Crystal structure of bis(*O*,*O′*-tetraisopropylmethylenediphosphonate) trinitrate neodymium(III), $Nd(NO_3)_3[(^iPrO)_2POCH_2PO(O^iPr)_2]_2$

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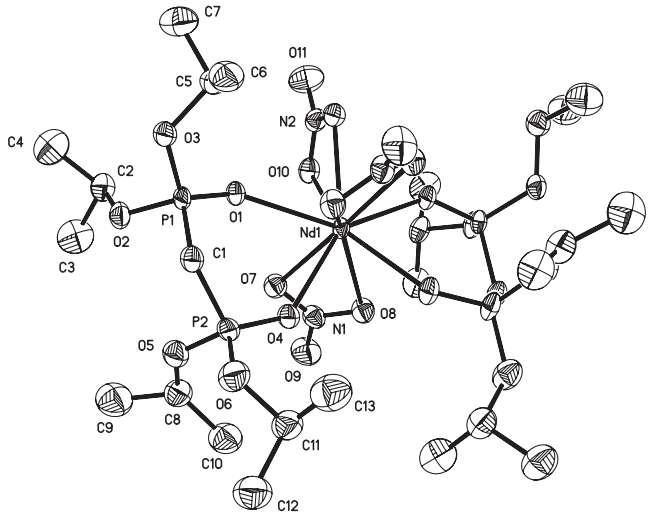

Abstract

$C_{26}H_{58}N_3NdO_{21}P_4$, monoclinic, *C*12/*c*1 (no. 15), a = 18.286(2) Å, b = 11.903(1) Å, c = 23.202(2) Å, β = 104.386(2)°, V = 4891.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.069, $wR_{ref}(F^2)$ = 0.210, T = 298 K.

Source of material

$Nd(NO_3)_3 \cdot nH_2O$ (0.1797 g, 0.4 mmol) was dissolved in 5 ml pyridine. Then tetrakis(*O*-isopropyl)-methylenediphosphonate (L = $(^iPrO)_2P(O)CH_2P(O)(^iPrO)_2$; 0.0689 g, 0.2 mmol) which was dissolved in 5 ml methylene dichloride was added under stiring. After three hours stiring, phen(1,10-phen-anthroline; 0.0793 g, 0.4 mmol) was added as the second ligand, the clear pink solution was stirred for another 6 hours at room temperature. Pink crystals $[Nd(NO_3)_3(L)_2]$ were obtained by chance through slowly evaporation of the solvent in the refrigerator.

Discussion

Lanthanide diphosphonate complexes have been widely studied in recent years and resulted in variety of structure types for the diphosphonate, which may be coordinated simultaneously to lanthanide ions in three different modes [1]. But the diphosphonate ligands in the compounds reported with crystal structure show only the chelating mode by now. As a consequence, the complexes form often dinuclear dimers, polymeric chain or network structures which are directed by the choice of metal and reaction conditions. If another ligand containing aromatic ring is added as an auxiliary one, the complexes obtained enhance the fluorescent properties and control the dimensionality. We have been interested in lanthanide with methylenediphosphonate complexes [2]. By attempt to synthesize Nd complex with mixed ligands tetrakis(*O*-isopropyl)methylene-diphosphonate (= L) and phen in a mild condition, an unexpected compound $[Nd(NO_3)_3(L)_2]$ is obtained.

The single crystal X-ray study shows that there are two kind of crystals mixed equally in one pot, one is $[Nd(NO_3)_3(L)_2]$, the other is made up of phen Nd^{3+} and $(NO_3)^-$. $[Nd(NO_3)_3(L)_2]$ is a mononuclear complex. The neodymium ion is coordinated by ten oxygen atoms, four from two L ligands, the other six from three nitrate ions. The NdO_{10} coordination motif is best described as a distorted bi-capped square antiprism. The average neodymium-oxygen(P) bond distances of 2.473 Å in the title compound is slightly longer than the average value of 2.438 Å reported for the complexe [2], the average value of 2.440 Å for $NdCl(NO_3)_2(MeO)_2P(O)]_2C(OH)^tBu_2$ [3], the average value of 2.457 Å for $Nd(NO_3)_3(MeO)_2P(O)]_2C(OH)Me_2$ [4]. The ∠O1–Nd1–O4 (74.32°) in the title compound is a bit wider than ∠O1–Nd1–O4 (73.62°) [5], and ∠O6–Nd1–O7 (72.71°) [4], but much smaller than the value of ∠O7–Nd1–O10 (121.2°) [2]. The bidentate nitrate ion shows neodymium-oxygen(N) bond distances of 2.580 Å which is almost equal to the average value of 2.588 Å [4]. The ∠O7–Nd1–O8 (47.92°) in the title compound is a bit wider than the ∠O3–Nd1–O4 (48.21°), and ∠O10–Nd1–O10′(49.53°) is almost equal to ∠O1–Nd1–O1′(49.40°) [4]. The ligands are disposed in a facial arrangement with ∠N–Nd–N being slightly narrower than 90°, with an average of 87.25°, whilst the ∠(P)O–Nd–O(P) display a narrow angle of 74.32°. This appear to be an electrostatic rather than steric effect, with the repulsions from two negative oxygen atoms per nitrate ion dominating the increased repulsions from the bulky diphosphonate groups. There is no hydrogen bond observed in the title compound.

The high R is caused by the crystal internal factors. Because the isopropyl group from the phosphate is bounded, thermal vibration of the carbon atoms from isopropyl group is severe.

Table 1. Data collection and handling.

Crystal:	pink block, size 0.42 × 0.49 × 0.53 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.61 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11874, 4301
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3773
$N(param)_{refined}$:	259
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*f*	–0.0183	0.4024	0.0509	0.082
H(2)	8*f*	0.1335	0.7504	0.1245	0.102
H(3A)	8*f*	0.2373	0.6028	0.1272	0.223
H(3B)	8*f*	0.2598	0.7301	0.1338	0.223
H(3C)	8*f*	0.2477	0.6705	0.0719	0.223
H(4A)	8*f*	0.1761	0.8311	0.0457	0.210
H(4B)	8*f*	0.0899	0.8018	0.0265	0.210
H(4C)	8*f*	0.1488	0.7229	0.0080	0.210
H(5)	8*f*	–0.0997	0.6916	0.1026	0.093
H(6A)	8*f*	–0.1566	0.6033	–0.0106	0.162
H(6B)	8*f*	–0.2100	0.6626	0.0233	0.162
H(6C)	8*f*	–0.1661	0.5536	0.0496	0.162
H(7A)	8*f*	–0.0574	0.8475	0.0536	0.191
H(7B)	8*f*	–0.1457	0.8487	0.0412	0.191
H(7C)	8*f*	–0.1070	0.8045	–0.0076	0.191

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8)	8*f*	0.2158	0.4081	0.2052	0.116
H(9A)	8*f*	0.3210	0.3731	0.1820	0.231
H(9B)	8*f*	0.2620	0.4306	0.1296	0.231
H(9C)	8*f*	0.2790	0.3019	0.1268	0.231
H(10A)	8*f*	0.2260	0.3066	0.2713	0.193
H(10B)	8*f*	0.2733	0.2251	0.2417	0.193
H(10C)	8*f*	0.1860	0.2074	0.2312	0.193
H(11)	8*f*	0.0463	0.1483	0.2030	0.119
H(12A)	8*f*	0.0431	–0.0358	0.1516	0.202
H(12B)	8*f*	0.1168	0.0356	0.1583	0.202
H(12C)	8*f*	0.0554	0.0346	0.0977	0.202
H(13A)	8*f*	–0.0787	0.1893	0.1680	0.215
H(13B)	8*f*	–0.0763	0.0586	0.1606	0.215
H(13C)	8*f*	–0.0819	0.1371	0.1054	0.215

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd(1)	4*e*	0	0.53944(5)	¼	0.0479(4)	0.0557(4)	0.0269(3)	0	0.0109(2)	0
N(1)	8*f*	0.1600(5)	0.4957(8)	0.3218(4)	0.058(5)	0.086(5)	0.062(5)	0.010(4)	0.012(4)	–0.004(4)
N(2)	4*e*	0	0.790(1)	¼	0.088(8)	0.058(7)	0.060(7)	0	0.027(6)	0
O(1)	8*f*	0.0314(3)	0.6128(5)	0.1596(2)	0.075(4)	0.070(4)	0.039(3)	0.006(3)	0.023(3)	–0.003(3)
O(2)	8*f*	0.1045(4)	0.6011(6)	0.0789(3)	0.082(4)	0.084(5)	0.058(4)	0.000(4)	0.032(3)	–0.001(3)
O(3)	8*f*	–0.0298(4)	0.6420(6)	0.0500(3)	0.087(4)	0.089(5)	0.043(3)	0.024(4)	0.019(3)	0.001(3)
O(4)	8*f*	0.0483(4)	0.3765(6)	0.2043(3)	0.081(4)	0.075(4)	0.050(3)	0.014(3)	0.024(3)	0.001(3)
O(5)	8*f*	0.1475(5)	0.3616(7)	0.1438(3)	0.095(5)	0.105(6)	0.068(4)	0.024(5)	0.024(4)	0.005(4)
O(6)	8*f*	0.0376(6)	0.2291(8)	0.1245(4)	0.143(8)	0.092(6)	0.076(5)	0.008(5)	0.029(5)	–0.001(5)
O(7)	8*f*	0.1482(4)	0.5429(6)	0.2729(3)	0.071(4)	0.087(5)	0.064(4)	0.006(3)	0.016(3)	0.004(4)
O(8)	8*f*	0.1028(4)	0.4684(6)	0.3387(3)	0.068(4)	0.097(5)	0.059(4)	0.005(4)	0.013(3)	0.003(3)
O(9)	8*f*	0.2228(5)	0.4732(9)	0.3518(5)	0.071(5)	0.16(1)	0.105(7)	0.028(5)	–0.003(5)	0.014(6)
O(10)	8*f*	0.0578(4)	0.7341(6)	0.2745(3)	0.074(4)	0.077(4)	0.058(4)	–0.010(3)	0.020(3)	–0.005(3)
O(11)	4*e*	0	0.890(1)	¼	0.15(1)	0.073(9)	0.15(1)	0	0.03(1)	0
P(1)	8*f*	0.0304(1)	0.5788(2)	0.09850(9)	0.061(1)	0.068(1)	0.0306(9)	0.009(1)	0.0175(8)	0.0006(9)
P(2)	8*f*	0.0639(2)	0.3470(2)	0.1466(1)	0.098(2)	0.066(2)	0.050(1)	0.023(1)	0.032(1)	–0.001(1)
C(1)	8*f*	0.0132(6)	0.4317(9)	0.0854(4)	0.085(7)	0.080(6)	0.044(5)	0.011(5)	0.020(4)	–0.005(4)
C(2)	8*f*	0.1473(7)	0.707(1)	0.0928(5)	0.090(8)	0.095(8)	0.072(7)	–0.004(6)	0.024(6)	0.000(6)
C(3)	8*f*	0.231(1)	0.675(2)	0.1078(9)	0.14(2)	0.14(2)	0.15(2)	–0.01(1)	0.02(1)	0.00(1)
C(4)	8*f*	0.140(1)	0.771(2)	0.0387(8)	0.14(1)	0.14(2)	0.13(1)	–0.02(1)	0.01(1)	0.01(1)
C(5)	8*f*	–0.1013(6)	0.689(1)	0.0600(5)	0.088(7)	0.089(7)	0.054(5)	0.024(6)	0.014(5)	–0.001(5)
C(6)	8*f*	–0.1638(8)	0.622(1)	0.0279(6)	0.097(9)	0.13(1)	0.090(9)	0.023(9)	0.005(7)	0.005(8)
C(7)	8*f*	–0.1030(9)	0.809(1)	0.0344(8)	0.13(1)	0.11(1)	0.12(1)	0.03(1)	0.00(1)	0.01(1)
C(8)	8*f*	0.2121(8)	0.337(1)	0.1832(6)	0.110(9)	0.102(9)	0.074(7)	0.018(8)	0.017(7)	0.007(7)
C(9)	8*f*	0.274(1)	0.363(2)	0.1526(9)	0.13(1)	0.18(2)	0.14(2)	0.03(1)	0.01(1)	0.01(1)
C(10)	8*f*	0.226(1)	0.262(2)	0.2366(7)	0.13(1)	0.14(1)	0.11(1)	0.03(1)	0.014(9)	0.01(1)
C(11)	8*f*	0.0246(9)	0.133(1)	0.1607(6)	0.12(1)	0.091(9)	0.083(8)	0.012(8)	0.028(7)	0.007(7)
C(12)	8*f*	0.064(1)	0.033(1)	0.1401(9)	0.16(2)	0.11(1)	0.13(2)	0.02(1)	0.03(1)	–0.00(1)
C(13)	8*f*	–0.061(1)	0.129(2)	0.1475(8)	0.16(2)	0.13(1)	0.13(1)	0.01(1)	0.02(1)	0.00(1)

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