

Molecular Complexes of Silver(I) Perchlorate and Tertiary Phosphines Containing Two-coordinate Silver

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Silver(I) salts containing relatively non-polarizable anions such as ClO_4^- , BF_4^- , and PF_6^- , are known to form cationic complexes [1–3] with tertiary phosphines. Complexes of the types $[\text{Ag}(\text{PR}_3)_4]\text{X}$ [1], $[\text{Ag}(\text{PR}_3)_3]\text{X}$ [2], $[\text{Ag}(\text{PR}_3)_2]\text{X}$, [2, 3], where $\text{X} = \text{ClO}_4$, BF_4 or PF_6 have been reported and their ionic constitution has been established by spectroscopic and conductance studies [1–3]. In the course of our investigations on the steric and electronic effects of phosphorus ligands in silver(I) complexes, it was found that the reaction of silver(I) perchlorate and a tertiary phosphine, in 1:1 mole ratio, affords hitherto unknown stable molecular complexes of the type $\text{R}_3\text{PAgOClO}_3$ which contain two-coordinate silver in the solid state as well as in solution. Although a linear two-fold coordination is quite common for silver(I) compounds [4], phosphine complexes of the type, R_3PAgX [5] are usually polymeric containing tetrahedrally coordinated silver. Except the recently reported $(\text{t-Bu})_3\text{PAgONO}_2$ [3], we are not aware of any molecular complexes of tertiary phosphines containing two-coordinate silver.

Stable complexes $\text{R}_3\text{PAgOClO}_3$, were isolated using bulky phosphines, $\text{P}(\text{t-Bu})_3$, PCy_3 ($\text{Cy} = \text{cyclohexyl}$), $\text{P}(\text{o-CH}_3\text{C}_6\text{H}_4)_3$, as well as less bulky triphenylphosphine and *para* substituted triarylphosphines, $\text{P}(\text{p-XC}_6\text{H}_4)_3$, where $\text{X} = \text{OCH}_3$, F and Cl . Unlike the cationic complexes [2, 3], the complexes $\text{R}_3\text{PAgOClO}_3$, are unionized in dichloromethane ($M = 0.1$ to $2.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The two coordinate structure of the complexes is evident from their infrared spectra. As shown by the data in Table I, the infrared spectrum of the complexes, in the solid state, show three bands at *ca.* 1150, 1000, and $915\text{--}850 \text{ cm}^{-1}$ which can be assigned unambiguously to the perchlorate moiety, showing that the perchlorate is monodentately [6–8] bonded to the silver atom. The two perchlorate bands in the 1150 and 1000 cm^{-1} regions were also observed in the spectra[†] of the solutions of

TABLE I. Infrared Absorption Bands^a Due to the Perchlorate Group for the $\text{R}_3\text{PAgOClO}_3$ Complexes in the $1200\text{--}800 \text{ cm}^{-1}$ Region.

R	cm^{-1}
t-Bu	1150S, 1002S, 910M
Cy	1150S, 1000S, 850M
<i>o</i> -CH ₃ C ₆ H ₄	1150S, 1010S, 880M
C ₆ H ₄	1145S, 1000S, 850S
<i>P</i> -CH ₃ OC ₆ H ₄	1155S, 995S, 915M
<i>p</i> -FC ₆ H ₄	1160S, 995S, 845M
<i>p</i> -ClC ₆ H ₄	1150S, 995S, 880M

^a In solid state. M, medium; S, strong.

the complexes in dichloromethane. Thus, the appearance of the three perchlorate bands in the solid state cannot be attributed to the lowering of the perchlorate symmetry due to solid state effects [9]. Further evidence for the monomeric molecular nature of the complexes was provided by the molecular weight measurements of the complexes $\text{Cy}_3\text{PAgOClO}_3$, $(\text{o-CH}_3\text{C}_6\text{H}_4)_3\text{PAgOClO}_3$, $(\text{p-ClC}_6\text{H}_4)_3\text{PAgOClO}_3$, and $(\text{p-FC}_6\text{H}_4)_3\text{PAgOClO}_3$, in 1,2-dichloroethane.

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[†]The presence of the perchlorate band in the $800\text{--}900 \text{ cm}^{-1}$ region could not be ascertained due to the interference with solvent bands.