

Die Oxochlorovanadate $\text{PPh}_4[\text{VOCl}_3\text{OH}]$, $\text{PPh}_4[\text{VOCl}_4]$, $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 2\text{CH}_3\text{CN}$ und $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 4\text{CH}_3\text{CN}$ mit auffälligen Abweichungen von der quadratisch-pyramidalen Anionenstruktur

The Oxochlorovanadates $\text{PPh}_4[\text{VOCl}_3\text{OH}]$, $\text{PPh}_4[\text{VOCl}_4]$, $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 2\text{CH}_3\text{CN}$,
and $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 4\text{CH}_3\text{CN}$ with Remarkable Deviations from the Square-Pyramidal
Anion Structure

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Trichloro-hydroxo-oxo-vanadate(V), Tetrachloro-oxo-vanadate(IV),
Tetrachloro-oxo-vanadate(V), Crystal Structure

Starting from vanadium which was not free of oxide, VCl_4 was prepared; its reaction with PPh_4Cl in the presence of K_2S_5 in dichloromethane yielded $\text{PPh}_4[\text{VOCl}_3\text{OH}]$. From V_2S_5 , PPh_4Cl and S_2Cl_2 in acetonitrile, sulfur crystallized first, then $\text{PPh}_4[\text{VOCl}_4]$, and then $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 4\text{CH}_3\text{CN}$. Upon standing with the mother liquor at -18°C , the latter was converted to $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 2\text{CH}_3\text{CN}$. According to its X-ray crystal structure determination, $\text{PPh}_4[\text{VOCl}_3\text{OH}]$ (space group $Pbca$, $a = 1105.5$, $b = 1920.8$, $c = 2242.8$ pm, $Z = 8$) has nearly square-pyramidal anions that are associated to chains by O-H \cdots Cl bridges. $\text{PPh}_4[\text{VOCl}_4]$ is isotypic with $\text{AsPh}_4[\text{VOCl}_4]$ and has strictly square-pyramidal anions (space group $P4/n$, $a = 1254.0$, $c = 765.0$ pm, $Z = 2$). In $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 4\text{CH}_3\text{CN}$ (space group $P\bar{1}$, $a = 1281.3$, $b = 1276.6$, $c = 1841.5$ pm, $\alpha = 84.11^\circ$, $\beta = 83.96^\circ$, $\gamma = 64.31^\circ$, $Z = 2$) the square pyramid of the VOCl_4^{2-} ion is distorted towards a trigonal-bipyramidal shape (C_{2v} symmetry) having *trans*-ClVCl angles of 145.88° and 156.87° and O=V-Cl angles of 107° and 101.6° . In $(\text{PPh}_4)_2[\text{VOCl}_4]\cdot 2\text{CH}_3\text{CN}$ (space group $P\bar{1}$, $a = 1017.1$, $b = 1029.3$, $c = 2416.0$, $\alpha = 77.74^\circ$, $\beta = 79.99^\circ$, $\gamma = 78.94^\circ$, $Z = 2$), the VOCl_4^{2-} structure is even closer to trigonal-bipyramidal, with *trans*-ClVCl angles of 133.25° and 165.80° and O=V-Cl angles of 113.3° and 97° .