

Structure of $\text{Tl}(\text{18-crown-6})\{\text{Cl}_3\text{CC}(\text{O})\text{NP}(\text{O})(\text{OCH}_3)_2\}$: Coordination of the Ionic Multidentate Weakens the Interaction of the Metal Atom with the Crown Ether

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The thallium(I) dimethyl-N-trichloroacetylamidophosphate complex with a 18-crown-6 of the composition $\text{Tl}(\text{18-crown-6})\{\text{L}\}$ ($\text{L} = \{\text{Cl}_3\text{CC}(\text{O})\text{NP}(\text{O})(\text{OCH}_3)_2\}^-$) has been prepared and characterized by means of IR spectroscopy and X-ray diffraction (orthorhombic, space group $\text{P2}_1\text{2}_1\text{2}_1$ with $a = 8.660(1)$, $b = 11.557(2)$, $c = 26.296(3)$ Å, $Z = 4$, $V = 2631.8(6)$ Å³; $R1 = 0.0285$ and $wR2 = 0.0558$ for 4314 unique reflections). It was shown that (L^-) is coordinated to the central atom in a bidentate manner *via* oxygen atoms of phosphoryl [$\text{Tl}-\text{O}(1)$ 2.678(4) Å] and carbonyl groups [$\text{Tl}-\text{O}(2)$ 3.012(6) Å]. The $\text{Tl}(\text{18-crown-6})^+$ moiety adopts a typical “sunrise” coordination with the metal atom laying 1.134(2) Å above the mean plane of the oxygen atoms of the macrocycle. This deviation is the highest value of the structurally examined $\text{Tl}(\text{18-crown-6})^+$ complexes. The Tl-O (etheric) separations are in the range 2.913(4) - 3.198(5) Å (av. 3.030(6) Å).

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