APPENDIX - I


Preparation of carbonato-bis(ethylenediamine) cobalt(III) chloride:

A solution of CoCl₂·6H₂O (80 gm) in water (100 ml) and HCl (667 ml, 1.00 N) was de-aerated by a continuous stream of CO₂ for 10 minutes at room temperature and anhydrous ethylenediamine (40 ml) was added slowly. The mixture was heated rapidly to 80° while being stirred mechanically, lead dioxide (60 gm) was added, and the stream of carbon dioxide gas was stopped. The stirring was maintained for 3 hours at 80° sufficiently vigorously to prevent the lead dioxide from caking. The hot solution then was filtered and lithium carbonate (48 gm) added to the filtrate, which was stirred occasionally and maintained at 80-90° on a water bath for 0.5 hour. The strongly alkaline red mixture was filtered, and the filtrate evaporated in a stream of air at 60° to a volume of 480 ml. Free carbonate ion was removed by the addition of CaCl₂·6H₂O (20 gm), and the calcium carbonate filtered off. Twice the volume of ethanol was added to the warm solution, which precipitated fine red crystals on cooling (yield 66 gm). The product was freed from a little tris(ethylenediamine) Co(III) chloride impurity by dissolution in water (310 ml) at 40°, and adding ethanol (620 ml)
while stirring. The precipitated crystals were washed with 80% alcohol and air dried. Yield - 62 gm i.e. 70%.

cis-Diaquo-bis(ethylenediamine cobalt(III) Nitrate:

A suspension of [Coen₂CO₃]Cl (4 gm) in water (30 ml) was shaken for 5 minutes with AgNO₃ (2.48 gm) in water (20 ml). The AgCl was removed, alcohol added to the filtrate and [Coen₂CO₃]NO₃ crystallised. This was collected, washed with alcohol and dried. The dry salt (3 gm) was added gradually to ice cold nitric acid (15 ml, 3 N) and when evolution of CO₂ was complete, a mixture of equal volumes of ethanol, acetone and ether was added. The resultant red oil which crystallised on the addition of methanol was collected, washed with acetone and dried over CaCl₂.
Methods used for elemental analysis

A. Estimation of Cobalt:–

Weighed amount of the sample was taken in a vitreosil crucible (which was previously ignited to redness, cooled in a dessicator and weighed). Few drops of conc. H$_2$SO$_4$ were added and the mixture was heated almost to 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. It was then cooled and evaporated after adding a little amount of conc. HCl almost to dryness on a very low flame. Finally few drops of conc. H$_2$SO$_4$ were added; the H$_2$SO$_4$ was almost completely driven off on a low flame. Few more drops of conc. H$_2$SO$_4$ were added and this too was driven off on a low flame. CoSO$_4$ thus formed (pink coloured) was kept in a furnace at 400° - 450°C for half an hour, cooled and weighed; the procedure was repeated until a constant weight was obtained.

B. Estimation of Nitrogen:

Nitrogen of the sample was determined by Duma's method.
C. Estimation of Sulphate (as \( \text{BaSO}_4 \)) :

The sample (weighed amount) was taken in a beaker, dissolved in water and heated in water-bath. Warm solution of \( \text{BaCl}_2 \) was added dropwise with stirring and the solution was kept in a hot condition for an hour and then filtered using Whatman No.540 filter paper. The precipitate was washed with hot water. The moist filter paper containing the precipitate (\( \text{BaSO}_4 \)) was placed in a weighed crucible, previously ignited to redness and cooled in a dessicator. 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 dessicator while still warm. It was kept in the dessicator till it attained room temperature and then weighed.
Method of Preparation of cis-$\left[ (\text{NH}_3\right)_2\text{Co(BigH)}_2\right]_{\text{OH}}\text{SO}_4\cdot 2\text{H}_2\text{O}$ as modified by us (Ref. of the original method - Ray, P.R. & Majumdar, A.N., J. Indian Chem. Soc., 23 (1946), 76.

Biguanide sulphate (13.2 g) dissolved in the least quantity (100 c.c) of 6(N) ammonium hydroxide solution was slowly added with stirring to that of 7.2 g of CoCl$_2\cdot 6\text{H}_2\text{O}$ in the smallest amount (15 c.c) of water. The mixture, containing the yellow precipitate of cobaltous bis-biguanidinium sulphate, was transferred to a flask; about 15 c.c of liquor ammonia were then added and air was passed through the mixture till the yellow product turned red. The flask was warmed gently till most of the precipitate dissolved and some unoxidised yellow compound remained behind. This was filtered off and the filtrate, to which again about 12 c.c of liquor ammonia were added, was left overnight in a refrigerator in a well stoppered vessel. Red crystals separated from the solution. After 24 hours these crystals were filtered and washed with 1:1 ammonia. The product was then recrystallised from warm ammoniacal water, washed first with dilute ammonia, then with alcohol saturated with ammonia gas, and finally dried in air.