

APPENDIX - I

A. Preparation of $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{SO}_4$ (Ref. Kauffman, G.B. and Pinnel, R.P., Inorg. Synthesis, Vol. VI, p. 176).

50 grams of ammonium carbonate are dissolved in 150 ml of water in a 600 ml beaker, and 125 ml of concentrated aqueous ammonia are added to it. Any undissolved solid will dissolve readily when the ammonia is added. A solution of 20 g (0.084 mol) of cobalt(II) chloride 6-hydrate in 30 ml of water is then added with continuous mechanical stirring. [A light blue precipitate of hydrated cobalt(II) hydroxide first forms, but it dissolves as stirring is continued.] 50 ml of 10% hydrogen peroxide are then slowly added over a period of 10 to 15 minutes with continuous, rapid stirring causing the color to change from a dull reddish brown to deep purple. Stirring is continued until all effervescence ceases. The solution is then transferred to a 525 ml evaporating dish and concentrated at 80°C with continuous mechanical stirring to a volume of around 100 ml. During this time 2 to 3 g of ammonium carbonate is added every 30 minutes to replace that lost by volatilization. The solution is then filtered through a Buchner funnel to remove any black hydrated cobalt(III) oxide that may have been formed from overheating, and then cooled in an ice-bath. The cooled filtrate is transferred to a 400 ml beaker, and a mixture of 62 ml of hydrochloric acid with 62 ml of water is added with continuous stirring over a period of

5 minutes. 75 ml of concentrated hydrochloric acid are then added, whereupon carmine-red crystals of carbonato tetrammine cobalt(III) chloride are deposited. The mixture is maintained at 60° on a hot plate with mechanical stirring for 45 minutes to 1 hour until the crystals have become deep purple. The mixture then is cooled in an ice-bath until crystallization of cis-aquochlorotetrammine cobalt(III) chloride seems to be complete (around 12 hours). The small purple crystals are collected on an 8 cm Buchner funnel, and this product is washed twice with 30 ml of an equivolume mixture of hydrochloric acid and water and once with 30 ml of ethanol. The crystals are then air-dried. The yield of impure cis-aquochlorotetrammine cobalt(III) chloride is 15.3 g [72.4%, based upon cobalt(II) chloride 6-hydrate]. The product is contaminated with small amounts of chloropentammine cobalt(III) chloride and trans-dichlorotetrammine cobalt(III) chloride. Purification is effected by precipitating the cis-aquochlorotetrammine cobalt(III) chloride as the more insoluble sulphates.

10 grams (0.0398 mol) of crude cis-aquochlorotetrammine cobalt(III) chloride are added to a mixture of 300 ml of water and 1 ml of sulphuric acid, and the mixture is mechanically stirred until no more solid dissolves (around 15 to 20 mins). The residual purple contaminants are removed by filtration through a small Buchner funnel, and 20 g (0.151 mol) of ammonium sulfate are dissolved in the filtrate. Minute deep purple crystals start to form immediately. The mixture

is then cooled with stirring in an ice-bath until crystallisation is complete (around 1 hour). The crystals are collected on a small Buchner funnel, washed twice with 10 ml of ice-water and once with 10 ml of ethanol, and then air dried. The yield is 9.9 g (65.2% based on cobalt(II) chloride 6-hydrate).

B. Preparation of $\text{cis-}[\text{Co}(\text{OH}_2)(\text{NH}_3)_4(\text{GH})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ [Ref. Fujita, J., Yasui, T., Shimura, Y., Bull. Chem. Soc. Japan, Vol. 38, p. 655 (1965)].

To an aqueous solution of 5 g of diaquotetrammine cobalt(III) perchlorate in 50 ml of water 1 g of glycine was added. The purple red solution obtained was warmed on a water bath at 80°C for 15 mins. and cooled in ice. Pink colored crystals were precipitated by adding concentrated perchloric acid, the crystals were then filtered and washed with ethanol. The complex was recrystallised from a cold aqueous solution by adding concentrated perchloric acid.

C. Preparation of $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{GH})_2](\text{ClO}_4)_3$ [Ref. Fujita, J., Yasui, T., Shimura, Y., Bull. Chem. Soc. Japan, Vol. 38, p. 655 (1965)].

The following procedure has been given in the above reference.

To 30 ml of an aqueous solution containing 5 g of diaquotetrammine cobalt(III) perchlorate a slight excess of glycine (1.8 g) was added. The resulting solution was gradually

evaporated on a water bath at 75-80°C to a volume of about 10 ml. After cooling, the drop-by-drop addition of absolute ethanol to this solution resulted in the formation of purple crude crystals, which were then filtered and washed with ethanol. These crystals were recrystallised by dissolving them in the minimum amount of water, then adding ethanol and a few drops of concentrated perchloric acid. Purple crystals were obtained after the solution had been kept in a refrigerator over night.

Following the above procedure we obtained crystals having the same chemical composition as that of $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{GH})_2](\text{ClO}_4)_4$. But the λ_{max} and ϵ values of the above product were not found to be the same as those of $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{GH})_2](\text{ClO}_4)_3$ as described in the literature. We have already referred to this point in the text of our paper.

We modified the above procedure by taking in place of 30 ml water for dissolving 5 g of $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$, only 10 ml of water and evaporated the mixture to a volume of 2-3 ml. Then we followed the same procedure as described above, and obtained the compound $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{GH})_2](\text{ClO}_4)_3$ yielding a spectrum described in the text and was almost the same as that given in the literature.

APPENDIX - II

Methods used for elemental analysis :

A) Estimation of cobalt - Cobalt was estimated gravimetrically as follows :

Weighed amount of the sample was taken in a vitreosil crucible (which was previously ignited to redness cooled in a desiccator and weighed). Few drops of concentrated H_2SO_4 were added and the mixture was heated to almost dryness on a very low flame. The mixture was then heated strongly until all organic matter had burned off and entire mass was converted to the black-oxide. Then it was cooled and evaporated after adding a little amount of conc. HCl almost to dryness on a very low flame. Finally few drops of concentrated H_2SO_4 were added; the H_2SO_4 was almost completely driven off on a low flame. Finally few more drops of conc. H_2SO_4 were added and this too was driven off on a low flame. Pink coloured $CoSO_4$ thus produced was kept in a furnace at $400-450^{\circ}C$ for half an hour. Cooled and weighed; the procedure was repeated until a constant weight was obtained.

B) Estimation of chlorine :

Weighed amount of the sample was taken in a beaker, dissolved in water by the addition of few drops of concentration HNO_3 and subsequent boiling. Then excess $AgNO_3$ solution was added and the solution was allowed to stand overnight. The $AgCl$ precipitated, was filtered, dried and weighed to constant weight in a previously weighed gooch crucible.

C) Estimation of nitrogen :

Nitrogen content of the samples was estimated by Duma's method.

D) Estimation of carbon and hydrogen :

Estimation of carbon and hydrogen were done by the Central Durg Research Institute, Lucknow, India.

E) Estimation of sulphate :

Sulphate was estimated as Barium sulphate by following the procedure described below. Weighed amount of the sample was taken in a beaker, dissolved in water and heated in water bath. Warm barium chloride solution was added dropwise with stirring and the solution was kept in a hot condition for an hour and then filtered using the filter paper Whatman No.540. The precipitate was washed with hot water. The moist filter paper containing the precipitate (BaSO_4) was placed in a weighed crucible, previously ignited to redness and cooled in a desiccator. The paper was dried on a small flame at first and then the flame was increased until the paper charred; the temperature of the flame was gradually increased until the attainment of dull red heat. When all black carbon particles were burnt off and the precipitate was white, the crucible was ignited to red heat for sometime more, cooled in air

and transferred in a desiccator while still warm. It was kept in the dessicator till it attained room temperature and then weighed.

F) Estimation of perchlorate :

Weighed amount of the sample was taken in a beaker, dissolved in cold double distilled water and the solution was passed through a hydrogen cation exchange column saturated with H^+ ions, and the column was washed with cold double distilled water. In the effluent, perchlorate, present as perchloric acid, was titrated with standerised N/10 NaOH solution using phenophthalein as indicator and the amount of perchlorate in the effluent was determined.