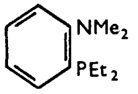
565. *The Constitution of Complex Metallic Salts. Part XVIII.*[1] *The Chelated Metallic Derivatives of* NNN′N′-*Tetramethylethylenediamine and of* 1 : 4-*Dimethylpiperazine.*

By Frederick G. Mann and H. R. Watson.

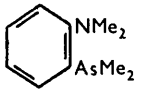
It is shown that the two diamines named in the title form stable chelated compounds of type [diamine MX_2], where X = halogen, with Pd^{2+}, Pt^{2+}, and Ir^{2+} ions, and the first diamine forms similar but less stable compounds with Cu^{2+} and Cd^{2+} ions. Compounds having two molecules of these diamines chelated to one metallic atom could not be prepared. These are apparently the first recorded examples of a simple ditertiary amine forming stable chelated metallic compounds. The composition, structure, and stability of these compounds are discussed.

It is well known that simple tertiary aliphatic amines very rarely co-ordinate stably with metallic salts, but that the co-ordinating power of a tertiary amino-group may be considerably reinforced if the group forms part of a molecule having a second strongly co-ordinating group in such a position that the two groups can form a chelating unit. For example, the detailed study of the co-ordinated palladium derivatives of *o*-dimethylaminophenyldiethylphosphine[1] (I) and *o*-dimethylaminophenyldimethylarsine[2] (II) has shown that these compounds form stable chelated palladium compounds, but that the advent of a strongly co-ordinating group such as the iodide ion almost certainly ruptures the N–Pd link, the amino-group becoming free and the iodine atom co-ordinating to the metal.

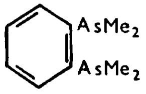
The co-ordinating groups in the compounds (I) and (II), and also in the strongly chelating *o*-phenylenebis(dimethylarsine) (III),[3,4] are however rigidly held in almost the ideal position for co-ordinated 5-membered ring formation.



(I)



(II)



(III)

A similar factor undoubtedly influences the co-ordination of 2 : 2′ : 2″-triaminotriethylamine[5] (IV), 3 : 3′ : 3″-triaminotripropylamine[6] (V), and *NNN′N′*-tetra-(2-aminoethyl)ethylenediamine[7] (VI), the tertiary amino-groups of which co-ordinate stably to metals: co-ordination of the primary amino-groups in the compounds (IV), (V), and (VI), around, for example, the 6-co-ordinate octahedron must bring the tertiary amino-groups into the precise position for co-ordination, and the stability of the whole complex will be enhanced by co-ordination of all available groups.

$N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$ (IV)

$N(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3$ (V)

$(H_2N{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}NH_2)_2$ (VI)

This factor cannot apply so powerfully to the *N*-alkylethylenediamines, in which the flexibility of the molecule enables the distance separating the nitrogen atoms to vary over a wide range. Yet Mann[8] has shown that *NN*-diethylethylenediamine (VII; R = Et)

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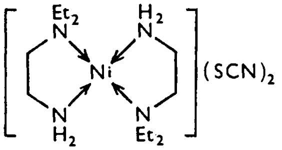
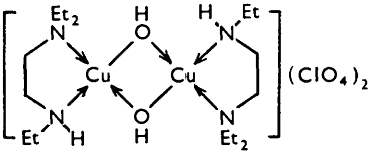
[1] Part XVII, Mann and Watson, *J.*, 1957, 3950.
[2] Mann and Stewart, *J.*, 1955, 1269.
[3] Chatt and Mann, *J.*, 1939, 1622.
[4] Nyholm, *J.*, 1950, 851 *et seq.*
[5] Mann and Pope, *Proc. Roy. Soc., A*, 1925, **109**, 444; *J.*, 1926, **129**, 482; Mann, *J.*, 1929, 409.
[6] Mann and Pope, *J.*, 1926, 489.
[7] Gauss, Moser, and Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2359; Schwarzenbach and Moser, *ibid.*, 1953, **36**, 581.
[8] Mann, *J.*, 1927, 2904.

gives stable nickel salts of type (XI), and Pfeiffer and Glaser[9] have shown that this diamine, and also *NN'*-diethylethylenediamine (VIII; R = Et) and the *N*-methyl-diamine (IX; R = Me) give cupric salts of type (XI), isolated as the diperchlorates, but that *NNN'*-triethylethylenediamine (X; R = Et) gives solely the bridged dicupric salt (XII).

Irving and Griffiths[10] have determined the stability constants of the cupric and nickel(II) salts of type (XI) formed by the diamines (VII; R = Me and Et) and (VIII; R = Me), and find the salts to be uniformly less stable than the corresponding salts formed from ethylenediamine. Since *N*-alkylation of ethylenediamine in general increases the basic strength of the amine groups, they attribute the weakening of the complex compounds mainly to increasing steric obstruction. A similar conclusion was drawn by Basolo and Murmann,[11] who found that the cupric and nickel salts of type (XI), formed from the diamines (VIII; R = Me, Et, and Pr^n), were less stable than those formed from the corresponding diamines (IX) and from ethylenediamine: it is noteworthy that the diamine (VIII; R = Pr^i) formed cupric salts solely of the bridged type (XII).

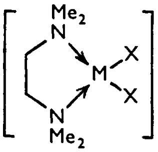
$R_2N{\cdot}C_2H_4{\cdot}NH_2$ (VII) $RHN{\cdot}C_2H_4{\cdot}NHR$ (VIII) $RHN{\cdot}C_2H_4{\cdot}NH_2$ (IX) $R_2N{\cdot}C_2H_4{\cdot}NHR$ (X)

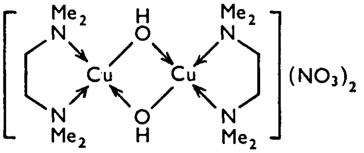

(XI)


(XII)

In view of the above results, we have been surprised to find that *NNN'N'*-tetramethylethylenediamine, $Me_2N{\cdot}C_2H_4{\cdot}NMe_2$, co-ordinates with palladium dichloride and dibromide, with platinum dichloride, and with iridium dichloride to give stable non-ionic yellow or orange compounds of type (XIII, where M represents the metal and X the co-ordinated halogen atom). These compounds have high melting points and can be readily recrystallised from boiling aqueous solution.

(XIII)




(XIV)

The preparation of the platinous compound (XIII; M = Pt, X = Cl) shows unusual features. When an aqueous solution of the diamine is steadily added to aqueous chloroplatinic acid, the orange chloroplatinate, $C_6H_{16}N_2,H_2PtCl_6$, is first precipitated, but is readily converted by the additional diamine into the pale yellow crystalline compound (XIII; M = Pt, X = Cl). The pure chloroplatinate, when set aside in aqueous suspension for several days, is slowly replaced by the chelated compound, a process which is accelerated if the suspension is boiled. The compound (XIII; M = Pt, X = Cl) can also be prepared less conveniently by the action of the diamine on aqueous sodium chloroplatinite. The preparations from the chloroplatinate clearly involve reduction of the latter with oxidation of the diamine, presumably to its *N*-mono- and di-oxide. We find similarly that the iridium compound (XIII; M = Ir, X = Cl) is best prepared by the action of the diamine on potassium chloroiridate, $K_2[IrCl_6]$, in which the diamine is again acting as a reducing and chelating agent.

This type of compound is not limited to metals giving 4-co-ordinate planar complexes,

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[9] Pfeiffer and Glaser, *J. prakt. Chem.*, 1938, **151**, 134.
[10] Irving and Griffiths, *J.*, 1954, 213.
[11] Basolo and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 211.

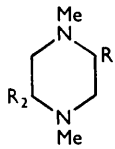
for cadmium chloride gives a similar but colourless compound (XIII; M = Cd, X = Cl), which can be recrystallised from ethanol but decomposes in boiling aqueous solution.

The addition of the diamine (1 equivalent) to an aqueous solution of copper sulphate gave a deep blue solution, which when treated with potassium thiocyanate gave the dithiocyanato-diamine-copper (XIII; M = Cu, X = SCN), and when treated with sodium picrate the dipicrato-diamine-copper (XIII; M = Cu; X = $O{\cdot}C_6H_2O_6N_3$), both forming very deep green crystals. The last compound has been recrystallised from acetone and identified by analysis and by its molecular weight in boiling acetone. It represents one of the very rare compounds in which the picrate group is directly co-ordinated to a metal.

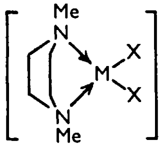
The addition of the diamine (1·4 equivalents) to copper nitrate in aqueous solution was necessary to redissolve the initial precipitate of cupric hydroxide: the clear solution when concentrated at room temperature gave deep blue crystals of the hydrated bistetramethylethylenediamine-$\mu\mu'$-dihydroxy-dicupric dinitrate (XIV), apparently identical in type with Pfeiffer and Glaser's salt (XII).

Dr. J. Chatt has kindly investigated the conductivities of nitrobenzene solutions of the compounds (XIII; M = Pd, X = Cl; M = Pt, X = Cl; M = Cd, X = Cl; M = Cu, X = $\cdot O{\cdot}C_6H_2O_6N_3$); these conductivities are virtually zero, *i.e.*, too small for accurate measurement, and the compounds cannot therefore be salts of the type $[(\text{diamine})_2M][MX_4]$. Further, these compounds are unaffected by the addition of an excess of the diamine to their solutions, and salts of type (XI) cannot be isolated (cf. p. 2778).

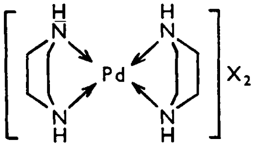
Even more surprising is the fact that 1 : 4-dimethylpiperazine (XV; R = H) gives similarly coloured compounds of type (XVI) with palladium dichloride and dibromide, platinum dichloride, and iridium dichloride. These compounds also have high stability, can be recrystallised unchanged from aqueous solution, are unaffected by additional 1 : 4-dimethylpiperazine, and give nitrobenzene solutions of negligible conductivity.



(XV)



(XVI)



(XVII)

The platinous dichloride derivative (XVI; M = Pt, X = Cl) can be prepared precisely similarly to the compound (XIII; M = Pt, X = Cl), *i.e.*, very readily by the addition of an excess of dimethylpiperazine to aqueous chloroplatinic acid, by spontaneous decomposition of the pure dimethylpiperazine chloroplatinate in aqueous suspension, or by the action of the piperazine on one equivalent of sodium chloroplatinite in aqueous solution. The iridium compound (XVI; M = Ir, X = Cl) has also been prepared by the action of the piperazine on potassium chloroiridate.

It is noteworthy that in compounds of type (XVI) the 1 : 4-dimethylpiperazine is clearly fixed in the boat form. Our attempts to prepare similar chelated metallic derivatives with 1 : 2 : 2 : 4 : 5 : 5-hexamethylpiperazine (XV; R = Me) uniformly failed. This is in harmony with the results of Mann and Senior,[12] who showed that both piperazines readily form dimethobromides and dimethiodides, but whereas 1 : 4-dimethylpiperazine also combines with ethylene dibromide to form triethylenediamine dimethobromide, the hexamethylpiperazine does not undergo a similar reaction. It was suggested that the two sets of *gem.*-dimethyl groups in the piperazine (XV; R = Me) " locked " the molecule in the chair form, which the cation of the crystalline hexamethylpiperazine dinitrate is known to possess.[12] If the molecule of the hexamethylpiperazine in solution is also held rigidly in the chair form, it clearly could not undergo either cyclic diquaternisation with ethylene dibromide or chelation with metals to form compounds of type (XVI).

[12] Mann and Senior, *J.*, 1954, 4476; cf. McElvain and Bannister, *J. Amer. Chem. Soc.*, 1954, **76**, 1126.

The structure of compounds of type (XIII) and (XVI) receives further confirmation from their infrared spectra. Dr. N. Sheppard reports:

" (1) In the spectrum of tetramethylethylenediamine there are medium-to-strong bands at 2800 and 2750 cm.$^{-1}$ and in that of 1 : 4-dimethylpiperazine a similar band at 2810 cm.$^{-1}$. Prominent bands in this region (2800 ± 50 cm.$^{-1}$) are found consistently when *N*-Me groups occur in free bases, and usually also when *N*-CH_2 groups are present. However, they apparently become shifted to higher frequencies (~2900 cm.$^{-1}$) and are then lost in other CH absorption bands, in the spectra of amine salts in which the nitrogen atom assumes a positive charge.[13]

" In the spectra of the compounds (XIII; M = Pd, X = Cl) and (XVI; M = Pd, X = Cl), the above bands are missing, and this shows clearly that in each compound there are no free *N*-Me groups, *i.e.*, that both tertiary amine nitrogen atoms in each compound are involved in the co-ordination with the palladium atom.

" (2) The infrared spectrum of the liquid 1 : 4-dimethylpiperazine in the ' fingerprint region ' (1400—700 cm.$^{-1}$) is very simple for such a complex molecule. There are indeed fewer absorption bands observable than there are infrared active fundamentals for the most highly symmetrical configuration of the molecule, even in the region below 1200 cm.$^{-1}$ where there is likely to be little overlapping of absorption bands. The spectrum therefore points to the most symmetrical structure for the molecule, *i.e.*, a centrosymmetrical configuration with the 6-membered ring in the ' chair ' conformation, and the *N*-Me groups either both axially (or both equatorially) disposed with respect to the ring.

" In the spectrum of the co-ordinated compound (XVI; M = Pd, X = Cl), the pattern of frequencies changes in many respects, and a number of additional bands of weak or medium strength appear. These changes are consistent with the change in conformation of the dimethylpiperazine molecule from the chair to the boat form caused by chelation with the palladium atom. No extra bands due to the palladium–halogen bonds are likely to be present in the region of the spectrum investigated."

Failure attended attempts to prepare stable co-ordination compounds of tetramethylethylenediamine with Co^{3+}, Rh^{3+}, and Ni^{2+}, and of 1 : 4-dimethylpiperazine with these ions and with Cu^{2+} and Cd^{2+}.

Two major features must be discussed regarding the structure and properties of the two parallel series of compounds (XIII) and (XVI), particularly the palladous, platinous, and iridous members: first, what is the reason for their unexpectedly high stability, both thermal and chemical, and secondly, why is co-ordination limited to one molecule of the diamine to each metallic atom?

There is apparently no intrinsic electronic factor responsible for the stability of these compounds, and their formation is presumably determined almost solely by the marked increase in the co-ordinating power of each tertiary amino-group when both groups are co-operating to form a chelated ring system. This increase in co-ordinating power is evidently much greater than has hitherto been recognised, since it enables two groups, each singly of very weak power, to form a firmly chelating molecule, and it is clearly not necessary (although helpful) for one of the groups to have strong co-ordinating power, as in the compounds (I) and (II).

The reason why only one molecule of tetramethylethylenediamine or 1 : 4-dimethylpiperazine will co-ordinate with one metallic atom is undoubtedly the steric obstruction of the *N*-methyl groups. The evidence for this is two-fold. (i) It is known that palladium and platinum dihalides readily react with ethylenediamine to give salts of type $[M(en)_2]X_2$, and we find that piperazine similarly gives palladium salts of type (XVII). (ii) Figs. 1 and 2 show the positions of a molecule of tetramethylethylenediamine and of dimethylpiperazine respectively when co-ordinated to a palladium atom of ionic radius 1·30 Å. For simplicity, the carbon atom of only one *N*-methyl group is shown attached to the

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[13] Nakaniski, Goto, and Ohashi, *Bull. Chem. Soc. Japan*, 1957, **30**, 403.

upper nitrogen atom in Fig. 1, and no such groups are shown attached to the lower nitrogen atoms in Figs. 1 and 2: circles drawn with thin lines and those with thick lines indicate atoms which are in the plane, and above the plane, of the paper respectively. The following bond lengths have been used: C–C, 1·54; C–H, 1·09; C–N$^+$, 1·49;[14] Pd–N, 2·02 Å.[15]

In Fig. 1, in order to accommodate the diamine molecule, the normal tetrahedral angles and also the right angle at the palladium atom have been modified by 4—5°, but this should cause a very small degree of strain. The curved dotted line in Fig. 1 indicates the probable extent of the complete methyl group.

It is clear that co-ordination of a second molecule of the diamine in Fig. 1 would bring the four pairs of substituent methyl groups (which would be held rigidly) impossibly close together. It is primarily this steric effect which prevents chelation by a second diamine molecule: a secondary and minor factor is the weaker bonding which would be involved if the palladium atom added further donor atoms, owing to the " ligand " effect.[16]

The same considerations apply to the analogous compounds of Pt^{2+} (1·32 Å) and Cu^{2+} (1·35 Å *) and it is probable that the diamine will co-ordinate stably only with metals having ionic radii in this region. No nickel complexes were isolated, and it is significant that Ni^{2+} has a much smaller ionic radius (0·69 Å). The Cd^{2+} ion (0·97 Å) is tetrahedral, and a similar calculation shows that the bond angles of the diamine are considerably strained in the compound (XIII; M = Cd, X = Cl): it is noteworthy that this compound was the least stable of those of type (XIII).

FIG. 1.

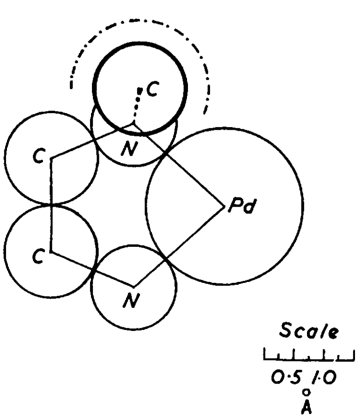
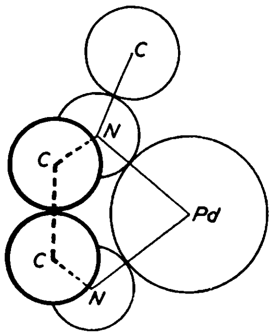


FIG. 2.



Figs. 1 *and* 2 *show the positions of a molecule of tetramethylethylenediamine and of* 1 : 4-*dimethylpiperazine respectively when co-ordinated to a palladium atom. Circles drawn in thin lines and in thick lines indicate atoms which are respectively in and above the plane of the paper. The carbon atom of only one* N-Me *group is shown attached to the upper nitrogen atom in Fig.* 1, *and no such groups are shown attached to the lower nitrogen atoms in Figs.* 1 *and* 2.

The structure of the dimethylpiperazine–palladium complex (Fig. 2) also shows the great steric obstruction to the chelation of a second molecule of this piperazine. The Figure has been drawn with the carbon angles of 109°, which brings the palladium bond angle very close to 90°: this structure does however reduce the C–N–Pd angle to 90°, but it is probable that the resulting bond strain is shared throughout the ring. Distortion of the more rigid dimethylpiperazine molecule would require more energy than that of the

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* This value is based on the Cu–N bond-length of 2·02 Å in $[py_2CuCl_2]$ (Dunitz, *Acta Cryst.*, 1957, **10**, 307) and of 2·07 Å in the cation $[en_2\,Cu]^{2+}$ (Scouloudi, *ibid.*, 1953, **6**, 651).

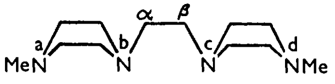
[14] Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495.

[15] Mann, Wells, and Purdie, *J.*, 1937, 1828.

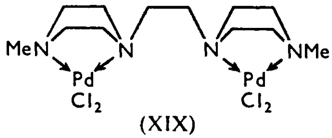
[16] Cf. Burkin, *Quart. Rev.*, 1951, **5**, 1.

tetramethylethylenediamine molecule: this factor may explain why the piperazine will not co-ordinate stably to the smaller cupric and cadmium ions. No values are apparently available for the ionic radius of Ir^{2+}, but it is undoubtedly very similar to that of Pt^{2+}.

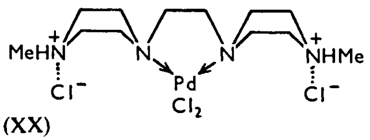
We have briefly investigated the co-ordinating properties of 1 : 2-di-(4-methyl-1-piperazinyl)ethane[17] (XVIII), since this compound consists essentially of two 1 : 4-disubstituted piperazine units linked by an ethylene group, which therefore acts as one of the substituents of each unit. Consideration of the structure of this tetramine indicates that it cannot act as a quadridentate co-ordinating molecule around one central metallic atom, because if, for example, the N^a and N^b atoms in (XVIII) were chelated to a metallic atom, the tetrahedral disposition of the co-ordinated N^b atom would direct the N^b–C^α valency into a position leading so far from the metallic atom that the N^b–C^α–C^β–N^c unit could not then co-ordinate as a chelate group with this atom. Experiment confirms this deduction. The only conditions discovered leading to a fully co-ordinated crystalline palladium derivative entailed treating the tetramine (XVIII) in aqueous solution with two equivalents of potassium chloropalladite, whereby pale yellow crystals of composition $C_{12}H_{26}N_4,2PdCl_2$, undoubtedly tetrachloro-[1 : 2-di-(4-methyl-1-piperazinyl)ethane]dipalladium (XIX), were obtained. The mother-liquor from this preparation, when set aside slowly yielded a crude deposit, which on digestion with hot water afforded deep orange crystals of composition $C_{12}H_{26}N_4,PdCl_2,2HCl,H_2O$. Although there is no evidence for the position of the co-ordinated palladium atom, it is highly probable that this compound is the monohydrated symmetric salt, dichloro-[1 : 2-di-(4-methyl-1-piperazinyl)-ethane 4 : 4′-dihydrochloride]palladium (XX). Unlike the compound (XIX), it is highly soluble in cold water, giving a solution in which only a portion of the chlorine is ionised.



(XVIII)



(XIX)



(XX)

It should be added that Bennett, Mosses, and Statham[18] claim to have prepared dichloro-*NN′*-dimethyl-*NN′*-diphenylethylenediaminepalladium by the interaction of the amine hydrochloride and potassium chloropalladite, but the compound was not further investigated, and its method of preparation, together with its physical properties ("an insoluble buff powder"), suggest that it may have had a much more complex structure.

EXPERIMENTAL

NNN′N′-Tetramethylethylenediamine, b. p. 121°/755 mm., was prepared by the formaldehyde–formic acid methylation of ethylenediamine, 1 : 4-dimethylpiperazine by Mann and Senior's method,[12] and 1 : 2-di-(4-methyl-1-piperazinyl)ethane as described by Mann and Baker.[17]

Metallic Derivatives of NNN′N′-*Tetramethylethylenediamine.*—In the following section this amine will be designated "diamine" for brevity.

Dichloro(diamine)palladium (XIII; M = Pd, X = Cl). The dropwise addition of the diamine (0·23 g.) in water to a stirred aqueous solution of potassium chloropalladite (0·65 g., 1 mol.) precipitated the *compound* (0·58 g., 100%), deep yellow-orange plates, m. p. 245—247° (decomp., darkening at 220°), from water (Found: C, 24·7; H, 5·6; N, 9·3. $C_6H_{16}N_2Cl_2Pd$ requires C, 24·5; H, 5·45; N, 9·5%).

Dibromo(diamine)palladium (XIII; M = Pd, X = Br), similarly prepared, formed deep

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[17] Mann and Baker, *J.*, 1957, 1881.

[18] Bennett, Mosses, and Statham, *J.*, 1930, 1668.

orange prisms, m. p. 226° (decomp.) after crystallisation from much hot water (Found: C, 18·7; H, 4·1; N, 7·2. $C_6H_{16}N_2Br_2Pd$ requires C, 18·8; H, 4·2; N, 7·3%).

These two compounds are sparingly soluble in hot water, very slightly soluble in other polar solvents and insoluble in non-polar solvents. Both crystallised unchanged from a hot aqueous solution containing a large excess of the diamine.

Dichloro(diamine)platinum (XIII; M = Pt; X = Cl). (*a*) The diamine in aqueous solution was added dropwise to pure aqueous chloroplatinic acid which was steadily shaken. The immediate fine precipitate of the orange chloroplatinate was rapidly converted by the additional diamine into the pale yellow *compound* (XIII; M = Pt, X = Cl), m. p. 303° (decomp.) after crystallisation from water (Found: C, 18·8; H, 4·7; N, 7·1. $C_6H_{16}N_2Cl_2Pt$ requires C, 18·8; H, 4·2; N, 7·3%). Addition of a moderate excess of the undiluted diamine to the aqueous acid precipitates this compound without apparent intermediate formation of the chloroplatinate. It is sparingly soluble in hot water and very slightly soluble in boiling ethanol and acetone.

(*b*) The chloroplatinate was precipitated when a solution of the diamine dihydrochloride (0·38 g.) in water (2 c.c.) was added to chloroplatinic acid (1·0 g., 1·2 mols.) in water (2·5 c.c.), and after cooling to 0° was collected, washed with ice-water, and dried. The orange leaflets had m. p. 246° (decomp.), unchanged by recrystallisation from water [(lit.,[19] sinters 245°, m. p. 252° (decomp.)] (Found: C, 13·4; H, 3·3; N, 5·3. Calc. for $C_6H_{16}N_2,H_2PtCl_6$: C, 13·7; H, 3·3; N, 5·3%). A concentrated aqueous solution of this salt, when boiled under reflux for 24 hr., became pale in colour and deposited some platinum. The solution, when filtered and cooled, deposited the above crystalline compound, m. p. and mixed m. p. 303° (decomp.). An aqueous suspension of the finely powdered chloroplatinate, when set aside for many days, gave the same result.

(*c*) Sodium chloroplatinite tetrahydrate and the diamine (1 mol.), each in 10% (w/v) aqueous solution, were mixed. No immediate change was apparent, but the solution when set aside for 5 days became colourless and deposited large crystals contaminated with metallic platinum. Recrystallisation of the deposit from hot water gave the above yellow compound, m. p. and mixed m. p. 303° (decomp.). If the initial mixed solution was heated, a copious deposit of black platinum readily separated.

Dichloro(diamine)iridium (XIII; M = Ir, X = Cl). A solution of the diamine (0·17 g., 3 mols.) in water (2 c.c.) was added dropwise to one of potassium chloroiridate, K_2IrCl_6 (0·24 g.), in water (7 c.c.), the colour of which rapidly changed from deep brown to pale olive-green. The mixture was set aside for 2 days, and the dark precipitate, when collected and recrystallised from much hot water, with filtration to remove iridium, deposited the *compound*, pale yellow prisms, m. p. 288° (decomp.) (Found: C, 19·0; H, 4·5; N, 7·3. $C_6H_{16}N_2Cl_2Ir$ requires C, 19·0; H, 4·25; N, 7·4%). A cold aqueous solution of this compound containing an excess of the diamine was unaffected when set aside for 4 weeks, but on warming rapidly deposited iridium.

The fact that aqueous solutions of potassium chloroiridite, K_3IrCl_6, are olive-green might suggest that the first stage in the above preparation is reduction of the chloroiridate to the chloroiridite: this however is apparently not the case, for we have been unable to prepare the compound (XIII; M = Ir; X = Cl) by the action of the diamine on aqueous solutions of the pure chloroiridite.

Copper derivatives. The diamine (0·46 g., 1 mol.) when added to copper sulphate pentahydrate (0·50 g.), both in aqueous solution, initially deposited cupric hydroxide, which then dissolved to form a very deep blue solution. One portion, diluted with saturated aqueous potassium thiocyanate, deposited *dithiocyanato(diamine)copper* (XIII; M = Cu, X = SCN), very deep green crystals giving an olive-green streak, m. p. 107° after thorough washing with ice-water (Found: C, 32·0; H, 5·7; N, 18·4. $C_8H_{16}N_4S_2Cu$ requires C, 31·6; H, 5·3; N, 18·4%). This compound is soluble in cold acetone and methanol, insoluble in benzene, and very sparingly soluble in cold water, the solution depositing cuprous thiocyanate when warmed.

A second portion of the original solution, when diluted with water and added to sodium picrate solution, deposited *dipicrato(diamine)copper* (XIII; M = Cu; X = $\cdot O\cdot C_6H_2O_6N_3$), very deep green crystals, black by reflected light, and giving an apple-green streak, m. p. 240° (decomp.) after crystallisation from acetone (Found: C, 34·0; H, 3·3; N, 17·35%; *M*, in boiling acetone, 615. $C_{18}H_{20}O_{14}N_8Cu$ requires C, 34·0; H, 3·15; N, 17·6%; *M*, 636).

A 10% (w/v) aqueous solution (3·3 c.c.) of the diamine (1·4 mols.) was added to a solution

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[19] Freund and Michaels, *Ber.*, 1897, **30**, 1385.

of cupric nitrate tetrahydrate (0·48 g.) in water (1·5 c.c.). The clear solution when concentrated at room temperature over sodium hydroxide deposited the *trihydrated bis(diamine)-μμ′-dihydroxy-dicupric dinitrate* (XIV), deep blue crystals, m. p. 178—179° when collected, washed with ice-water and dried in air (Found: C, 25·7; H, 7·5. N, 14·75. $C_{12}H_{34}O_8N_6Cu_2,3H_2O$ requires C, 25·2; H, 7·0; N, 14·7%). These crystals, when confined in a vacuum over sodium hydroxide, effloresced to give the *monohydrate*, a deep royal-blue powder, m. p. 178—179° (Found: C, 27·2; H, 7·0; N, 16·2. $C_{12}H_{34}O_8N_6Cu_2,H_2O$ requires C, 26·9; H, 6·7; N, 16·2%). An aqueous solution of the dinitrate, when either warmed or treated cautiously with dilute nitric acid, gave a copious precipitate of cupric hydroxide.

Dichloro(diamine)cadmium (XIII; M = Cd; X = Cl). Addition of the diamine to aqueous cadmium chloride caused deposition of cadmium hydroxide, which did not dissolve even in a large excess of the diamine. A solution of the diamine (0·47 g., 2 mols.) in ethanol (2 c.c.) was therefore added dropwise to an agitated solution of cadmium chloride (0·46 g.) in ethanol (12 c.c.). The *compound* rapidly separated as colourless silky needles, m. p. 254—255° (in a sealed tube, immersed at 250°), resolidifying to a crystalline mass at 260°, after crystallisation from much ethanol (Found: C, 24·3; H, 5·4; N, 9·6. $C_6H_{16}N_2Cl_2Cd$ requires C, 24·1; H, 5·3; N, 9·35%). It is sparingly soluble in hot ethanol and acetone, and its hot aqueous solution rapidly deposits cadmium hydroxide.

An ethanolic solution, when diluted with an excess of the diamine, boiled under reflux and cooled, deposited the unchanged compound.

Metallic Derivatives of 1 : 4-*Dimethylpiperazine* (XV; R = H).—*Dichloro(dimethylpiperazine)palladium* (XVI; M = Pd; X = Cl). Addition of the piperazine (0·23 g.; 1 mol.) to potassium chloropalladite (0·65 g.), each in aqueous solution, gave a quantitative deposition of the *compound*, deep orange tabular crystals, m. p. 190° (decomp.) after crystallisation from water (Found: C, 24·35; H, 4·6; N, 9·6; Pd, 36·9%; *M*, in boiling water, 294. $C_6H_{14}N_2Cl_2Pd$ requires C, 24·7; H, 4·8; N, 9·6; Pd, 36·8%; *M*, 292).

The *dibromo-compound* (XVI; M = Pd, X = Br), similarly prepared and crystallised, formed deep russet-red prisms, m. p. 172—172·5° (decomp.) (Found: C, 19·3; H, 3·75; N, 7·35. $C_6H_{14}N_2Br_2Pd$ requires C, 18·9; H, 3·7; N, 7·35%).

These two compounds have similar solubilities to those of their tetramethylethylenediamine analogues. Each crystallised unchanged from an aqueous solution containing an excess of the piperazine.

Dichloro(dimethylpiperazine)platinum (XVI; M = Pt, X = Cl). (*a*) An aqueous solution of the piperazine, when added slowly in ultimate excess to chloroplatinic acid solution, first precipitated the orange chloroplatinate, which readily redissolved; the orange solution then deposited the *compound*, pale yellow prisms, m. p. 249° (decomp.; immersed at 240°) from much hot water (Found: C, 19·1; H, 3·5; N, 7·5; Pt, 51·05%; *M*, in boiling water, 350. $C_6H_{14}N_2Cl_2Pt$ requires C, 18·9; H, 3·7; N, 7·4; Pt, 51·3%; *M*, 380). A cold aqueous suspension of the chloroplatinate, $C_6H_{14}N_2,H_2PtCl_6$, behaved similarly when treated with the diamine. The successful preparation of this chloroplatinate [17] depends therefore on the use of an excess of chloroplatinic acid in hydrochloric acid (cf. p. 2778), otherwise the above compound may be formed.

(*b*) An aqueous suspension of the chloroplatinate, when set aside for 21 days, became initially clear and then deposited the above compound, m. p. and mixed m. p. 247° (decomp. as before).

(*c*) The above compound (Found: N, 7·2%) was also prepared from sodium chloroplatinite, as described for the compound (XIII; M = Pt, X = Cl).

Dichloro(dimethylpiperazine)iridium (XVI; M = Ir, X = Cl). This compound was prepared precisely as its tetramethylethylenediamine analogue, and from water formed pale yellow crystals, m. p. 242·5—243·5° (decomp.) (Found: C, 19·2; H, 3·8; N, 7·45. $C_6H_{14}N_2Cl_2Ir$ requires C, 19·1; H, 3·7; N, 7·4%).

Dimethylpiperazine was added to nickel succinimide,[20] both in ethanolic solution, in an unsuccessful attempt to prepare co-ordinated derivatives: the solution, when treated subsequently with an excess of ethanolic sodium iodide, deposited *disodium tetrasuccinimidonickel*, pale mustard-yellow plates, m. p. 328° (decomp.) (Found: C, 38·2; H, 3·7; N, 11·2; Ni, 11·4. $C_{16}H_{16}O_8N_4Na_2Ni$ requires C, 38·5; H, 3·2; N, 11·3; Ni, 11·8%). When sodium succinimide (2 mols.) was added to nickel succinimide, both in ethanolic solution, rapid crystallisation of

[20] Tschugaev, *Ber.*, 1906, **39**, 3197.

this salt, m. p. and mixed m. p. 329° (decomp.), occurred. It is insoluble in organic solvents, but readily soluble in water to give a yellow solution which rapidly deposits nickel hydroxide.

Bis(piperazine)palladium dipicrate (XVII; $X = \cdot O\cdot C_6H_2O_6N_3$). An aqueous solution of piperazine (2 mols.) was added to aqueous potassium chloropalladite, giving immediately a clear pale yellow solution of the dichloride (XVII; $X = Cl$). This solution, when added to an excess of aqueous sodium picrate, precipitated the *dipicrate*, yellow plates, m. p. 113° (decomp.) (Found: C, 32·6; H, 3·7; N, 18·8. $C_{20}H_{24}O_{14}N_{10}Pd$ requires C, 32·7; H, 3·3; N, 19·1%).

Metallic Derivatives of 1 : 2-*Di*-(4-*methyl*-1-*piperazinyl*)*ethane* (XVIII). (This base will be designated the " tetramine " in this section.)—A solution of the tetramine (0·44 g.) in water (10 c.c.) was added rapidly to a stirred solution of potassium chloropalladite (1·36 g., 2 mols.) in water (20 c.c.), a buff-coloured amorphous precipitate being immediately formed. After 2 min., the mixture was centrifuged, and the upper layer then filtered as rapidly as possible. Almost immediately, there started the slow separation of the pale yellow microcrystalline *tetrachloro*(*tetramine*)*dipalladium* (XIX) (0·3 g.) which, when collected after 2 hr., washed with water and acetone, and dried, had m. p. 226° (decomp.) (Found: C, 24·8; H, 4·5; N, 9·5. $C_{12}H_{26}N_4Cl_4Pd_2$ requires C, 24·8; H, 4·5; N, 9·6%): it is insoluble in all the common solvents.

The mother-liquor when set aside for several days continued to deposit the crystals (XIX), contaminated later with minute deep brown needles, probably the tetramine di(chloropalladite), $C_{12}H_{26}N_4,2H_2PdCl_4$. The mixture was collected, and digested with much water at 100° for 2 hr. It was then filtered hot to remove a deep brown sludge, and the filtrate when concentrated and cooled yielded the *monohydrated dichloro*(*tetramine dihydrochloride*)*palladium* (XX), hygroscopic deep orange tablets, m. p. 219° (decomp.) after crystallisation from aqueous acetone and drying over silica gel at 20 mm. (Found: C, 28·8; H, 6·2; N, 11·6. $C_{12}H_{26}N_4Cl_2Pd,2HCl,H_2O$ requires C, 29·1; H, 6·1; N, 11·3%). This compound is very soluble in cold water but insoluble in ethanol, acetone, and ether. A dilute aqueous solution, when treated with aqueous silver nitrate, deposits silver chloride but remains orange in colour, showing that the co-ordinated ring system remains intact. The addition of sodium hydroxide to an aqueous solution causes no apparent change.

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