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# CCLXXVI.—Researches on Residual Affinity and Coordination. Part XXV. A Quadridentate Group Contributing Four Associating Units to Metallic Complexes.

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FUNDAMENTAL advances were made in the experimental verification of the co-ordination theory when Werner showed that certain compounds and compound radicals were capable of furnishing two associating units to the co-ordination complex surrounding a metallic atom, for by means of such complexes he was able to identify the three-dimensional structure of many co-ordination compounds. Of chemical substances contributing two associating units the following may be cited : ethylenediamine,  $\alpha\alpha$ -dipyridyl, dimethyldithiolethylene, and tetramminodihydroxycobaltic bromide, (NH<sub>3</sub>)<sub>4</sub>Co(OH)<sub>2</sub>Br, the last of these being noteworthy owing to its completely inorganic character. There are also numerous complex radicals which function as two associating units : the carbonato-, malonato-, and oxalato-groups and the monoenolic radicals of acetvlacetone and its homologues, R·CO·CH:C(OH)R', R and R' being alkyl or aryl groups. To these compounds and compound radicals capable of occupying two positions in the co-ordination complex the generic name of chelate groups has been given (J., 1920, 117, 1457) because their tenacious grip of the implicated metallic atom leads to the formation of remarkably stable coordination complexes.

Werner also identified groups capable of treble attachment to metallic atoms, such tridentate residues containing three fused chelate groups. The tridentate groups recognised by Werner already contained, however, one metallic atom, so that on association of these tridentate groups with the co-ordinating nuclear atoms the complexes became binuclear, as, for instance, in the case of triamminocobaltic hydroxide,  $(NH_3)_3Co(OH)_3$ , identified in the complex cation of the salt in which the three hydroxyl groups

$$\left[ (\mathrm{NH}_3)_3\mathrm{Co} \begin{array}{c} \mathrm{OH} \\ \mathrm{OH} \\ \mathrm{OH} \\ \mathrm{OH} \end{array} \right] \mathrm{Br}_3$$

contribute simultaneously three units to the co-ordination numbers of each of two cobalt atoms.

Recently Pope and Mann have proved that  $\alpha\beta\gamma$ -triaminopropane,  $NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2$ , is capable of treble attachment to metallic atoms. Two molecular proportions of this triacidic base

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(tp) occupy six co-ordination positions round cobalt and rhodium atoms, forming the complex cations  $[Co tp_2]'''$  and  $[Rh tp_2]'''$ . This demonstration constitutes the first example of a tridentate non-metallic group in complexes containing a single nuclear atom (Compt. rend., 1924, **178**, 2085; Proc. Roy. Soc., 1925, **107**, 80).

We have now succeeded in identifying a group capable of quadruple attachment to metallic atoms, this being the first known case of a quadridentate group in co-ordination complexes. This quadridentate group is furnished by the bivalent radical of *ethylenediaminobisacetylacetone*,  $C_{12}H_{20}O_2N_2$ , a compound first prepared by Combes (*Compt. rend.*, 1889, **108**, 1252) on condensing two molecules of acetylacetone with one molecule of ethylenediamine with elimination of two mols. of water. Combes showed that this product is a dienolic diketone,

 $CH_3 \cdot C(OH): CH \cdot C(CH_3): N \cdot CH_2 \cdot CH_2 \cdot N: C(CH_3) \cdot CH: C(OH) \cdot CH_3$ , yielding a violet cupric salt containing one atomic proportion of copper to one molecular proportion of the dienolic radical.

In attempting to prepare an additive co-ordination compound of cupric acetylacetone and ethylenediamine we obtained accidentally the green monohydrate of Combes's violet salt, copper ethylenediaminobisacetylacetone, which separated from the indigo-blue solution of copper acetylacetone in ethylenediamine hydrate. This observation led to other experiments on Combes's ethylenediaminobisacetylacetone and particularly to the preparation of its *cobaltous* salt,\* a non-ionised complex which proved to be dihydrated, and,

$$\left[ (\mathbf{H_{2}O})_{2} \operatorname{Const}^{\mathrm{II}} \left( \mathbf{N}_{N} \right) \mathbf{C_{12}H_{18}} \right] \quad (\mathbf{I}.)$$

as the co-ordination number of bivalent cobalt is usually six, this composition suggested that the organic group might occupy four of the six co-ordination positions. Since, however, the co-ordination number of tervalent cobalt is invariably six, the oxidation of this cobaltous salt in the presence of ammonia should, on the foregoing supposition, lead to a cobaltammine containing two of ammonia and one molecular proportion of the supposed quadridentate group per cobaltic atom with a single univalent acidic ion outside the complex.

On reaction with ammonium chloride, excess of ammonia, and hydrogen peroxide, this supposition was verified, for the cobaltous salt yielded the anticipated cobaltammine readily and almost

<sup>\*</sup> The co-ordination compounds of ethylenediaminobisacetylacetone with several other bivalent metals have been investigated and will be discussed subsequently.

quantitatively. The chloride radical present was wholly ionised, immediately precipitable with silver nitrate, and yielded the less soluble *bromide*, *iodide*, *chlorate*, *perchlorate*, *nitrite*, *nitrate*, and d-*camphorsulphonate* (Reychler) by double decomposition with the sodium or potassium salts of the corresponding acids.

Excepting the chloride and *d*-camphorsulphonate, all the salts prepared were anhydrous when crystallised from water, thus confirming the view that the cobaltic co-ordination number of six is made up solely of two ammonia molecules and the organic radical. Hence this organic radical, which contributes four to the cobaltic co-ordination number, is actually a quadridentate group.

The univalent complex cobaltammine ion is thus demonstrated to have the following chemical constitution :



Five stereochemical arrangements of the groups present in this coordination complex are, however, possible, depending on the positions taken up on the octahedron by the ammonia molecules and by the bivalent quadridentate group,  $C_{12}H_{18}N_2O_2$  or

 $-\dot{O}\cdot C(CH_3):CH\cdot C(CH_3):N\cdot CH_2\cdot CH_2\cdot N:C(CH_3)\cdot CH:C(CH_3)\cdot O-$ . If the two ammonia molecules are in the antipodal *trans*-positions (Diagram 1) the quadridentate group must be wrapped equatorially round the octahedron. This configuration contains two planes of symmetry and the compound is optically inactive and irresolvable. If the two ammonia molecules are in contiguous *cis*-positions, then three associating units of the quadridentate group must occupy the corners of one triangular face of the octahedron with the fourth associating unit overlapping on to an adjacent face, and this arrangement can be made in four different ways, giving rise to four stereo-isomeric modifications. None of these four isomerides possesses a plane, a centre, or an alternating axis of symmetry and hence they are all optically active. Two of them are mirror images of the other two and the four isomerides comprise two enantiomorphous pairs.

Conclusive evidence has now been obtained that the product actually isolated contains two racemoid modifications which have been resolved into optically active forms by *d*-camphorsulphonic (Reychler) acid, and that all these active forms on keeping are spontaneously transformed into the single inactive and irresolvable form. The lack of optical activity in the last indicates that it is the *trans*-form (Diagram 1), in which the pair of ammonia molecules is in the *trans*-octahedral position. The active form with the low optical activity is in all probability the *cis-trans*-form (Diagram 2),

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in which only the dyad axis of symmetry of the *trans*-form is retained, the pair of ammonia molecules here being in the *cis*position while the pair of oxygen atoms is retained in the *trans*position. The active form with the very high activity may thus be regarded as the *cis*-form (Diagram 3), in which none of the elements of symmetry is retained, the pair of oxygen atoms as well as the pair of ammonia molecules being in *cis*-positions.



It has not been possible, however, to confirm these structures by chemical means, for the compounds are not decomposed by hot concentrated hydrochloric or hydrobromic acid to yield either the *cis* (violeo)- or *trans* (praseo)-dichlorodiamminoethylenediamminocobaltic halides which could be identified by their respective violet and green colours.

Whatever be the exact chemical structure of the organic group in the complex, the evidence is conclusive that it is a quadridentate group and moreover that it can be arranged spatially round the coordination sphere so as to yield the *cis*- and *trans*-configurations with respect to the ammonia molecules (Diagrams 1, 2 and 3). The tricyclic system of the three chelate components of the quadridentate group associated with the octahedral cobalt atom is shown in plan in Diagram 4; two of the rings are six-membered and one is fivemembered.



EXPERIMENTAL.

 $C_2H_4(N:C\cdot CH_3\cdot CH\cdot CO\cdot CH_3)_2 = ec$  (ethylenediaminobisacetyl-acetone).

Diaquocobaltous Ethylenediaminobisacetylacetone,  $[(H_2O)_2 \text{ ec Co}]$ (Formula I).—Hexa-aquocobaltous chloride (4·8 g. = 1 mol.) was dissolved in hot water (20 c.c.), and ethylenediaminobisacetylacetone (4·5 g. = 1 mol.) and 5N-sodium hydroxide (8 c.c. = 2 mols.) added, forming a green paste. On boiling, the mixture turned brownishyellow and a reddish-orange, crystalline precipitate separated. After washing with water and air-drying, bright orange-red prisms were obtained in yield varying from 85 to 45%, the higher yields being obtained with exclusion of air during the reaction (Found : Co, 18·7.  $C_{12}H_{22}O_4N_2Co$  requires Co, 18·6%). The compound was insoluble in water and readily dissolved in most organic solvents to orange solutions which darkened in air owing to oxidation. It readily dissolved in dilute mineral acids with complete decomposition into acetylacetone and cobaltous and ethylenediamine salts.

Diamminoethylenediaminobisacetylacetonocobaltic Chloride Dihydrate,  $[(NH_3)_2Coec]Cl(H_2O)_2$ .—This salt was readily obtained in 83% yield on oxidation of the foregoing cobaltous salt by the calculated amount of 6N-hydrogen peroxide in the presence of excess of 18N-ammonia and ammonium chloride. The salt separated from the cooled mixture in pale fawn needles which were recrystallised from hot water, washed with alcohol, and air dried [Found : Co, 15·2; N (as NH<sub>3</sub>), 7·35; H<sub>2</sub>O, 8·1. C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>N<sub>4</sub>ClCo requires Co, 15·3; N (as NH<sub>3</sub>), 7·25; 2H<sub>2</sub>O, 9·3%).

This feebly coloured cobaltic salt was moderately soluble in water to a brownish-red, neutral solution, from which silver nitrate solution immediately precipitated silver chloride. Concentrated solutions of the appropriate sodium or potassium salts precipitated

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the bromide, iodide, nitrite, nitrate, chlorate, perchlorate, and *d*-camphorsulphonate of the complex base from concentrated solutions of the chloride. The chloride dissolved in boiling concentrated hydrochloric or hydrobromic acid solutions, but was not decomposed. It dissolved in boiling caustic soda solution, evolving ammonia and forming a clear reddish-brown solution which appeared to contain the complex diaquo-base. The chloride was quite insoluble in all organic solvents.

The following salts were prepared in quantitative yield by precipitation from concentrated solutions of the chloride by concentrated solutions of the appropriate alkali salt. All except the *d*-camphorsulphonate (Reychler) were very sparingly soluble in water and were precipitated as fine, yellowish-brown needles, which were washed with water and alcohol and air-dried. The camphorsulphonate, which is moderately soluble in water and in moist alcohol, was recrystallised from water and washed with acetone and ether and air-dried.

Bromide,  $[(NH_3)_2 \text{ ec Co}]Br$ . Found : Co, 14.7;  $H_2O$  at 100°, nil.  $C_{12}H_{24}O_2N_4BrCo$  requires Co, 14.9%.

Iodide,  $[(NH_3)_2 \text{ ec Co}]I$ . Found : Co, 13.4; N (as NH<sub>3</sub>), 6.4; H<sub>2</sub>O at 100°, nil. C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>ICo requires Co, 13.4; N (as NH<sub>3</sub>), 6.3%.

*Nitrate*,  $[(NH_3)_2 \text{ ec Co}]NO_3$ . Found : Co, 15.7; H<sub>2</sub>O at 100°, nil. C<sub>12</sub>H<sub>24</sub>O<sub>5</sub>N<sub>5</sub>Co requires Co, 15.7%).

Chlorate,  $[(NH_3)_2 \text{ ec Co}]ClO_3$ . Found : Co, 14.8; H<sub>2</sub>O at 100°, nil. C<sub>12</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub>ClCo requires Co, 14.8%.

Perchlorate,  $[(NH_3)_2 \text{ ec Co}]ClO_4$ . Found : Co, 14.2; H<sub>2</sub>O at 100°, nil. C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>N<sub>4</sub>ClCo requires Co, 14.2%.

d-Camphorsulphonate,  $[(NH_3)_2 \text{ ec Co}]C_{10}H_{15}O_4S, H_2O$ . Found : Co, 10.6;  $H_2O$  at 100°, 3.1.  $C_{22}H_{41}O_7N_4SCo$  requires Co, 10.6;  $H_2O$ , 3.2%.

Resolution of the Racemoid Mixture.—Aqueous solutions of the salts were transparent only in the darker red of the spectrum, and the light of the lithium line 6708 Å. ( $10^{-8}$  cm.) was used throughout the polarimetric measurements. Owing to the intensity of colour, solutions stronger than about 1% of the camphorsulphonates and 0.5% of the bromides in 0.5-dcm. tubes could not be used.

cis-dextro-Bromide.—On mixing saturated solutions of the complex chloride and the sodium salt of *d*-camphorsulphonic (Reychler) acid, fine, pale fawn needles of the *d*-camphorsulphonate separated, isolated in six crops, which were washed with acetone and ether and air-dried. The first crop was found to be strongly dextrorotatory. The second crop was redissolved in water and decomposed with a solution of potassium bromide, the complex bromide immediately separating in fine, fawn needles, which were washed with alcohol and ether and air-dried (Found : Co, 14.7%). This bromide was indistinguishable in appearance and general properties from the racemoid bromide, but was strongly dextrorotatory,  $[\alpha]_{\text{Li}} = +$  $452^{\circ}$ ,  $[M] = + 1784^{\circ}$ . Owing to the evanescent nature of this optical activity it was very fortunate that the specimens were submitted to independent observers.\*

cis-trans-dextro-dextro-Camphorsulphonate.—The third crop from the above resolution had  $[\alpha]_{\text{Li}} = +36^{\circ}$ ,  $[M] = +202\cdot0^{\circ}$ , and deducting  $+51\cdot7^{\circ}$  for the *d*-camphorsulphonate ion, [M] = + $150\cdot3^{\circ}$  for the cobaltic ion (Found : Co,  $19\cdot6^{\circ}_{0}$ ). Subsequent crops possessed successively diminishing activities. Recrystallisation of the crops failed to raise the activity for the cobaltic ion above  $[M] = +150^{\circ}$ , and the most soluble crops invariably had a strong lavorotation. The highest lavorotation ever observed was [M] $= -108^{\circ}$  for the cobaltic ion.

cis-trans-dextro-Bromide.—The corresponding cis-trans-d-dcamphorsulphonate was decomposed with potassium bromide solution, and the bromide isolated as in the case of the cis-bromide (Found: Co,  $14\cdot8\%$ ).  $[\alpha]_{\text{Li}} = +40^{\circ}$ ,  $[M] = +158^{\circ}$ . This cistrans-bromide alone was invariably obtained after the first preparation, and was indistinguishable, except for optical activity, from the racemoid bromide.

Inactive (or trans) Bromide.—The foregoing optically active salts, on keeping a few days, were found to be completely inactive, the camphorsulphonates having only the activity due to the camphorsulphonate ion, and being irresolvable. Once these inactive salts had been identified, it was found impossible to prepare active salts again. Numerous preparations were performed at ordinary and low temperatures, in sunlight and in darkness, and even in new apparatus in a different building, but optically active salts were never again obtainable. A specimen of the first preparation, which had originally yielded both the *cis*- and the *cis-trans*bromides, was found to be quite irresolvable after 10 days. We

<sup>\*</sup> A specimen of the racemoid bromide (S. 2) and of the *cis*-bromide (S. 1) was submitted to Mr. C. E. Wood for polarimetric examination without informing him which or if either of the specimens was optically active. His report is as follows: S. 1.—Weight, 0.0664 g., dissolved in 12.5 c.c. of water and examined in 0.5-dcm. tube with light of lithium line 6708 Å.,  $[\alpha]_{Li} = +531^{\circ}$ ,  $[M] = +2097 \cdot 4^{\circ}$ . S. 2.—Weight, 0.0666 g., dissolved in 12.5 c.c. of water of water and examined in 0.5 dcm. tube—inactive.—C. E. W.

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are unable to assign the precise cause of the inability to obtain active salts after the first ten or so preparations, but it is worthy of remark that active salts could not be obtained after the inactive salts had been brought into existence, pointing to the probability that the result is due to infection. This possibility is not wholly ruled out by preparation in new apparatus in a different building, because the inactive salt may have been a partial product only in later preparations and the active salts simultaneously formed thus infected at the moment of coming into existence. Found for the inactive *bromide*: Co, 14.8%. The inactive bromide was indistinguishable in appearance and general properties from the racemoid and active bromides.

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