CCCLXXXVII.—*The Complex Salts of Nickel with Various Aliphatic Diamines.*

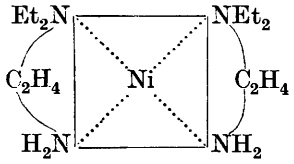
By FREDERICK GEORGE MANN.

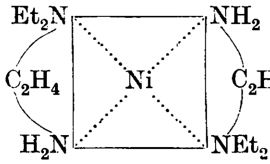
WERNER first suggested (*Z. anorg. Chem.*, 1893, **3**, 298) that when a metal shows a co-ordination number of 6, as in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$, the co-ordinated groups lie at the apices of a regular octahedron described around the metallic atom. The resolution into optically active forms of various complex salts of eight different metals (Co, Cr, Rh, Fe, Pt, Ir, Ru, and Al : also As), all having a co-ordination number of 6, leaves little doubt of the correctness of Werner's views.

Very great uncertainty still exists, however, with regard to the configuration of the complex salts of metals having a co-ordination number of 4, *e.g.*, tetramminonickelous chloride, $[Ni(NH_3)_4]Cl_2$. Biltz and Fetkenheuer (*Z. anorg. Chem.*, 1914, **89**, 121) claim to have prepared two distinct forms of the neutral non-ionic dichlorodiamminocobalt, $[Cl_2Co(NH_3)_2]$, and of the corresponding dibromo- and di-iodo-compounds, a result which would indicate that the four co-ordinated groups lie at the corners of a square with the metallic atom at the centre. This configuration would also explain the existence of two distinct forms of nickel iodate dihydrate, $[(H_2O)_2Ni(IO_3)_2]$ (Meusser, *Ber.*, 1901, **34**, 2438). Tschugaev (*Ber.*, 1906, **39**, 3192), however, failed to detect any similar *cis-trans*-isomerism in a series of salts such as bissuccinimidobismethylaminenickel, $[(C_4H_4O_2N)_2Ni(CH_3{\cdot}NH_2)_2]$. Moreover, the existence of the stable salts, $\beta\beta'\beta''$-triaminotriethylaminenickel thiocyanate, $[NiN(C_2H_4{\cdot}NH_2)_3](SCN)_2$, and $\gamma\gamma'\gamma''$-triaminotripropylaminenickel thiocyanate (Mann and Pope, J., 1926, 482, 489) is more easily explained by assuming that the four co-ordination valencies of the nickel atom are directed to the apices of a regular tetrahedron. Schlesinger (*Ber.*, 1925, **58**, 1877) found that copper, of co-ordination number 4, combines with certain bisimino-carboxylic acids to give compounds existing in two forms, and concludes that the copper complex has therefore the uniplanar configuration, a deduction opposed by Reihlen (*Z. anorg. Chem.*, 1926, **151**, 72), who considers the isomerism to be due to the presence of the two asymmetric nitrogen atoms in these compounds. Moreover, the recent resolution into optically active forms of 4-co-ordination derivatives of copper, zinc, and beryllium by Mills and Gotts (J., 1926, 3121) shows that such metallic complexes have the tetrahedral configuration, thus confirming the conclusions of Lowry and Burgess (J., 1924, **125**, 2081) with regard to the beryllium complex. On the other hand, the existence of two forms of many derivatives of bivalent platinum and palladium, *e.g.*, dichlorodiamminoplatinum, $[Cl_2Pt(NH_3)_2]$, led Werner (*loc. cit.*, p. 310) to consider that here the complex was uniplanar and the two forms *cis-trans*-isomerides. Reihlen and Nestle (*Annalen*, 1926, **447**, 211) consider these compounds to be merely polymeric forms having the tetrahedral configuration,* a conclusion opposed on experimental grounds by Grunberg (*Z. anorg. Chem.*, 1926, **157**, 299) and Hantzsch (*Ber.*, 1926, **59**, 2761). Finally, the uniplanar configuration has been given to the dimethyltelluronium dihalides by Vernon (J., 1920, **117**, 90) to explain the existence of two isomeric forms.

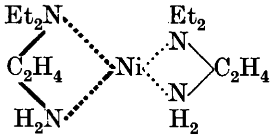
Attempts were therefore made to obtain more decisive evidence with regard to the configuration of the 4-co-ordination nickel complex by preparing certain complex salts which, if possessing the uniplanar configuration, should show *cis-trans*-isomerism, and, if possessing the tetrahedral configuration, should be resolvable into optically active forms. Nickel was first combined with β-aminotriethylamine to give *bis-β-aminotriethylaminenickelous thiocyanate*, $[Ni\{(C_2H_5)_2N\cdot C_2H_4\cdot NH_2\}_2](SCN)_2$. This compound, if possessing the uniplanar configuration, should exist in the *cis* (I*a*)

(I*a*.)





(I*b*.)



(II.)

and the *trans* (I*b*) form, whilst if possessing the tetrahedral configuration (II),† it should be resolvable into optically active forms owing to its dissymmetric nature. No evidence of *cis-trans*-isomerism could be detected in this compound, whilst the presence of the tertiary nitrogen atoms rendered the complex so unstable that attempts at resolution could not be completed.

In order to avoid the presence of tertiary nitrogen atoms, a new type of complex salt was prepared by co-ordinating nickel with β-bromo-αγ-diaminopropane to give *bis-β-bromo-αγ-diaminopropane-*

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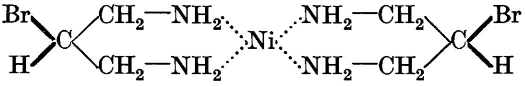
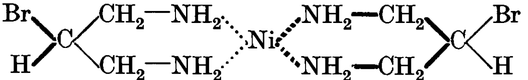
* Reihlen goes further and states (*Annalen*, 1926, **448**, 316) that all 4-co-ordination elements have the tetrahedral configuration.

† The thick bonds are in the plane of the paper, the thin ones at right angles to it.

nickelous thiocyanate, $[\{(NH_2{\cdot}CH_2)_2CHBr\}_2Ni](SCN)_2$. If this complex has the uniplanar configuration, the two co-ordinated ring systems lie in one plane, which is at right angles to that in which the terminal bromine and hydrogen atoms lie : the complex should therefore show *cis-trans*-isomerism according as the two bromine atoms are both on one side of the co-ordinated plane (III) or are on opposite sides, respectively. If, however, the complex has the


(III.)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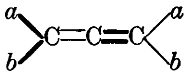
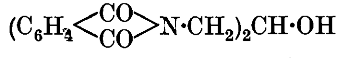

(V.)

tetrahedral configuration, the two ring systems are at right angles to each other (IV) : the complex thus possesses molecular dissymmetry, being structurally of the same type as the allene compounds (V), and should be resolvable into optically active forms. Here again, however, the highly crystalline dithiocyanate showed no signs of *cis-trans*-isomerism, whilst attempts at resolution failed because of the labile character of the bromine atoms; *e.g.*, the bis-β-bromo-αγ-diaminopropanenickelous thiocyanate in hot aqueous solution changed rapidly into the highly crystalline *bis-β-thiocyano-αγ-diaminopropanenickelous thiocyanate*,

$$[\{(NH_2{\cdot}CH_2)_2CH(SCN)\}_2Ni](SCN)_2.$$

Although this compound is of the required type for the purposes of this investigation, its low solubility in water made it unsuitable for use. Attempts were made to join a more stable group to the central carbon atom, and in particular to prepare αγ-diamino*iso*propyl methyl ether, $(NH_2{\cdot}CH_2)_2CH{\cdot}O{\cdot}CH_3$. αγ-Dichlorohydrin reacts readily with potassium phthalimide to give αγ-diphthalimido*iso*propyl alcohol,  $(C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH_2)_2CH{\cdot}OH$: the hydroxyl group is, however, so well protected (probably sterically) that it is extremely inert and could not be methylated. Dichlorohydrin was itself methylated to give dichloro*iso*propyl methyl ether (Hess and Fink, *Ber.*, 1915, **48**, 2003), but the chlorine atoms were now extremely inert and would not react with potassium phthalimide even when heated in a sealed tube at 180° for 4 hours.

Nickel was next combined with the easily obtained αγ-diamino*iso*propyl alcohol to give *bis-αγ-diamino-β-hydroxypropanenickelous thiocyanate*, $[\{(NH_2{\cdot}CH_2)_2CH{\cdot}OH\}_2Ni](SCN)_2$. Since, however, bivalent nickel may show a co-ordination number of 4 or of 6, it is difficult to decide whether in this compound the nickel has a co-ordination number of 4 and is combined solely with the four amino-groups, or of 6 and is combined with the four amino-groups and with the two hydroxyl groups. It was found, however, that the diamine co-ordinates with cobalt to give *dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic monochloride*,

$$[\{(NH_2{\cdot}CH_2)_2CH{\cdot}OH\}_2Co(OH)_2]Cl,$$

a compound in which the alcohol molecules must be co-ordinated by the amino-groups alone, and it was considered probable that the same held true of the above nickel compound, which should therefore be of the desired type. Again, however, no trace of *cis-trans*-isomerism was detected, and all attempts at resolution failed.

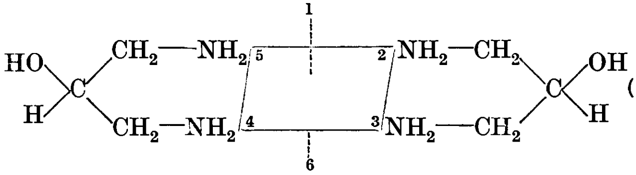
β-*Methyltrimethylenediamine* was now synthesised by converting β-methyltrimethylene dibromide into the corresponding *diphthalimido*-compound and hydrolysing it. The diamine was combined with nickel to give *bis-β-methyltrimethylenediaminenickelous thiocyanate*, $[\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2Ni](SCN)_2$. This compound, although highly crystalline, showed no evidence of *cis-trans*-isomerism, and all attempts at resolution again failed.

These repeated failures to resolve the nickel compounds may have been due either to the complex possessing the uniplanar configuration, or to the complex, if dissymmetric, undergoing such rapid racemisation that no evidence of resolution could be detected. The latter is presumably the reason for repeated failures in the past to resolve 6-co-ordination nickel derivatives, *e.g.*, trisethylenediaminenickel salts, and also tristriaminotriethylaminebisnickelous salts (Mann and Pope, *loc. cit.*, p. 486).

An interesting point arises here. It is well known that the complex compounds of nickel in which the metal has a co-ordination number of 4 are much more stable than those in which the co-ordination number is 6 : yet nickel will combine with three molecules of the simplest aliphatic diamines, *e.g.*, ethylenediamine and propylenediamine, to give compounds such as trisethylenediaminenickel chloride, $[Ni\,en_3]Cl_2$, which are sufficiently stable to be isolated and sometimes even recrystallised, in spite of the fact that the metal here has a co-ordination number of 6. Yet in the present investigation it was found that even if a nickel salt (nickel chloride in aqueous solution : nickel succinimide in alcoholic solution) was treated with a very large excess of the various diamines employed, *viz.*, β-aminotriethylamine, αγ-diamino*iso*propyl alcohol, and β-methyltrimethylenediamine, only two molecules of the diamine co-ordinated with the metal and no trace of a compound in which the metal had a co-ordination number of 6 could be isolated. Similarly *roseo*cobaltic chloride on treatment with a large excess of diamino*iso*propyl alcohol gave always dihydroxybisdiaminohydroxypropanecobaltic monochloride, and again no compound in which three molecules of the diamine co-ordinated with the cobalt atom could be prepared. Many similar instances have previously been recorded. Thus nickel combines with only two molecules of dimethylglyoxime, to give $[Ni(ON{:}CMe{\cdot}CMe{:}N{\cdot}OH)_2]$, and never with three molecules, whilst cobalt will give diamminobisdimethylglyoximecobaltic monochloride, $[(ON{:}CMe{\cdot}CMe{:}N{\cdot}OH)_2Co(NH_3)_2]Cl$, but will not combine with three molecules of the dioxime. Dicyanodiamidine gives diaquobisdicyanodiamidinenickel,

$$[\{NH_2{\cdot}(NH{:})C{\cdot}N{\cdot}CO{\cdot}NH_2\}_2Ni(H_2O)_2],$$

but the two molecules of water cannot be replaced by a third molecule of the diamidine. This inability of nickel * to combine with more than two molecules of any but the simplest double-bridging groups cannot be ascribed to the general instability of 6-co-ordination nickel compounds, since tristriaminotriethylaminebisnickelous tetraiodide is a very stable compound, in spite of the presence of two weakly co-ordinating aliphatic tertiary nitrogen atoms : it is more probably due to the difficult access of the third molecule of the diamine. Thus if, when nickel is treated with an excess of, *e.g.*, diamino*iso*propyl alcohol, two molecules of the diamine co-ordinate first to give a 4-co-ordination complex having the uniplanar configuration (VI), co-ordination of a third molecule of the diamine would involve bridging the potential 1 : 6-positions, which is structurally probably impossible. Similarly, with tervalent cobalt it is probable that the first two molecules of the diamine again occupy the 2 : 3- and 4 : 5-positions respectively; whence the distant 1- and 6-positions have to be occupied by simple unbridged groups as in dihydroxybisdiaminohydroxypropanecobaltic chloride and diamminobisdimethylglyoximecobaltic chloride.



(VI.)

Although the extreme difficulty of co-ordinating a third double-bridging group to the nickel atom can thus be explained on the assumption that the 4-co-ordination nickel complex has the uniplanar configuration, it is, on the other hand, significant that in the present investigation the five different complex salts showed no

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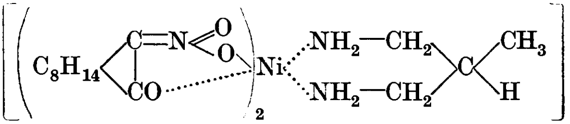
* Tervalent cobalt does not always share this inability : it will combine, *e.g.*, with 3 molecules of α-nitroso-β-naphthol (Morgan and Smith, J., 1921, **119**, 704).

evidence of *cis-trans*-isomerism, although all were highly crystalline compounds in which such isomerism should have been easily detected. The evidence for the configuration of the nickel complex thus remains conflicting.

A novel and apparently quite general reaction of 4-co-ordination nickel salts arose in the present investigation. Werner, in order to resolve certain complex salts of chromium (*Ber.*, 1912, **45**, 865), had recourse to crystallisation of the camphornitronates of the complex, prepared by simple double decomposition with the normal salts. Similar attempts were made with these nickel complex salts, since crystallisation of the camphorsulphonates had failed to effect resolution. When, however, bis-β-methyltrimethylenediaminenickelous nitrate is treated in cold aqueous solution with an excess of ammonium nitrocamphor, ammonia is at once liberated, the solution changes in colour from deep blue to green, and a rapid precipitation of the green, neutral, non-ionic *biscamphornitronate-β-methyltrimethylenediaminenickel* occurs, in accordance with the equation

$$[\mathrm{Ni}\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2](NO_3)_2 + 2C_{10}H_{14}O{\cdot}NO_2NH_4 = [(C_{10}H_{14}O{\cdot}NO_2)_2\mathrm{Ni}\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}] + CH_3{\cdot}CH(CH_2{\cdot}NH_2,HNO_3)_2 + 2NH_3.$$

A precisely similar reaction occurs with the corresponding compounds of β-aminotriethylamine and diamino*iso*propyl alcohol, thus providing further evidence that the latter diamine occupies only two co-ordination positions, *i.e.*, is co-ordinated by the amino-groups alone and not by the hydroxyl group. The three compounds so obtained are soluble in the usual organic liquids, but insoluble in water, a property common to many neutral, non-ionic co-ordination compounds. It is probable that in these compounds the ketonic group in the camphor molecule is also linked by a subsidiary valency to the nickel atom, which has therefore a co-ordination number of 6 (VII). In this case the complex as a whole becomes dissymmetric (in addition to the dissymmetric character of the constituent camphor residues) and the recrystallised compounds in solution might be expected to show mutarotation owing to slow racemisation of the complex itself. No such mutarotation was shown in chloroform solution, however, by the three compounds of this type available.



(VII.)

It is obvious that the new diamine, β-methyltrimethylenediamine, should prove extremely useful in the solution of various problems connected with the stereochemistry of complex salts. Its use will unfortunately be limited, because the preparation of β-methyltrimethylene dibromide is extremely slow and tedious and the yield of the diphthalimido-compound is very small owing to side reactions. The diamine, however, co-ordinates with bivalent platinum to give *bis-β-methyltrimethylenediamineplatinous chloride*, $[Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2]Cl_2$. This compound is now being further investigated, since the occurrence of *cis-trans*-isomerism or of optical activity would solve the vexed question of the configuration of the complex platinous salts.

EXPERIMENTAL.

All rotations given in this paper have been measured at 15° in a 4-dcm. polarimeter tube.

The Complex Salts of β-Aminotriethylamine.

β-*Aminotriethylamine*, $N(C_2H_5)_2\cdot CH_2\cdot CH_2\cdot NH_2$.—In view of the low solubility of phthal-β-bromoethylimide in diethylamine, Ristenpart's preparation of this base can with advantage be modified as follows : Phthal-β-bromoethylimide (23 g.), diethylamine (18·3 c.c.), and anhydrous xylene (50 c.c.) were confined in a round-bottomed bottle and heated at 100° for 10 hours, diethylamine hydrobromide slowly crystallising from the clear solution. The cold mixture was acidified with hydrochloric acid (1 : 1 by vol.), the xylene removed by steam distillation, and the residue hydrolysed by boiling under reflux, with the addition of fresh acid, for 3 hours. The product was then made alkaline and steam-distilled. The mixture of bases which separated when the distillate was saturated with potassium hydroxide was dried over fresh potash and then fractionally distilled. β-Aminotriethylamine was obtained as a colourless liquid, b. p. 144—146°.

Bis-β-aminotriethylaminenickelous Thiocyanate.—β-Aminotriethylamine (15·8 c.c.; 3 mols.) was added to a solution of nickel succinimide (15·0 g.) in hot absolute alcohol (500 c.c.), and the whole boiled under reflux for 4 hours. The cooled filtrate from the concentrated solution, when treated with an equal volume of a saturated alcoholic solution (90%) of potassium thiocyanate, yielded almost immediately the above *thiocyanate*, which, after 3 hours, was washed with water, alcohol, and ether (yield 10·4 g., *i.e.*, 68% calculated on the nickel taken). The yield was considerably decreased if the alcohol used in the preparation was not absolute, or if the above large excess of the amine was not employed. In spite of this excess, no compound in which the nickel had combined with more than two molecules of the amine could be isolated. The thiocyanate crystallised from absolute alcohol in lilac-blue needles, m. p. 213—214° (decomp.) after shrinking at 204° (Found: C, 41·5; H, 8·0; N, 20·7; Ni, 14·4. $C_{14}H_{32}N_6S_2Ni$ requires C, 41·3; H, 7·9; N, 20·65; Ni, 14·4%).

The *chloroplatinate*, $[\{N(C_2H_5)_2{\cdot}C_2H_4{\cdot}NH_2\}_2Ni]PtCl_6$, was precipitated on addition of a solution of the thiocyanate (0·5 g.) in acetone (35 c.c.) to a solution of sodium chloroplatinate (0·9 g.) in water (5 c.c.) and acetone (30 c.c.), and was obtained, after being washed with water, acetone and ether, as an apricot-coloured powder, insoluble in boiling water and alcohol. It darkens at 165—168° and shrinks to a plastic rod at 179—181° (Found: C, 20·4; H, 4·6. $C_{12}H_{32}N_4Cl_6NiPt$ requires C, 20·6; H, 4·6%).

Attempted Preparation of the d-*Camphor-β-sulphonate of the Complex.*—Hot solutions of bisaminotriethylaminenickelous thiocyanate (5 g.) in alcohol (300 c.c.) and of silver *d*-camphorsulphonate (8·3 g.) in alcohol (100 c.c.) were mixed, boiled for 5 minutes, and filtered. The fine, very pale blue, crystalline precipitate deposited on cooling was difficult to filter off and recrystallise. Eventually, 1 g. portions were dissolved in a little boiling absolute alcohol, and the solutions filtered quickly. The filtrates deposited very pale blue (almost white) crystals, m. p. 175—176°. This very pale blue colour is characteristic of many neutral non-ionic nickel complex salts, such as nickel succinimide, $[(H_2O)_2Ni(NC_4H_4O_2)_2]$: the camphorsulphonate, moreover, in alcoholic solution gave no precipitate with sodium chloroplatinate, although the chloroplatinate of the complex $[\{N(C_2H_5)_2{\cdot}C_2H_4{\cdot}NH_2\}_2Ni]''$ is insoluble in alcohol. It is probable, therefore, that the camphorsulphonate radicals had entered the complex, and the nickel had thus increased its co-ordination number to 6, giving the neutral non-ionic *bis*-d-*camphorsulphonatebisaminotriethylaminenickel*,

$$[(C_{10}H_{15}O{\cdot}SO_3)_2Ni\{N(C_2H_5)_2{\cdot}C_2H_4{\cdot}NH_2\}_2]$$

(Found: N, 7·4; S, 8·4; Ni, 7·45. $C_{32}H_{62}O_8N_4S_2Ni$ requires N, 7·4; S, 8·5; Ni, 7·8%).

The d-*α-bromocamphor-π-sulphonate* was obtained from the thiocyanate (5 g. in hot alcohol, 300 c.c.) and silver *d*-α-bromocamphor-π-sulphonate (10·7 g. in alcohol, 150 c.c.), the conditions and difficulties of the preparation being similar to those described above. Also, for reasons similar to those mentioned above, the very pale blue product, m. p. 165—168° (decomp.), probably has the constitution $[(C_{10}H_{14}BrO{\cdot}SO_3)_2Ni\{N(C_2H_5)_2{\cdot}C_2H_4{\cdot}NH_2\}_2]$ (Found: N, 5·9; Ni, 6·7, 6·65. $C_{32}H_{60}O_8N_4S_2Br_2Ni$ requires N, 6·15; Ni, 6·4%).

The alcoholic solution from which this compound originally separated was concentrated and cooled, and the precipitate of the nickel complex compound filtered off. The filtrate was evaporated to dryness, and the residue twice recrystallised from benzene, from which the d-*α-bromocamphorsulphonate* of *β-aminotriethylammonium hydroxide*, $(C_{10}H_{14}OBr{\cdot}SO_3H,NH_2{\cdot}C_2H_4){\cdot}NH(C_2H_5)_2{\cdot}OH$ separated in white crystals, m. p. 80—82° (Found: C, 43·5; H, 7·4; N, 6·5; Br, 17·9. $C_{16}H_{33}O_5N_2BrS$ requires C, 43·15; H, 7·5; N, 6·3; Br, 17·95%). The identity of this compound was confirmed by mixed melting-point determinations with the product obtained by treating bromocamphorsulphonic acid in alcoholic solution with an excess of the base, evaporating the solution to dryness, and recrystallising the residue from benzene. The presence of this compound in the original preparation shows that further decomposition of the complex occurs in hot alcoholic solution, the diamine being split off from the metal and becoming partially neutralised by the sulphonic acid.

Bis-d-*camphornitronateaminotriethylaminenickel*,
$[(C_{10}H_{14}O{\cdot}NO_2)_2NiN(C_2H_5)_2{\cdot}C_2H_4{\cdot}NH_2]$.
—Finely-powdered silver *d*-camphornitronate (4·5 g.) was added to a solution of bis-β-aminotriethylaminenickelous thiocyanate (3·0 g.) in boiling alcohol (300 c.c.). After being boiled for 10 minutes and filtered, the deep olive-green solution was evaporated under reduced pressure to small bulk, again filtered, and then diluted with a little hot water. The precipitate was recrystallised from hot aqueous alcohol (95%), and the product thus obtained in deep olive-green crystals, m. p. 258—260° (decomp.) after softening at 248° (Found: C, 54·9; H, 7·6; N, 9·8. $C_{26}H_{44}O_6N_4Ni$ requires C, 55·0; H, 7·8; N, 9·9%). A 0·212% solution in chloroform had $\alpha_{5461} + 2{\cdot}33°$, whence $[\alpha]_{5461} + 275°$, and $[M]_{5461} + 1560°$: this rotation remained unchanged for 20 hours.

The Complex Salts of β-Bromo-αγ-diaminopropane.

β-Bromo-αγ-diaminopropane, $(NH_2{\cdot}CH_2)_2CHBr$.—Gabriel's preparation of the dihydrobromide of this base (*Ber.*, 1889, **22**, 225) was modified as follows: A mixture of diphthalimido*iso*propyl alcohol (7·0 g.) and a saturated solution of hydrogen bromide in acetic acid (23 c.c.) was heated in a sealed tube at 100° for 30 hours with occasional shaking. After cooling, the precipitate was filtered off, washed with alcohol, and recrystallised from acetic acid, from which *αγ-diphthalimido*iso*propyl bromide* separated in colourless crystals, m. p. 196—198° (Found: N, 6·6; Br, 19·2. $C_{19}H_{13}O_4N_2Br$ requires N, 6·8; Br, 19·3%). This compound was boiled under reflux with hydrobromic acid of constant b. p., and the clear solution was chilled, filtered from phthalic acid, and evaporated until, on cooling, the dihydrobromide of β-bromo-αγ-diaminopropane crystallised. The latter, when washed with alcohol and dried, was pure.

Bis-β-bromo-αγ-diaminopropanenickelous Thiocyanate.—A solution of β-bromo-αγ-diaminopropane dihydrobromide (13·0 g.) in 15% aqueous sodium hydroxide (19·0 c.c.) was added to one of nickel succinimide (6·0 g.) in boiling alcohol (240 c.c.), the green colour of the nickel solution changing at once to blue. The solution was boiled for 15 minutes, filtered, reduced to small bulk, and treated with a saturated solution of potassium thiocyanate in 95% alcohol. The precipitate was filtered off after 2 hours and washed with water, alcohol and ether. The *thiocyanate* was thus obtained as a fine pink powder, m. p. 200—203° (decomp.) after shrinking and darkening at 160°. It is insoluble in all the usual organic liquids, and is decomposed by hot water (Found: C, 20·0; H, 3·8; Br, 33·2; Ni, 12·2. $C_8H_{18}N_6Br_2S_2Ni$ requires C, 20·0; H, 3·8; Br, 33·25; Ni, 12·2%). If this compound is kept in contact with the original solution for more than 2 hours, it becomes contaminated with deep blue crystals of *bis-β-thiocyano-αγ-diaminopropanenickelous thiocyanate*. The latter compound was obtained pure by boiling bis-β-bromo-αγ-diaminopropanenickelous thiocyanate with water, a deep blue solution being obtained. The concentrated solution on quick cooling gave a fine blue, crystalline powder, whilst the dilute solution on slow cooling gave deep blue, heavy prisms; both deposits, after being washed with water, alcohol and ether, had m. p. 247—248° (decomp.) (Found: C, 27·5, 27·6; H, 4·4, 4·3; S, 29·4; Ni, 13·4. $C_{10}H_{18}N_8S_4Ni$ requires C, 27·5; H, 4·15; S, 29·3; Ni, 13·4%).

αγ-Dichloro*iso*propyl methyl ether, $(CH_2Cl)_2CH{\cdot}O{\cdot}CH_3$, was obtained as a colourless liquid, b. p. 66·5—67°/24 mm., having a characteristic peppermint-like odour (Found: C, 33·5; H, 5·7. Calc. for $C_4H_8OCl_2$: C, 33·6; H, 5·6%). When it was heated with an excess of potassium phthalimide in a sealed tube at 180° for 4 hours, much remained unchanged and no diphthalimido-derivative could be isolated.

*The Complex Salts of αγ-Diamino*iso*propyl Alcohol.*

*αγ-Diamino*iso*propyl Alcohol Dihydrochloride,* $(CH_2{\cdot}NH_2,HCl)_2CH{\cdot}OH$. —Diphthalimido*iso*propyl alcohol, prepared by Gabriel's method (*Ber.*, 1889, **22**, 224), was boiled under reflux with concentrated hydrochloric acid; the clear solution obtained, when chilled, filtered, and evaporated, gave the pure crystalline dihydrochloride.

Dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic Monochloride.—A solution of diamino*iso*propyl alcohol dihydrochloride (12·2 g.; 2 mols.) in 10% aqueous sodium hydroxide (59 c.c.) was added to a mixture of *roseo*-cobaltic chloride (10 g.) and water (150 c.c.), and the whole heated under reflux on a water-bath for 3 hours, ammonia being freely evolved. The solution was then boiled for 30 minutes, filtered, and evaporated until crystals appeared. After cooling, the latter were collected and recrystallised from hot water, the *cobaltic monochloride* separating in dark red needles (Found: C, 23·6; H, 7·2; N, 17·9; Cl, 11·6. $C_6H_{22}O_4N_4ClCo$ requires C, 23·3; H, 7·2; N, 18·1; Cl, 11·5%). If the original solution was treated with potassium thiocyanate before the chloride started to crystallise, the corresponding *monothiocyanate* separated; after recrystallisation from water, it was obtained in fine, dark red crystals, decomp. 240—250° after shrinking at about 230° (Found: C, 25·2; H, 6·7; N, 21·0. $C_7H_{22}O_4N_5SCo$ requires C, 25·3; H, 6·7; N, 21·1%). A solution of the pure chloride, when treated with potassium iodide, gave the *monoiodide*, which also recrystallised from water in deep red leaflets (Found: C, 18·1; H, 5·5; I, 31·5. $C_6H_{22}O_4N_4ICo$ requires C, 18·0; H, 5·5; I, 31·7%).

Bis-αγ-diamino-β-hydroxypropanenickelous Thiocyanate.—A solution of diamino*iso*propyl alcohol dihydrochloride (17 g.) in water (50 c.c.) was treated with 10% aqueous sodium hydroxide (80·5 c.c.), and the whole added to a solution of hydrated nickel chloride (12 g.) in water (100 c.c.). The solution so obtained was heated under reflux on a water-bath for 4 hours, filtered, and concentrated. The addition of potassium thiocyanate solution gave the *thiocyanate* as a violet precipitate, which separated from hot water as a pale violet, crystalline powder, m. p. (to a clear blue liquid) 161—163° after shrinking at 105° (Found: C, 27·2; H, 5·6; N, 23·4; Ni, 16·7. $C_8H_{20}O_2N_6S_2Ni$ requires C, 27·1; H, 5·7; N, 23·7; Ni, 16·5%).

The original solution, when diluted with potassium iodide solution, slowly deposited the corresponding *di-iodide*, which separated from water, in which it was very soluble, in deep bluish-violet crystals, m. p. 239—242° (decomp.) (Found: C, 14·7; H, 4·1; I, 51·4. $C_6H_{20}O_2N_4I_2Ni$ requires C, 14·6; H, 4·1; I, 51·5%).

Bis-αγ-diamino-β-hydroxypropanenickelous d-*Camphor-β-sulphonate*, $[\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}_2Ni](C_{10}H_{15}O{\cdot}SO_3)_2$.—Hot aqueous solutions of the thiocyanate (10 g.) and of silver *d*-camphorsulphonate (19·2 g.) were mixed, boiled for 5 minutes, filtered, and evaporated to dryness. The powdered residue was recrystallised from alcohol (charcoal), and the d-*camphor-β-sulphonate* obtained in pale lilac-blue crystals (Found: N, 8·2, 8·1; Ni, 8·6. $C_{26}H_{50}O_{10}N_4S_2Ni$ requires N, 8·0; Ni, 8·4%).

This camphorsulphonate was recrystallised seven times from alcohol, and its rotation for the mercury violet line (the only light which would penetrate the deep violet solutions) was then compared with those of the actual specimens of highly purified zinc and magnesium dicamphorsulphonates which Graham (J., 1912, **101**, 746) had prepared for rotatory determinations. The following readings were all made at 15° in a 4-dcm. tube. $\lambda = 4062$; c = concentration of the solution in g./100 c.c.; A denotes $C_{10}H_{15}O{\cdot}SO_3$.

Substance.	c.	α.	$[\alpha]$.	$[M]$.
$[\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}_2Ni]A_2$ ...	1·7466	+ 3·60°	+ 51·5°	+ 361°
$MgA_2,6H_2O$	1·8824	+ 4·60	+ 61·1	+ 363
$ZnA_2,6H_2O$	1·8699	+ 4·25	+ 56·8	+ 361

These results show that the activity of the complex nickel salt is due solely to the camphorsulphonate radicals, and not to the complex itself. This was confirmed by reconverting the camphorsulphonate into the thiocyanate: the latter was inactive.

Bis-d-*camphornitronate*-$\alpha\gamma$-*diamino*-β-*hydroxypropanenickel*, $[(C_{10}H_{14}O{\cdot}NO_2)_2Ni\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}]$.—Hot aqueous solutions of the above thiocyanate and of silver nitrate (2 mols.) were mixed, boiled for 5 minutes, filtered, concentrated and chilled, a solution of the very soluble bis-$\alpha\gamma$-diamino-β-hydroxypropanenickelous nitrate being thus obtained. The addition of a concentrated cold aqueous solution of ammonium nitrocamphor (2·5 mols.) caused the violet colour to change immediately to green, and the solution, after 12 hours, deposited a fine, green precipitate. This, when dry, was soluble in nearly all the usual organic solvents: it was finally recrystallised from anhydrous benzene, from which *bis*-d-*camphornitronate*-$\alpha\gamma$-*diamino*-β-*hydroxypropanenickel* separated as a fine, olive-green powder with a molecule of benzene of crystallisation (Found: C, 56·5; H, 7·2; Ni, 9·3; C_6H_6, 12·3. $C_{29}H_{44}O_7N_4Ni$ requires C, 56·25; H, 7·2; Ni, 9·5; C_6H_6, 12·6%), which was lost in a vacuum at 80°, leaving the pure product as an olive-green powder; this shrank and blackened up to 210° (Found: C, 51·2; H, 7·0; Ni, 10·8. $C_{23}H_{38}O_7N_4Ni$ requires C, 51·0; H, 7·05; Ni, 10·85%). A 0·272% solution of the benzene-free material in chloroform had $\alpha_{5461} + 2{\cdot}89°$, whence $[\alpha]_{5461} + 266°$ and $[M]_{5461} + 1440°$. No change in rotation occurred during 20 hours.

The Complex Salts of β-*Methyltrimethylenediamine.*

$\alpha\gamma$-*Diphthalimido*-β-*methylpropane*, $CH_3{\cdot}CH(CH_2{\cdot}N{:}C_2O_2{:}C_6H_4)_2$.—A uniform mixture of potassium phthalimide (32 g.) and β-methyltrimethylene dibromide (Faworski, *Annalen*, 1907, **354**, 384) (10 c.c.) was heated at 175—180° for 6 hours. The cold product was pulverised and extracted twice with boiling carbon tetrachloride

(200 + 80 c.c.), giving 16 + 1·5 g. of the crude diphthalimido-compound and leaving a residue of potassium bromide and a small quantity of phthalimide. The phthalimido-compound was twice crystallised from boiling alcohol (400 c.c. each time), and *αγ-di-phthalimido-β-methylpropane* obtained in fine, white, crystalline scales, m. p. 169—171° (Found : C, 68·8; H, 4·8; N, 8·1. $C_{20}H_{16}O_4N_2$ requires C, 68·9; H, 4·6; N, 8·05%).

β-Methyltrimethylenediamine Dihydrochloride, $CH_3{\cdot}CH(CH_2{\cdot}NH_2,HCl)_2$.—αγ-Diphthalimido-β-methylpropane (12 g.) and concentrated hydrochloric acid (50 c.c.), heated in a sealed tube at 160° for 18 hours, the tube being inverted from time to time to mix the contents, gave a clear pale brown solution; this, when cold, was filtered from phthalic acid and concentrated. The *dihydrochloride* was now obtained in three successive crops by (*a*) crystallisation from the concentrated aqueous solution, (*b*) diluting the filtrate from the first crop with alcohol, and (*c*) further dilution with ether [Found : (*a*) Cl, 43·9, (*b*) C, 29·8; H, 8·7; Cl, 44·0, (*c*) Cl, 43·9. $C_4H_{14}N_2Cl_2$ requires C, 29·8; H, 8·8; Cl, 44·0%]. It separated in deliquescent, fine, white crystals, m. p. 195—197°, very soluble in water, but insoluble in alcohol and ether.

The *dihydrobromide* was similarly obtained by means of concentrated hydrobromic acid, and separated, when the final concentrated solution was diluted with alcohol, in colourless needles, m. p. 227—229° (decomp.) (Found : Br, 64·0. $C_4H_{14}N_2Br_2$ requires Br, 64·0%).

The *dibenzoyl* derivative, $CH_3{\cdot}CH(CH_2{\cdot}NHBz)_2$, prepared in the usual way, after crystallising twice from benzene and once from acetone, was obtained in fine, white crystals, which melted with effervescence at 92—93°, rapidly resolidified, and remelted at 136—138° (Found : C, 73·2; H, 6·85. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8%).

Bis-β-methyltrimethylenediaminenickelous Thiocyanate.—A mixture of a solution of β-methyltrimethylenediamine dihydrochloride (9·0 g.; 2·2 mols.) in 10% aqueous sodium hydroxide (20 c.c.) with a solution of nickel succinimide (10 g.) in boiling alcohol (300 c.c.) rapidly became blue. It was boiled under reflux for 1 hour, filtered from a small quantity of an apple-green precipitate, and concentrated. The cold solution, on treatment with a concentrated aqueous solution of potassium thiocyanate, rapidly gave a bluish-red precipitate of the thiocyanate of the nickel complex. The latter can be recrystallised quickly from hot water, but prolonged boiling causes the precipitation of a green sludge. After two recrystallisations, the *thiocyanate* was obtained in deep blue needles,

m. p. 226—228° (decomp.) (Found: C, 33·9; H, 6·9; N, 24·0. $C_{10}H_{24}N_6S_2Ni$ requires C, 34·2; H, 6·9; N, 23·9%).

Bis-β-methyltrimethylenediaminenickelous d-*Camphor-β-sulphonate*, $[Ni\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2](C_{10}H_{15}O{\cdot}SO_3)_2$.—Solutions of the above thiocyanate (6 g.) in hot water (120 c.c.) and of silver *d*-camphorsulphonate (11·8 g.) in water (100 c.c.) were slowly mixed and then boiled for 5 minutes. Filtration gave a clear blue solution which, when concentrated and chilled, furnished the d-*camphorsulphonate* in fine, lilac-blue scales. These were recrystallised twice from alcohol, and then had m. p. 287—288° (decomp.) (Found: C, 48·5; H, 7·7; N, 8·05; Ni, 8·4. $C_{28}H_{54}O_8N_4S_2Ni$ requires C, 48·2; H, 7·8; N, 8·0; Ni, 8·4%). This material was recrystallised seven times from alcohol, and so obtained as pale blue, minute crystals (Found: C, 48·3; H, 7·7%): a 1·098% aqueous solution had α_{4062} + 2·11°, whence $[\alpha]_{4062}$ + 48·0° and $[M]_{4062}$ + 335°. This sulphonate was reconverted in cold aqueous solution into the thiocyanate, which was inactive. A further preparation of the camphorsulphonate was recrystallised six times from water, and so obtained as the *monohydrate* (Found: C, 46·8; H, 8·2. $C_{28}H_{54}O_8N_4S_2Ni,H_2O$ requires C, 47·0; H, 7·9%): this, in 1·059% aqueous solution, had α_{4062} + 2·17°, whence $[\alpha]_{4062}$ + 51·2° and $[M]_{4062}$ + 366°, but once again furnished an inactive thiocyanate.

Bis-d-*camphornitronate-β-methyltrimethylenediaminenickel*, $[(C_{10}H_{14}O{\cdot}NO_2)_2Ni\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}]$.—A solution of the *d*-camphorsulphonate (5 g.) in water (50 c.c.) was treated with an excess of ammonium nitrocamphor (3·5 g.), also dissolved in water (25 c.c.). A green precipitate rapidly appeared, and the solution smelt strongly of ammonia. The precipitate was washed with water and recrystallised from alcohol, from which the *nitronate* separated in fine, olive-green crystals, m. p. 293—295° (decomp.) (Found: C, 53·4; H, 7·4; Ni, 10·8. $C_{24}H_{40}O_6N_4Ni$ requires C, 53·4; H, 7·5; Ni, 10·9%). A 0·273% solution in chloroform had α_{5461} + 3·52°, whence $[\alpha]_{5461}$ + 322° and $[M]_{5461}$ + 1736°: the activity remained unchanged for 24 hours. This compound is only slightly soluble in water, but is soluble in nearly all the usual organic solvents.

The Complex Salts of β-Methyltrimethylenediamine with Bivalent Platinum.—A solution of ammonium chloroplatinite (4 g.) in water (20 c.c.) was added to one of methyltrimethylenediamine dihydrochloride (5·4 g.; 3 mols.) in 10% aqueous sodium hydroxide (12·8 c.c.). A pale yellow precipitate slowly separated, and after 2 hours the mixture was heated under reflux on a water-bath for a further 8 hours, and then chilled. The precipitate was filtered off and recrystallised from hot water, from which *dichloro-β-methyltri-*

methylenediamineplatinum, $[Cl_2Pt\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}]$, separated in very pale yellow crystals, m. p. 273—276° (decomp.) (Found: C, 13·5; H, 3·45; Pt, 55·0. $C_4H_{12}N_2Cl_2Pt$ requires C, 13·5; H, 3·4; Pt, 55·1%). The original filtrate was now evaporated to about half its original volume, and on quick cooling, *bis-β-methyltrimethylenediamineplatinous chloride*, $[Pt\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2]Cl_2$, separated as a fine, white, crystalline powder, m. p. 266—267° (decomp.) after darkening at about 240° (Found: C, 21·4; H, 5·45; Pt, 44·2. $C_8H_{24}N_4Cl_2Pt$ requires C, 21·7; H, 5·5; Pt, 44·1%). The filtrate, on standing several days, deposited a mixture of colourless crystals of sodium chloride and very pale yellow crystals of the platinous dichloride compound. The latter could be very easily separated by hand, and no indication of *cis-trans*-isomeric forms could be detected.

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