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Crystallographic report

Thallium(18-crown-6) hexafluorophosphate, [Tl(18-crown-6)](PF_6)

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Thallium(18-crown-6) hexafluorophosphate was prepared and its structure was determined by X-ray diffraction analysis. The Tl^+ ion is surrounded by six oxygen atoms of 18-crown-6 and three fluorine atoms of PF_6^-, forming a sandwiched structure. If the three Tl–F interactions were considered significant, the coordination number in the title compound would be nine. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: thallium; 18-crown-6; hexafluorophosphate; crystal structure

COMMENT

Thallium(18-crown-6) hexafluorophosphate is a mononuclear complex. The thallium atom is coordinated by six oxygen atoms of the crown ether, and weakly interacts with three fluorine atoms of the hexafluorophosphate ion. The Tl–O bond distances are in the range of 2.875(3)–3.010(4) Å, which are usual for thallium(I) complexes. The Tl–F bond distances are in the range of 3.138(5)–3.347(6) Å, which are relatively long, indicating weak interactions between Tl(I) and PF_6^-. In crystalline salts, the Tl^+ ion is usually six- or eight-coordinate.[1] The coordination number of Tl^+ in the title compounds reaches nine if the three Tl–F interactions are taken into account, as shown in Fig. 1.

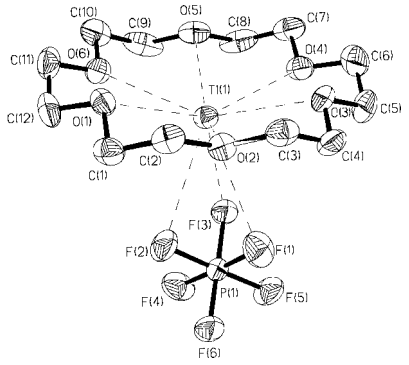

Figure 1. Molecular structure of [Tl(18-crown-6)](PF_6). Important geometric parameters: Tl–F(1) 3.347(6), Tl–F(2) 3.250(5), Tl–F(3) 3.138(5), Tl–O(1) 2.981(4), Tl–O(2) 2.875(3), Tl–O(3) 2.954(5), Tl–O(4) 2.889(4), Tl–O(5) 3.010(4), Tl–O(6) 2.880(4) Å; O(2)–Tl–O(6) 115.50(11), O(2)–Tl–O(4) 116.11(13), O(4)–Tl–O(6) 115.08(13), O(2)–Tl–O(3) 58.15(11), O(3)–Tl–O(6) 146.84(11), O(3)–Tl–O(4) 58.06(13), O(1)–Tl–O(2) 58.40(11), O(1)–Tl–O(6) 57.21(12), O(1)–Tl–O(4) 147.15(11), O(1)–Tl–O(3) 109.02(12), O(2)–Tl–O(5) 147.67(11), O(5)–Tl–O(6) 57.72(14), O(4)–Tl–O(5) 57.49(14), O(3)–Tl–O(5) 108.42(13), O(1)–Tl–O(5) 108.04(13), O(2)–Tl–F(3) 115.64(11), O(6)–Tl–F(3) 105.43(11), O(4)–Tl–F(3) 84.78(11), O(3)–Tl–F(3) 105.99(11), O(1)–Tl–F(3) 127.72(10), O(5)–Tl–F(3) 95.96(11), O(2)–Tl–F(2) 87.87(12), O(6)–Tl–F(2) 93.60(11), O(4)–Tl–F(2) 124.53(11), O(3)–Tl–F(2) 117.31(11), O(1)–Tl–F(2) 88.30(11), O(5)–Tl–F(2) 122.72(13), F(2)–Tl–F(3) 40.72(11), O(2)–Tl–F(1) 76.20(12), O(6)–Tl–F(1) 133.15(11), O(4)–Tl–F(1) 95.41(13), O(3)–Tl–F(1) 79.23(11), O(1)–Tl–F(1) 112.50(12), O(5)–Tl–F(1) 133.38(12), F(1)–Tl–F(3) 40.16(11), F(1)–Tl–F(2) 39.84(11)°.

EXPERIMENTAL

Synthesis

To a solution of $TlPF_6$ (0.35 g, 1.0 mmol) in water (5 ml) was added 18-crown-6 (0.27 g, 1.0 mmol). The mixture was stirred and maintained at 40 °C for 2 h. Slow evaporation of the resulting colorless solution yielded crystals after a few days. Yield: 42%. Anal. Found: C, 23.16; H, 4.08. Calc. for $C_{12}H_{24}F_6O_6PTl$: C, 23.49; H, 3.94%.

Crystallography

Intensity data for the title compound were collected at room temperature on a Brucker CCD 1000 diffractometer for a colorless crystal with a dimension of 0.18 × 0.20 × 0.59 mm^3. Crystallographic data: $C_{12}H_{24}F_6O_6PTl$, $M = 613.65$, monoclinic, $P2_1/n$, $a = 12.539(7)$ Å, $b =$

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8.792(5) Å, $c = 18.624(11)$ Å, $\beta = 93.786(10)°$, $V = 2049(2)$ Å^3, $Z = 4$, $D = 1.990$ Mg m^{-3}, 11 751 reflections collected, 4513 independent reflections ($R_{int} = 0.068$), R indices [$I > 2\sigma(I)$], 0.038, 0.091, R indices (all data): 0.049, 0.095. Largest diff. peak 1.835 e$^-$ Å^{-3}. Programs used: SAINT, SHELXL97, ORTEP. CCDC number: 204 305.

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