113. *The Interactions of Cobalt Chloride and Ethylenediamine.*

By H. D. K. Drew and N. H. Pratt.

An aqueous solution containing cobalt chloride and ethylenediamine in molecular proportion, when kept in a limited supply of air, deposited minute pink crystals containing both cobaltic and cobaltous cobalt; the mother-liquor, on slow evaporation, yielded the purplish *cis*-compound (I), and other products. The pink substance proved to be trans-*hydroxoaquobisethylenediaminocobaltic cobaltochloride* (II), which appears to be the only known example of this type. The structure of (II) was determined by conversion into the brownish-pink trans-*plato-salt* (III) by means of potassium chloroplatinite, and then, by double decomposition with tetramminoplatinous chloride, into the reddish *trans*-chloride (IV), together with the insoluble green salt of Magnus. The chloride (IV) was recognised as the *trans*-compound by its properties (Werner, *Ber.*, 1907, **40**, 272); and reconversion of (IV) into (III) showed, as would be anticipated, that change of configuration had not taken place.

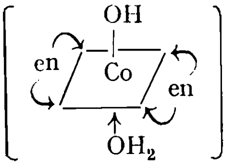
The action of dilute hydrochloric acid on (II) gave dark green trans-*dichlorobisethylenediaminocobaltic cobaltochloride monohydrate* (V), which with potassium chloroplatinite gave the green *trans*-plato-salt (VI) of Jörgensen (*J. pr. chem.*, 1890, **41**, 440). With less dilute hydrochloric acid, (II) gave bluish-green trans-*trichloroethylenediaminocobaltiethylenediamine hydrochloride*, (VII), a dihydrated form of which has been described by Jörgensen (*ibid.*, 1889, **39**, 24), although we have not been able to obtain it; (VII) readily lost hydrogen chloride to give Jörgensen's light green *trans*-salt (VIII), which with potassium chloroplatinite yielded (VI) (see Werner, *Ber.*, 1901, **34**, 1705). It follows that both (V) and (VII) belong to the *trans*-(praseo)series and that the action of hydrochloric acid on

(II) is configuratively normal. It is evident also that the hydrochloride (VII), for which a structural formula has not hitherto been proposed, must be constituted as shown, with

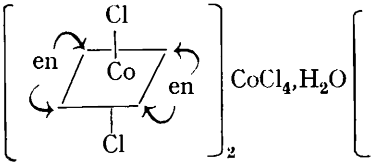
$[CoCl_2en_2]Cl$ (I.)

$[Co(H_2O)(OH)en_2]PtCl_4$ (III.)

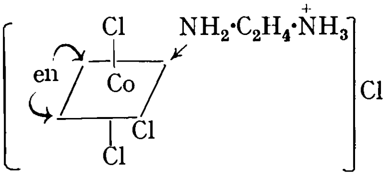
$[Co(H_2O)(OH)en_2]Cl_2$ (IV.)



(II.)



(V.)



(VII.)

$[CoCl_2en_2]_2PtCl_4$ (VI.)

$[CoCl_2en_2]Cl$ (VIII.)

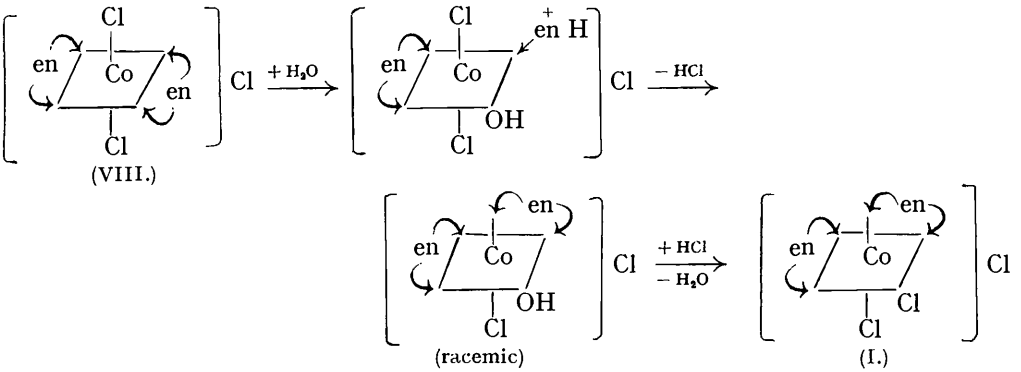
$[CoCl(NH_3)en_2]Cl_2$ (IX.)

the free positive charge located upon an opened ethylenediamino-loop of (VIII). This is in agreement with the results previously obtained in the opening of chelate loops attached to platinum (Drew and Tress, J., 1932, 2328; 1933, 1335).

The reconversion of (V) into (II) was effected by treatment with a very little alkali, and that of (VIII) into (II) by the same means in presence of aqueous cobalt chloride. The removal of chlorine by alkali in the above reactions is thus again configuratively normal.

The configuration of (V) was further confirmed by transforming it, by means of nitric acid, into the green *trans*-nitrate, $[CoCl_2en_2]NO_3$, identical with that obtained from (VIII) (Jörgensen, *J. pr. Chem.*, 1889, **39**, 23). When (V) was treated with a small excess of ammonia, however, it gave the *cis*-chloride (IX), which is red and forms a red plato-salt; this substance was recognised as the *cis*-form by transformation into the dithionate, $[CoCl(NH_3)en_2]S_2O_6$ (Werner, *Annalen*, 1912, **386**, 165). The action of ammonia upon (V) is therefore configuratively abnormal, as is the case also with (VIII) (Werner, *loc. cit.*, p. 58).

Jörgensen's remarkable transformation (*J. pr. Chem.*, 1889, **39**, 16) of the praseo (*trans*)-chloride (VIII) into the violeo (*cis*)-isomeride (I), by evaporation with water at 100°, was confirmed; the change is never quite complete, and moreover, it is not effected by slow evaporation at laboratory temperature. No explanation of the change has yet been given; the following scheme is suggested by the present experiments:



(VIII.)

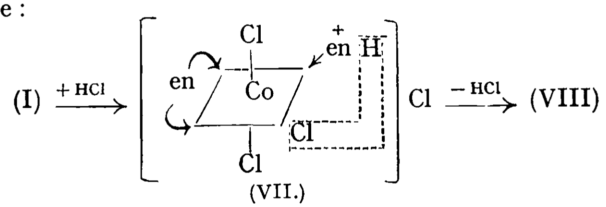
(racemic)

(I.)

It will be seen that the elimination of hydrogen chloride could involve either of two similarly situated chlorine atoms in the kation of the second formula, giving enantiomorphous products, the final product (I) being therefore racemic.

The reverse transformation of the violeo- into the praseo-chloride (Jörgensen, *ibid.*, 1890, **41**, 449) by evaporation with dilute hydrochloric acid was likewise confirmed. The plato-salts (green and purple, respectively) of the two chlorides were shown to be isomeric.

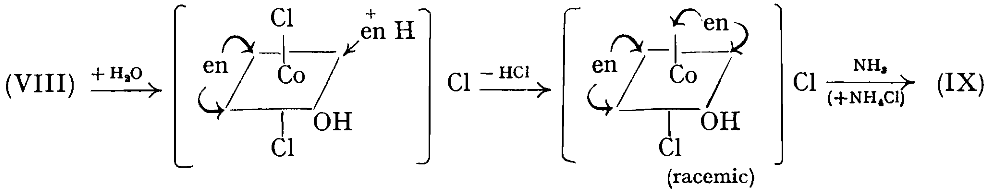
Here the formation of the hydrochloride (VII), which is known to condense to (VIII), explains the change :



(VII.)

In the case of either of the enantiomorphous *cis*-chlorides, (I), the chelate loop must open at a nitrogen atom in the *cis*-position with respect to both nitrogens of the unopened loop.

In accord with the foregoing, the following scheme explains why the replacement of halogen by ammonia, through the action of aqueous ammonia upon (VIII), or upon (V), is configuratively abnormal :



The last stage represents a displacement of hydroxyl by ammonia.

In other cases in which ammonia is known to bring about a change of configuration in a cobaltic salt, the application of this mechanism leads to the observed result without ambiguity at any stage, as may be seen in the following :

trans-$[\mathrm{CoCl(NH_3)en_2}]\mathrm{Cl_2} \longrightarrow$ *cis*-$[\mathrm{Co(NH_3)_2en_2}]\mathrm{Cl_3}$;

cis-$[\mathrm{Co(NO_3)(NH_3)en_2}](\mathrm{NO_3})_2 \longrightarrow$ *trans*-$[\mathrm{Co(NH_3)_2en_2}](\mathrm{NO_3})_3$.

Where, as in the case of *cis*- or *trans*-$[\mathrm{CoCl(SCN)en_2}]\mathrm{Cl}$, the configuration of the product depends upon the experimental conditions, a second mechanism (probably that of direct replacement of halogen by ammonia) may be assumed to accompany the suggested mode of reaction.

Kurnakow (*Z. anorg. Chem.*, 1898, **17**, 223) combined cobalt chloride with the yellowish-brown salt $[\mathrm{Co\,en_3}]\mathrm{Cl_3,3H_2O}$ by evaporating an aqueous solution at 100°, and obtained dark green needles of the dihydrate (X). In our hands, his procedure invariably gave yellowish-green needles of the trihydrate (or, less probably, the tetrahydrate) (XI), which had the properties of a compound formulated by Werner (*ibid.*, 1900, **22**, 155) as $[\mathrm{Co\,en_3Cl_3}]_2\mathrm{CoCl_2,4H_2O}$; on one occasion only we obtained Kurnakow's compound by acidifying the solution with hydrochloric acid. These substances (X) and (XI), which are at once decomposed by water, are evidently assemblages of ions; their structures may be expressed, respectively, as (X*a*) (compare the case of $\mathrm{Cs_3CoCl_5}$; Powell and Wells, J., 1935, 359) and (XI*a*). The blue ethylenediammonium salt of Kurnakow (*loc. cit.*, p. 215), of composition $\mathrm{CoCl_2,en_2,4HCl}$, likewise unstable to water, probably has the structure $[\mathrm{en\,H_2}]_2\mathrm{CoCl_6}$, as written by Meyer and Hoehne (*Z. anorg. Chem.*, 1935, **222**, 163). On treating it with cobalt chloride in boiling hydrochloric acid, we obtained light blue crystals of an *octachloride* of composition $(\mathrm{en\,2HCl})_3\mathrm{CoCl_2}$, which might be formulated as (XII) but for the lack of independent evidence of a co-ordination number of 8 for cobalt (compare Clément and Duval, *Compt. rend.*, 1935, **200**, 399). We have not been able to repeat the preparation of (XII). In several preparations of this series, very slight variations in the conditions lead to failure.

$\mathrm{CoCl_3\,en_3,CoCl_2,2H_2O}$ (X.)

$\mathrm{2CoCl_3\,en_3,CoCl_2,3H_2O}$ (XI.)

$[\mathrm{en\,H_2}]_3\mathrm{CoCl_8}$ (XII.)

$[\mathrm{Co\,en_3}]\genfrac{}{}{0pt}{}{\mathrm{CoCl_4}}{\mathrm{Cl}}$ (X*a*.)

$[\mathrm{Co\,en_3}]_2\genfrac{}{}{0pt}{}{\mathrm{CoCl_6}}{\mathrm{Cl_2}}$ or $[\mathrm{Co\,en_3}]_2\genfrac{}{}{0pt}{}{\mathrm{CoCl_4}}{\mathrm{Cl_4}}$ (XI*a*.)

EXPERIMENTAL.

trans-*Hydroxoaquobisethylenediaminocobaltic cobaltochloride* (II) was prepared by gradually adding ethylenediamine (5 g.) to an ice-cold solution of hydrated cobalt chloride (19·8 g.) in water (50 c.c.), with constant stirring. The red-brown solution was left (1—2 days) in a stoppered vessel. The pink precipitate (1·5—2 g.) was filtered off (filtrate A), washed with water, alcohol, and ether, and dried over calcium chloride (Found: C, 11·7, 11·8; H, 5·2, 5·1; N, 13·6; Co, 28·2, 28·4. $C_4H_{19}O_2N_4Cl_4Co_2$ requires C, 11·6; H, 4·6; N, 13·5; Co, 28·4%). The substance formed minute transparent red rods, sparingly soluble in cold water but readily soluble in hot, and insoluble in alcohol. It was slowly decomposed by boiling water. The water molecule was not lost at 120°, but at 150° decomposition set in. Hydrogen peroxide oxidised the compound in the cold. It formed a brownish-pink trans-*plato-salt* (III) (Found: C, 8·6, 8·9; H, 3·8, 4·1; N, 10·4, 10·5. $C_4H_{19}O_2N_4Cl_4CoPt$ requires C, 8·7; H, 3·45; N, 10·2%). The plato-salt, ground with an equivalent aqueous solution of $[Pt(NH_3)_4]Cl_2$, gave Magnus's salt, which was filtered off, and a deep red solution which, on being allowed to evaporate, yielded red leaf-like crystals, with a bluish tinge, of the chloride (IV) (Found: C, 17·1; H, 6·6; N, 19·8; Co, 21·0. Calc.: C, 16·8; H, 6·7; N, 19·2; Co, 20·7%).

trans-*Dichlorobisethylenediaminocobaltic cobaltochloride monohydrate* (V) was prepared: (1) by treating the filtrate A (foregoing preparation) with an equal volume of concentrated hydrochloric acid, and evaporating the deep red liquid to about one-third of its volume; the resulting bluish-green liquid deposited dark green spangles, which were washed with concentrated hydrochloric acid, alcohol, and ether, and dried over phosphoric oxide; the compound may be recrystallised from 16% hydrochloric acid; (2) by evaporating a solution of (II) in 16% hydrochloric acid to crystallisation. The compound (Found: C, 13·3, 13·5; H, 5·1, 5·1; N, 15·4, 15·7; Co, 24·5, 24·6. $C_8H_{34}ON_8Cl_8Co_3$ requires C, 13·3; H, 4·7; N, 15·6; Co, 24·6%) was very soluble in water to a green neutral solution, becoming violet and then red on boiling; it was insoluble in alcohol. Addition of a little concentrated nitric acid to the aqueous solution precipitated light green crystals of the corresponding nitrate (Found: C, 15·55, 15·2; H, 5·6, 5·2; N, 22·6; Co, 18·9, 18·8. Calc.: C, 15·4; H, 5·1; N, 22·4; Co, 18·9%), the aqueous solution of which gave no precipitate with silver nitrate unless first boiled (whereupon it became red). Compound (V) formed the plato-salt (VI), dark green prisms (Found: C, 11·5, 11·7; H, 4·0, 3·9; N, 13·4. Calc.: C, 11·5; H, 3·8; N, 13·4%), which was also obtained from the above nitrate (Found: C, 11·6; H, 4·1; N, 13·4%). When the plato-salt was warmed with concentrated hydrochloric acid, it decomposed, giving yellow prisms of ethylenediammonium chloroplatinate, $(en\,H_2)PtCl_6$ (Found: C, 5·3; H, 2·4; N, 6·0; Pt, 41·2. Calc.: C, 5·1; H, 2·5; N, 5·9; Pt, 41·3%), described by Schacht (*Arch. Pharm.*, 1897, **235**, 459).

trans-*Trichloroethylenediaminocobaltiethylenediamine hydrochloride* (VII) was prepared by allowing the deep bluish-green solution of (II), or of (V), in concentrated hydrochloric acid to stand (1 or 2 days); the green rhombic plates which separated were washed with concentrated hydrochloric acid and dried over sulphuric acid (Found: C, 14·7; H, 5·5; N, 17·2; Co, 18·1. $C_4H_{17}N_4Cl_4Co$ requires C, 14·9; H, 5·3; N, 17·4; Co, 18·3%). The compound lost hydrogen chloride readily in air; its green solution in water was strongly acid. Attempts to repeat Jörgensen's method of preparation (*J. pr. Chem.*, 1889, **39**, 24) gave only ethylenediamine dihydrochloride and bisethylenediammonium cobalt chloride. When (VII) was powdered and heated at 100° (2 hours), it gave the *trans*-chloride (VIII); this formed green prisms from water (Found: C, 16·8; H, 5·9; N, 19·9; Co, 20·6. Calc.: C, 16·7; H, 5·6; N, 19·65; Co, 20·7%), and afforded the green plato-salt (VI) (Found: C, 11·6; H, 4·2; N, 13·7. Calc.: C, 11·5; H, 3·8; N, 13·4%). Aqueous solutions of (V) or (VIII), treated with ammonia until the green colour just became red, and then concentrated, gave red crystals of *cis*-chloroamminobisethylenediaminocobaltic chloride (IX) (Found: C, 15·8; H, 6·6; N, 22·9; Cl, 34·9; Co, 19·5. Calc.: C, 15·9; H, 6·3; N, 23·1; Cl, 35·2; Co, 19·5%); conversion of this into the dithionate by means of sodium dithionate yielded compact red prisms, distinct from the long needles of the *trans*-isomeride; the plato-salt of (IX) formed red cubes (Found: N, 12·5. Calc.: N, 12·3%).

Conversion of trans-*Dichlorobisethylenediaminocobaltic Chloride into its* cis-*Isomeride.*—The aqueous solution of the *trans*-chloride, evaporated to dryness on a water-bath, gave the *cis*-chloride (I), mixed with a little of the unchanged material. Repeated redissolution in water and evaporation failed to remove it, showing that the change is never completed. However, washing on a filter with a little water readily removed the more soluble praseo-salt. After being washed with water and alcohol and dried over phosphoric oxide, the violeo-salt appeared to retain $\frac{1}{2}H_2O$ (Found: C, 16·2; H, 6·3; N, 19·2; Cl, 35·8; Co, 20·0, 20·1. Calc. for $C_4H_{16}N_4Cl_3Co,\frac{1}{2}H_2O$: C, 16·3; H, 5·8; N, 19·0; Cl, 36·2; Co, 20·0%). Evaporation of the violeo-chloride with dilute hydrochloric acid changed it almost completely into the anhydrous praseo-isomeride (Found: Co, 20·6%). The violeo-chloride was obtained also by allowing the filtrate in the preparation of (II) to evaporate slowly, small quantities of (II), (V), tris-ethylenediaminocobaltic chloride (XIII), and (XI) being removed, until the purplish-red hexagonal prisms of (I) separated; the crystals were violet when powdered. The plato-salt of (I) formed purple octahedra (Found: C, 11·6; H, 4·3; N, 13·5. Calc.: C, 11·5; H, 3·8; N, 13·4%).

The above chloride, $[Co\,en_3]Cl_3$ (XIII), prepared as its trihydrate by passing air through an aqueous solution of cobalt chloride and ethylenediamine, formed brownish-yellow prisms (Found: C, 18·2, 17·9; H, 7·6, 7·6; N, 20·9; Co, 15·0; H_2O, 13·5. Calc.: C, 18·0; H, 7·5; N, 21·0; Co, 14·8; H_2O, 13·5%), which readily lost the water at 110°; it formed a pale yellow plato-salt, $[Co\,en_3]_2(PtCl_4)_3$ (Found: C, 9·9; H, 3·6; N, 11·3. Calc.: C, 9·7; H, 3·2; N, 11·3%).

The compound (XI) was obtained by concentrating on the water-bath a solution of (XIII) (1 g.) and cobalt chloride (2 g.) in water (40 c.c.); it separated on cooling in yellowish-green needles, which were washed with alcohol and ether and dried over phosphoric oxide (Found: C, 16·6; H, 6·3; N, 19·2, 19·0; Cl, 31·9; Co, 20·0, 20·2. Calc. for $C_{12}H_{48}N_{12}Co_3Cl_8,3H_2O$: C, 16·5; H, 6·2; N, 19·2; Cl, 32·45; Co, 20·2%). The compound (X) was similarly obtained from a solution of (XIII) (1 g.) and cobalt chloride (4 g.) in dilute hydrochloric acid; the green crystals were washed and dried as above (Found: C, 14·2; H, 6·0; N, 16·6; Cl, 34·4; Co, 23·1. Calc.: C, 14·2; H, 5·5; N, 16·4; Cl, 34·7; Co, 23·1%). $[en\,H_2]_2CoCl_6$ was obtained in dark blue leaflets from cobalt chloride (10 g.) and ethylenediamine (5 g.) in 80 c.c. of 16% hydrochloric acid (Found: C, 12·3; H, 5·4; N, 14·2; Co, 14·9. Calc.: C, 12·1; H, 5·1; N, 14·1; Co, 14·9%). The *octachloride* (XII) was obtained by acidifying with hydrochloric acid an aqueous solution of the last chloride (1 part) and cobalt chloride (3 parts), and concentrating to half-bulk; addition of concentrated hydrochloric acid caused the separation of long pale blue prisms, which were washed with concentrated hydrochloric acid, alcohol, and ether, and dried over phosphoric oxide (Found: C, 13·6; H, 6·3; N, 16·0; Cl, 53·8; Co, 11·0. $C_6H_{30}N_6Cl_8Co$ requires C, 13·6; H, 5·7; N, 15·9; Cl, 53·7; Co, 11·15%).

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