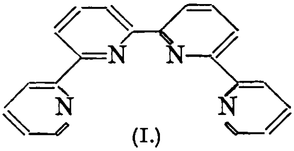
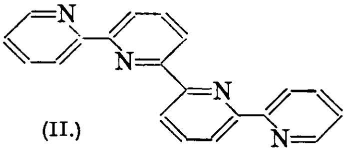
313. *Researches on Residual Affinity and Co-ordination. Part XXXVIII. Complex Metallic Salts containing 6 : 6′-Di-2″-pyridyl-2 : 2′-dipyridyl (2 : 2′ : 2″ : 2‴-Tetrapyridyl).*

By Sir Gilbert Morgan and Francis H. Burstall.

The tetramine 6 : 6′-di-2″-pyridyl-2 : 2′-dipyridyl (2 : 2′ : 2″ : 2‴-tetrapyridyl; I) combines with many metallic salts, forming co-ordination compounds of the types [M tetrpy]X, [M tetrpy]X_2 and [M X_2 tetrpy]X. These derivatives differ considerably from co-ordination compounds containing 2 : 2′-dipyridyl and 2 : 6-di-2′-pyridylpyridine and contain only one molecule of the base in combination with one atom of metal. The salts described in this memoir comprise those containing iron, cobalt, nickel, copper, silver, zinc, cadmium, and platinum. The stereochemistry of these complex salts is discussed.

IN the course of a study on the polypyridyls (preceding paper) the preparation and properties of 6 : 6′-di-2″-pyridyl-2 : 2′-dipyridyl (2 : 2′ : 2″ : 2‴-tetrapyridyl; I) were recorded, and it was then anticipated that this tetramine would function as a quadridentate co-ordinating unit in combination with metallic salts. This view has been justified by the preparation of a number of complex salts in which only one molecule of the base is combined with one molecule of metallic salt.


(I.)


(II.)

I. *With Univalent Metallic Salts.*—In alcoholic solution 2 : 2′ : 2″ : 2‴-tetrapyridyl and silver nitrate yield filamentous, yellow needles of the co-ordinated *salt* [Ag tetrpy]NO_3, which resembles the univalent 2 : 2′-dipyridyl derivative [Ag 2dipy]NO_3 in appearance but differs from it in its failure to react with aqueous persulphates with production of a bivalent silver derivative. In the presence of nitric acid, electrolytic oxidation or treatment with persulphate furnishes only brown mixtures, so that a pure complex argentic salt with this tetramine has not been obtained.

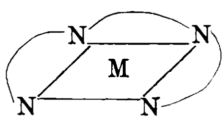
II. *With Bivalent Metallic Salts.*—In aqueous-alcoholic solution ferrous sulphate yields sparingly soluble reddish-brown 2 : 2′ : 2″ : 2‴-*tetrapyridylferrous sulphate tetrahydrate* [Fe tetrpy]SO_4,$4H_2O$, which gives a greenish-yellow anhydrous *sulphate* at 120°. The foregoing sulphate forms a yellow solution in water, which yields the hydrated *bromide* [Fe tetrpy]Br_2,$2H_2O$ and *iodide* [Fe tetrpy]I_2,$3H_2O$ with potassium bromide and iodide respectively. Both these complex halides possess a green tint, but the former sometimes separates in large, almost black crystals of the same composition. Cobalt chloride and the tetramine give pink leaflets of the dihydrated *chloride* [Co tetrpy]Cl_2,$2H_2O$, which readily yields a *monohydrate* and finally the anhydrous salt on gentle warming. Both nickel and cupric bromides form green complex *salts* [Ni tetrpy]Br_2,$2H_2O$ and [Cu tetrpy]Br_2,$\frac{1}{2}H_2O$ with the tetrapyridyl, and zinc and cadmium chlorides furnish yellowish-white crystals of [Zn tetrpy]Cl_2,$2H_2O$ and [Cd tetrpy]Cl_2,H_2O respectively. With potassium platinochloride in neutral medium the green *platinochloride* [Pt tetrpy]$PtCl_4$ is isolated, whereas in the presence of hydrochloric acid the *salt* tetrpy,H_2PtCl_4 is formed.

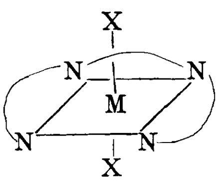
III. *With Tervalent Metallic Salts.*—The foregoing cobaltous salt [Co tetrpy]Cl_2,$2H_2O$ is readily oxidised with hydrogen peroxide in acid solution, forming grey-green 2 : 2′ : 2″ : 2‴-*tetrapyridyldichlorocobaltic chloride trihydrate,* [Co Cl_2 tetrpy]Cl,$3H_2O$, whereas potassium iridochloride and the tetramine furnish brown [Ir Cl_2 tetrpy]$_3$$IrCl_6$.

Stereochemistry of 2 : 2′ : 2″ : 2‴-*Tetrapyridyl Complex Salts.*—The constitution of 6 : 6′-di-2″-pyridyl-2 : 2′-dipyridyl has been proved by synthesis and, following modern ideas on mesomerism among aromatic compounds, may be regarded as having four pyridine rings in one plane. In the free base the arrangement of the rings may be as in (I) or (II) according as the nitrogen atoms are on the same or on opposite sides of the rings, or possibly there may exist some intermediate arrangement between these two limiting structures. When the four nitrogen atoms are all co-ordinated to one metallic atom, however, the arrangement (III) should prevail, with the base and metal in one plane. This structure does not exclude in certain cases an octahedral distribution (IV) when two additional associating units are involved.

With compounds of the types [M tetrpy]X and [M tetrpy]X_2 a simple planar arrange-

(III.)





(IV.)

ment (III) is most in keeping with physical and chemical properties. The latter type could have the alternative octahedral structure [M tetrpyX_2] (IV), but this formulation is regarded as improbable. A planar configuration has already been shown to be present in four-covalent derivatives of bivalent copper, silver, cobalt, nickel, platinum, palladium, tin, lead, and manganese, and there seems no reason for excluding a planar structure for the complex compounds of bivalent iron, zinc, and cadmium described in this paper. In such compounds a tetrahedral arrangement appears to be inadmissible. Tervalent cobalt and iridium derivatives are of the type [M X_2 tetrpy]X with octahedral distribution of addenda (IV), but, as the tetramine and metal are still planar, the groups X_2 must be in the *trans*-positions. It is noteworthy that only one isomer is obtained in each case.

EXPERIMENTAL.

6 : 6′-Di-2″-pyridyl-2 : 2′-dipyridyl (2 : 2′ : 2″ : 2‴-tetrapyridyl) was obtained as described in the preceding paper.

2 : 2′ : 2″ : 2‴-*Tetrapyridylargentous nitrate* crystallised in filamentous, pale yellow needles when an alcoholic solution containing silver nitrate (1·7 g.) and the tetramine (3·1 g.) was cooled (Found: Ag, 22·4; N, 14·7. $C_{20}H_{14}O_3N_5Ag$ requires Ag, 22·6; N, 14·6%). This complex was sparingly soluble in water and not altered by addition of potassium persulphate. Dilute nitric acid gave a bulky white product soluble in excess of concentrated nitric acid.

2 : 2′ : 2″ : 2‴-*Tetrapyridylferrous sulphate tetrahydrate.* Ferrous sulphate (2·7 g.) in water (150 c.c.) was treated with the tetrapyridyl (3·1 g.) and alcohol (50 c.c.), the mixture being boiled until the base had dissolved and most of the alcohol had evaporated. After the hot dark red liquid had been filtered, the hydrated sulphate crystallised on cooling in reddish-brown needles, which were air-dried (Found: Fe, 10·7; N, 10·4; H_2O, 12·9. $C_{20}H_{14}O_4N_4SFe,4H_2O$ requires Fe, 10·5; N, 10·5; H_2O, 13·5%). This moderately soluble sulphate and the following bromide and iodide gave yellow solutions in water which were easily decomposed by 2N-hydrochloric acid and 2N-sodium hydroxide. When maintained over concentrated sulphuric acid, or on warming to 110°, this hydrated complex salt became converted into the green anhydrous *sulphate* (Found: N, 12·2. $C_{20}H_{14}O_4N_4SFe$ requires N, 12·1%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylferrous bromide dihydrate.* When aqueous solutions of the foregoing sulphate and excess of aqueous sodium bromide were mixed, the complex *bromide* separated in either green needles or massive black rhombic crystals, which were air-dried (Found: Fe, 9·3; Br, 28·3; H_2O, 6·2. $C_{20}H_{14}N_4Br_2Fe,2H_2O$ requires Fe, 9·9; Br, 28·4; H_2O, 6·4%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylferrous iodide trihydrate.* By double decomposition between the complex ferrous sulphate and an excess of sodium iodide solution, the dark green *iodide* was obtained in needles, which were recrystallised from hot water and air-dried (Found: I, 38·0; H_2O, 7·5. $C_{20}H_{14}N_4I_2Fe,3H_2O$ requires I, 37·6; H_2O, 8·0%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylcobaltous chloride dihydrate.* Cobaltous chloride (1·2 g.) in water (20 c.c.) was treated with an alcoholic solution of the tetramine (1·6 g.); after being boiled to dissolve the base and to remove alcohol, the mixture was filtered and cooled; the red solution then deposited pink leaflets of the dihydrated *chloride* (Found: Co, 12·2; H_2O, 7·6. $C_{20}H_{14}N_4Cl_2Co,2H_2O$ requires Co, 12·4; H_2O, 7·6%). This chloride readily lost one molecule of water over sulphuric acid and gave a brown *monohydrate* (Found: N, 12·5; Cl, 15·4. $C_{20}H_{14}N_4Cl_2Co,H_2O$ requires N, 12·2; Cl, 15·5%). Solutions of this cobalt salt were easily decomposed by dilute mineral acids and alkalis.

2 : 2′ : 2″ : 2‴-*Tetrapyridyldichlorocobaltic chloride trihydrate.* A solution of the foregoing cobaltous salt when treated with 2N-hydrochloric acid and hydrogen peroxide yielded on warming silvery plates of the cobaltic salt. This sparingly soluble complex *chloride* was air-dried after crystallisation from hot water. It formed greenish-grey crystals soluble in water to a yellow solution, which was not decomposed by dilute acids and only slowly by hot 2N-caustic soda (Found: Co, 10·9; N, 10·7; Cl, 19·4; H_2O, 10·8. $C_{20}H_{14}N_4Cl_3Co,3H_2O$ requires Co, 11·1; N, 10·6; Cl, 20·1; H_2O, 10·2%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylnickel bromide dihydrate* separated in sparingly soluble, green crystals when a hot solution containing nickel bromide (1·1 g. of anhydrous salt) and the tetramine (1·6 g.) was cooled (Found: Ni, 10·0; N, 10·2; Br, 28·1. $C_{20}H_{14}N_4Br_2Ni,2H_2O$ requires Ni, 10·4; N, 9·9; Br, 28·3%). The water of crystallisation in this compound was not removed at 120°. Hot 2N-acids and -alkalis decomposed this bromide and the following cupric salt.

2 : 2′ : 2″ : 2‴-*Tetrapyridylcupric bromide hemihydrate.* A solution containing cupric sulphate (1·2 g.) and the tetramine (1·6 g.) was treated with an excess of aqueous potassium bromide, whereupon green leaflets of the complex bromide separated. After recrystallisation from much water this *compound* was air-dried (Found : Cu, 11·7; N, 10·2; Br, 29·3; H_2O, 1·7. $C_{20}H_{14}N_4Br_2Cu,\frac{1}{2}H_2O$ requires Cu, 11·7; N, 10·3; Br, 29·5; H_2O, 1·7%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylzinc chloride dihydrate.* An aqueous solution of zinc chloride (0·7 g.) was boiled with the tetramine (1·6 g.) and a little alcohol, and the solution filtered; faintly yellow leaflets of the complex chloride separated on cooling. After recrystallisation from hot water this *compound* was air-dried (Found : Zn, 13·8, 13·7; Cl, 14·8; H_2O, 7·0. $C_{20}H_{14}N_4Cl_2Zn,2H_2O$ requires Zn, 13·6; Cl, 14·7; H_2O, 7·5%). This complex salt was decomposed by dilute acids or aqueous alkalis.

2 : 2′ : 2″ : 2‴-*Tetrapyridylcadmium chloride hydrate.* Pale yellow needles of this sparingly soluble, complex *chloride* separated from a hot solution containing equimolecular proportions of cadmium chloride and the tetrapyridyl. This product, which was decomposed by hot acids or alkalis, was crystallised from much hot water and dried (Found : Cd, 22·1; Cl, 14·0; H_2O, 3·0. $C_{20}H_{14}N_4Cl_2Cd,H_2O$ requires Cd, 22·0; Cl, 13·9; H_2O, 3·5%).

2 : 2′ : 2″ : 2‴-*Tetrapyridyldichloroiridium iridochloride.* Potassium iridochloride (1·0 g.) in water (100 c.c.) was boiled with the tetramine (0·6 g.) and alcohol (100 c.c.) until the green solution changed to orange-brown with concurrent formation of a brown salt. When the hot filtrate was cooled, small orange-brown crystals of the *iridochloride* separated. Further quantities of this compound were obtained by extracting the residue with much boiling water (Found : Ir, 36·2. $C_{60}H_{42}N_{12}Cl_{12}Ir_4$ requires Ir, 36·3%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylplatinous platinochloride.* The tetramine (1·0 g.) in 250 c.c. of alcohol was treated with aqueous potassium platinochloride (2·0 g.); the green microcrystalline *plato-salt* which separated was collected and washed successively with water, alcohol, and benzene (Found : Pt, 46·3. $C_{20}H_{14}N_4Cl_4Pt_2$ requires Pt, 46·3%). This insoluble derivative was very slowly decomposed with dissolution by aqueous ammonia, whereas silver nitrate furnished a reddish-yellow solution which gave an immediate precipitate of the green plato-salt with potassium platinochloride. On heating, the platinochloride yielded a black compound, also formed when potassium platinichloride and tetrapyridyl in aqueous-alcoholic media were boiled vigorously for several hours (Found : Pt, 58·3%).

2 : 2′ : 2″ : 2‴-*Tetrapyridyl platinochloride.* The tetrapyridyl in excess of 2N-hydrochloric acid was treated with potassium platinochloride; the yellow, insoluble, microcrystalline *salt* then separated (Found: Pt, 29·8. $C_{20}H_{14}N_4Cl_4Pt$ requires Pt, 30·1%). Alkalis decomposed this salt into its generators.

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