X-Ray Structure of the Novel Ligand-bridged Olefinic Tertiary Arsine Complex $C_{11}H_{15}AsAg_2(NO_3)_2$

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Summary *X*-ray structure analysis has shown that in the complex $C_{11}H_{15}AsAg_2(NO_3)_2$ the normally chelating *o*-allylphenyldimethylarsine ligand is bonded *via* its arsine and olefin groups to two different silver atoms.

TERTIARY phosphine and arsine groups have been used to stabilize the otherwise weak mono-olefin complexes of transition metals, the olefin group being held in proximity to the metal by the strong phosphine or arsine metal bond.[1] In attempts to prepare the 1:1 adduct of *o*-allylphenyldimethylarsine and silver nitrate,[2] for use as an intermediate, we obtained a new compound analysing as $C_{11}H_{15}As(AgNO_3)_2$. An *X*-ray analysis has shown that the structure consists of chains of silver atoms bridged by the

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o-allylphenyldimethylarsine and nitrate groups. This is the first time that a mono-olefin ligand of this type has been shown to bond to two different metal atoms. Structures of related types may be envisaged for other silver nitrate mono-olefin arsine and phosphine complexes.

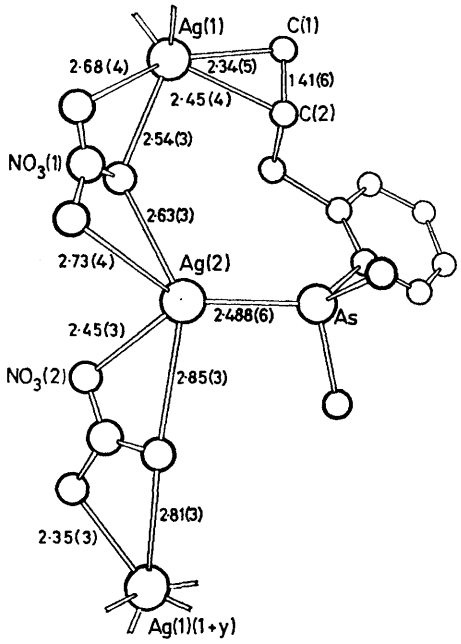

FIGURE. Structure of the complex $C_{11}H_{15}As(AgNO_3)_2$ showing the principal bond lengths (e.s.d.'s in parentheses).

Colourless needle shaped crystals of $C_{11}H_{15}AsAg_2(NO_3)_2$ are orthorhombic, space group $P2_12_12_1$ with $a = 7{\cdot}17$, $b = 10{\cdot}16$, $c = 22{\cdot}02$ Å, $U = 1605$ Å^3, $D_m = 2{\cdot}35$, $D_c = 2{\cdot}33$ g cm^{-3}, $Z = 4$. With isotropic temperature factors for all non-hydrogen atoms block diagonal least-squares refinement, using 774 independent visually estimated reflections corrected for absorption (Mo-K_α radiation, $\mu = 34$ cm^{-1}), has given an R-value of 0·078.

The structure and the principal bond lengths are shown in the Figure. The ligand links two silver atoms, the olefin group being π-bonded to Ag(1) and the arsenic atom co-ordinated to Ag(2). These two silver atoms are also bridged by a doubly-bidentate nitrate group with four similar Ag–O bond lengths. A second bridging nitrate completes the chain-like structure, forming two unsymmetrically bidentate linkages with two Ag–O distances (2·85, 2·81 Å) significantly longer than the other two (2·43, 2·35 Å) The co-ordination of each silver atom is completed by a long bond (2·90 Å in each case) from an oxygen atom of a neighbouring chain.

The molecular weight of the complex measured in methanol [0·007—0·025 M $C_{11}H_{15}AsAg_2(NO_3)_2$] is half the formula weight consistent with the dissociation

$$C_{11}H_{15}AsAg_2(NO_3)_2 \longrightarrow C_{11}H_{15}AsAg_2NO_3^+ + NO_3^-$$

and indicating that the ligand-bridged binuclear unit persists in solution.

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[1] R. S. Nyholm, *Rev. Pure Appl. Chem.*, 1971, **27**, 127 and references therein.
[2] M. A. Bennett, W. R. Keen, and R. S. Nyholm, *Inorg. Chem.*, 1968, **7**, 552.