part, by adding carefully drops of the aqueous ammonia, the remainder of the crystals being dissolved by cautiously warming the closed flask. On cooling to room temperature no immediate precipitation occurs, but on being kept undisturbed in an ice refrigerator which maintained in general a temperature between 8 and 12°, but sometimes was even colder, crystals begin to deposit after two or three days.

Both of these methods always yield hexagonal crystals of the tetrammine dihydrate.

When a fresh quantity of crude dihydrate was dissolved, by warming, in the final filtrate obtained by the first method, on cooling, long needles of the monohydrate appeared. When the closed Erlenmeyer flask containing these crystals was allowed to stand at room temperature for three months, with a daily variation of 4 or 5°, the needles of the monohydrate were slowly absorbed and replaced by the large six-sided plates of dihydrate until finally only the dihydrate, analytically pure, in typical hexagonal tablets remained. The final solution contained 19.3% of ammonia which was, of course, partly in the copper complex.

CHEMICAL INSTITUTE OF
THE UNIVERSITY OF BERLIN
BERLIN, GERMANY

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Some Arsine Derivatives of Silver Salts

BY G. J. BURROWS AND R. H. PARKER

Various compounds of silver salts with basic substances are described in the literature. In most of these silver has a coördination valency of two. Thus silver halides (or nitrate) are known to combine with two molecules of ammonia, pyridine, aniline, quinoline, etc.[1] In addition, silver ammines have been described with compositions corresponding to the formulas, $AgCl{\cdot}NH_3$, $AgCl{\cdot}3NH_3$ and $2AgCl{\cdot}3NH_3$.

It was decided to investigate the action of phenyldimethylarsine and diphenylmethylarsine on silver salts. These two particular arsines were chosen on account of their ease of preparation and the fact that they are known to combine with the iodides of phosphorus, arsenic, antimony, bismuth and tin.[2] When silver chloride was digested with an aqueous alcoholic solution of phenyldimethylarsine a clear solution was readily obtained, from which white needles separated on cooling. These, on examination, were found to be bisphenyldimethylarsine silver chloride $[Ag(PhMe_2As)_2]Cl$. Compounds of other silver salts with phenyldimethylarsine and diphenylmethylarsine were prepared and examined. The

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(1) *Cf.* Weinland, "Einfuhrung in die Chemie der Komplex-Verbindungen," p. 270.

(2) Burrows and Turner, *J. Chem. Soc.*, **119**, 1449 (1921).

compounds isolated were all of the same type, the coördination valency of the silver being two. The relative proportions of silver salt and arsine were varied in attempts to obtain the analogs of the other ammine silver salts described, but in all cases the compound isolated was one in which two molecules of arsine were coördinated with one atom of silver.

The arsine derivatives are white crystalline compounds with characteristic melting points and are quite stable and unaffected by light. The following list, containing the salts so far prepared, illustrates the variations in melting point.

Bis-phenyl Dimethyl and Bis-diphenyl Methyl Arsine Silver Salts

		Yield, %	M. p., °C.	Arsenic, %		Silver halide, %	
				Calcd.	Found	Calcd.	Found
Diphenyl methyl	Chloride	60	121	23.8	23.5	22.7	22.4
	Bromide	50	110	22.2	21.9	27.8	27.6
	Iodide	..	132	..	..	32.5	32.5
	Nitrate	81	112	..	..	Ag, 16.2	16.3
Phenyl dimethyl	Chloride	..	97	29.6	29.2	28.3	28.1
	Bromide	..	79	..	..	34.1	33.9

It is interesting to note that the bromide has a lower melting point than the corresponding chloride in both series, while in the case of diphenylmethylarsine derivatives the iodide has the highest melting point. The iodide can only be prepared from the nitrate and as we have been unable to prepare the nitrate in the case of phenyldimethylarsine the corresponding iodide could not be isolated. Attempts to prepare arsine silver sulfate were also unsuccessful.

Although the chlorides and bromides are easily prepared by heating the silver halide and arsine in aqueous alcohol and allowing to cool, it was found that they could not be redissolved in aqueous alcohol or absolute alcohol or methyl alcohol except in the presence of excess of the arsine; the compounds appear to be decomposed on heating in these solvents. The halides are also insoluble in acetone, ether and benzene, undergoing decomposition on heating in the two latter liquids with loss of arsine. Bisdiphenylmethylarsine silver nitrate is remarkable in being soluble in aqueous alcohol, ethyl or methyl alcohol, acetone or benzene.

Unsuccessful attempts were made to isolate arsine derivatives of silver salts of optically active acids such as *d*-mandelic and *d*-bromocamphor sulfonic acids. Experiments were carried out with both diphenylmethylarsine and phenylmethylethylarsine. A derivative of the latter should contain arsenic as a center of asymmetry and it was therefore hoped that fractions differing in optical activity would be obtained. On warming the arsine and silver salt in alcohol, reaction undoubtedly took place and a clear solution was obtained but this could not be induced to crystallize. On concentrating the solution *in vacuo* a thick sirup (and ultimately a glassy residue) resulted which very slowly darkened on keeping. This portion of the investigation is being studied further.

Experimental

For the preparation of bis-diphenylmethylarsine silver chloride or the corresponding bromide, freshly precipitated silver chloride (1 mol) or silver bromide was well washed with hot water, then with 96% alcohol. It was then treated in hot alcohol on the water-bath with diphenylmethylarsine (2 mols) until the silver halide had dissolved. On cooling the complex salt separated in white needles. These were removed and washed once with ether. (N. B. Excessive treatment with ether appears to decompose the compound by removal of arsine.) A further crop of crystals was obtained by careful concentration of the mother liquor.

These compounds do not darken on exposure to light; they are insoluble in water, alcohol, acetone, ether or benzene. They are decomposed by concentrated nitric acid. In the analysis, a known weight was treated with excess of silver nitrate (crystals) and a few cc. of concentrated nitric acid and the silver halide precipitate well washed with water, and then alcohol (or acetone) and dried.

Bis-diphenylmethylarsine Silver Nitrate $[Ag(Ph_2MeAs)_2]NO_3$.—This compound was very readily obtained by adding an aqueous alcoholic solution of diphenylmethylarsine (2 mols) to a saturated solution (aqueous) of silver nitrate (1 mol). On agitating the solution the complex salt separated as a micro crystalline precipitate. This was washed with a little ether and dried over sulfuric acid.

Bis-diphenylmethylarsine Silver Iodide $[Ag(Ph_2MeAs)_2]I$.—Attempts to prepare this compound by the action of the arsine on silver iodide were unsuccessful. The relative solubilities of silver chloride, bromide and iodide in diphenylmethylarsine are similar to their relative solubilities in ammonia. The iodide was prepared from the nitrate. An aqueous alcoholic solution of bisdiphenylmethylarsine silver nitrate was treated with the calculated quantity of hydriodic acid, when a very pale yellow finely crystalline precipitate separated. This was filtered off, washed with a little ether and dried over sulfuric acid. It is quite insoluble in the ordinary solvents. During an analysis of this compound it was noticed that on warming with nitric acid and excess of silver nitrate the substance melted and crystallized on cooling. The crystalline mass was removed, washed with water, alcohol and finally ether. It melted at 113° and on analysis was found to be the nitrate.

When decomposed with nitric acid alone, silver iodide is formed, and this can be filtered and washed with acetone or alcohol and weighed.

Bis-phenyldimethylarsine silver chloride and the corresponding bromide were prepared in a similar manner to the bis-diphenylmethylarsine silver compounds using phenyldimethylarsine in place of diphenylmethylarsine. Their solubilities resemble those of the other series.

THE UNIVERSITY OF SYDNEY
NEW SOUTH WALES, AUSTRALIA

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