Crystal structure of cyclohexyl-*tert*-butylammonium dichlorophosphate, $(C_{10}H_{20}NH_2)PCl_2O_2$

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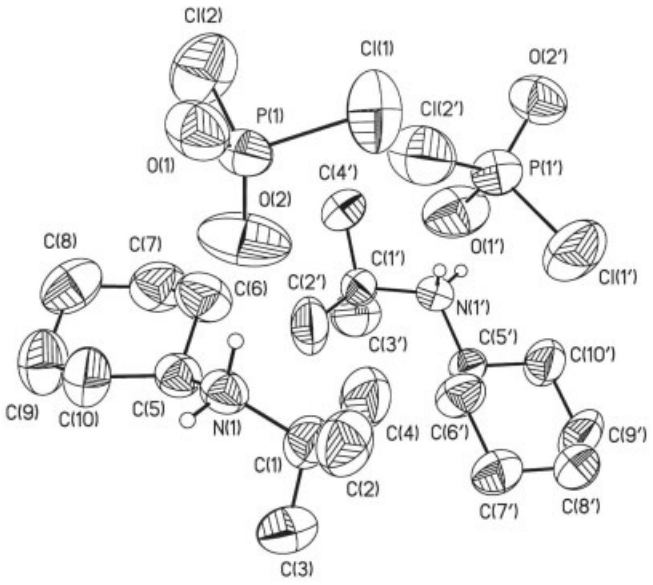

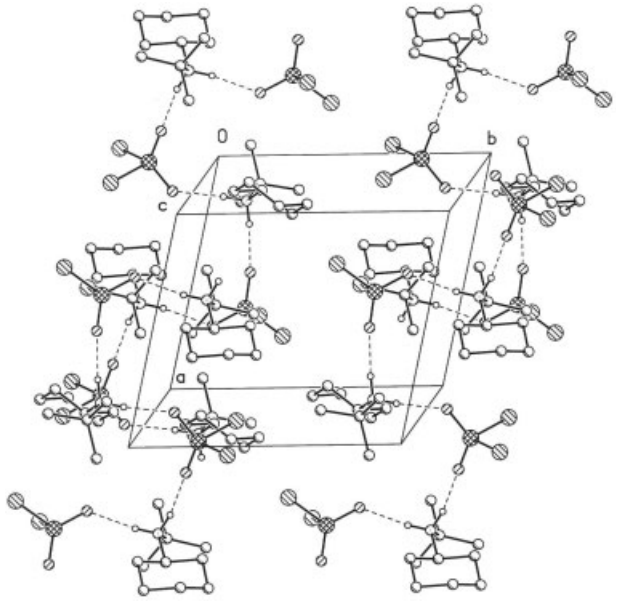

Abstract

$C_{10}H_{22}Cl_2NO_2P$, triclinic, $P\bar{1}$ (no. 2), a = 9.358(1) Å, b = 10.433(1) Å, c = 16.186(2) Å, α = 98.571(3)°, β = 92.727(3)°, γ = 101.392(3)°, V = 1526.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.063, $wR_{ref}(F^2)$ = 0.133, T = 293 K.

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Source of material

The title compound was synthesized by the reaction of phosphoryl chloride (1 mmol) with cyclohexyl *tert*-butylamine in chloroform under stirring 4 hours at 343 K. Single crystals were obtained from a mixture of *n*-heptane and chloroform after slow evaporation at room temperature. Elemental analysis: found – C, 41.32 %; H, 7.61 %; N, 4.84 %; calc. for $C_{10}H_{22}Cl_2NO_2P$ – C, 41.39 %; H, 7.64 %; N, 4.83 %.

Discussion

Phosphate derivatives act as oxygen-donor ligands [1] and are used to the extraction of rare earth metal cations [2]. The crystal structure of the title compound consists of two symmetrically independent dichlorophosphate anions as well as cyclohexyl-*tert*-butylammonium cations (figure, top) linked by intermolecular hydrogen bonds. The P1—O1, P1—O2, P1′—O1′ and P1′—O2′ bond lengths are 1.476(3) Å, 1.428(3) Å, 1.441(3) Å and 1.455(2) Å, respectively, despite the presence of one negative charge on the anion, the P—O bond lengths are in agreement with normal double bond lengths (1.45 Å [2]). The phosphorus atoms P1 and P1′ have slightly distorted tetrahedral coordination. The bond angles around P1 are in the range of 99.20° – 122.80°. The minimum and maximum values of angles are observed for angles Cl1–P1–Cl2 and O2–P1–O1, respectively. For P1′, they are in the region of 99.51° – 122.24° with smallest angle Cl1′–P1′–Cl2′ and largest angle O1′–P1′–O2′. The bond angles C5–N1–C1 and C5′–N1′–C1′ in cyclohexyl-*tert*-butylammonium component, are 120.2° and 119.7°, respectively. These deviations from sp^3 hybridization angles are depending on the steric influence of two bulk groups, *tert*-butyl and cyclohexyl.

In the crystal structure, infinite zigzag chains are built from $[PO_2Cl_2]^-$ anions alternating with $[NH_2(tert\text{-}C_4H_9)(C_6H_{11})]^+$ cations by four different kinds of intermolecular hydrogen bonds. The $[PO_2Cl_2]^-$ and $[NH_2(tert\text{-}C_4H_9)(C_6H_{11})]^+$ ions are placed between two symmetrically different $[NH_2(tert\text{-}C_4H_9)(C_6H_{11})]^+$ cations and $[PO_2Cl_2]^-$ anions, respectively (figure, bottom). The concept of H bonds has been extended to C–H···*Y* bonding (where *Y* is an electronegative atom). Previous studies have suggested that C–H···O hydrogen bonds occur in the range of 3.0 – 4.0 Å for C···O distances and more than 110° for the bond angles [3]. According to these results, it can be said that each $[PO_2Cl_2]^-$ anion (labeled with prime) provides O2′ as acceptor which forms a hydrogen bond with C2 in neighboring cation (C–H···O bond). In C2–H2C···O2′, d(C2···O2′) = 3.449 Å and ∠C2–H2C···O2′ = 137.0°. Another $[PO_2Cl_2]^-$ anion provides O1 as acceptor and forms an hydrogen bond with C4′. The distance between C4′ and O1 in C4′–H4′B···O1 is 3.386 Å with the bond angle 136.4°. Also another weak hydrogen bond is formed by Cl1 and C3 as acceptor and as donor, respectively, with C3···Cl1 distance of 3.821 Å and the bond angle of 152.4°.

Table 1. Data collection and handling.

Crystal:	colorless cube, size 0.3 × 0.3 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.19 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	54.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10864, 6715
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3283
$N(param)_{refined}$:	289
Programs:	SADABS [4], SHELXTL [5]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.5878	0.9416	0.2587	0.068
H(1B)	2*i*	0.6478	0.8232	0.2482	0.068
H(2A)	2*i*	0.7366	0.8473	0.3892	0.139
H(2B)	2*i*	0.6369	0.8840	0.4605	0.139
H(2C)	2*i*	0.6874	0.9836	0.3989	0.139
H(3A)	2*i*	0.3125	0.8543	0.3288	0.126
H(3B)	2*i*	0.4246	0.9877	0.3603	0.126
H(3C)	2*i*	0.3755	0.8892	0.4228	0.126
H(4A)	2*i*	0.3953	0.6417	0.3060	0.154
H(4B)	2*i*	0.4586	0.6627	0.3996	0.154
H(4C)	2*i*	0.5598	0.6387	0.3268	0.154
H(5A)	2*i*	0.3593	0.7858	0.1981	0.071
H(6A)	2*i*	0.4650	0.5996	0.1795	0.102
H(6B)	2*i*	0.5800	0.6681	0.1236	0.102

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(7A)	2*i*	0.3899	0.5230	0.0362	0.111
H(7B)	2*i*	0.2741	0.5955	0.0789	0.111
H(8A)	2*i*	0.3210	0.6692	–0.0477	0.121
H(8B)	2*i*	0.4891	0.7106	–0.0200	0.121
H(9A)	2*i*	0.2718	0.8329	0.0559	0.114
H(9B)	2*i*	0.3890	0.9005	0.0009	0.114
H(10A)	2*i*	0.5773	0.9070	0.1035	0.097
H(10B)	2*i*	0.4590	0.9764	0.1460	0.097
H(1′A)	2*i*	0.1170	0.0732	0.2284	0.058
H(1′B)	2*i*	0.2328	0.1902	0.2380	0.058
H(2′A)	2*i*	0.0532	0.3765	0.1863	0.177
H(2′B)	2*i*	0.0884	0.3553	0.0921	0.177
H(2′C)	2*i*	0.2139	0.3752	0.1634	0.177
H(3′A)	2*i*	–0.1332	0.1655	0.1666	0.144
H(3′B)	2*i*	–0.0893	0.0316	0.1313	0.144
H(3′C)	2*i*	–0.1081	0.1331	0.0714	0.144
H(4′A)	2*i*	0.1482	0.1381	0.0284	0.126
H(4′B)	2*i*	0.1589	0.0315	0.0860	0.126
H(4′C)	2*i*	0.2773	0.1635	0.0982	0.126
H(5′A)	2*i*	–0.0261	0.2317	0.2938	0.063
H(6′A)	2*i*	0.2651	0.3430	0.3605	0.093
H(6′B)	2*i*	0.1685	0.4140	0.3080	0.093
H(7′A)	2*i*	0.1673	0.4929	0.4524	0.108
H(7′B)	2*i*	0.0081	0.4242	0.4147	0.108
H(8′A)	2*i*	0.0555	0.3500	0.5392	0.119
H(8′B)	2*i*	0.1944	0.3038	0.5051	0.119
H(9′A)	2*i*	–0.0964	0.1902	0.4411	0.130
H(9′B)	2*i*	0.0035	0.1206	0.4924	0.130
H(10C)	2*i*	0.1559	0.1035	0.3827	0.102
H(10D)	2*i*	–0.0054	0.0406	0.3461	0.102

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}
P(1)	2*i*	0.9718(1)	0.77170(9)	0.20554(6)	0.0566(6)	0.0579(5)	0.0764(6)	0.0179(4)	0.0102(5)	0.0073(4)
Cl(1)	2*i*	1.0392(1)	0.6556(1)	0.28201(8)	0.117(1)	0.0999(8)	0.1019(9)	–0.0028(7)	–0.0135(7)	0.0448(7)
Cl(2)	2*i*	0.9380(2)	0.6424(1)	0.09653(7)	0.142(1)	0.1148(9)	0.0706(7)	0.0073(8)	–0.0019(7)	–0.0061(6)
O(1)	2*i*	1.0979(3)	0.8796(2)	0.2006(2)	0.080(2)	0.055(1)	0.113(2)	0.014(1)	0.015(2)	0.018(1)
O(2)	2*i*	0.8329(3)	0.7954(3)	0.2289(2)	0.060(2)	0.131(3)	0.197(4)	0.037(2)	0.023(2)	–0.007(2)
N(1)	2*i*	0.5651(3)	0.8532(2)	0.2569(2)	0.048(2)	0.057(2)	0.070(2)	0.016(1)	0.009(1)	0.014(1)
C(1)	2*i*	0.5219(4)	0.8281(4)	0.3444(2)	0.073(3)	0.075(2)	0.063(2)	0.014(2)	0.014(2)	0.020(2)
C(2)	2*i*	0.6585(4)	0.8917(4)	0.4038(2)	0.086(3)	0.122(4)	0.070(3)	0.023(3)	–0.004(2)	0.021(2)
C(3)	2*i*	0.3973(4)	0.8960(4)	0.3661(2)	0.079(3)	0.095(3)	0.079(3)	0.026(2)	0.019(2)	0.002(2)
C(4)	2*i*	0.4800(5)	0.6790(4)	0.3442(3)	0.151(4)	0.077(3)	0.087(3)	0.024(3)	0.026(3)	0.030(2)
C(5)	2*i*	0.4591(4)	0.7958(3)	0.1804(2)	0.051(2)	0.062(2)	0.065(2)	0.015(2)	0.006(2)	0.011(2)
C(6)	2*i*	0.4805(5)	0.6610(4)	0.1397(3)	0.093(3)	0.071(2)	0.090(3)	0.027(2)	–0.001(2)	0.000(2)
C(7)	2*i*	0.3734(5)	0.6082(4)	0.0623(3)	0.107(3)	0.082(3)	0.082(3)	0.020(2)	0.005(3)	–0.010(2)
C(8)	2*i*	0.3922(5)	0.7030(5)	0.0000(3)	0.102(4)	0.126(4)	0.065(3)	0.014(3)	0.009(2)	–0.003(3)
C(9)	2*i*	0.3717(5)	0.8392(4)	0.0407(3)	0.108(4)	0.098(3)	0.074(3)	0.009(3)	–0.015(2)	0.023(2)
C(10)	2*i*	0.4775(5)	0.8922(4)	0.1194(2)	0.095(3)	0.075(2)	0.069(3)	0.007(2)	0.000(2)	0.019(2)
P(1′)	2*i*	0.5845(1)	0.24544(9)	0.29008(6)	0.0533(6)	0.0662(6)	0.0719(6)	0.0043(5)	0.0057(5)	0.0036(5)
Cl(1′)	2*i*	0.5858(2)	0.3162(2)	0.41361(7)	0.153(1)	0.166(1)	0.0676(7)	0.046(1)	0.0076(7)	–0.0076(8)
Cl(2′)	2*i*	0.7153(1)	0.4014(1)	0.25393(9)	0.111(1)	0.0795(7)	0.168(1)	0.0171(7)	0.0495(9)	0.0392(8)
O(1′)	2*i*	0.4385(3)	0.2321(3)	0.2525(2)	0.054(2)	0.151(3)	0.110(2)	0.016(2)	0.002(2)	–0.008(2)
O(2′)	2*i*	0.6610(3)	0.1361(2)	0.2816(2)	0.086(2)	0.061(2)	0.114(2)	0.019(1)	0.015(2)	0.013(1)
N(1′)	2*i*	0.1351(3)	0.1617(2)	0.2310(1)	0.046(2)	0.046(1)	0.053(2)	0.010(1)	0.003(1)	0.005(1)
C(1′)	2*i*	0.0844(4)	0.1897(3)	0.1459(2)	0.083(3)	0.062(2)	0.045(2)	0.029(2)	0.002(2)	0.006(2)
C(2′)	2*i*	0.1125(6)	0.3377(4)	0.1470(3)	0.226(6)	0.074(3)	0.064(3)	0.050(3)	0.006(3)	0.022(2)
C(3′)	2*i*	–0.0764(4)	0.1239(5)	0.1271(2)	0.084(3)	0.136(4)	0.068(3)	0.045(3)	–0.018(2)	–0.005(2)
C(4′)	2*i*	0.1756(4)	0.1247(4)	0.0839(2)	0.104(3)	0.099(3)	0.057(2)	0.037(2)	0.020(2)	0.010(2)
C(5′)	2*i*	0.0722(3)	0.2193(3)	0.3093(2)	0.052(2)	0.060(2)	0.049(2)	0.016(2)	0.009(1)	0.008(2)
C(6′)	2*i*	0.1658(4)	0.3529(3)	0.3478(2)	0.091(3)	0.070(2)	0.065(2)	0.013(2)	0.014(2)	–0.004(2)
C(7′)	2*i*	0.1049(5)	0.4088(4)	0.4278(2)	0.122(4)	0.084(3)	0.065(3)	0.031(3)	0.013(2)	–0.004(2)
C(8′)	2*i*	0.0966(6)	0.3143(4)	0.4891(2)	0.144(4)	0.109(3)	0.056(2)	0.061(3)	0.004(2)	0.001(2)
C(9′)	2*i*	0.0036(6)	0.1810(5)	0.4522(3)	0.168(5)	0.102(3)	0.065(3)	0.033(3)	0.046(3)	0.029(3)
C(10′)	2*i*	0.0605(5)	0.1229(4)	0.3706(2)	0.127(4)	0.066(2)	0.065(2)	0.023(2)	0.019(2)	0.016(2)

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