

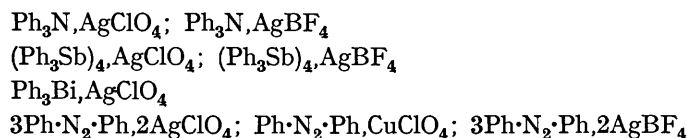
**558.** *The Formation of Complexes of Triphenylamine, Triphenylbismuth, and Azobenzene with Some Copper and Silver Salts.*

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New adducts have been prepared of triphenylamine, triphenylstibine, and triphenylbismuth with some silver salts, and of azobenzene with some silver and cuprous salts.

THE ability of the triaryl derivatives of elements of Group V to form complexes with metal ions seems to be greatest for triphenyl-phosphine and -arsine although in recent years a number of triphenylstibine complexes have been reported.<sup>1</sup> No metal complex of triphenylamine or triphenylbismuth has previously been described although the amine forms adducts with boron trichloride and tribromide and forms triphenylammonium salts,<sup>2</sup> whilst triphenylbismuth forms an adduct with sulphur trioxide.<sup>3</sup> In the case of triphenylamine the lack of basicity is probably due to interaction of the *p*-electrons of the nitrogen atom with the  $\pi$ -electron systems of the aromatic rings.<sup>2</sup>

In order to form complexes of very weak bases from solution, it is necessary that the basicity of the solvent towards the metal ion should be less than the complex-forming power of the base and that any anions present should have only weak powers of complex-formation. Previous workers have shown that complexes of triaryl-phosphines and -arsines are readily prepared from solutions in ethanol. The present work has shown that the following compounds with the weakly basic ligands triphenylamine, triphenylbismuth, and azobenzene may be prepared from solutions in diethyl ether:



The 4:1 complexes formed by interaction of triphenylstibine with silver salts are almost certainly similar to the 4:1 complexes of triphenylphosphine and triphenylarsine described by Cotton and Goodgame<sup>4</sup> and will not be discussed further. The triphenylamine adducts are formulated as complexes on the basis of their virtual insolubility in diethyl ether and on physical studies on the adducts. Triphenylamine silver perchlorate gives an X-ray powder pattern completely distinct from those of either of the components, and the ultraviolet spectra of the complex in both the solid state and in solution show extra bands which are due to modifications of the electronic structure of the triphenylamine molecule when it is donating electrons to the silver ion. The infrared spectra of the solid adducts show that the anions must be considered free and unco-ordinated. The

<sup>1</sup> Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

<sup>2</sup> Kemmitt, Nuttall, and Sharp, *J.*, 1960, **46**; Sharp, *Chem. and Ind.*, 1958, 1235.

<sup>3</sup> Becke-Goehring and Thielemann, *Z. anorg. Chem.*, 1961, **308**, 33.

<sup>4</sup> Cotton and Goodgame, *J.*, 1960, 5267.

infrared spectra of the organic part of the adducts show only slight modifications from those of the free organic derivatives.

Co-ordination from triphenylamine or triphenylbismuth could be from either the Group V atoms or from the  $\pi$ -electron systems of the aromatic rings. Co-ordination from the Group V atoms would be expected to alter the co-ordination about that atom from planar<sup>2,5</sup> to tetrahedral and would account for the small changes in the infrared spectra from the spectra of the free ligands. Aromatic systems give rise only to weak complexes with copper and silver<sup>6</sup> but again some slight modification of the infrared spectrum would be expected. On the basis of the stoichiometry, co-ordination by the first mechanism would involve one-co-ordinate silver and we prefer a model in which a nitrogen atom of one molecule of triphenylamine is co-ordinated to the silver which is further bonded to the aromatic systems of a further molecule of triphenylamine. However, it is impossible to prove this point without complete X-ray structure determinations.

As an extension of this work, the formation of complexes to silver and copper by the weakly basic azobenzene was investigated. Azomethane fairly readily acts as a ligand, but as the only azobenzene complexes recorded in the literature are with platinum<sup>7</sup> and titanium<sup>8</sup> it must be presumed that the basicity of the molecule is low because of interaction between the lone-pairs of electrons on the nitrogen atoms and the  $\pi$ -electron systems of the phenyl rings. The present work shows that azobenzene complexes of silver(I) and copper(I) are readily formed from ethereal solution. The ratio of ligand to metal is unusual in the silver salts, but the complexes may be polymeric<sup>9</sup> with the azo-groups acting as bridges, and there is the possibility of interaction between the aromatic systems and the metal ions as has been postulated above for the triphenylamine complexes. The infrared spectra of the complexes indicate that the anions are completely free in the solid adducts; the ultraviolet spectra of the complexes are different from those of the free ligand, in agreement with changes in electronic structure which occur on complex formation.

#### EXPERIMENTAL

All anhydrous salts were handled in the dry-box. Silver fluoroborate was prepared by the action of boron trifluoride on a suspension of silver fluoride in sulphur dioxide<sup>10</sup> or by the action of bromine trifluoride on silver borate.<sup>11</sup> A solution of cuprous perchlorate was prepared by shaking an excess of copper powder with an ethereal solution of silver perchlorate.<sup>12</sup> Complexes were prepared by mixing solutions in diethyl ether of the silver salts and of the ligands. If immediate precipitation did not occur the mixed solutions were gently warmed; precipitation then occurred almost at once. Analytical data for the *adducts* are tabulated.

Adduct	Found (%)			Required (%)		
	C	H	Ag	C	H	Ag
Ph <sub>3</sub> N, AgClO <sub>4</sub> .....	47.8	3.9	24.2	47.8	3.3	23.9
(Ph <sub>3</sub> Sb) <sub>4</sub> , AgClO <sub>4</sub> .....	53.0	3.9	6.7	53.3	3.7	6.7
Ph <sub>3</sub> Bi, AgClO <sub>4</sub> .....	33.3	2.9	—	33.3	2.3	—
3Ph·N <sub>2</sub> ·Ph, 2AgClO <sub>4</sub> .....	45.4	4.0	22.2	45.0	3.1	22.5
Ph <sub>3</sub> N, AgBF <sub>4</sub> .....	48.5	3.95	—	49.1	3.65	—
(Ph <sub>3</sub> Sb) <sub>4</sub> , AgBF <sub>4</sub> .....	53.2	4.2	—	53.8	3.7	—
3PhN <sub>2</sub> Ph, 2AgBF <sub>4</sub> .....	46.6	3.6	—	46.2	3.2	—
Ph·N <sub>2</sub> ·Ph, CuClO <sub>4</sub> .....	45.4	4.1	—	45.7	3.3	—

All the compounds obtained were non-explosive at room temperature but readily ignited on gentle heating. Azobenzencopper(I) perchlorate detonated at 75°.

<sup>5</sup> Sasaki, Kimura, and Kubo, *J. Chem. Phys.*, 1959, **31**, 477; Whetsel, *Z. Krist.*, 1942, **104**, 305.

<sup>6</sup> Sharp and Sharpe, *J.*, 1958, 1855, 1858.

<sup>7</sup> Kharash and Ashford, *J. Amer. Chem. Soc.*, 1936, **58**, 1736.

<sup>8</sup> Dermer and Fernelius, *Z. anorg. Chem.*, 1934, **221**, 83.

<sup>9</sup> Cf. Brown and Dunitz, *Acta Cryst.*, 1960, **13**, 28.

<sup>10</sup> Russell and Sharp, *J.*, 1961, 4689.

<sup>11</sup> Sharpe, *J.*, 1952, 4538.

<sup>12</sup> Moss and Sharp, unpublished work.

X-Ray powder photographs were taken on a 9 cm. powder camera with  $\text{Cu-K}_\alpha$  radiation. Ultraviolet spectra of solutions over the range 250—700  $\text{m}\mu$  were taken on an Optika spectrophotometer. Bands recorded in solution were: for triphenylamine in ether, 300  $\text{m}\mu$ ; for triphenylamine silver perchlorate, 300vs, 420w  $\text{m}\mu$ .

We are greatly indebted to Dr. T. M. Dunn of University College, London, for measurement of reflectance spectra of the solids over the range 320—700  $\text{m}\mu$ . Bands recorded were: for triphenylamine, 350  $\text{m}\mu$ ; for triphenylamine silver perchlorate, 350vs, 420w, 510vw  $\text{m}\mu$ ; for azobenzene, 370s, 450s  $\text{m}\mu$ ; for trisazobenzene bis(silver perchlorate), 330m, 420m  $\text{m}\mu$ .

The ultraviolet spectra of triphenylamine and triphenylamine silver perchlorate in the solid are slightly different from those in solution, the position of the main peak being shifted by 50  $\text{m}\mu$ , probably owing to some form of intermolecular electronic interactions in the solid lattice.

Infrared spectra were recorded for Nujol or hexachlorobutadiene mulls on a Perkin-Elmer model 21 or a Grubb-Parsons model 54 spectrophotometer. The following peaks ( $\text{cm}^{-1}$ ) were found: triphenylamine, 3040m, 3030m, 1940w, 1850w, 1775w, 1700w, 1585s, 1490s, 1330m, 1305m, 1285s, 1185m, 1175m, 1075m, 1050m, 898w, 833w, 750s, 700s; silver perchlorate, 1080s, 920w; triphenylamine silver perchlorate, 3030w, 1590s, 1480s, 1330m, 1280m, 1230m, 1160m, 1090s ( $\text{ClO}_4^-$ ),\* 1030m, 910w,\* 900w, 780s, 760s, 690s.

Broad perchlorate peaks were recorded for the other complexes as follows:  $(\text{Ph}_3\text{Sb})_4\text{AgClO}_4$ , 1080;  $\text{Ph}_3\text{Bi}\cdot\text{AgClO}_4$ , 1095;  $3\text{PhN}_2\text{Ph}\cdot 2\text{AgClO}_4$ , 1060;  $\text{Ph}\cdot\text{N}_2\cdot\text{Ph}\cdot\text{CuClO}_4$ , 1095. Fluoroborate peaks were recorded as follows:  $\text{Ph}_3\text{N}\cdot\text{AgBF}_4$ , 1050, 970;  $(\text{Ph}_3\text{Sb})_4\cdot\text{AgBF}_4$ , 1060, 1045;  $3\text{Ph}\cdot\text{N}_2\cdot\text{Ph}\cdot 2\text{AgBF}_4$ , 1065, 1020;  $\text{AgBF}_4$ ,\* 1026, 1064.

In all cases the appearance and position of these peaks were in agreement with the presence of free anions.

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