Crystal structure of tetra(triphenylphospine oxide-κO)-bis(nitrate-$\kappa O,O',N$)yttrium(III) nitrate — ethanol (1:1), $[Y(C_{18}H_{15}PO)_4(NO_3)_2][NO_3] \cdot C_2H_5OH$

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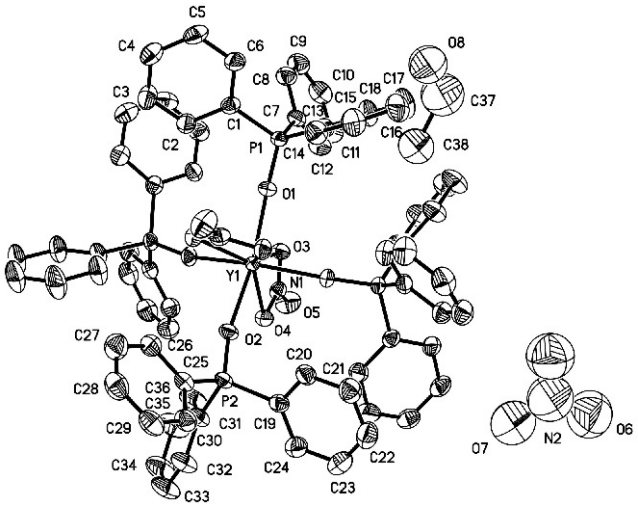

Abstract

$C_{74}H_{66}N_3O_{14}P_4Y$, orthorhombic, *Pccn* (no. 56), a = 16.076(1) Å, b = 16.930(1) Å, c = 26.916(2) Å, V = 7325.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.069, $wR_{ref}(F^2)$ = 0.246, T = 298 K.

Source of material

$Y(NO_3)_3 \cdot 6H_2O$ (0.253 g, 0.66 mmol) was dissolved in 5 ml ethanol, then Ph_3PO (triphenylphosphine oxide; 1.113 g, 4 mmol), dissolved in 5 ml ethanol, was added under stirring. The clear yellow solution was stirred for 6 hours at room temperature. Colorless crystals were obtained by chance through slow evaporation of the solvent in the refrigerator.

Experimental details

Because the crystal data was collected at room temperature, there is significant thermal vibration of the free NO_3^- anion, leading to large U_{ii} values for N2, O6 and O7.

Discussion

Phosphine oxides are popular ligands for complexing rare earth metal ions and have been used widely in solvent extraction and separation processes of rare earth metals. In recent years, they have attracted attention for their remarkable function as a catalyst for a variety of organic reactions [1]. For a long time, we have been involved in coordination chemistry of P=O ligands and studied their coordination capabilities toward selected *f*-block elements [2].

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The asymmetric unit of the title crystal structure is composed of $[Y(Ph_3PO)_4(NO_3)_2][NO_3]$ and one solvent ethanol molecule. The Y(III) atom is ten-coordinated by four oxygen atoms from Ph_3PO groups, four oxygen atoms and two nitrogen atoms from two nitrate anions. The coordination geometry about the yttrium ion is a distorted two-capped square antiprism. The free ethanol molecule is outside the coordination sphere of yttrium. The Y—O bond lengths fall in the range 2.237(4)-2.469(4) Å, which is slightly shorter than those found in similar complexes [3]. The distances between the center ion and the oxygen atom of Ph_3PO agree with those of $[YCl_2(Ph_3PO)_4]Cl \cdot 2.5EtOH \cdot H_2O$ [4]. The Y—O bond lengths in the chelating ring are significantly shorter than the other Y—O (O from Ph_3PO) bonds in the title complex. The angles ∠O–Y–O vary from 52.1(1)° to 147.1(2)°.The O–Y–O–N four-membered ring, with the angle ∠O–Y–O much smaller than 90°, is seriously distorted. There are two types of hydrogen bond formed by OH group from ethanol and O atom from Ph_3PO. The hydrogen bond with the symmetry code of $[-x+1,-y+1,-z]$ has the angle ∠O8–H8···O6 = 175.61° and distance d(O8···O6) = 3.223 Å, while the hydrogen bond with the symmetry code of $[x-½,y+½,-z]$ has the corresponding angle of 127.23° and the distance of 3.223 Å. The hydrogen bonds further stablize the title crystal structure. It is interesting that the Y(III) atom is coordinated by the N atom of nitrate with d(Y—N) = 2.864(6) Å, a phenomenon which is rarely reported.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.28 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.47 cm^{-1}
Diffractometer, scan mode:	Smart-1000 CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	35378, 6448
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4137
$N(param)_{refined}$:	445
Programs:	SHELXS-97, SHELXL-97, SHELXTL [5]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(8A)	8*e*	0.50	0.2334	0.7595	0.0007	0.196
H(2)	8*e*		0.0193	0.3054	0.2885	0.071
H(3)	8*e*		–0.0963	0.3711	0.3171	0.089
H(4)	8*e*		–0.1738	0.4466	0.2648	0.084
H(5)	8*e*		–0.1449	0.4497	0.1808	0.085
H(6)	8*e*		–0.0301	0.3826	0.1511	0.074

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(8)	8*e*		–0.0621	0.2234	0.1523	0.076
H(9)	8*e*		–0.1080	0.1015	0.1221	0.095
H(10)	8*e*		–0.0175	–0.0027	0.1184	0.098
H(11)	8*e*		0.1171	0.0109	0.1442	0.099
H(12)	8*e*		0.1632	0.1308	0.1746	0.080
H(14)	8*e*		0.1464	0.4377	0.1856	0.084
H(15)	8*e*		0.2016	0.5159	0.1223	0.096
H(16)	8*e*		0.2268	0.4630	0.0464	0.109
H(17)	8*e*		0.1969	0.3339	0.0299	0.116
H(18)	8*e*		0.1397	0.2536	0.0918	0.091
H(20)	8*e*		0.4403	0.4056	0.2937	0.069
H(21)	8*e*		0.5521	0.4299	0.2432	0.090
H(22)	8*e*		0.6813	0.3820	0.2631	0.099
H(23)	8*e*		0.6999	0.3101	0.3345	0.101
H(24)	8*e*		0.5869	0.2815	0.3857	0.084

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(26)	8*e*		0.2660	0.4154	0.4049	0.076
H(27)	8*e*		0.2383	0.5363	0.4427	0.099
H(28)	8*e*		0.3471	0.6158	0.4674	0.096
H(29)	8*e*		0.4809	0.5768	0.4554	0.089
H(30)	8*e*		0.5095	0.4573	0.4184	0.073
H(32)	8*e*		0.5164	0.3275	0.4706	0.095
H(33)	8*e*		0.5401	0.2379	0.5342	0.119
H(34)	8*e*		0.4642	0.1234	0.5383	0.127
H(35)	8*e*		0.3701	0.0945	0.4773	0.131
H(36)	8*e*		0.3498	0.1794	0.4109	0.101
H(37A)	8*e*	0.50	0.3264	0.6692	0.0071	0.237
H(37B)	8*e*	0.50	0.2395	0.6366	0.0221	0.237
H(38A)	8*e*	0.50	0.3379	0.6787	0.1012	0.182
H(38B)	8*e*	0.50	0.3681	0.6051	0.0708	0.182
H(38C)	8*e*	0.50	0.2799	0.6047	0.0957	0.182

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y(1)	4*c*		¼	¼	0.29428(3)	0.0310(4)	0.0376(4)	0.0294(4)	–0.0009(3)	0	0.0
P(1)	8*e*		0.0921(1)	0.2788(1)	0.19402(6)	0.0379(9)	0.051(1)	0.0372(9)	0.0015(7)	–0.0044(7)	0.0057(7)
P(2)	8*e*		0.4112(1)	0.3273(1)	0.38249(6)	0.0475(9)	0.049(1)	0.0344(9)	–0.0064(7)	–0.0080(7)	–0.0011(7)
N(1)	8*e*		0.2875(3)	0.0847(3)	0.2970(2)	0.045(3)	0.045(3)	0.055(4)	0.001(3)	0.006(3)	–0.007(3)
N(2)	4*d*		¾	¼	0.108(3)	0.30(9)	0.31(6)	0.30(9)	0.02(5)	0	0.0
O(1)	8*e*		0.1526(3)	0.2611(2)	0.2353(2)	0.043(2)	0.058(3)	0.041(2)	0.004(2)	–0.009(2)	0.002(2)
O(2)	8*e*		0.3388(3)	0.2980(3)	0.3526(2)	0.048(3)	0.056(3)	0.041(2)	–0.009(2)	–0.011(2)	–0.002(2)
O(3)	8*e*		0.2321(3)	0.1111(3)	0.2683(2)	0.051(3)	0.052(3)	0.049(3)	0.002(2)	–0.010(2)	–0.004(2)
O(4)	8*e*		0.3255(3)	0.1342(2)	0.3240(2)	0.049(3)	0.048(3)	0.050(3)	0.002(2)	–0.007(2)	–0.001(2)
O(5)	8*e*		0.3051(4)	0.0140(3)	0.2989(2)	0.086(4)	0.043(3)	0.117(5)	0.015(3)	–0.014(3)	–0.010(3)
O(6)	8*e*		0.810(2)	0.224(2)	0.083(1)	0.31(4)	0.32(3)	0.31(3)	0.02(2)	0.02(2)	0.01(2)
O(7)	4*d*		¾	¼	0.155(1)	0.26(3)	0.30(3)	0.30(4)	0.01(2)	0	0.0
O(8)	4*d*		¼	¾	0.0301(6)	0.16(1)	0.17(2)	0.15(1)	0.03(1)	0	0.0
C(1)	8*e*		0.0050(4)	0.3347(4)	0.2159(3)	0.043(4)	0.049(4)	0.055(4)	0.001(3)	–0.002(3)	0.011(3)
C(2)	8*e*		–0.0141(4)	0.3335(4)	0.2665(3)	0.060(5)	0.063(5)	0.055(5)	0.012(4)	0.005(4)	0.008(4)
C(3)	8*e*		–0.0822(5)	0.3739(5)	0.2836(3)	0.075(5)	0.074(6)	0.072(5)	0.012(4)	0.022(5)	0.006(4)
C(4)	8*e*		–0.1291(5)	0.4179(5)	0.2523(3)	0.059(5)	0.061(5)	0.091(7)	0.012(4)	0.006(5)	0.001(4)
C(5)	8*e*		–0.1115(5)	0.4207(5)	0.2023(3)	0.055(5)	0.067(5)	0.092(7)	0.019(4)	–0.007(4)	0.013(4)
C(6)	8*e*		–0.0434(4)	0.3797(4)	0.1847(3)	0.055(4)	0.071(5)	0.059(5)	0.009(4)	–0.002(4)	0.016(4)
C(7)	8*e*		0.0547(4)	0.1887(4)	0.1675(2)	0.050(4)	0.057(4)	0.042(4)	–0.006(3)	–0.007(3)	0.007(3)
C(8)	8*e*		–0.0259(5)	0.1806(5)	0.1512(3)	0.056(4)	0.072(5)	0.062(5)	–0.009(4)	–0.008(4)	–0.002(4)
C(9)	8*e*		–0.0533(6)	0.1076(6)	0.1328(3)	0.072(6)	0.094(7)	0.071(6)	–0.021(5)	–0.011(4)	–0.009(5)
C(10)	8*e*		0.0007(6)	0.0457(6)	0.1306(3)	0.100(7)	0.071(6)	0.073(6)	–0.025(5)	–0.010(5)	–0.001(4)
C(11)	8*e*		0.0808(6)	0.0536(5)	0.1460(3)	0.095(7)	0.067(5)	0.085(6)	0.004(5)	–0.017(5)	–0.004(5)
C(12)	8*e*		0.1083(5)	0.1253(4)	0.1643(3)	0.073(5)	0.059(5)	0.068(5)	0.000(4)	–0.016(4)	–0.001(4)
C(13)	8*e*		0.1373(4)	0.3364(4)	0.1451(2)	0.051(4)	0.064(5)	0.043(4)	–0.004(3)	–0.001(3)	0.007(3)
C(14)	8*e*		0.1561(5)	0.4161(5)	0.1543(3)	0.073(5)	0.068(5)	0.068(5)	–0.008(4)	0.004(4)	0.005(4)
C(15)	8*e*		0.1895(6)	0.4630(5)	0.1163(4)	0.091(6)	0.069(5)	0.080(6)	–0.015(5)	0.013(5)	0.018(5)
C(16)	8*e*		0.2041(6)	0.4315(6)	0.0713(4)	0.099(7)	0.102(8)	0.072(6)	–0.016(6)	0.015(5)	0.030(6)
C(17)	8*e*		0.1864(7)	0.3545(7)	0.0613(3)	0.123(9)	0.107(8)	0.060(6)	–0.018(7)	0.025(5)	0.009(5)
C(18)	8*e*		0.1522(5)	0.3061(5)	0.0986(3)	0.090(6)	0.079(6)	0.059(5)	–0.014(5)	0.017(4)	0.000(4)
C(19)	8*e*		0.5020(4)	0.3404(4)	0.3451(2)	0.050(4)	0.052(4)	0.049(4)	–0.008(3)	–0.006(3)	–0.007(3)
C(20)	8*e*		0.4924(5)	0.3855(4)	0.3020(2)	0.059(4)	0.068(5)	0.047(4)	–0.012(4)	–0.002(3)	0.004(3)
C(21)	8*e*		0.5592(6)	0.4003(5)	0.2720(3)	0.078(6)	0.082(6)	0.065(5)	–0.019(5)	0.007(4)	0.003(4)
C(22)	8*e*		0.6363(6)	0.3719(6)	0.2838(4)	0.075(6)	0.088(7)	0.083(7)	–0.015(5)	0.022(5)	–0.015(5)
C(23)	8*e*		0.6472(5)	0.3286(6)	0.3262(4)	0.056(5)	0.092(7)	0.104(8)	0.003(5)	0.003(5)	–0.003(6)
C(24)	8*e*		0.5795(5)	0.3117(5)	0.3572(3)	0.063(5)	0.077(5)	0.070(5)	0.004(4)	–0.004(4)	0.005(4)
C(25)	8*e*		0.3900(4)	0.4225(4)	0.4091(2)	0.061(4)	0.055(4)	0.039(4)	–0.003(3)	–0.005(3)	–0.004(3)
C(26)	8*e*		0.3097(5)	0.4472(5)	0.4155(3)	0.066(5)	0.065(5)	0.060(5)	–0.002(4)	–0.002(4)	–0.009(4)
C(27)	8*e*		0.2929(6)	0.5200(5)	0.4378(3)	0.087(6)	0.080(6)	0.080(6)	0.017(5)	0.004(5)	–0.008(5)
C(28)	8*e*		0.3580(7)	0.5674(5)	0.4525(3)	0.107(8)	0.065(5)	0.069(6)	0.006(5)	–0.001(5)	–0.015(4)
C(29)	8*e*		0.4375(6)	0.5442(5)	0.4454(3)	0.101(7)	0.060(5)	0.061(5)	–0.014(5)	–0.010(5)	–0.009(4)
C(30)	8*e*		0.4546(5)	0.4725(4)	0.4236(3)	0.068(5)	0.059(5)	0.056(4)	–0.007(4)	–0.005(4)	–0.012(4)
C(31)	8*e*		0.4319(5)	0.2613(4)	0.4332(3)	0.070(5)	0.067(5)	0.039(4)	–0.014(4)	–0.010(3)	0.004(3)
C(32)	8*e*		0.4878(6)	0.2797(6)	0.4711(3)	0.095(6)	0.083(6)	0.059(5)	–0.017(5)	–0.027(5)	0.007(4)
C(33)	8*e*		0.5009(7)	0.2266(7)	0.5098(3)	0.125(9)	0.113(8)	0.061(6)	–0.019(7)	–0.038(6)	0.020(5)
C(34)	8*e*		0.4564(7)	0.1582(7)	0.5120(4)	0.140(9)	0.109(8)	0.069(6)	–0.024(7)	–0.028(6)	0.036(6)

Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(35)	8*e*		0.4005(7)	0.1412(6)	0.4755(4)	0.14(1)	0.100(7)	0.085(7)	–0.047(7)	–0.033(7)	0.043(6)
C(36)	8*e*		0.3879(6)	0.1922(5)	0.4357(3)	0.107(7)	0.081(6)	0.065(5)	–0.033(5)	–0.029(5)	0.023(5)
C(37)	8*e*	0.50	0.284(3)	0.672(3)	0.033(2)	0.19(4)	0.21(4)	0.20(4)	–0.03(3)	0.00(3)	0.00(3)
C(38)	8*e*	0.50	0.321(2)	0.637(1)	0.079(1)	0.12(2)	0.11(2)	0.13(2)	–0.07(2)	–0.01(2)	0.00(2)

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