*Inorganica Chimica Acta,* 8 (1974) 25–26

# Bidentate Group VB Chelates
## Part V. Silver(I) Complexes of Some Diphosphine and Diarsine Ligands[1]

W. LEVASON and C. A. McAULIFFE*
*Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.*
Received February 3, 1973

*Silver(I) nitrate reacts with bisdiphenylphosphinomethane, 1,2-bisdiphenylphosphinoethane, 1,3-bisdiphenylphosphinopropane, cis-1,2-bisdiphenylphosphinoethylene, and o-phenylenebisdimethylarsine to form non-conducting complexes* [$(AgNO_3)_2.L$]. *The infrared spectra indicate monodentate nitrato groups, and the complexes are assigned a dimeric structure with single ligand bridges, a type of complex hitherto unknown for* $Ag^I$ *with bidentate phosphines and arsines. Attempts to prepare silver(II) complexes were unsuccessful.*

### Introduction

The reported[2] silver(I) ditertiary phosphine complexes are of the types $[AgL_2][AgX_2]$, $[AgL_2]X$, and, in rare cases, $Ag_2L_3X_2$ (L = ditertiary phosphine, X = halide or nitrate). Similarly, with *o*-phenylenebisdimethylarsine Lewis *et al.*[3] obtained complexes of types $[AgL_2][AgX_2]$ (X = Cl, Br, I, $NO_2$) and $[AgL_2]Y$ (Y = $NO_3$, $ClO_4$). The ability of the heavier group VB donor ligands to stabilise high oxidation states of many transition metals is well known; however, silver(II) complexes of phosphorus or arsenic donor ligands have not been reported. Silver(II) is known[4] only in $AgF_2$, fluorocomplexes,[5] and in compounds with various nitrogen heterocycles.[4]

Here we report new silver(I) complexes of stoichiometry $(AgNO_3)_2.L$, where L = bisdiphenylphosphinomethane (dPm), 1,2-bisdiphenylphosphinoethane (dPe), 1,3-bisdiphenylphosphinopropane (dPp), *cis*-1,2-bisdiphenylphosphinoethylene (VPP), and *o*-phenylenebisdimethylarsine (DAS), and attempts to oxidise these to silver(II) complexes.

### Experimental

The ligands were prepared by standard methods available in the literature.[2] The method used to prepare the complexes is exemplified by that used to prepare $[(AgNO_3)_2.dPe]$: warm ethanolic solutions of dPe (2.0 g; 5.0 mmole) and silver nitrate (1.7 g; 10.0 mmole) were mixed and stirred for 1 h. The slightly cloudy solution was filtered and rotatory evaporated until crystals began to appear. The solution was allowed to stand overnight, filtered, and the greyish–white product dried *in vacuo*. Yield 3.1 g (84%). Analyses: Found: C, 42.2; H, 3.4; N, 3.7%. Calculated for $[(AgNO_3)_2.dPe]$: C, 42.3; H, 3.3; N, 3.8%. M.P. 215° C.

Similarly were prepared $[(AgNO_3)_2.VPP]$. Found: C, 42.0; H, 2.8; N, 3.6%. Calculated: C, 42.4; H, 3.0; N, 3.8%. M.P. 182° C.

$[(AgNO_3)_2.dPm]$. Found: C, 41.1; H, 2.9; N, 3.9%. Calculated: C, 41.5; H, 3.1; N, 3.9%. M.P. 196° C (decomposition).

$[(AgNO_3)_2.dPp]$. Found: C, 42.9; H, 3.6; N, 3.6%. Calculated: C, 43.2; H, 3.5; N, 3.8%. M.P. 72° C (decomposition).

$[(AgNO_3)_2.DAS]$. Found: C, 19.2; H, 2.6; N, 3.8%. Calculated: C, 19.2; H, 2.5; N, 4.0%. M.P. 180° C (decomposition).

The $[Ag(DAS)_2]NO_3$ complex was prepared as previously described.[3] Found: C, 32.6; H, 4.5; N, 1.9%. Calculated: C, 32.3; H, 4.3; N, 1.9%.

Conductivity measurements were obtained on a Cambridge Instruments Ltd. conductivity bridge in nitromethane ($10^{-3}M$ at 20° C). Infrared spectra were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer.

### Discussion

The ligands dPm, dPe, dPp, VPP, and DAS react with silver nitrate in a 1:2 molar ratio to produce $[(AgNO_3)_2.L]$ complexes. These compounds are effectively non-conductors in nitromethane solution ($\Lambda_M$ values of $\leqq 6$ ohm$^{-1}$ cm$^2$ $M^{-1}$), ruling out ionic structures, and suggesting a structure of type

---

* Author to whom correspondence should be addressed.

$$O_2NO{-}Ag \leftarrow L \frown L \rightarrow Ag{-}ONO_2 \qquad (L = P,As)$$

This type of structure, in which a single diphosphine or diarsine ligand bridges two metal ions, is well known in gold(I) chemistry,[2] but has not been reported previously for $Ag^I$. A few silver(I) complexes with multiple ligand bridges, $Ag_2(dPe)_3X_2$,[6] are known, as are complexes with bridging bisdiphenylphosphinoacetylene ligands.[7]

The complex $[(AgNO_3)_2.DAS]$ contains a rare example of DAS behaving as a bridging rather than a chelating ligand. The only other example of bridging DAS reported is $[\{(MeC_5H_4)Mn(CO)_2\}_2.DAS]$.[8] For comparison purposes $[Ag(DAS)_2]NO_3$[3] was prepared and, as expected, exhibited conductivity in nitromethane equivalent to a 1:1 electrolyte ($\Lambda_M = 91$ ohm$^{-1}$ cm$^2$ $M^{-1}$).

The infrared spectra of these complexes provide some evidence about the mode of coordination of the nitrato ligands (see Table I), although in the absence of Raman data it is not possible to unequivocally distinguish between mono- and bi-dentate nitrato groups.[9] The IR spectrum of $[Ag(DAS)_2]NO_3$ is clearly different from those of the other complexes. Ionic nitrate groups absorb at ~1390, 830, and 720 cm$^{-1}$, whilst coordination lifts the degeneracy of the $\nu_3$ (the 1390 cm$^{-1}$ band), resulting in a splitting of this absorption into two components, one at higher, and one at lower frequency.[9] The infrared spectrum of $[Ag(DAS)_2]NO_3$ points to the presence of ionic nitrate, consistent with the conductivity data. The $[(AgNO_3)_2.L]$ complexes show three absorptions due to nitrato groups at ~1430, ~1280, and ~820 cm$^{-1}$, which can be assigned to the $\nu_4$ ($B_1$), $\nu_1$ ($A_1$) and $\nu_6$ ($B_2$) vibrations of monodentate nitrato groups. There are also weak bands at ~1030 cm$^{-1}$ which could be due to the $\nu_2$ ($A_2$) vibrations, but ligand vibrations also occur in the region making positive assignments difficult. The assignment of monodentate nitrato groups is in keeping with the linear stereochemistry of silver(I) complexes.

Attempts to oxidise these complexes to silver(II) failed. No reaction was observed on stirring them with aqueous ammonium persulphate solution. The complexes dissolved in nitric acid but were not oxidised; whilst reaction with chlorine or bromine in dichloromethane solution resulted in decomposition and precipitation of AgX (X = Cl, Br).

TABLE I. Infrared Spectra (Nitrate Bands), cm$^{-1}$

| Compound | Absorptions |
|---|---|
| $(AgNO_3)_2.dPm$ | 1430, 1275, 805 |
| $(AgNO_3)_2.dPe$ | 1430, 1295, 810 |
| $(AgNO_3)_2.dPp$ | 1430, 1285, 808 |
| $(AgNO_3)_2.VPP$ | 1430, 1280, 810, 805 |
| $(AgNO_3)_2.DAS$ | 1435, 1280, 810, 805 |
| $[Ag(DAS)_2]NO_3$ | 1375, 828, 720 |

## Acknowledgement

W.L. is grateful to the Science Research Council for the award of a Research Studentship.

## References

1 Part IV. K.K. Chow, W. Levason, and C.A. McAuliffe, *Inorg. Chim. Acta.*, in press.

2 W. Levason and C.A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, *14*, 173 (1972).

3 J. Lewis, R.S. Nyholm, and D.J. Phillips, *J. Chem. Soc.*, 2177 (1962).

4 J.A. McMillan, *Chem. Rev.*, *62*, 65 (1962), and refs. therein.

5 R.H. Odenthal and R. Hoppe, *Z. Anorg. Allgem. Chem.*, *385*, 92 (1971).

6 S.S. Sandhu and R.S. Sandhu, *Ind. J. Chem.*, *9*, 482 (1971).

7 W.A. Anderson, A.J. Carty, and A. Efraty, *Can. J. Chem.*, *47*, 3361 (1969).

8 R.S. Nyholm, S.S. Sandhu, and M.H.B. Stiddard, *J. Chem. Soc.*, 5916 (1963); M.J. Bennett and R. Mason, *Proc. Chem. Soc.*, 395 (1964).

9 C.C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, *6*, 71 (1964); C.C. Addison and D. Sutton, *Prog. Inorg. Chem.*, *8*, 195 (1967).