

centages of the bromide, the azeotropic mixture was found to contain 70.7 mole per cent. of *sec*-butyl bromide. Data for the series of mixtures are shown in Table II.

Bromine was directly determined in the constant boiling fraction by the method of Lemp and Broderson.⁴ These determinations gave values of 71.0 and 71.4 mole per cent. of bromide in the mixture.

TABLE II
REFRACTIVE INDICES OF MIXTURES OF SEC-BUTYL ALCOHOL AND BROMIDE

Weight per cent. of bromide.....	15.02	27.39	39.08	51.70	60.06	
Mole per cent. of bromide.....	8.51	16.94	25.75	36.67	44.86	
n_D^{20}	1.3983	1.4013	1.4042	1.4073	1.4117	1.4138
Weight per cent. of bromide.....	70.41	79.25	84.85	93.34	100	
Mole per cent. of bromide.....	56.27	67.36	75.20	88.33	100	
n_D^{20}	1.4192	1.4242	1.4275	1.4329	1.4370	

Conclusion

Secondary-butyl alcohol and secondary-butyl bromide form an azeotropic mixture boiling at 87.2° at 749 mm., having a refractive index n_D^{20} of 1.4256, and containing 71.0 ± 0.4 mole per cent. of the bromide.

(4) J. F. Lemp and H. J. Broderson, *THIS JOURNAL*, **39**, 2069-2074 (1917).

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Note

Copper Selenate Tetrammine Dihydrate

BY WILLY LANGE AND GERDA V. KRUEGER

We recently described a method for preparing copper selenate tetrammine dihydrate in large crystals.¹ Slight variations in the procedure, however, often result in failure and occasionally no crystals at all are deposited from the ammoniacal solution. We have now perfected two new procedures which are entirely dependable.

(1) Fifteen grams of crystalline copper selenate (Kahlbaum) is dissolved by boiling in 25 cc. of 25% aqueous ammonia and, after filtering and cooling with ice, alcohol is added, the precipitate filtered off, washed with acetone and ether, and dried on a porous plate. Ten grams of this product is dissolved, for the greater part, by warming in 8 to 10 cc. of 25% aqueous ammonia and the hot solution is filtered as quickly as possible but without suction. The hot filtrate is then placed in a closed Erlenmeyer flask partially submerged in a large amount of hot water so that it will cool slowly. It is important that the solution be not shaken during this period.

(2) The same procedure is followed except that the hot solution in the Erlenmeyer flask is rapidly chilled to room temperature, whereupon needles of monohydrate precipitate. These are redissolved, for the greater

(1) *THIS JOURNAL*, **53**, 4013 (1931).

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.

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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 amines have been described with compositions corresponding to the formulas, $\text{AgCl}\cdot\text{NH}_3$, $\text{AgCl}\cdot 3\text{NH}_3$ and $2\text{AgCl}\cdot 3\text{NH}_3$.

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 $[\text{Ag}(\text{PhMe}_2\text{As})_2]\text{Cl}$. Compounds of other silver salts with phenyldimethylarsine and diphenylmethylarsine were prepared and examined. The

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

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