

## Silver (I) Complexes with Triphenylphosphine & Aniline

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The mixed ligand complexes of the type  $[AgX(PPh_3)(An)]_2$  (where  $X = Br^-, I^-, NO_3^-$  or  $SCN^-$ ;  $PPh_3$  = triphenylphosphine and  $An$  = aniline) have been obtained and characterized on the basis of elemental analyses and IR data. The anionic groups are suggested to form bridge between the two silver (I) atoms.

In a recent communication<sup>1</sup> two of the authors reported mixed ligand complexes of silver (I) of the type  $[AgX(PPh_3)(HOx)]_n$  containing triphenylphosphine and 8-hydroxyquinoline. In this note a few mixed ligand complexes of Ag(I) with triphenylphosphine and aniline have been prepared and characterized.

$[AgBr(PPh_3)(An)]_2$  was prepared by refluxing  $[AgBr(PPh_3)_2]$  (ref. 2) and aniline in equimolar ratio in benzene for 4 hr. On cooling to room temperature, light brown crystals of the complex crystallized out; yield 70%, m.p. 160°C (Found: C, 52.89; H, 3.96; N, 2.32; Br, 14.21; P, 5.10; Ag, 19.41. Req'd.: C, 53.03; H, 4.05; N, 2.57; Br, 14.73; P, 5.70; Ag, 19.88%). Similar procedure was applied to prepare  $[AgI(PPh_3)(An)]_2$ , pale white crystals, yield 75%, m.p. 170°C (Found: C, 48.53; H, 3.50; N, 2.16; I, 21.12; P, 5.05; Ag, 17.98; Req'd.: C, 48.81; H, 3.73; N, 2.37; I, 21.52; P, 5.25; Ag, 18.30%).

$[AgSCN(PPh_3)(An)]_2 \cdot H_2O$  was prepared by refluxing  $AgSCN(PPh_3)_2$  (ref. 3) and aniline in 1:2 ratio in chloroform for 6 hr. On cooling to room temperature brown crystals of the complex separated out, yield 75%, m.p. 200 (d) (Found: C, 55.23; H, 4.23; N, 4.86; S, 5.38; P, 5.44; Ag, 19.88. Req'd.: C, 55.66; H, 4.45; N, 5.19; S, 5.94; P, 5.75; Ag, 20.04%).

$[AgNO_3(PPh_3)(An)]_2 \cdot H_2O$  was prepared by refluxing  $AgNO_3(PPh_3)_2$  (ref. 3) and aniline in 1:2 ratio in methanol for 4 hr. On cooling to room temperature the complex separated out as dark brown crystals, yield 65%, m.p. 120 (d) (Found: C, 52.53; H, 4.08; N, 4.98; P, 5.08; Ag, 19.13. Req'd.: C, 53.03; H, 4.42; N, 5.15; P, 5.71; Ag, 19.38%).

The compounds prepared are sparingly soluble in common organic solvents thus prohibiting their molecular weight determinations. The colour of the complexes may be due to charge transfer, since the complexes are diamagnetic.

The IR spectra of the complexes exhibit bands in the regions 1090-1118 and 698  $cm^{-1}$  assignable to  $\nu P-C$  modes<sup>4</sup>. The shift to higher frequency of  $\nu P-C$  at 1089  $cm^{-1}$  indicates coordination of triphenylphosphine. Whenever phosphine acts as a donor or if it is in the four-coordinated state<sup>5</sup>, it exhibits an absorption near 720  $cm^{-1}$ . This band in our complexes occurs in the region 706-720  $cm^{-1}$ .

A weak band in the region 1250-1370  $cm^{-1}$  is assigned to  $\nu C-N$  (ref. 6). The occurrence of  $NH_2$  scissor deformation in the complexes at 1575-1620  $cm^{-1}$  indicates coordination of aniline through the lone pair of nitrogen atom<sup>7</sup>.

The presence of coordinated thiocyanate group in  $[AgSCN(PPh_3)(An)]_2$ , forming the bridge between the two metal atoms is shown by the occurrence of a sharp band at 2094  $cm^{-1}$ , this somewhat lower value than required<sup>8</sup> for a bridged thiocyanato group (2150-2185  $cm^{-1}$ ) may be due to unsymmetrically bonded thiocyanato group or due to the presence of two ligands having large difference in basicity and  $\pi$  bonding ability towards the Ag(I) atoms<sup>9</sup>.

The structure and vibrational spectra of a large number of nitrate complexes have been reviewed by Addison *et al.*<sup>10</sup> and Rosenthal<sup>11</sup>. The nitrate complex,  $[AgNO_3(PPh_3)(An)]_2 \cdot H_2O$  exhibits bands at 1466, 1288 and 1020  $cm^{-1}$  assignable to  $\nu NO$ , indicating the presence of (chelating) bidentate nitrate group as has been observed by Gatehouse *et al.*<sup>12</sup> in the complex  $[Ni(en)_2NO_3]ClO_4$ .

In our complexes water molecules are present in the lattice form, as revealed by the absorptions in the region 3340-3450  $cm^{-1}$  in the form of small splittings<sup>13,14</sup>. If the spectrum is examined under high resolution, the fine structure of these bands is observed. The presence of  $\delta HOH$  rules out the presence of coordinated water.

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### References

- 1 Najma S, Irshad A K & Naqvi S R R, *Rev Roum Chim*, **25** (1980) 105.
- 2 Boon-Keng T & Joseph C C, *J Am chem Soc*, **97** (1975) 1256.

- 3 Vohra A G, *Ph D thesis*, University of London, London (1969).
- 4 Deacon G B & Green S H J, *Spectrochim Acta*, **24A** (1968) 345.
- 5 Sheldon B & Tyree S, *J Am chem Soc*, **80** (1958) 2117.
- 6 Skrbljak J, *J chem Soc*, (1957) 843.
- 7 Barnes G & Williams V, *Analyt Chem*, **20** (1948) 402.
- 8 Chatt J & Duncanson L A, *Nature (Lond)*, **178** (1956) 997.
- 9 Toeiniskoetler R H & Solomon S, *Inorg Chem*, **7** (1968) 617.
- 10 Addison C C, Logan N, Wallwork S C & Barner C D, *Q Rev*, **25** (1971) 289.
- 11 Rosenthal M R, *J chem Educ*, **50** (1973) 331.
- 12 Gatehouse B M, Livingstone S E & Nyholm R S, *J chem Soc*, (1957) 4222; *J inorg nucl Chem*, **8** (1958) 75.
- 13 Miller F A & Wilkins C H, *Analyt Chem*, **24A** (1952) 1253.
- 14 Nakagawa I & Shimanouchi T, *Spectrochim Acta*, **20** (1964) 429.