XCIV.—*The Stability of Complex Metallic Salts.*

By FREDERICK GEORGE MANN.

THE stability of the complex metallic salts is commonly considered to be based on the electronic structure of the metal when so co-ordinated, since the metal in its simple salts, when co-ordinating with amine molecules or further acid radicals, endeavours to increase the number of its electrons to that of the next inert gas (Lowry, *Chem. and Ind.*, 1923, **1**, 318; Sidgwick, J., 1923, **123**, 725; " The Electronic Theory of Valency," 1927, 113). If, then, it is assumed that co-ordinated amine, water, sulphide, or other molecules are bound to the metal by " semi-polar double bonds " (Lowry) or " co-ordinate links " (Sidgwick), contributing in each case 2 electrons per molecule to the metal, and that co-ordinated acid radicals are bound by covalencies, contributing 1 electron per monobasic radical to the metal, a reasonable explanation is afforded of the great stability of, *e.g.*, the complex salts of tervalent cobalt and rhodium and of quadrivalent platinum, all of co-ordination number 6. For instance, cobalt of atomic number 27 requires 9 electrons to attain the 36 electrons of krypton, and these are obtained in the hexammino-series, *e.g.*, $[Co(NH_3)_6]Cl_3$, where the metal gains $(2 \times 6) - 3 = 9$, and in the hexacido-series, *e.g.*, $Na_3[Co(NO_2)_6]$, where it again gains $(3 + 6) = 9$. Quadrivalent platinum, of atomic number 78, requires 8 electrons to equal emanation (86), and therefore gives compounds such as $[Pt(NH_3)_6]Cl_4$ and $Na_2[PtCl_6]$, in both of which the necessary electrons, $(12 - 4)$ and $(2 + 6)$, respectively, are acquired.

These considerations would explain why, for instance, the complex salts of tervalent iron are usually less stable than those of bivalent iron. Iron, of atomic number 26, requires 10 electrons to attain the 36 electrons of krypton. In potassium ferrocyanide, $K_4[FeCy_6]$, these are acquired $(4 + 6)$, but in the ferricyanide, $K_3[FeCy_6]$, the co-ordinated metal is still one short $(3 + 6)$. This deficiency is presumably the cause of the comparative instability of the ferri-complex salts. Werner prepared and resolved the chemically stable tris-$\alpha\alpha'$-dipyridylferrous bromide, $[Fe''(Dpy)_3]Br_2$ (*Ber.*, 1912, **45**, 433) : on the other hand, the trisethylenediamineferric salts, $[Fe''' en_3]Cl_3$, are extremely unstable, and the ferrioxalates, $Na_3[Fe(C_2O_4)_3]$, merely on exposure to light break down to the corresponding ferro-oxalates (Thomas, J., 1921, **119**, 1140).

There are, however, various metals that give at least two series of complex salts, in one of which the co-ordinated metal has a deficiency, and in the other an excess, of electrons compared with the next inert gas. It is usually found in such cases that the metal can tolerate a deficiency of electrons more readily than an excess, and that the series of salts having an excess of electrons is the least stable of all, usually readily reverting to a lower series by the loss of co-ordinated addenda. For instance, nickel, of atomic number 28, requires 8 electrons to attain the number in krypton. In the tetrammino-series, *e.g.*, $[Ni(NH_3)_4]Cl_2$, the metal gains only 6, *i.e.*, $(8 - 2)$, and has thus a deficiency of 2 electrons; in the hexammino-series, *e.g.*, $[Ni(NH_3)_6]Cl_2$, the metal gains 10, *i.e.*, $(12 - 2)$, and has an excess of 2 : salts of the hexammino-series are generally much less stable than those of the tetrammino-series, and usually revert easily to the latter in aqueous solution. Again, copper, of atomic number 29, requires similarly 7 electrons. In the tetrammino-series, *e.g.*, $[Cu(NH_3)_4]Cl_2$, it has a deficiency of

1 electron, and in the hexammino-series, *e.g.*, $[Cu(NH_3)_6]Cl_2$, an excess of 3 : the latter series is much less stable than the former.

It has recently been shown, however, by the author (J., 1928, 893) that the stability of salts containing polyamines or other "multidentate" molecules is also dependent on a second factor, *viz.*, the ease with which the polyamine molecule, for purely structural reasons, can arrange itself around a complex which may be a square or tetrahedron, an octahedron, or a cube according as the metal has a co-ordination number of 4, 6, or 8, respectively. This factor, dependent on the molecular structure of the co-ordinating addendum, may have a greater effect on the stability of the complex salt than the former factor, which is dependent on the electronic structure of the metal itself.

This is well illustrated in the complex metallic salts of $\alpha\beta\gamma$-triaminopropane. There is considerable evidence to show that this triamine can arrange itself readily and very firmly around the 6-co-ordination octahedron (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **107**, 80; J., 1926, 2675), and thus gives extremely stable salts such as bistriaminopropanecobaltic chloride,

$$[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Co]Cl_3,$$

and the corresponding bistriaminopropanerhodium trichloride. When, however, nickel chloride is treated with triaminopropane in any proportion, the bistriaminopropanenickelous salt, *e.g.*, $[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Ni]I_2$, is always formed. Here the metal, of co-ordination number 6, has an excess of 2 electrons, and the salt should therefore be very unstable : actually it is extremely stable, and shows no sign of degradation to a salt of co-ordination number 4, such, *e.g.*, as monoaquotriaminopropanenickelous iodide, $[H_2O\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}Ni]I_2$. Again, bivalent platinum has the characteristic co-ordination number of 4, *e.g.*, $[Pt(NH_3)_4]Cl_2$, and in this series the metal has a deficiency of 2 electrons. It has been shown, however (Mann, J., 1928, 890), that with triaminopropane, bivalent platinum gives salts such as bistriaminopropaneplatinous iodide, $[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Pt]I_2$: these are the only salts known in which bivalent platinum has a co-ordination number of 6, and, since the metal has an excess of 2 electrons, they should be very unstable. Actually they are remarkably stable, and can be recrystallised repeatedly from boiling water. The stability of these nickel and platinous salts is therefore to be attributed primarily to the ease with which the triaminopropane molecule can co-ordinate around the octahedron : the metal in each case has adopted the exceptional co-ordination number of 6 in order to provide the octahedron necessary for maximum stability of the completed complex salt.

The possibility that in salts of this type the metal has a co-ordination number of 4, and not of 6, being bound to only two of the three amino-groups in each molecule of the base, has already been discussed and disproved (Mann, *loc. cit.*, p. 893). When such salts separate from aqueous solution, each of the free and unco-ordinated amino-groups would almost undoubtedly add on a molecule of water to give a substituted ammonium hydroxide. Moreover, such salts, on treatment in solution with an excess of picric acid, should give a tetrapicrate, since in addition to the complex forming a dipicrate, each free amino-group would also combine with a molecule of picric acid. It has been shown, however, that when, *e.g.*, bistriaminopropaneplatinous iodide is treated with picric acid, a *dipicrate* alone results, showing conclusively that all six amino-groups are co-ordinated to the metal.

Further evidence of the stability of this 6-co-ordination grouping has now been obtained by investigating the complex salts of triaminopropane with other bivalent metals. Zinc, of atomic number 30, requires 6 electrons to attain the number in krypton. In the tetrammino-series, *e.g.*, $[Zn(NH_3)_4]Cl_2$, these are obtained $(8 - 2)$, and the salts of this series are of moderate stability. In the hexammino-series, *e.g.*, $[Zn(NH_3)_6]Cl_2$, the metal has an excess of 4 electrons, and the salt is in consequence extremely unstable: in fact, it exists only in the solid state, and even on exposure to air loses ammonia, reverting to a salt of the lower series. With triaminopropane, however, zinc readily unites to give salts such as *bistriaminopropanezinc iodide*,

$$[\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2Zn]I_2 :$$

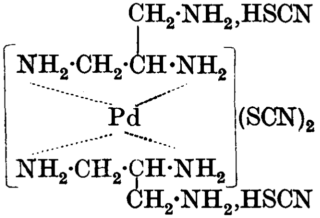
here again the metal has a co-ordination number of 6 and an excess of 4 electrons, yet the salt is extremely stable and, like the above nickelous and platinous salts, can be recrystallised repeatedly from boiling water without change.

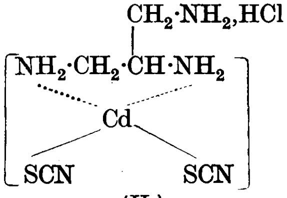
The reactions of bivalent palladium with the triamine are (as might be expected) precisely similar to those of bivalent platinum. Palladium, of atomic number 46, requires 8 electrons to attain the state of xenon. The quadrivalent metal has a co-ordination number of 6, and in compounds such as $[Pd(NH_3)_6]Cl_4$ acquires the requisite 8 electrons $(6 \times 2 - 4)$. The bivalent metal has, like platinum, the characteristic co-ordination number 4, and in compounds such as $[Pd(NH_3)_4]Cl_2$ has therefore a deficiency of 2 electrons. With triaminopropane, however, it gives compounds such as *bistriaminopropanepalladous iodide*, $[\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2Pd]I_2$: here the bivalent metal has a co-ordination number of 6, and an excess of 2 electrons, yet in spite of the latter factor the salt is very stable. These compounds, again, are the only known derivatives of bivalent palladium in which the metal shows a co-ordination number of 6.

It follows, therefore, that bivalent nickel, zinc, platinum, and palladium give complex salts with triaminopropane in all of which the metal shows the unusual (and, for the last two metals, quite abnormal) co-ordination number of 6. In each case, the co-ordinated metal has electrons in excess of the number in the next inert gas—a condition normally causing considerable instability. Actually, all these salts possess great stability, due presumably to the very firm attachment of the triamine molecule around the 6-co-ordination octahedron, a factor outweighing the former in its effect on the stability of the complex salt.

Bivalent palladium also unites with the triamine to give *bis(triaminopropane-monothiocyanate)palladous dithiocyanate* (I), in which the metal has its normal co-ordination number of 4 and each molecule of the triamine is co-ordinated by only two of its three amino-groups, the third group being free to form a salt with further hydrogen thiocyanate. This compound is identical in type with the platinous salt already described (*loc. cit.*, p. 892), and its stereochemistry has been fully described.

(I.)





(II.)

Cadmium, however, does not behave like the above four bivalent metals, inasmuch as it, like bivalent copper, shows a co-ordination number of 4 in all its complex salts with triaminopropane. For instance, it forms a series of salts such as *tetrakistriaminopropanetriscadmium hexaiodide*, $[\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_4Cd_3]I_6$, identical in type with the cupric salts already described (J., 1926, 2682). These salts are unstable, and on being warmed with water readily lose part of the base to give very stable and slightly soluble salts such as *monoiodotriaminopropanecadmium monoiodide*,

$$[I\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}Cd]I.$$

The metal also gives salts such as *dithiocyanato(triaminopropane-monohydrochloride)cadmium* (II). This salt, like the corresponding platinous salt (J., 1928, 890), contains an asymmetric β-carbon atom, and should therefore be resolvable into optically active forms. Since it tends to lose hydrogen chloride, however, giving the very stable *monothiocyanatotriaminopropanecadmium monothio-*

cyanate, $[SCN\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}Cd]SCN$, its resolution was not attempted.

A further example of the stability of the complex salts of certain polyamines is furnished by ββ′β″-triaminotriethylamine, $N(C_2H_4{\cdot}NH_2)_3$. Mann and Pope showed (J., 1926, 482) that this tetramine combines with nickel salts to give tristriaminotriethylaminebisnickelous tetraiodide, $[\{N(C_2H_4{\cdot}NH_2)_3\}_3Ni_2]I_4$. Here, again, the nickel has a co-ordination number of 6, and an excess of 2 electrons, yet this salt and the corresponding tetrabromide are extremely stable and may be recrystallised repeatedly from boiling water without change.

EXPERIMENTAL.

In the following formulæ, the symbol "ptn" represents one molecule of αβγ-triaminopropane.

Bistriaminopropanezinc Iodide, $[Zn\,ptn_2]I_2$.—Triaminopropane trihydrochloride (6·6 g.; 3 mols.), dissolved in 15% sodium hydroxide solution (24 c.c.), is added with stirring to a solution of zinc nitrate (3 g.) in water (40 c.c.). The white precipitate which is first formed rapidly redissolves, and the clear solution is concentrated on the water-bath, chilled, and filtered. The addition of concentrated potassium iodide solution gives a crystalline precipitate, which, when recrystallised from water, gives the above *iodide* as fine white crystals; these have no melting point, but decompose slowly between 255° and 270° (Found: C, 14·6; H, 4·5; I, 50·6. $C_6H_{22}N_6I_2Zn$ requires C, 14·5; H, 4·4; I, 51·0%).

Bistriaminopropanepalladous Iodide, $[Pd\,ptn_2]I_2$.—A solution of ammonium chloropalladite (15 g.) in water (200 c.c.) is slowly added to a solution of triaminopropane trihydrochloride (34·5 g.; 3 mols.) in 15% sodium hydroxide solution (127 c.c.); the whitish-yellow precipitate produced rapidly redissolves. The clear solution is concentrated on the water-bath, much ammonia being given off, and is then chilled and treated with saturated potassium iodide solution, a fine white powder being steadily deposited: after 24 hours, this is collected, and recrystallised three times from hot water to eliminate traces of potassium iodide. The above *iodide* is thus obtained as a fine, white, crystalline powder, m. p. 230° (decomp.), freely soluble in cold water (Found: C, 13·3; H, 4·0; I, 46·9; Pd, 20·0. $C_6H_{22}N_6I_2Pd$ requires C, 13·3; H, 4·1; I, 47·1; Pd, 19·8%).

Bis(triaminopropane-monothiocyanate)palladous Dithiocyanate (I).—The clear concentrated solution obtained in the preparation of the above iodide is treated with a concentrated solution of potassium thiocyanate containing free acetic acid. A voluminous white precipitate slowly separates: this is recrystallised three times from hot water, the solid product being each time thoroughly drained by suction to remove the last trace of potassium thiocyanate solution, which is held very tenaciously by the crystalline substance. The *dithiocyanate* is obtained as a fine white crystalline powder, m. p. 166—168° (decomp.), freely soluble in water (Found: C, 22·9; H, 4·7; N, 27·3; Pd, 20·5; SCN, 44·5. $C_{10}H_{24}N_{10}S_4Pd$ requires C, 23·1; H, 4·7; N, 27·0; Pd, 20·6; 4SCN, 44·7%).

Tetrakistriaminopropanetriscadmium Hexaiodide, $[Cd_3\,ptn_4]I_6$.—A solution of hydrated cadmium chloride (4 g.) in water (20 c.c.) is slowly added to a solution of triaminopropane trihydrochloride (12 g.; 3 mols.) in 15% sodium hydroxide solution (44·4 c.c.). The white precipitate formed rapidly redissolves, and the clear solution, after 1 hour, is treated with saturated potassium iodide solution. The heavy white crystals which slowly separate are washed with much cold water and dried in a vacuum over sulphuric acid (Found: C, 9·9; H, 3·3; N, 11·6; I, 52·2. $C_{12}H_{44}N_{12}I_6Cd_3$ requires C, 9·9; H, 3·1; N, 11·6; I, 52·35%). The crystalline *hexaiodide* is only slightly soluble in cold water, in which it is quite stable: boiling water, however, converts it into the monoiodide described below.

The corresponding *hexabromide*, $[Cd_3\,ptn_4]Br_6,3H_2O$, is prepared by treating the clear solution, obtained in the preparation of the above hexaiodide, with saturated sodium bromide solution. The white crystals of the hexabromide separate very slowly in the course of several days: they are washed with cold water and dried (Found: N, 13·7; Br, 39·1. $C_{12}H_{44}N_{12}Br_6Cd_3,3H_2O$ requires N, 13·7; Br, 39·1%).

Monoiodotriaminopropanecadmium monoiodide, [I ptn Cd]I, is obtained by adding the above hexaiodide to much boiling water. The clear solution is rapidly filtered, and the monoiodide separates in large white crystals, m. p. 210—213°, only slightly soluble in boiling water (Found: C, 7·9; H, 2·5; N, 9·3; I, 55·8. $C_3H_{11}N_3I_2Cd$ requires C, 7·9; H, 2·4; N, 9·2; I, 55·7%).

Monobromotriaminopropanecadmium monobromide, [Br ptn Cd]Br, is obtained similarly by treating the hexabromide with boiling water, and separates as white crystals, m. p. 221—223° (decomp.) (Found: C, 9·9; H, 3·35; N, 11·6; Br, 44·3. $C_3H_{11}N_3Br_2Cd$ requires C, 10·0; H, 3·1; N, 11·6; Br, 44·2%).

Monothiocyanatotriaminopropanecadmium Monothiocyanate, [SCN ptn Cd]SCN.—If the clear solution obtained by treating the base with cadmium chloride (as in the preparation of the hexaiodide) is treated with potassium thiocyanate solution, no trace of a corresponding hexathiocyanate can be detected. The addition of the potassium salt gives a white precipitate, which dissolves readily in excess of thiocyanate. The clear solution obtained slowly deposits large white crystals of the above *monothiocyanate*: these are almost insoluble in cold water, and only slightly soluble in boiling water, from which they crystallise unchanged in composition, and of m. p. 201—202° (decomp.) (Found : for the crude material, N, 22·3; for the recrystallised material, N, 22·1; S, 20·1. $C_5H_{11}N_5S_2Cd$ requires N, 22·1; S, 20·2%). This compound is extremely stable, and in the estimation of sulphur by Carius's method the heating with nitric acid must be continued for 12 hours at 260° to ensure conversion of all the sulphur into sulphuric acid.

Dithiocyanato(triaminopropane-monohydrochloride)cadmium (II).—The clear solution obtained as before is treated with potassium thiocyanate solution containing free acetic acid. Large colourless crystals slowly separate: after 24 hours, these are collected and recrystallised twice from hot water. The *compound* is thus obtained as fine white crystals, m. p. 150—154° (decomp.), moderately easily soluble in water: if the hot aqueous solution is cooled too rapidly, the compound separates as an oil (Found : C, 17·0; H, 3·4; N, 19·9; SCN + Cl, 42·5. $C_5H_{12}N_5ClS_2Cd$ requires C, 17·0; H, 3·4; N, 19·8; 2SCN + Cl, 42·8%). The compound on exposure to air slowly loses hydrogen chloride, apparently with the formation of the monothiocyanate described above.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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