CXIX.—*Complex Metallic Ammines. Part IV. cis-Sulphoacetato-, cis-Methionato- and cis-Dimethylmalonato-diethylenediaminecobaltic Salts.*

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WERNER (*Annalen*, 1911, **386**, 79) has shown that complex cobalt-ammines containing the malonato-radicle are easily prepared, but he was of the opinion (*ibid.*, pp. 26, 81) that complexes containing a higher number of atoms to the ring than six could not be obtained. Price and Brazier (T., 1915, **107**, 1367) showed, however, that when a sulphur atom forms one of the components of the ring, an eight-ring can be obtained, and were successful in preparing *cis*-sulphonyldiacetatodiethylenediaminecobaltic salts. The part played by the sulphur in enabling such compounds to be isolated is not clear. It may be that the presence of sulphur in the acid radicle enabled ring-formation to take place readily, or it may be that the compounds could be isolated, because they were readily obtained in the crystalline form, whereas the attempts by Werner to obtain products containing the succinato- and other radicles only gave rise to uncrystallisable syrups or glasses. It was therefore of interest to investigate the behaviour of other dibasic acids containing sulphur, and the present communication details the results obtained with sulphoacetic acid,

and with methionic acid, $\text{CH}_2(\text{SO}_3\text{H})_2$, both of which give rise to crystalline compounds.

In a previous paper (Price and Brazier, T., 1915, **107**, 1713) it has been shown that malonic acid forms an additive compound with dichlorodiethylenediaminecobaltic hydrogen malonate, namely, $[\text{Cl}_2\text{Co en}_2]\text{HA}, \text{H}_2\text{A}$, where $\text{H}_2\text{A} = \text{CH}_2(\text{CO}_2\text{H})_2$, but that the substituted malonic acids do not give rise to such additive compounds, and a tentative explanation of the results obtained was advanced. It was therefore of interest to ascertain whether the substituted malonic acid residue could be introduced into the cobalt complex, giving compounds similar to the malonato-compounds, or whether some such steric hindrance as is postulated in the aforementioned paper prevented their formation. The first experiments were made with dimethylmalonic acid, and we have been successful in preparing dimethylmalonatodiethylenediaminecobaltic salts. The other substituted malonic acids have not yet been investigated, but owing to the fact that one of us (T.S.P.) is taking up other duties, it is considered advisable to publish the results hitherto obtained.*

* These researches are being continued by Mr. Duff (T.S.P.).

The fact that the dimethylmalonic acid residue can be introduced into the nucleus does not necessarily invalidate the explanation given previously of the formation of additive compounds, since, as will be seen in the experimental part, a higher temperature than the ordinary was used, whereby the formation of a ring complex may be greatly facilitated.

As will be seen later, sulphoacetic and methionic acids do not form additive compounds with their dichlorodiethylenediamine-cobaltic acid salts, thus differing markedly from their analogue, malonic acid. No explanation of this is offered at present, since further work is necessary.

EXPERIMENTAL.

cis-Sulphoacetatodiethylenediaminecobaltic Salts, YX, where

To obtain the *bromide*, YBr, 5 grams of carbonatodiethylenediaminecobaltic bromide were dissolved in 80 c.c. of warm water, and a solution of 2.19 grams of sulphoacetic acid in 20 c.c. of water was added. Evaporation of the mixed solution on the water-bath to a small bulk only resulted in a very poor yield of crystals. It was found best to heat the solution, after the evolution of carbon dioxide had slackened, in a closed bottle at 105° for four hours, and then evaporate to small bulk on the water-bath. After remaining in the ice-chest overnight, the anhydrous bromide separated in small, carmine-red plates, which were collected and washed with water and alcohol. The yield was 2.4 grams, but a further small quantity was obtained by evaporation of the filtrate (Found: Co = 14.87; Br = 20.08. $\text{C}_6\text{H}_{18}\text{O}_5\text{N}_4\text{BrSCo}$ requires Co = 14.85; Br = 20.15 per cent.).

The *nitrate*, YNO_3 , was obtained in brick-red, elongated plates by precipitating a solution of 2 grams of the bromide in 50 c.c. of water with the equivalent quantity (0.86 gram) of silver nitrate. After shaking for one hour, the silver bromide was collected and the filtrate evaporated to low bulk on the water-bath. The crystals of the nitrate separated slowly on keeping in the ice-chest. Yield, 0.8 gram (Found: Co = 15.39; N = 18.24. $\text{C}_6\text{H}_{18}\text{O}_8\text{N}_5\text{SCo}$ requires Co = 15.56; N = 18.47 per cent.).

The *thiocyanate*, YSCN, was obtained by adding 1.5 grams of solid potassium thiocyanate to a saturated solution containing 3 grams of the bromide. The potassium thiocyanate dissolved, and, after leaving overnight in the ice-chest, microscopic, brick-red crystals of the complex thiocyanate separated (Found: Co = 15.62;

N=18.91. $C_7H_{18}O_5N_5S_2Co$ requires Co=15.73; N=18.67 per cent.).

The *platinichloride*, Y_2PtCl_6 , was prepared by filtering a saturated solution containing 2 grams of the bromide into a 5 per cent. solution of chloroplatinic acid. Microscopic, pale brown crystals slowly separated; these were collected after two hours and washed with alcohol and ether, and dried in a vacuum desiccator [Found: Co=11.11; Pt=18.95. $(C_6H_{18}O_5N_4SCo)_2PtCl_6$ requires Co=11.32; Pt=18.72 per cent.].

The *hydrogen sulphoacetate*, $YSO_3 \cdot CH_2 \cdot CO_2H$, was obtained by dissolving 6 grams of the carbonato-bromide in 120 c.c. of water and shaking the cooled solution with 4 grams of freshly prepared moist silver oxide for half an hour. The product was then filtered into an aqueous solution of 5.25 grams of sulphoacetic acid, the proportions being two molecules of the acid to one of the carbonato-base. The resulting solution was evaporated to low bulk on the water-bath, and, after keeping overnight in the ice-chest, deposited microscopic, pink crystals, which dissolve readily in cold water. Yield, 2.8 grams (Found: Co=12.79; N=12.33. $C_8H_{21}O_{10}N_4S_2Co$ requires Co=12.93; N=12.28 per cent.).

cis-Methionatodiethylenediaminecobaltic Salts, YX , where

The *bromide*, $YBr_2 \cdot 2H_2O$, was only obtained after several attempts had been made to prepare it from the carbonato-bromide according to the method used by Price and Brazier in making sulphonyldiacetatodiethylenediaminecobaltic bromide (*loc. cit.*). It was found that on mixing solutions of the carbonato-bromide and methionic acid in equivalent quantities and evaporating on the water-bath, pink, microscopic crystals separated in increasing quantity as evaporation proceeded. These crystals, however, contained no bromine, and were later identified as the methionato-methionate (Found: Co=13.20). On further evaporation, the mother liquor gave no crystals of the bromide, a syrupy liquid resulting which contained some unused carbonato-bromide. To avoid this formation of the methionate, it was found best to dissolve 5 grams of the carbonato-bromide in 120 c.c. of water and add a solution of 2.73 grams of methionic acid in 40 c.c. of water. The whole solution was then well boiled for twenty minutes, keeping the volume at about 150 c.c. by the addition of boiling water.* After evaporating the resulting solution on the water-bath to low

* This method of treatment has already given successful results in the case of succinato-compounds, which will be dealt with in a later paper by one of us.

bulk and keeping for two days in the ice-chest, the pure methionato-bromide separated in purplish-red plates, which were collected and washed with water and alcohol. Yield, 1.4 grams [Found: Co=12.50; Br=17.02; S=13.28; H₂O (at 100°)=7.74. C₅H₁₈O₆N₄BrS₂Co.2H₂O requires Co=12.57; Br=17.04; S=13.64; H₂O=7.68 per cent.].

The *nitrate*, YNO₃.2H₂O, was obtained by shaking for one hour a solution of 3 grams of the hydrated bromide in 60 c.c. of water with the equivalent quantity (1.08 grams) of silver nitrate. The silver bromide was then collected and the filtrate evaporated to low bulk on the water-bath. After keeping for several days in the ice-chest, the nitrate separated in carmine-red, elongated plates. Yield, 0.5 gram [Found: Co=13.42; N=15.76; H₂O (at 110°)=7.94. C₅H₁₈O₉N₅S₂Co.2H₂O requires Co=13.08; N=15.52; H₂O=7.98 per cent.].

The *thiocyanate*, YSCN, was prepared by adding 1.5 grams of solid potassium thiocyanate to a saturated solution of 3 grams of the methionato-bromide. After keeping overnight, the complex thiocyanate separated in microscopic, dark red crystals (Found: Co=14.68; N=17.40. C₆H₁₈O₆N₅S₃Co requires Co=14.35; N=17.03 per cent.).

The *platinichloride*, Y₂PtCl₆, was obtained by filtering a saturated solution of the methionato-bromide into a 5 per cent. solution of chloroplatinic acid. Microscopic, light brown crystals readily separated, which were washed with alcohol and ether and dried in a vacuum desiccator [Found: Co=10.34; Pt=17.83. (C₅H₁₈O₆N₄S₂Co)₂PtCl₆ requires Co=10.58; Pt=17.52 per cent.].

The hydrogen methionate could not be obtained, although the same method was used that has always been successful in similar cases. When two molecular proportions of methionie acid in solution were mixed with one of the carbonato-base, the crystals which separated on evaporation always proved to be the normal methionate. When this was dissolved in a boiling solution of methionie acid, only the unchanged salt separated on evaporation. The *normal methionate*, CH₂(SO₃Y)₂, was prepared by dissolving 7 grams (2 mols.) of the carbonato-bromide in 120 c.c. of warm water, shaking for half an hour with 3.8 grams of freshly prepared silver oxide, and filtering from the silver bromide into a solution containing 5.78 grams (3 mols.) of methionie acid. The mixed solution was then evaporated to low bulk on the water-bath. Complete separation of the normal methionate in pink, microscopic crystals only occurred when a little water was added to the resulting syrup and the whole well stirred. The yield was 7.3 grams. The salt is almost insoluble in cold water, but dis-

solves readily in hot water (Found: Co=13.56; N=12.64; S=21.37. $C_{11}H_{38}O_{18}N_8S_6Co_2$ requires Co=13.41; N=12.72; S=21.82 per cent.).

The normal methionate dissolves readily in cold dilute ammonia or sodium carbonate solution, but is not reprecipitated on acidifying. Barium hydroxide solution also dissolves it, giving a blood-red solution, from which barium methionate separates on keeping. Excess of barium hydroxide is required for solution, so that the reaction cannot be used as a method for obtaining the methionato-hydroxide, and hence the chloride. When the normal methionate is heated with a solution of barium chloride, a blood-red solution results, from which barium methionate separates on cooling. The filtrate from these crystals changes to a purple colour on evaporation, and small, purple crystals of *cis*-dichlorodiethylenediaminecobaltic chloride separate after a time (Found: Co=20.86. Calc.: Co=20.67 per cent.).

Concentrated solutions of the methionato-bromide do not give any precipitate when mixed with a solution of mercuric bromide in potassium bromide solution. On boiling the resulting solution, however, there is at once formed the green double salt of mercuric bromide and the *trans*-dibromo-bromide, $[Br_2Co en_2]Br, HgBr_2$, which separates from the hot solution in small, flattened needles (Found: Co=7.47; Br=49.83. Calc.: Co=7.56; Br=51.28 per cent.).

trans-Dichlorodiethylenediaminecobaltic Salts.

Since both sulphoacetic acid and methionie acid may be considered to be analogues of malonic acid, it was expected that they would give additive compounds with their acid salts of dichlorodiethylenediaminecobalt. This was found not to be the case, however, the substitution of $\cdot CO_2H$ by $\cdot SO_3H$ thus playing a part which requires further investigation. Price and Brazier (*loc. cit.*, p. 1737) found that sulphonyldiacetic acid, which contains an SO_2 -group in place of one of the CH_2 -groups of glutaric acid, did give rise to such additive compounds.

trans-Dichlorodiethylenediaminecobaltic hydrogen sulphoacetate, $[Cl_2Co en_2]SO_3 \cdot CH_2 \cdot CO_2H$, separates immediately as emerald-green, striated, and elongated plates when 3 grams of the *trans*-dichlorochloride are stirred into a cold solution of 4.3 grams of sulphoacetic acid in 15 c.c. of water. Yield, 3.1 grams (Found: Co=15.24; Cl=18.37. $C_6H_{19}O_5N_4Cl_2SCo$ requires Co=15.16; Cl=18.23 per cent.).

cis-Sulphoacetatodiethylenediaminecobaltic chloride could not be obtained from the above hydrogen sulphoacetate in the same way as oxalatodiethylenediaminecobaltic chloride was obtained from the

dichloro-hydrogen oxalate (Price and Brazier, *loc. cit.*, p. 1726). When a solution of the hydrogen sulphoacetate was boiled, the colour changed to the blood-red colour of a *cis*-salt, but on evaporation to small bulk, only green crystals could be separated. Repeated boiling of the solution and evaporation only resulted in the recovery of the green crystals of the unchanged hydrogen sulphoacetate.

trans-Dichlorodiethylenediaminecobaltic methionate;

separated in green, elongated plates when 3 grams of the *trans*-dichloro-chloride were stirred into a cold solution of 4.5 grams of methionic acid in 15 c.c. of water. The separation of crystals was complete after two hours in the ice-chest. Yield, 2.4 grams (Found: Co=17.29; Cl=20.81; S=9.07. $\text{C}_9\text{H}_{34}\text{O}_6\text{N}_8\text{Cl}_4\text{S}_2\text{Co}_2$ requires Co=17.50; Cl=21.04; S=9.49 per cent.).

When this salt was dissolved in water, together with a molecular proportion of methionic acid, and the solution boiled for fifteen minutes, the colour became deep red, but, on evaporating almost to dryness, only green crystals of the original substance separated. The acid salt could not be obtained.

cis-Dimethylmalonatodiethylenediaminecobaltic Salts, YX,

Before commencing the preparation of these salts, the method described by Price and Brazier (*loc. cit.*, p. 1373) for the preparation of *cis*-sulphonyldiacetatodiethylenediaminecobaltic bromide was tested in the case of the malonato-bromide. This consisted in the preparation of the bromide directly by the interaction of one molecular proportion of the carbonato-bromide and one molecular proportion of malonic acid, whereas Werner's method of preparation of such compounds is first to prepare the carbonato-hydroxide and then add two molecular proportions of malonic acid. The method was found to be satisfactory, *cis*-malonatodiethylene-diaminecobaltic bromide, $[\text{CH}_2(\text{CO}_2)_2\text{Co en}_2]\text{Br}, x\text{H}_2\text{O}$, being obtained in large, rhombic, dark red plates, which very readily effloresced on exposure to the air. A freshly prepared specimen, which had slightly effloresced, gave Co=14.48, whereas $\text{C}_7\text{H}_{18}\text{O}_4\text{N}_4\text{BrCo}, x\text{H}_2\text{O}$ requires Co=14.21 for $3\text{H}_2\text{O}$ and Co=14.86 for $2\text{H}_2\text{O}$. The anhydrous substance gave Co=16.25, theory requiring Co=16.34 per cent. The corresponding thiocyanate, $\text{C}_8\text{H}_{18}\text{O}_4\text{N}_5\text{SCo}$, was readily obtained, and possessed the properties described by Werner (*Annalen*, 1911, **386**, 81) (Found: Co=17.19. Calc.: Co=17.39 per cent.).

To obtain *cis-dimethylmalonatodiethylenediaminecobaltic bromide*, $\text{YBr} \cdot 2\text{H}_2\text{O}$, 5 grams of the carbonato-bromide were dissolved in 80 c.c. of warm water and 2.07 grams (1 mol. equiv.) of dimethylmalonic acid added. The resulting solution was evaporated to low bulk on the water-bath, and, after keeping in the ice-chest overnight, crimson-red, microcrystalline plates of the desired salt separated in small quantity. Crystallisation, or, it may be, the introduction of the dimethylmalonato-residue into the complex, takes place very slowly, and it was necessary repeatedly to collect the crystals, wash with alcohol, and evaporate the filtrate and washings in order to obtain any quantity of the salt. The solution cannot be boiled, as was found to be effective in the case of the methionato-compound, owing to decomposition of the dimethylmalonic acid [Found: $\text{Co} = 13.82$; H_2O (at 130°) = 8.44. $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_4\text{BrCo} \cdot 2\text{H}_2\text{O}$ requires $\text{Co} = 13.87$; $\text{H}_2\text{O} = 8.47$ per cent. Found: $\text{Br} = 18.54$. $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_4\text{BrCo}$ requires $\text{Br} = 18.80$ per cent.].

The *nitrate*, $\text{YNO}_3 \cdot 2\text{H}_2\text{O}$, was prepared by the interaction in solution of equivalent quantities of the bromide (1.134 grams) and silver nitrate (0.4532 gram). After shaking for one hour, the silver bromide was collected and the filtrate evaporated to low bulk on the water-bath. The salt crystallised out very slowly as a crimson, microcrystalline powder or in dark red crusts of indefinite shape * [Found: H_2O (at 130°) = 8.85.

requires $\text{H}_2\text{O} = 8.85$ per cent. Found: $\text{Co} = 15.58$; $\text{N} = 19.19$. $\text{C}_9\text{H}_{22}\text{O}_7\text{N}_5\text{Co}$ requires $\text{Co} = 15.89$; $\text{N} = 18.87$ per cent.].

The *chloride*, $\text{YCl} \cdot 2\text{H}_2\text{O}$, was obtained by shaking a solution of the bromide with an excess of freshly precipitated silver chloride, collecting the precipitate, and evaporating the filtrate to low bulk. It separated in microcrystalline prisms, which are very soluble in water [Found: H_2O (at 130°) = 9.95.† $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_4\text{ClCo} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 9.47$ per cent. Found: $\text{Co} = 16.86$. $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_4\text{ClCo}$ requires $\text{Co} = 17.11$ per cent.].

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* Both in the case of the nitrate and the chloride, which are very readily soluble in water, it was difficult to obtain a solution which was just of the right concentration for crystallisation; if too concentrated it formed a viscid mass.

† Only 0.2 gram of the salt was obtained, so that the estimation of the water of crystallisation could not be repeated. The high value found was probably due to the salt not being quite air-dry, owing to the abnormally damp weather which prevailed at the time: $3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 13.56$ per cent.