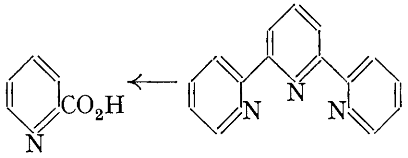
347. *Researches on Residual Affinity and Co-ordination. Part XXXVII. Complex Metallic Salts containing 2 : 6-Di-2′-pyridylpyridine (2 : 2′ : 2″-Tripyridyl).*

By Sir Gilbert Morgan and Francis H. Burstall.

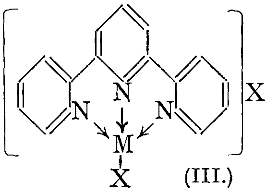
A number of reactions of the triamine 2 : 6-di-2′-pyridylpyridine (2 : 2′ : 2″-tripyridyl) are described. Oxidation of the base with alkaline permanganate yields only pyridine-2-carboxylic acid, thus indicating that it is the central one of three pyridine rings which is preferentially attacked. The triamine acts as a tridentate group and furnishes many stable and characteristic co-ordination compounds. This group of salts is divided into two series which contain severally one and two molecular proportions of base to each atom of metal. The first series is of monotridentate types [M tripy X] and [M tripy X]X, where M = copper, univalent and bivalent silver, zinc, cadmium, mercury, palladium and platinum. Tervalent iridium chloride yields [$IrCl_3$ tripy]. The second series is of bistridentate type represented by the general formulæ [M 2tripy]X_2 and [M 2tripy]X_3,nH_2O, where M = bivalent iron, bi- and ter-valent cobalt, nickel, bivalent ruthenium, bivalent osmium and tervalent chromium.

In the course of a comprehensive study of the dehydrogenation of pyridine by anhydrous metallic chlorides (J., 1932, 20; *J. Indian Chem. Soc.*, 1933, Ray Commemoration Vol.,

p. 1) we recorded the isolation of a new triamine, 2 : 6-di-2′-pyridylpyridine (2 : 2′ : 2″-tripyridyl) (I), as one of some twenty products identified in these condensations. This base was characterised by the formation of a deep purple coloration with ferrous salts and a noteworthy series of complex platinum derivatives (J., 1934, 1498). In the first communication dealing with this base (J., 1932, 20) two triamines designated as 2 : 2′ : 2″-tripyridyl and 2 : 2′ : *x*″-tripyridyl were described, but it has now been found that these products are dimorphous forms of the same substance. Although these two crystalline species differ slightly in melting point, 88—89° and 85—86°, they both give the same compounds and are readily converted one into the other. In order to obtain formal proof of its constitution, 2 : 6-di-2′-pyridylpyridine was oxidised with alkaline potassium permanganate solution. The only acid of the pyridine series isolated from the oxidised base was pyridine-2-carboxylic acid (picolinic acid) (II), which was obtained in such yield as to indicate that it is the centre ring of the triamine which is preferentially attacked. There is no evidence of the formation of either pyridine-2 : 6-dicarboxylic acid or of 2 : 2′-dipyridyl-6-carboxylic acid.



(II.) (I.)



(III.)

In combination with metallic salts, notably those of the transition elements, 2 : 6-di-2′-pyridylpyridine yields two series of derivatives containing severally one and two molecules of base to each atom of metal. The former type is represented by the salts of copper, silver, zinc, cadmium, mercury, palladium, iridium and platinum, whereas the latter series comprises the complex derivatives of iron, cobalt, nickel, ruthenium, osmium and chromium.

The bivalent compounds of copper, silver, palladium and platinum are regarded as possessing a planar configuration (III), which is in keeping with the known structure of other 4-co-ordinated derivatives of these metals. The arrangement of addenda round the univalent silver ion and the bivalent zinc, cadmium and mercury atoms is more speculative; a planar configuration is not excluded, although a tetrahedral arrangement appears to be inadmissible if these salts are to be regarded as monomeric. Moreover, the triamine should possess a planar distribution of its three pyridine rings in order to satisfy the mesomerism possible in such a molecule. If this effect is manifested, this tridentate base cannot span the three sides of a tetrahedron without some distortion of its molecule and accordingly a planar arrangement of four covalent complex salts is favoured.

The remaining compounds described in this paper are those in which the metal manifests a co-ordination number of 6. Accordingly, these derivatives will have the characteristic octahedral arrangement of their addenda round a central metallic atom.

Monotridentate Types, [MX tripy] *and* [MX tripy]X.

Copper Salt.—In aqueous solution cupric chloride and 2 : 6-di-2′-pyridylpyridine (2 : 2′ : 2″-tripyridyl) yield a bright green, sparingly soluble *chloride*, [CuCl tripy]Cl,$2H_2O$, even in presence of excess of the base. Although the presence of a salt containing a larger proportion of the triamine is indicated by an increased solubility of the foregoing compound in an aqueous alcoholic solution of the base, a further combination could not be isolated.

Univalent Silver Salts.—Silver nitrate and the triamine yield a compound of the empirical formula [tripy $AgNO_3$] and as univalent silver salts manifesting a co-ordination number of 4 usually possess a tetrahedral structure which, for reasons already given, is regarded as inadmissible, it is doubtful whether a simple formula will suffice to interpret the constitution of this compound. It is possible that only one or perhaps two of the three associating foci of the organic base are co-ordinated to one atom of the metal. The corresponding *perchlorate*, [tripy $AgClO_4$], is of similar type.

Bivalent Silver Salts.—In the presence of dilute nitric acid the foregoing nitrate [tripy $AgNO_3$] is readily oxidised at the anode of an electrolytic cell with the formation of 2 : 2′ : 2″-*tripyridylargentic nitrate*, [$AgNO_3$ tripy]NO_3. This dark brown derivative containing bivalent silver is soluble in water and from the solution the corresponding *chlorate*, [$AgClO_3$ tripy]ClO_3, *perchlorate*, [$AgClO_4$ tripy]ClO_4, and *dithionate*, [AgS_2O_6 tripy], can be obtained by double decomposition. An alternative mode of preparation follows from the oxidation of the univalent silver salt [tripy $AgNO_3$] with aqueous potassium persulphate, brown insoluble 2 : 2′ : 2″-*tripyridylargentic persulphate*, [AgS_2O_8 tripy], being formed :

$$2[\text{tripy Ag}^{I}\text{NO}_3] + 3K_2S_2O_8 = 2[\text{Ag}^{II}S_2O_8\text{ tripy}] + 2KNO_3 + 2K_2SO_4.$$

This persulphate yields the corresponding bivalent nitrate with nitric acid. Following the results obtained by Cox, Wardlaw, and Webster (J., 1936, 775) with argentic picolinate $(C_6H_4O_2N)_2Ag$, the foregoing 2 : 2′ : 2″-tripyridylargentic salts are regarded as having a planar configuration. This arrangement of addenda may with equal justice be extended to complex silver salts containing pyridine [Ag 4py]X_2 (Barbieri, *Gazzetta*, 1912, **42**, 7; *Ber.*, 1927, **60**, 2424), α-phenanthroline [Ag 2phenan]X_2 (Hieber and Mühlbauer, *Ber.*, 1928, **61**, 2149), and 2 : 2′-dipyridyl [Ag 2dipy]X_2 (Morgan and Burstall, J., 1930, 2594; Barbieri, *Atti R. Accad. Lincei*, 1932, **16**, 44).

Moreover, there is no indication of the formation of a bivalent silver derivative containing more than one molecule of the triamine in combination with each atom of silver.

Zinc, Cadmium and Mercuric Salts.—Salts of these three elements yield characteristic compounds with the triamine. Zinc chloride and cadmium chloride in aqueous solution furnish the sparingly soluble *chlorides* [ZnCl tripy]Cl and [CdCl tripy]Cl, whereas mercuric nitrate yields [$HgNO_3$ tripy]NO_3.

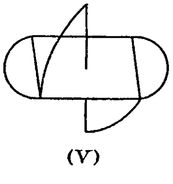
4-Co-ordinated derivatives in this group of elements are normally tetrahedral in structure. Accordingly the constitution of the zinc, cadmium and mercury compounds will probably be more complicated than is indicated by the foregoing formulæ. This possibility has already been mentioned in the case of univalent silver.

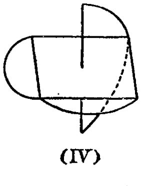
It is noteworthy that neither beryllium nor magnesium chloride gives compounds under similar conditions.

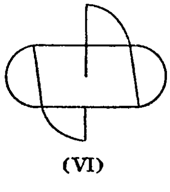
Palladium, Platinum and Iridium Salts.—In aqueous medium, potassium palladochloride or palladium dichloride and 2 : 2′ : 2″-tripyridyl unite to form the stable complex chloride [PdCl tripy]Cl,$3H_2O$. This soluble yellow derivative is very similar to the corresponding orange-red platinous salt [PtCl tripy]Cl,$3H_2O$ which has already been described (J., 1934, 1498). It is concluded that both these chlorides have a planar configuration, in keeping with the known structure of many 4-covalent palladium and platinum salts. Potassium iridochloride, $K_3[IrCl_6]$, and 2 : 2′ : 2″-tripyridyl in aqueous solution afford the sparingly soluble chloride [tripy $IrCl_3$] corresponding with the platinic derivative [$PtCl_3$ tripy]Cl,$2H_2O$. Both these salts possess 6-co-ordinated structures characterised by an octahedral distribution of addenda round the metallic atom.

Bistridentate Types, [M 2tripy]X_2 *and* [M 2tripy]X_3,nH_2O.

An octahedral structure is also advanced for a group of complex metallic salts containing two molecules of 2 : 6-di-2′-pyridylpyridine. The compounds are all of the general type [M 2tripy]$X_{2\text{ or }3}$,yH_2O, where M = iron, ruthenium osmium, cobalt, nickel, or chromium and X is a univalent acid radical. The arrangement of two tridentate groups round the six vertices of an octahedron leads to the three stereoisomeric compounds represented by the structures (IV), (V) and (VI).


(V)


(IV)


(VI)

Of these three possibilities, the arrangement (IV) is regarded as the most probable, since it is the one formed with the least distortion of the triamine. The structure (VI) cannot be excluded, whereas (V) should exist in optically active forms, but there is no evidence of any resolution among nickel and ruthenium derivatives, which are among the most stable salts of this series.

Iron, Ruthenium and Osmium Salts.—2 : 2′ : 2″-Tripyridyl was first discovered from the intense purple colour which it gave with ferrous salts. On addition of a soluble bromide to the concentrated red aqueous solution of ferrous sulphate and the base, *bis*-2 : 2′ : 2″-*tripyridylferrous bromide tetrahydrate*, [Fe 2tripy]Br_2,$4H_2O$, separates and this tetrahydrated bromide yields a *monohydrate* when left over sulphuric acid. The *iodide*, [Fe 2tripy]I_2,H_2O, is obtained from the bromide by double decomposition. The intense purple colour of these salts provides a specific and sensitive test for ferrous ions up to dilutions of about 1 in 2 million parts of water. This fact has been utilised in the determination of iron in the sea and marine plankton (Cooper, *Proc. Roy. Soc.*, 1935, *B*, **118**, 419). The ruthenium salts are represented by the red chloride, [Ru 2tripy]Cl_2,$4H_2O$, which arises from the condensation of 2 : 2′ : 2″-tripyridyl, ruthenium trichloride and metallic ruthenium at 250—260°. This bivalent ruthenium salt possesses the noteworthy stability associated with the corresponding 2 : 2′-dipyridyl analogue (J., 1936, 173), although precipitation with ammonium *d*-tartrate, followed by regeneration of the chloride, gives only optically inactive preparations. The osmium series of salts results from the reaction between the triamine, potassium osmichloride and metallic osmium at 250—260°. The green chloride, [Os 2tripy]Cl_2,$4H_2O$, furnishes an almost black iodide, [Os 2tripy]I_2,H_2O. The bivalent ion [Os 2tripy]$^{\cdot\cdot}$ is remarkably stable to both acids and alkalis.

Cobalt, Nickel and Chromium Salts.—Cobaltous salts and 2 : 2′ : 2″-tripyridyl furnish stable, deep brown solutions, from which soluble bromides precipitate almost black crystals of the *hydrated bromide*, [Co 2tripy]Br_2,$3\frac{1}{2}H_2O$; this yields a *monohydrate* over sulphuric acid. The *iodide* also is monohydrated. Chlorine oxidises a solution of cobalt chloride and the triamine in water, forming the stable, pale yellow cobaltic *chloride*, [Co 2tripy]Cl_3,$7H_2O$.

Nickel salts furnish light brown salts exemplified by the *bromide*, [Ni 2tripy]Br_2,1 and $3\frac{1}{2}H_2O$, *iodide* ($1H_2O$), and *tartrate* ($4H_2O$). These salts are quite comparable with the corresponding 2 : 2′-dipyridylnickel salts in stability towards aqueous acids and alkalis, but there is no evidence of optical resolution of the ion [Ni 2tripy]$^{\cdot\cdot}$ after fractional deposition of the foregoing tartrate.

The complex chromium chloride [Cr 2tripy]Cl_3,$2H_2O$ arising from combination of its generators in hot aqueous medium is a yellow salt very similar to the analogous cobaltic derivative.

EXPERIMENTAL.

2 : 6-*Di*-2′-*pyridylpyridine* (2 : 2′ : 2″-*Tripyridyl*) (I).—This base, which arose from the reaction between pyridine and ferric chloride or pyridine ferrichloride, was purified according to the method already described (J., 1932, 28). It was usually obtained in hard white tabular crystals, m. p. 88—89°, but rapid crystallisation from a concentrated ethereal solution yielded fine needles, m. p. 85—86°. A mixture of the two forms gave no perceptible lowering in m. p. The compound formerly described as 2 : 2′ : *x*″-tripyridyl (*ibid.*, p. 29) was shown to be identical with this base after repeated crystallisation from ether or petroleum (b. p. 40—60°).

2 : 2′ : 2″-*Tripyridyl trihydrochloride tetrahydrate* separated in colourless crystals on evaporation of the triamine with excess of hydrochloric acid. It was extremely soluble in water and decomposed without melting at 280—285° (Found: Cl, 25·3. $C_{15}H_{22}O_4N_3Cl_3$ requires Cl, 25·8%).

Oxidation of 2 : 2′ : 2″-*Tripyridyl.*—The base (7 g.), suspended in water (200 c.c.) and 2N-caustic potash (50 c.c.), was treated gradually with potassium permanganate (47 g.) in water (2 l.), and the mixture refluxed until the pink colour of the permanganate had disappeared. The hot mixture was filtered, and the residue of hydrated manganese oxide washed with alcohol to remove unchanged base. The filtrate and alcoholic washings were mixed and evaporated to about 700 c.c., cooled, and the unchanged base (2 g.) separated. The aqueous liquor after acidification with acetic acid was evaporated further and treated with excess of aqueous copper acetate. After 24 hours the precipitate of copper picolinate was suspended in water and treated with hydrogen sulphide. Evaporation of the filtrate from copper sulphide yielded picolinic acid, m. p. 135° (2·0 g.). A further small quantity was obtained from the residue left after separation of the copper picolinate by treatment with hydrogen sulphide, followed by evaporation with excess of hydrochloric acid and extraction of the residue with alcohol; this alcoholic extract then gave a little more copper picolinate (0·5 g.) with copper acetate.

2 : 2′ : 2″-*Tripyridylcupric Chloride Dihydrate.*—Cupric chloride (1·7 g.) and 2 : 2′ : 2″-tripyridyl (2·3 g.) were heated in water (500 c.c.) until a homogeneous blue solution was obtained. On cooling, bright green crystals of the complex *chloride* were deposited. A further quantity was obtained by evaporating the filtrate. This salt was air-dried (Found : Cu, 15·6; Cl, 17·3; N, 10·4. $C_{15}H_{15}O_2N_3Cl_2Cu$ requires Cu, 15·8; Cl, 17·6; N, 10·5%). The same salt was produced when twice the quantity of triamine (4·6 g.) was heated with cupric chloride (1·7 g.) in water. It was sparingly soluble in water and alcohol.

2 : 2′ : 2″-*Tripyridylargentous Nitrate.*—Silver nitrate (1·7 g.) and 2 : 2′ : 2″-tripyridyl (2·3 g.) were heated in aqueous alcohol until a clear solution resulted; evaporation and cooling then gave white needles of the complex *nitrate*, which was recrystallised from water or aqueous alcohol and dried over sulphuric acid (Found : Ag, 26·5; N, 13·6. $C_{15}H_{11}O_3N_4Ag$ requires Ag, 26·8; N, 13·9%). It was moderately easily soluble in water or alcohol.

2 : 2′ : 2″-*Tripyridylargentous perchlorate* was precipitated as a sparingly soluble, white, crystalline powder when aqueous sodium perchlorate was added to a solution of the foregoing nitrate. After being washed with cold water, it was recrystallised from boiling water (Found : Ag, 24·3; N, 9·7. $C_{15}H_{11}O_4N_3ClAg$ requires Ag, 24·5; N, 9·5%).

2 : 2′ : 2″-*Tripyridylargentic Nitrate.*—75 C.c. of a solution containing 2 : 2′ : 2″-tripyridylargentous nitrate (3·0 g.) and concentrated nitric acid (8 g.) were placed in a porous pot which constituted the anode compartment of an electrolytic cell. The anode consisted of platinum foil; the cathode was a length of platinum wire dipping into a solution of N/5-nitric acid. A current of 8 volts and 2—3 amps. was passed through this cell for 3 hours. The contents of the anode compartment, which were cooled, if necessary, and stirred by a stream of air, speedily became deep brown and brown crystals separated on the bottom and sides of the porous vessel. At the end of the electrolysis the anodic products were cooled to 0° after the addition of concentrated aqueous ammonium nitrate. The deep brown, almost black crystals were then separated and recrystallised from water (40°) by cooling at 0° (Found : C, 38·4; H, 2·2; N, 15·0; Ag, 22·9, 23·3; active O, 1·6. $C_{15}H_{11}O_6N_5Ag$ requires C, 38·7; H, 2·4; N, 15·1; Ag, 23·2; active O, 1·7%). This complex *nitrate* dissolved readily in water to a deep brown solution, which soon decomposed; the solid product, however, was stable under normal conditions. Aqueous solutions were at once decomposed by alcohol, alkalis, and halogen acids. The reaction with potassium iodide formed the basis for estimating bivalent silver in the molecule :

$$2[AgNO_3 \text{ tripy}]NO_3 + 4KI = 2AgI + 2\text{tripy} + 4KNO_3 + I_2$$

Each molecule of the bivalent nitrate contains the equivalent of half an atomic proportion of active oxygen. The iodine liberated was titrated with N/10-sodium thiosulphate. This complex nitrate was the starting material for the preparation of the following three compounds containing bivalent silver.

2 : 2′ : 2″-*Tripyridylargentic chlorate*, obtained in almost black, lustrous crystals on addition of excess of a concentrated solution of sodium chlorate to a saturated solution of the nitrate, was purified by dissolution in water and addition of aqueous sodium chlorate (Found : Ag, 20·8; N, 8·4; active O, 1·6. $C_{15}H_{11}O_6N_3Cl_2Ag$ requires Ag, 21·2; N, 8·3; active O, 1·6%).

2 : 2′ : 2″-*Tripyridylargentic perchlorate* was precipitated as a russet-brown crystalline salt when aqueous sodium perchlorate was added to a solution of the corresponding nitrate. It was also formed by the anodic oxidation of a suspension of the univalent silver salt, 2 : 2′ : 2″-tripyridylargentous perchlorate, in aqueous perchloric acid in a divided cell. It was sparingly soluble in water (Found : Ag, 19·9; N, 8·0; active O, 1·45. $C_{15}H_{11}O_8N_3Cl_2Ag$ requires Ag, 20·0; N, 7·8; active O, 1·5%).

2 : 2′ : 2″-*Tripyridylargentic dithionate* separated in dark brown crystals when concentrated solutions of sodium dithionate and 2 : 2′ : 2″-tripyridylargentic nitrate were mixed; it was washed with ice-cold water and dried (Found : Ag, 21·4; N, 8·5; active O, 1·56. $C_{15}H_{11}O_6N_3S_2Ag$ requires Ag, 21·5; N, 8·4; active O, 1·6%).

2 : 2′ : 2″-*Tripyridylargentic Persulphate.*—The white crystals of the univalent silver salt [tripy $AgNO_3$], when added in aqueous suspension to an aqueous solution containing an excess of potassium persulphate, slowly changed to the characteristic brown crystals of the bivalent *persulphate*. After 12 hours this was separated, washed with cold water, and dried (Found : Ag, 20·1; N, 8·1; active O, 2·9. $C_{15}H_{11}O_8N_3S_2Ag$ requires Ag, 20·3; N, 7·9; active O, 3·0%).

It gave 2 : 2′ : 2″-tripyridylargentic nitrate when stirred with cold nitric acid (50% nitric acid, *d* 1·4, and 50% water).

2 : 2′ : 2″-*Tripyridylzinc Chloride.*—Zinc chloride (1·3 g.) and 2 : 2′ : 2″-tripyridyl (2·3 g.) were mixed in water (50 c.c.) and heated until the base gave place to the complex *chloride.* The product crystallised from much hot water in pale yellow needles, which were air-dried (Found : Zn, 17·9; Cl, 19·2. $C_{15}H_{11}N_3Cl_2Zn$ requires Zn, 17·7; Cl, 19·2%). This complex salt and 2 : 2′ : 2″-tripyridyl were mutually soluble in water, but the resulting compound was too unstable to be isolated. The excess of base could be recovered by evaporation and extraction with acetone.

2 : 2′ : 2″-*Tripyridylcadmous Chloride.*—Cadmium chloride (1·8 g.) and 2 : 2′ : 2″-tripyridyl (2·3 g.) were boiled in an aqueous medium (100 c.c.). The microcrystalline *chloride* was separated and recrystallised from much water, forming anhydrous, small, pale yellow crystals even less soluble in water than the foregoing zinc derivative (Found : Cd, 27·2; Cl, 16·7. $C_{15}H_{11}N_3Cl_2Cd$ requires Cd, 27·0; Cl, 17·0%).

2 : 2′ : 2″-*Tripyridylmercuric nitrate* was formed when equimolecular quantities of its generators were mixed in an aqueous medium. This pale yellow, sparingly soluble nitrate was crystallised from hot water and air-dried (Found: Hg, 36·3. $C_{15}H_{11}O_6N_5Hg$ requires Hg, 36·0%).

2 : 2′ : 2″-*Tripyridylpalladous Chloride Trihydrate.*—Palladium dichloride (1·7 g.) in water (100 c.c.) was boiled with 2 : 2′ : 2″-tripyridyl (2·3 g.). The deep yellow solution was cooled, filtered, and acidified with hydrochloric acid; the complex *chloride* then separated in primrose-yellow leaflets. After crystallisation from water acidified with hydrochloric acid, the salt was air-dried (Found: Pd, 23·3; N, 9·0; H_2O, 11·1. $C_{15}H_{11}N_3Cl_2Pd,3H_2O$ requires Pd, 23·0; N, 9·0; H_2O, 11·6%). It was also formed by heating equimolecular quantities of potassium palladochloride and 2 : 2′ : 2″-tripyridyl in an aqueous medium.

2 : 2′ : 2″-*Tripyridyliridium Trichloride.*—Molecular quantities of sodium iridochloride, $Na_3[IrCl_6]$, and 2 : 2′ : 2″-tripyridyl were heated in aqueous solution; the green tint of the iridochloride speedily changed to orange-yellow and the sparingly soluble, orange-yellow complex *salt* separated. It was crystallised from aqueous alcohol containing a little of the triamine and washed with water and alcohol (Found: Ir, 36·1; N, 8·0; Cl, 19·9. $C_{15}H_{11}N_3Cl_3Ir$ requires Ir, 36·3; N, 7·9; Cl, 20·0%).

Bis-2 : 2′ : 2″-*tripyridylferrous Bromide Tetrahydrate.*—When ferrous sulphate (2·7 g.) in water (150 c.c.) and 2 : 2′ : 2″-tripyridyl (4·6 g.) were warmed together, the base slowly dissolved with formation of a deep purple solution, which was evaporated to half its volume, filtered, and treated with excess of a concentrated solution of potassium bromide. The separated complex *bromide* was slowly crystallised from a cold solution in water and air-dried (Found: Fe, 7·2; Br, 21·0; H_2O, 9·4. $C_{30}H_{22}N_6Br_2Fe,4H_2O$ requires Fe, 7·4; Br, 21·2; H_2O, 9·55%). Exposure over sulphuric acid gave the *monohydrate* with loss of three molecules of water (Found: Br, 22·75; H_2O, 2·5. $C_{30}H_{22}N_6Br_2Fe,H_2O$ requires Br, 22·9; H_2O, 2·6%). The sesquihydrate ($1\frac{1}{2}H_2O$) recorded in an earlier communication (J., 1932, 22) consisted mainly of this monohydrate together with a small proportion of the tetrahydrate.

Bis-2 : 2′ : 2″-*tripyridylferrous iodide monohydrate* was obtained in deep purple crystals by addition of aqueous potassium iodide to a solution of the foregoing bromide (Found: Fe, 6·9; N, 10·7; I, 31·6; H_2O, 2·5. $C_{30}H_{22}N_6I_2Fe,H_2O$ requires Fe, 7·0; N, 10·6; I, 32·0; H_2O, 2·3%).

Bis-2 : 2′ : 2″-*tripyridylruthenous Chloride Tetrahydrate.*—Ruthenium trichloride (1·0 g.), metallic ruthenium (0·5 g.), and 2 : 2′ : 2″-tripyridyl (10 g.) were heated at 250—260° with stirring. After 3 hours the cooled melt was extracted with benzene to remove the excess of triamine. The residue was treated with water and filtered, and the red solution evaporated to crystallising point. The red crystals were recrystallised from water and air-dried (Found: Ru, 14·6; N, 11·7; Cl, 10·15; H_2O, 10·4. $C_{30}H_{22}N_6Cl_2Ru,4H_2O$ requires Ru, 14·3; N, 11·8; Cl, 10·0; H_2O, 10·2%). This dark red ruthenium *salt* was not decomposed by concentrated hydrochloric acid or concentrated aqueous alkali hydroxide. A 10% solution of the chloride gave a crystalline tartrate when stirred with ammonium *d*-tartrate at 0°. Regeneration of the chloride from the tartrate yielded a preparation which gave no perceptible rotation in a polarimeter.

Bis-2 : 2′ : 2″-*tripyridylosmous Chloride Tetrahydrate.*—Potassium osmichloride, $K_2[OsCl_6]$ (1·0 g.), metallic osmium (0·5 g.), and 2 : 2′ : 2″-tripyridyl were heated at 250—260° with stirring for 3 hours. The product was extracted successively with benzene and water. The aqueous extract after filtration and evaporation yielded green needles of the *chloride*, which were recrystallised from the minimum quantity of water (Found: Os, 23·7; Cl, 9·2. $C_{30}H_{22}N_6Cl_2Os,4H_2O$ requires Os, 23·9; Cl, 8·9%). This osmium salt gave a red solution in water or alcohol and was notably stable towards aqueous halogen acids and alkali hydroxides.

Bis-2 : 2′ : 2″-*tripyridylosmous Iodide Hydrate.*—The addition of potassium iodide solution to a solution of the foregoing chloride gave almost black crystals of the *iodide* (Found : Os, 20·3. $C_{30}H_{22}N_6I_2Os,H_2O$ requires Os, 20·6%).

Bis-2 : 2′ : 2″-*tripyridylcobaltous Bromide Hydrate.*—An aqueous solution of cobalt bromide (2·2 g. in 100 c.c. of water) and 2 : 2′ : 2″-tripyridyl (4·6 g.) were boiled together until the base dissolved. The deep brown solution was evaporated and cooled; dark brown crystals of the complex *bromide* then separated (Found : Co, 7·8; H_2O, 8·3. $C_{30}H_{22}N_6Br_2Co,3\frac{1}{2}H_2O$ requires Co, 7·9; H_2O, 8·4%). After desiccation over sulphuric acid the *monohydrate* was formed (Found: Co, 8·2; N, 11·9; Br, 22·4; H_2O, 2·5. $C_{30}H_{22}N_6Br_2Co,H_2O$ requires Co, 8·4; N, 11·9; Br, 22·7; H_2O, 2·6%). This bromide was slowly decomposed by 2N-hydrochloric acid and 2N-aqueous alkali hydroxide.

Bis-2 : 2′ : 2″-*tripyridylcobaltous iodide hydrate* was obtained by double decomposition of the foregoing bromide with potassium iodide in aqueous solution (Found : N, 10·7; I, 32·0; H_2O, 2·0. $C_{30}H_{22}N_6I_2Co,H_2O$ requires N, 10·6; I, 31·9; H_2O, 2·3%). It was much less soluble than the foregoing bromide.

Bis-2 : 2′ : 2″-*tripyridylcobaltic Chloride Heptahydrate.*—Cobalt chloride (2·4 g.) and 2 : 2′ : 2″-tripyridyl (4·6 g.) were boiled with water until the base dissolved. Chlorine was passed into the mixture, the deep brown colour becoming lighter, and the solution was evaporated to a syrup at 90° and stirred with alcohol at 0°; the yellow crystals that separated were recrystallised from water by cooling a concentrated solution at 0°. This hygroscopic *salt* was kept over sulphuric acid (Found : Co, 7·7; Cl, 13·8; H_2O, 16·5. $C_{30}H_{22}N_6Cl_3Co,7H_2O$ requires Co, 7·8; Cl, 14·0; H_2O, 16·7%). It was decomposed by alkali hydroxide, but not by 2N-mineral acid.

Bis-2 : 2′ : 2″-*tripyridylnickel Bromide Hydrate.*—Nickel sulphate (2·8 g.) and 2 : 2′ : 2″-tripyridyl (4·6 g.) were boiled with water (100 c.c.) until the base dissolved. The brown liquid was evaporated, cooled, and treated with an excess of potassium bromide solution. The pale brown, crystalline deposit slowly crystallised from warm water and when air-dried consisted of a complex bromide with $3\frac{1}{2}H_2O$ (Found : H_2O, 8·7. Calc., 8·4%). After keeping over sulphuric acid the *monohydrate* was formed (Found: Ni, 8·2; N, 11·9; Br, 22·5; H_2O, 2·4. $C_{30}H_{22}N_6Br_2Ni,H_2O$ requires Ni, 8·35; N, 12·0; Br, 22·7; H_2O, 2·6%). This complex bromide was decomposed by warm 2N-hydrobromic acid, but was rather more stable towards the same strength of caustic alkali.

Bis-2 : 2′ : 2″-*tripyridylnickel iodide hydrate* was obtained from the foregoing bromide by double decomposition with aqueous potassium iodide. This sparingly soluble iodide crystallised in light brown needles from hot water (Found : Ni, 7·4; N, 10·7. $C_{30}H_{22}N_6I_2Ni,H_2O$ requires Ni, 7·4; N, 10·6%).

Bis-2 : 2′ : 2″-*tripyridylnickel Tartrate Tetrahydrate.*—A saturated solution of the complex bromide in water was stirred at 0° with excess of solid ammonium *d*-tartrate; brown leaflets of the complex d-*tartrate* separated slowly. This product and the liquid were decanted from undissolved ammonium tartrate and the separated solid was crystallised from water and dried (Found : Ni, 7·7; H_2O, 9·9. $C_{34}H_{26}O_6N_6Ni,4H_2O$ requires Ni, 7·9; H_2O, 9·7%). Addition of potassium bromide to this tartrate gave the complex bromide, which was optically inactive.

Bis-2 : 2′ : 2″-*tripyridylchromic Chloride Dihydrate.*—Anhydrous chromic chloride (1·5 g.) and 2 : 2′ : 2″-tripyridyl (4·6 g.) with a trace of zinc dust as catalyst were boiled with water until most of the reagents dissolved. The filtered, deep brown solution was evaporated to a small volume and treated with acetone; a brown oil then separated which gradually yielded small yellowish-brown crystals. This *chloride* was purified by repetition of this precipitation of the aqueous solution with acetone and dried over sulphuric acid (Found : Cr, 7·95; N, 12·55. $C_{30}H_{22}N_6Cl_3Cr,2H_2O$ requires Cr, 7·9; N, 12·7%). A solution of this salt deposited some chromic oxide on boiling.

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