

Antimony as a Donor Atom in Silver Coordination Chemistry: Synthesis, IR Spectra and Structure of the Silver(I) Cyanoximate Complexes with Triphenylstibine and Triphenylphosphine Model Compounds

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Silver(I) cyanoximate complexes $\text{Ag}\{\text{ONC}(\text{CN})\text{-R}\}$ ($\text{R} = \text{COPh}$, $\{\text{L}^1\}$; $\text{COC}(\text{CH}_3)_3$, $\{\text{L}^2\}$; benzothiazol-2-yl, $\{\text{L}^3\}$) with triphenylphosphine and -stibine of compositions $\text{Ag}(\text{PPh}_3)_n\{\text{L}\}$ ($n = 2, 4$) and $\text{Ag}(\text{SbPh}_3)_n\{\text{L}\}$ ($n = 3$ for $\{\text{L}^1\}$ and $\{\text{L}^2\}$, $n = 2$ for $\{\text{L}^3\}$) were synthesized by the reaction of the components in acetonitrile solution and characterized by elemental analyses and IR spectroscopy. The crystal structures of $\text{Ag}(\text{SbPh}_3)_3\{\text{L}\}$ ($\text{L} = \{\text{L}^1\}$ (**1**), $\{\text{L}^2\}$ (**2**), $\text{Ag}(\text{SbPh}_3)_2\{\text{L}^3\} \cdot \text{CH}_3\text{CN}$ (**3**) and $\text{Ag}(\text{PPh}_3)_2\{\text{L}^1\} \cdot \text{CH}_3\text{CN}$ (**4**), have been determined by X-ray diffraction. For all the compounds examined the coordination environment of the silver atom has the geometry of a distorted tetrahedron ($[\text{AgP}_2\text{NO}]$ (**4**); $[\text{AgSb}_3\text{N}]$ (**1**), (**2**); $[\text{AgSb}_2\text{N}_2]$ (**3**)). The *bis* adducts $\text{Ag}(\text{EPh}_3)_n\{\text{L}\}$ adopt molecular structures, in which the organic anions are coordinated in bidentate chelate fashion *via* the nitroso nitrogen atom and the oxygen (nitrogen for $\{\text{L}^3\}$) atom of the substituent R. In the *tris*-stibino complexes (Ag-Sb 2.670(4) - 2.7748(8) Å; Sb-Ag-Sb 108.87(4) - 115.00(2) $^\circ$) the cyanoximates are unidentate ligands and coordinated *via* the nitroso nitrogen atoms (Ag-N *ca.* 2.35(1) Å). The different behaviour of N,O and N,N chelating cyanoximes under the same conditions suggests, that the Sb donor triphenylstibine is able to substitute the oxygen atoms in the silver(I) coordination sphere, but not the nitrogen ones. This causes the formation of 1:3 adducts of $\text{Ag}\{\text{L}\}$ with SbPh_3 for N,O donors $\{\text{L}^1\}$ and $\{\text{L}^2\}$, and only 1:2 for N,N donor anionic $\{\text{L}^3\}$.