arrangement.

Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.026
wR factor = 0.067
Data-to-parameter ratio = 25.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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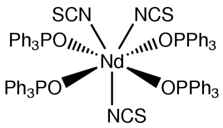
Comment

Lanthanide metals have become particularly interesting in the preparation of new materials owing to their unique physical and chemical properties (Benelli *et al.*, 1992). More importantly, since the removal of lanthanides from radioactive high-level liquid waste (HLLW) has been shown to improve the transmutation of long-lived transuranic elements to short-lived or even stable nuclides (Modolo & Odoj, 1998), the coordination chemistry of the 4*f* metals continues to attract interest. In particular, complexes of lanthanide nitrates and *N*-thiocyanates have been studied with a multitude of mono- and polyfunctional ligands containing P═O, C═O, or N—O donors (Cunningham & Kautz, 2000; Farmer *et al.*, 2000; Gan *et al.*, 1996; Levason *et al.*, 2000, and references therein). Phosphine oxides, above all, have proved to be popular complexing ligands and are often used in solvent extraction and separation processes specific to lanthanide metals (Levason *et al.*, 2000). In the light of these considerations, the present study is aimed at the synthesis and structural characterization of the molecular neodymium(III) complex $[Nd(NCS)_3\{OP(C_6H_5)_3\}_4]$, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The Nd^{III} metal center is coordinated by three $[NCS]^-$ anions [average Nd—N = 2.50 (3) Å] and four triphenylphosphine oxide ($OPPh_3$) ligands [average Nd—O = 2.37 (2) Å]. The C and S atoms of the N2/C74/S2 thiocyanate group are disordered over two sites. The occupancies of the major and minor components were refined to 88.4 (2) and 11.6 (2)%, respectively; the analogous atoms in each component were refined with identical anisotropic displacement parameters. Selected geometric parameters are included in Table 1 and are reasonable when compared to similar Nd^{III}–thiocyanate complexes.

The Nd^{III} ion exists in a slightly distorted capped trigonal prismatic (CTP) arrangement. The atoms N2/O2/O3 and N1/O1/O4 define the two triangular faces of the prism and exhibit

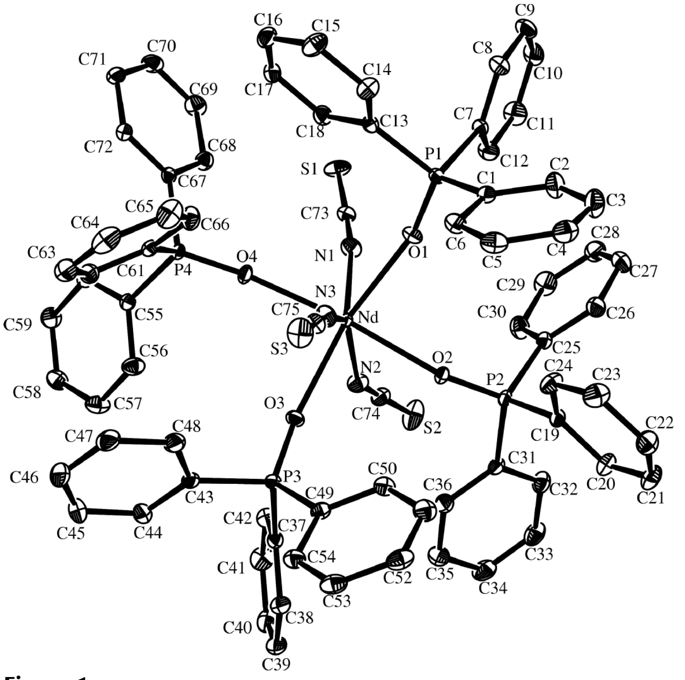


Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 40% probability level. H atoms and the minor disorder component have been omitted.

a dihedral angle of 4.81 (5)°; atom N3 caps the O1/O2/O3/O4 face, with Nd—N3 = 2.5144 (14) Å. The $L—M—L$ geometric parameters in (I) are fairly typical for the CTP coordination environment (Howard *et al.*, 1998; Yao *et al.*, 2001). The other plausible option for a coordination polyhedron of (I) is a capped octahedron, although the distortions when attempting to fit the atoms of (I) to this system are significant. As such, the four unique O atoms from the $OPPh_3$ groups comprise the equatorial plane with an r.m.s. deviation of 0.1811 Å. Atoms N2, Nd and N3 form the octahedral axis and exhibit a bond angle of 147.80 (5)°. Atom N1 caps the O1/O4/N2 face, with Nd—N1 = 2.5230 (14) Å, and is the longest Nd—ligand bond in the system. As a general note, there are three archetypal forms for seven-coordinate systems: the pentagonal bipyramid (PBP, D_{5h}), the capped octahedron (COC, C_{3v}), and the capped trigonal prism (CTP, C_{2v}). The COC is considered an intermediate on the PBP/CTP interconversion pathway (Kepert, 1979). As such, the geometric distortions of the CTP in (I) indicate a COC coordination environment.

In the past, there has been significant discussion about the nature of the P—O bond order in phosphine oxides (X_3PO). Much of this work has been reviewed (Gilheany, 1994). In these complexes, the P—O bond has been described anywhere from a formal triple bond (Messmer, 1991) to roughly a single bond (Reed & Schleyer, 1990). There are several methods available for the estimation of bond order including the bond-distance–bond-order relationship, first described by Pauling (1960) and later modified as the Bond Valence Model (Brese & O'Keeffe, 1991; Brown, 1992; Burdett & Hawthorne, 1993; O'Keeffe & Brese, 1991; Urusov, 1995), along with an analysis of IR force constants. See *et al.* (1998) recently published an analysis of the P—O bond using these methods on several triarylphosphine oxides, including the compounds (p-ClPh)$_3$PO and (p-OMePh)$_3$PO along with the ubiquitous $OPPh_3$ ligand. Similar calculations for the P—O bond in (I) yield an average bond order of 1.71 (1) from the bond-distance–bond-order relationship and 1.65 when considering IR force constants (based on the peak at 1152 cm^{-1}). These are slightly lower than those predicted for the discrete triphenylphosphine molecules discussed by See *et al.* – an expected observation after considering coordination of the triphenylphosphine oxide ligand to the Nd^{III} metal center *via* the O atom. The P—O single-bond distance has been calculated by O'Keeffe & Brese (1991) as 1.70 Å. The average P—O distance in (I) is 1.501 (3) Å.

The geometry about the various phosphorus atoms is distorted tetrahedral, with O—P—C angles *ca.* 5° larger than the C—P—C angles on average. This result agrees with a structural study of a monoclinic polymorph of $OPPh_3$ by Spek (1987), discussed in detail by Gilheany (1994).

Experimental

Ethanol solutions of neodymium(III) nitrate hydrate (1 mmol) and KSCN (3 mmol) were combined. The resulting precipitate (KNO_3) was discarded. The filtrate was then combined with an ethanol solution of triphenylphosphine oxide (4 mmol). The total solution volume was reduced to 10 ml and a pale-purple precipitate was isolated. X-ray quality crystals were grown from a dichloromethane solution of the crude product layered with light petroleum ether. IR (KBr disc, Nicolet FT–IR): ν(CN) 2074, 2060, 2050 (*vs*); ν(PO) 1152 (*vs*) cm^{-1}. UV–Vis (Shimadzu UV-2101PC dilute ethanol solution): λ_{max} 522.5, 583.5, 744.5, 802.0 nm.

Crystal data

$[Nd(NCS)_3(C_{18}H_{15}OP)_4]$
$M_r = 1431.56$
Monoclinic, $P2_1/c$
$a = 13.1276$ (6) Å
$b = 23.4257$ (10) Å
$c = 22.4129$ (10) Å
$\beta = 102.660$ (2)°
$V = 6724.9$ (5) Å^3
$Z = 4$

$D_x = 1.414$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8594 reflections
$\theta = 2.9$–29.8°
$\mu = 1.01$ mm^{-1}
$T = 110$ (2) K
Block, purple
0.26 × 0.25 × 0.19 mm

Data collection

Bruker X8 SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.769$, $T_{max} = 0.827$
172262 measured reflections

20530 independent reflections
17010 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 30.5°$
$h = -18 \rightarrow 18$
$k = -33 \rightarrow 33$
$l = -31 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.067$
$S = 1.04$
20530 reflections
818 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 2.6415P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Nd—N1	2.5230 (14)	O3—P3	1.4968 (11)
Nd—N3	2.5144 (14)	O4—P4	1.5024 (10)
Nd—O1	2.3508 (11)	N2—C74	1.175 (2)
Nd—O4	2.3649 (10)	C74—S2	1.629 (2)
Nd—O2	2.3767 (10)	C74A—S2A	1.569 (13)
Nd—O3	2.4075 (10)	C73—N1	1.162 (2)
Nd—N2	2.4730 (14)	C73—S1	1.6361 (16)
O1—P1	1.4992 (11)	C75—N3	1.166 (2)
O2—P2	1.5043 (10)	C75—S3	1.6353 (17)
O1—Nd—O4	103.45 (4)	O4—Nd—N1	75.91 (4)
O1—Nd—O2	79.30 (4)	O2—Nd—N1	115.77 (4)
O4—Nd—O2	168.13 (4)	O3—Nd—N1	138.75 (4)
O1—Nd—O3	148.61 (4)	N2—Nd—N1	73.27 (5)
O4—Nd—O3	87.36 (4)	N3—Nd—N1	138.57 (5)
O2—Nd—O3	84.72 (4)	P1—O1—Nd	159.36 (7)
O1—Nd—N2	125.77 (4)	P2—O2—Nd	150.26 (6)
O4—Nd—N2	107.50 (4)	P3—O3—Nd	167.22 (7)
O2—Nd—N2	79.20 (4)	P4—O4—Nd	169.53 (7)
O3—Nd—N2	76.49 (4)	C74—N2—Nd	154.93 (17)
O1—Nd—N3	78.91 (4)	C73—N1—Nd	171.79 (13)
O4—Nd—N3	82.34 (4)	C75—N3—Nd	170.74 (13)
O2—Nd—N3	86.93 (4)	N2—C74—S2	178.0 (3)
O3—Nd—N3	73.38 (4)	N1—C73—S1	178.05 (16)
N2—Nd—N3	147.80 (5)	N3—C75—S3	178.80 (16)
O1—Nd—N1	72.61 (4)		

H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.93 Å and $U_{\rm iso}(\rm H) = 1.2U_{\rm iso}(\rm C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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References

Benelli, C., Guerriero, P., Tamburini, S. & Vigato. P. A. (1992). *Mater. Chem. Phys.* **31**, 137–144.

Brese, N. E. & O'Keeffe, M. O. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.

Bruker (2000). *SADABS* (Version 2.03) and *SAINT* (Version 5.624). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SMART*. Version 6.04. Bruker AXS Inc., Madison, Wisconsin, USA.

Burdett, J. K. & Hawthorne, F. C. (1993). *Am. Mineral.* **78**, 884–892.

Cunningham, B. P. & Kautz, J. A. (2000). *J. Chem. Crystallogr.* **30**, 671–675.

Farmer, J. M., Kautz, J. A., Kwon, H. S. & Mullica, D. F. (2000). *J. Chem. Crystallogr.* **30**, 301–309.

Gan, X., Duesler, E. N., Paine, R. T. & Smith, P. H. (1996). *Inorg. Chim. Acta*, **247**, 29–34.

Gilheany, D. G. (1994). *Chem. Rev.* **94**, 1339–1374.

Howard, J. A. K., Copley, R. C. B., Yao, J. W. & Allen, F. H. (1998). *Chem. Commun.* pp. 2175–2176.

Kepert, D. L. (1979). *Prog. Inorg. Chem.* **25**, 41–144.

Levason, W., Newman, E. H. & Webster, M. (2000). *Polyhedron*, **19**, 2697–2705.

Messmer, R. P. (1991). *J. Am. Chem. Soc.* **113**, 433–440.

Modolo, G. & Odoj, R. (1998). *J. Alloys Compd.* **271**–**273**, 248–251.

O'Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press.

Reed, A. E. & Schleyer, P. v. R. (1990). *J. Am. Chem. Soc.* **112**, 1434–1445.

See, R. F., Dutoi, A. D., Fettinger, J. C., Nicastro, P. J. & Ziller, J. W. (1998). *J. Chem. Crystallogr.* **28**, 893–898.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Spek, A. L. (1987). *Acta Cryst.* C**43**, 1233–1235.

Urusov, V. S. (1995). *Acta Cryst.* B**51**, 641–649.

Yao, J. W., Copley, R. C. B., Howard, J. A. K., Allen, F. H. & Motherwell, W. D. S. (2001). *Acta Cryst.* B**57**, 251–260.

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