CCCXLIV.—*Researches on Residual Affinity and Co-ordination. Part XXXII. Complex Salts of Bivalent Silver.*

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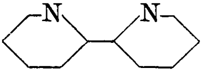
In earlier communications of this series it was shown that co-ordination between copper salts and a diamine such as ethylenediamine stabilises the bivalent condition of this metal so that it becomes possible to isolate complex cupric salts of the less electronegative anions such as iodide, thiosulphate, selenocyanate, and hypophosphite (J., 1926, 2018, 2028; 1927, 1260). These results suggested that the employment of a suitable diamine might lead to a similar increase in the valency of silver. Ethylenediamine itself was tried without complete success, but we have since noticed that αα′-dipyridyl (I) furnishes a sufficiently powerful chelate group to hold together a stable bivalent argentic complex.



(I.)

$[Ag2dipy]^{I}NO_3$ (II.)

$[Ag2dipy]^{II}S_2O_8$ (III.)

$[Ag3dipy]^{II}(NO_3)_2,(ClO_3)_2$ or $(ClO_4)_2$. (IV.)

$[Ag2dipy]^{II}(HSO_4)_2$ (V.)

When light yellow bis-αα′-dipyridylargentous nitrate (II) is added to cold aqueous potassium persulphate the following reaction occurs and reddish-brown *bis-αα′-dipyridylargentic persulphate* (III) is obtained in practically quantitative yield :* $2[Ag2dipy]^{I}NO_3 + 3K_2S_2O_8 = 2[Ag2dipy]^{II}S_2O_8 + 2KNO_3 + 2K_2SO_4$. From this complex persulphate the following salts of bivalent silver have been prepared by suitable double decompositions : *Tris-αα′-dipyridylargentic nitrate* and *chlorate* (IV) are both highly coloured, crystalline salts decomposing quietly above 170° and soluble in water to intense reddish-brown solutions. *Tris-αα′-dipyridylargentic perchlorate* (IV) is a sparingly soluble, orange-brown salt which detonates on heating. *Bis-αα′-dipyridylargentic hydrogen sulphate* (V) is a brown, sparingly soluble powder.

In addition to these mononuclear salts a well-defined complex binuclear diargentic persulphate, $[Ag_2 5dipy](S_2O_8)_2$, has been identified and an acid argentosoargentic nitrate,

$$[Ag2dipy](NO_3)_2,AgNO_3,HNO_3,$$

has been recognised as a by-product in the formation and decomposition of tris-αα′-dipyridylargentic nitrate (IV).

The bivalency of silver in the foregoing complex argentic salts is demonstrated by estimating the iodine liberated by these compounds from potassium iodide. In the case of the two argentic persulphates this effect is accompanied by a further liberation of iodine due to the oxidising action of the anion on the iodide.

In general these complex argentic salts remain unchanged if kept in a cool dry place shaded from direct sunlight. They are decomposed immediately by halogen acids or aqueous alkalis. Mild reducing agents such as ethyl alcohol decolorise their aqueous solutions.

The earliest observations on bivalent silver salts were made by Barbieri, who first obtained tetrapyridinoargentic persulphate (VI) on mixing aqueous solutions of persulphate and silver nitrate containing excess of pyridine (*Gazzetta*, 1912, **42**, ii, 7) and subsequently prepared the corresponding nitrate (VI) electrolytically by anodic oxidation of aqueous silver nitrate in presence of pyridine (*Ber.*, 1927, **60**, 2424).

(VI.) $[Ag4py]S_2O_8$ or $(NO_3)_2$ $[Ag2phenan]S_2O_8$ or X_2 (VII.)

More recently Hieber and Mühlbauer (*Ber.*, 1928, **61**, 2149) have prepared a series of complex argentic salts having the general formula (VII, where $X = HSO_4, NO_3, ClO_3$ or ClO_4), using α-phenanthroline as the co-ordinating diamine.

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* It is noteworthy by way of comparison that, although argentous persulphate readily decomposes with formation of silver peroxide (Marshall and Inglis, J., 1891, **59**, 775), the univalent condition can be stabilised for this salt by co-ordination with a sulphur-containing addendum. Colourless triethylenethiocarbamidodiargentous persulphate, $[Ag_2 3etu]S_2O_8$, is stable up to 160° and only slowly decomposed by warm water (J., 1928, 150).

The series of complex argentic salts described in the present communication differ from those containing α-phenanthroline in containing complexes with three as well as two molecules of the diamine, thus indicating both co-ordination numbers 4 and 6 for bivalent silver.

EXPERIMENTAL.

αα′-Dipyridyl was prepared by heating pyridine and ferric chloride in steel autoclaves fitted with stirring gear, the method being essentially that described by Hein and Retter (*Ber.*, 1928, **61**, 1790). When, however, these reagents are employed in considerable amounts, notable proportions of by-products are obtained which are still under examination.

Bis-αα′-dipyridylargentous nitrate (II) separated when hot aqueous-alcoholic solutions of 16·9 g. of silver nitrate and 31·2 g. of αα′-dipyridyl were mixed and a further amount was obtained by concentration of the mother-liquor. Recrystallised from hot dilute alcohol, this complex nitrate formed felted masses of yellow needles (Found: Ag, 22·1; NO_3, 12·5. $C_{20}H_{16}O_3N_5Ag$ requires Ag, 22·4; NO_3, 12·9%). The salt, which was only sparingly soluble in hot water or in organic solvents other than the alcohols, was decomposed by either acids or aqueous alkalis. It was slowly darkened by light and decomposed at 155°.

Bis-αα′-dipyridylargentic Persulphate (III).—When bis-αα′-dipyridylargentous nitrate was stirred into a cold saturated solution containing excess of potassium persulphate, the filamentous needles of the argentous salt were soon replaced by a deep reddish-brown microcrystalline precipitate of the complex *argentic persulphate* and after 2 hours the reaction was complete. The precipitate, thoroughly washed with cold water, was obtained in almost quantitative yield (Found: Ag, 17·3; S, 10·6; dipy, 48·5. $C_{20}H_{16}O_8N_4S_2Ag$ requires Ag, 17·6; S, 10·5; dipy, 51·0%).

With aqueous potassium iodide, this persulphate decomposed in accordance with the equation

$$[\mathrm{Ag2dipy}]S_2O_8 + 4KI = AgI + 2K_2SO_4 + 2\mathrm{dipy} + 3I.$$

0·2032 G. required 9·0 c.c. of *N*/10-thiosulphate, the calculated amount being 9·0 c.c. The complex persulphate decomposed rapidly at 137° and on exposure to the air at the ordinary temperature it was slowly transformed into the corresponding bisulphate (*v. infra*). It was only very sparingly soluble in water and insoluble in the ordinary organic media.

Pentakis-αα′-dipyridyldiargentic persulphate, $[Ag_2 5\mathrm{dipy}](S_2O_8)_2$, was formed when the foregoing persulphate was triturated with cold dilute nitric acid (60% HNO_3, *d* 1·4, and 40% H_2O) and was precipitated from the brown filtrate by dilution with four volumes of cold water (Found: Ag, 15·8; S, 9·4; dipy, 54·9. $C_{50}H_{40}O_{16}N_{10}S_4Ag_2$ requires Ag, 15·7; S, 9·3; dipy, 56·5%). With aqueous potassium iodide the binuclear persulphate reacted in a similar manner to the mononuclear persulphate: 0·1013 g. required 4·5 c.c. of *N*/10-thiosulphate, the calculated amount being 4·4 c.c.

This complex persulphate was insoluble in water or alcohol but dissolved in moderately concentrated nitric acid and crystallised from the brown solution in small reddish-purple needles which decomposed rapidly at 159°.

Tris-αα′-dipyridylargentic Nitrate (IV).—The residue remaining after the trituration of bis-αα′-dipyridylargentic persulphate with 60% nitric acid in the preceding experiment consisted largely of complex nitrate; it was drained from excess of acid and extracted with warm water. Excess of aqueous ammonium nitrate was added to the brown filtrate and when the solution was cooled in ice the complex *argentic nitrate* separated in small, dark brown needles, which were dissolved in warm water and reprecipitated by addition of ammonium nitrate (Found: Ag, 15·5; NO_3, 18·0; dipy, 65·8. $C_{30}H_{24}O_6N_8Ag$ requires Ag, 15·4; NO_3, 17·7; dipy, 66·9%. 0·2032 G. required 2·85 c.c. of *N*/10-thiosulphate; calc., 2·93 c.c.). When kept in a cool dark place, this complex argentic nitrate remained unchanged, but it decomposed at 176°. Its aqueous solution, which slowly decomposed with evolution of oxygen, behaved as a powerful oxidising agent. Aqueous alkalis caused an immediate precipitation of silver peroxide, whereas nitric acid promoted the formation of the complex *argentosoargentic nitrate*,

$$[Ag2dipy](NO_3)_2,AgNO_3,HNO_3,$$

obtained in small brown needles and also separating from a solution of bis-αα′-dipyridylargentic persulphate in nitric acid (64% HNO_3, *d* 1·4, and 36% H_2O) (Found: Ag, 27·8; NO_3, 32·3. $C_{20}H_{17}O_{12}N_8Ag_2$ requires Ag, 27·8; NO_3, 31·9%. 0·2058 G. required 2·55 c.c. of *N*/10-thiosulphate; calc., 2·65 c.c.).

Some of the univalent silver may be removed from this complex substance by repeated extraction with cold alcohol. The complex argentosoargentic salt, which decomposed at 161°, dissolved readily in water to a dark solution, from which tris-αα′-dipyridylargentic nitrate separated on addition of ammonium nitrate.

Tris-αα′-dipyridylargentic chlorate (IV) was readily obtained in dark purple plates or needles when aqueous sodium chlorate was added to solutions of either of the preceding complex nitrates, and the product recrystallised from water by addition of sodium chlorate (Found: Ag, 14·8; ClO_3, 22·1; dipy, 62·7. $C_{30}H_{24}O_6N_6Cl_2Ag$ requires Ag, 14·5; ClO_3, 22·5; dipy, 63·0%).

This chlorate dissolved readily in water to a deep brown solution in which the salt slowly decomposed; it decomposed quietly at 171°.

Tris-αα′-dipyridylargentic perchlorate (IV) separated as an orange-brown microcrystalline precipitate when sodium perchlorate was added to a solution of either nitrate or chlorate (Found: Ag, 13·8; ClO_4, 25·6; dipy, 58·9. $C_{30}H_{24}O_8N_6Cl_2Ag$ requires Ag, 13·9; ClO_4, 25·7; dipy, 60·4. 0·2067 G. required 2·80 c.c. of *N*/10-thiosulphate; calc., 2·7 c.c.). It was very sparingly soluble in water and detonated violently on heating.

Bis-αα′-dipyridylargentic hydrogen sulphate (V) was prepared when bis-αα′-dipyridylargentic persulphate was treated with cold 40% sulphuric acid. It has also been obtained by adding sodium sulphate and sulphuric acid to solutions of the foregoing chlorate or nitrate. The brown crystalline powder was washed with cold water and dried over concentrated sulphuric acid. It decomposed at 157° (Found: Ag, 17·9; S, 10·5; dipy, 49·5. $C_{20}H_{18}O_8N_4S_2Ag$ requires Ag, 17·6; S, 10·4; dipy, 50·7. 0·2010 G. required 3·2 c.c. of *N*/10-thiosulphate; calc., 3·27 c.c.).

Analytical Methods.—Bivalent silver was estimated by treating the complex salt with cold aqueous potassium iodide: $AgX_2 + 2KI = 2KX + AgI + I$.

Total silver was estimated by decomposing the complex salt with hydrochloric or hydrobromic acid and weighing the precipitated silver halide. Alternatively the complex salt was heated to leave a residue of metallic silver.

The nitrate and perchlorate radicals were precipitated and weighed as nitron salts, after silver had been removed by decomposition of the complex salt with pure caustic soda. The chlorate radical was estimated by distilling the compound with hydrochloric acid (1 concentrated acid : 1 water) in a stream of carbon dioxide, the distillate being received in aqueous potassium iodide.

αα′-Dipyridyl furnishes sparingly soluble mercurihalides and the *mercuri-iodide*, $C_{10}H_8N_2,HgI_2$, was found to be sufficiently insoluble for use in the gravimetric estimation of the base (Found: I, 41·0. $C_{10}H_8N_2I_2Hg$ requires I, 41·6%).

The silver of the complex salt was first removed as chloride or bromide and the filtrate was treated successively with sodium hydroxide, acetic acid, and a solution of mercuric iodide in aqueous potassium iodide. The αα′-dipyridyl was then precipitated as white granular mercuri-iodide, which was readily collected and washed.

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