CHAPTER 5

RESULTS AND DISCUSSION

1. COBALT (II) SUCCINIMIDATE COMPLEXES
2. COBALT (II) CHROMATE COMPLEXES
3. COBALT (II) PERCHLORATE COMPLEXES
4. COBALT (III) COMPLEXES
STRUCTURE OF COBALT (II) SUCCINIMIDATE COMPLEXES

The electronic configuration of cobalt atom may be represented as follows:

\[
\text{Co}_{27}, \; 1s^2, \; 2s^2 \; p^6, \; 3s^2 \; p^6 \; d^7, \; 4s^2
\]

and the configuration of the cobalt (II) ion is given by

\[
\text{Co}^{2+}, \; 1s^2, \; 2s^2 \; p^6, \; 3s^2 \; p^6 \; d^7
\]

There are two possibilities of the existence of the general molecular formula of cobalt (II) succinimidate complexes, as derived from the basis of elemental (metal, nitrogen, carbon, hydrogen) analysis; one having co-ordination No. 4 and the other 6. The two formulae may be represented as \( \text{CoAm}_2 \; \text{Succ}_2 \) and \( \text{CoAm}_4 \; \text{Succ}_2 \) (where, \( \text{Am} \) represents ammonia, methyl-, ethyl-, propyl-, butyl-, amyl-, ethylenedi-, propylenedi-, O-phenanthroline, 2-2-Dipyridylamine, dimethyl glyoxime, pyridine, quinoline, aniline, dimethyl-, or diethylamine). Examination of the above complexes enables one to conclude that two molecules in the case of monodentated ligand and one molecule in the case of bidented
ligand is attached per molecule of cobalt (II) succinimidate in cases where co-ordination no. is 4 (tetrahedral complexes), and four molecules of monodented or two molecules of bidented ligand per molecule of cobalt (II) succinimidate complexes in octahedral or distorted octahedral cases (co-ordination no. 6).

On the basis of colour, it could be assumed that these complexes possess a tetrahedral or octahedral stereo-chemistry, since the complexes show a variable colour, i.e., blue, pink, orange, brown, pinkish brown, etc. The data presented in the present investigations supports this hypothesis.

The complexes are highly stable but decomposed on heating, giving a characteristic odour of amines. With an increase in the molecular weight of amines the stability of the complexes decreases. The cobalt (II) succinimidate complexes with pyridine, quinoline, aniline, methyl-, ethyl-, and dimethylamines are insoluble in water, and various organic solvents like ethyl alcohol, methyl alcohol, acetone, chloroform, benzene, nitrobenzene, carbon tetrachloride, carbon di sulphide and ether. The cobalt (II) succinimidate complexes with ammonia have two types of stereo-chemistry, one tetrahedral and the other octahedral. The complex having tetrahedral stereochemistry is blue in colour and insoluble in the above mentioned organic solvents and water, whereas the other possessing octahedral stereochemistry is pink and soluble in water and various other
organic solvents. All the other remaining complexes of cobalt (II) succinimidate with propyl-, butyl-, amyl-, ethylenedi-, propylene di-, 2-2-dipyridyl-, ortho-phenanthroline amine, dimethyl glyoxime and 2-4-6 collidine are soluble in water and other organic solvents.

Evidence is available to show that cobalt (II) succinimidate complexes (of ammonia, methyl-, ethyl-amine, pyridine, quinoline, aniline) react with water since on keeping a suspension of the complex in water for two weeks, its colour changes to pink with change of the tetrahedral stereochemistry to octahedral one. This change obviously is taking place due to the attachment of two water molecules to the tetrahedral form to convert it to the octahedral one.

The molar conductance data indicates a very low ($\sim 10 \text{ ohm}^{-1} \text{ cm}^2$) value for these complexes, which falls in the correct range of non-electrolytes, thus confirming the expectation that these compounds are non-electrolytes, neutral and undissociated in solution. Since the stability of a complex ion is often greatly affected by a change in temperature, the cryoscopic method is by far the best for determining its molecular weight for purposes of investigating the complex ions, since it involves minimum departure from atmospheric temperature. The molecular weight so obtained for non-electrolyte fully co-ordinated compounds, would correspond to the calculated value. The data presented
in this respect clearly indicate that the compounds investigated are neutral, undissociated and non-electrolyte, thus supporting the conclusion drawn from the molar conductance measurements.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS:

The magnetic moment measurements have been used to distinguish between the cobalt (II) ion in tetrahedral, octahedral and tetragonally distorted octahedral stereochemistry. Magnetic susceptibility measurements have proved very useful in the study of complexes of cobalt (II). The magnetic moments observed for the spin-free octahedral and tetragonally distorted octahedral complexes is found to be greater than spin only value by an amount 0.8 to 1.3 B.M., which is due to the contribution of unquenched orbital of both the ground state, $t_{2g}^5 e_g^2$ and the first excited state $t_{2g}^4 e_g^3$. Since the ground state configuration $t_{2g}^6 e_g^3$ allows no orbital contribution, the magnetic moments observed for spin paired octahedral complexes is very close to the calculated value.

In tetrahedral complexes many a times high magnetic moments have been observed, which may be due to the mixing of energy levels, e.g., $t_{2g}^3 e_g^3 t_{2g}^3$ with higher (4p$^1$) ones—this postulate becomes necessary since the symmetrical ground state

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$\text{eg}^4 \text{t}_{2g}^3$ being densely populated, would not permit any orbital contribution to magnetic moment.

In cases where the ground state must necessarily contribute to the orbital moment, the magnetic moment observed for the octahedral and tetrahedral cases are lower. The argument for spin-free cobalt (II) complexes whose magnetic moments fall in the range 4.8 to 5.2 B.M. to be square planar, is not conclusive, and there is every possibility that these may be tetragonal.

The magnetic susceptibilities of cobalt (II) succinimidate complexes with ammonia, methyl amine and ethyl amine fall in the acceptable range (4.4 to 4.8 B.M.) for the tetrahedral cobalt (II) complexes.3-5 The observed values being 4.52, 4.57 and 4.67 B.M. respectively. It is, therefore, inferred that these complexes are paramagnetic and tetrahedral, with three impaired electrons.

Since there is a very small stability difference between octahedral and tetrahedral stereochemistry, several such cases

have been reported in which the two types\(^6,7\) occur with the same ligand. The author has also reported such a case, e.g., Cobalt (II) succinimide complexes with ammonia have been found to have both stereo-chemistry, i.e., octahedral and tetrahedral having pink and blue colours respectively.

The tetrahedral cobalt (II) ion in the electronic configuration \(1s^2, 2s^2 \, p^6, 3s^2 \, p^6 \, d^7\) has a ground state \(4A_2\) which has no inherent angular momentum. The magnetic moments data reported for these complexes which is in the range of 4.4 to 4.8 B.M. and is considerably in excess of spin only value i.e., 3.89 B.M.\(^8\) has already been explained by the crystal field theory.

The cobalt (II) ion with electronic configuration \(d^7\) has its ground state configuration in weaker fields \(t_{2g}^5 \, e_g^2\), and in stronger fields \(t_{2g}^6 \, e_g^1\). It has been seen that in such cases where octahedral field has a very high value, a '2E' state which originates in the 2G state of the free ion, will become the ground, state showing that a very high value of ligand field strength, is required. From this it may be concluded that

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ligands lying very far of the strong end of the spectrochemical series may give rise to a low spin octahedral cobalt (II) complexes.

The most widely acceptable range of magnetic moments for octahedral stereo-chemistry of spin-free cobalt (II) ion is 4.7 to 5.2 B.M.\(^9\). The data presented for cobalt (II) succinimidate complexes with ammonia, propyl-, butyl-, amyl-, ethylenedi-, propylenedi-, 2-2 Dipyridyl-, O-phenanthroline amine, and dimethyl glyoxime are 4.72, 4.62, 4.72, 4.60, 5.21, 5.13, 5.17, 5.14 and 5.19 B.M. respectively which fall in the acceptable range of octahedral stereo-chemistry. The magnetic moments of these complexes are most readily interpreted in terms of essentially octahedral environment and in general exclude the possibility of the metal ions having either a tetrahedral or square planar environment. Some lower values reported for cobalt (II) complexes with ammonia, propyl-, butyl- and amyl amine are probably indicative of distortion from cubic symmetry splitting the \(4 T_{1g} \) ground state term\(^10,11\) which has not been pursued by carrying out low temperature

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measurements on account of the ambiguities that often arise in the interpretation of the distortion parameters.\textsuperscript{12}

The magnetic data observed for cobalt (II) succinimidate complexes with dimethylamine, diethyl amine, aniline, pyridine, quinoline and 2 : 4 : 6 collidine are 4.51, 4.54, 4.45, 4.41, 4.38 and 4.40 B.M. respectively which are slightly less than the expected high spin octahedral cobalt (II) complexes, but these fall in the range 4.2 to 4.8 B.M. accepted for high spin tetrahedral cobaltous complexes. Such behaviour, however, has been observed in several hexa coordinated cobalt (II) complexes which in general arise due to incomplete quenching of the orbital contribution to the magnetic moment.\textsuperscript{13,14}

Thus on the basis of magnetic studies, analytical data and colour the cobalt (II) succinimidate complexes may be divided in three groups, the first having tetrahedral, the second low spin octahedral and the third high spin octahedral stereo-chemistry.

\textsuperscript{13} Selwood, P.W.; Magneto-chemistry, p. 159, Interscience, New York, 1953.
The absorption spectra of coordination compounds have been thoroughly studied by numerous investigators to distinguish between three possible structures, i.e., octahedral, tetrahedral and distorted tetragonally octahedral cobalt (II) complexes. Since the molar extinction coefficient of these three possible structures are quite different. Shibata and Urbain\textsuperscript{15} worked with the cobalt (II) complexes and noticed that there were always two bands of maximum absorption, one of which occurs in the visible range while the other near the ultraviolet. The spectra of the complexes under investigation have been observed in solution in order to ascertain their molar extinction coefficients, the latter being necessary to determine whether or not the band intensities fall in the correct range for octahedral and tetrahedral\textsuperscript{16} complexes.

The present investigation shows that the octahedral complexes in the solid state have the same structure as in solution except those of cobalt (II) succinimidate complexes with ammonia, methyl-, and ethyl amine which are tetrahedral in the solid state but change to octahedral when a suspension in water is kept for two weeks. For the remaining complexes the colour of the complexes in solution remains the same as in

\textsuperscript{15} Shibata and Urbain, Compt rend., \textbf{157}: 593, 1914.
the solid state. The value of the various d-d transitions in octahedral symmetry have been reported in literature to be within the range 1.50 to 20.0 l. mol\(^{-1}\) cm\(^{-1}\). Similar values have also been found within the complexes examined by the present author, confirming their structure.

The electronic absorption spectra of cobalt (II) succinimidate complexes with propyl-, butyl-, and amyl amine have been found to show three bands in the range of 350 nm to 1050 nm (29570 cm\(^{-1}\) to 9524 cm\(^{-1}\)) while the complexes with ammonia, 2 : 4 : 6 collidine, ethylenedi-, propylenedi-, 8-phenanthroline-, 2:2-dipyridylamine and dimethylygly oxime show only two absorption bands in the range of 250 nm to 600 nm (40,000 to 16,670 cm\(^{-1}\)) irrespective of the ligand. The molar extinction coefficients of the above complexes (10.0 to 21.0 l. mol\(^{-1}\) cm\(^{-1}\)) fall in the range accepted for the octahedral complexes. The octahedrally co-ordinated cobalt (II) ion has three spin allowed d-d transition, i.e., \(4 T_1g(F)\) to \(4 T_{2g}\), \(4 A_{2g}\) and \(4 T_{1g}(F)\) States.\(^{17}\) It should be noted that the visible absorption which is in the blue part of the spectrum and rather weak accounts for the pink colour of the complexes.

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The first absorption band near ~ 1030 nm (9709 cm⁻¹) corresponds to 4 T₁g(F) → 4 T₂g transition. The second band observed near ~ 515 nm (19420 cm⁻¹) is the consequence of 4 T₁g(F) → 4 A₂g and the third absorption band at ~ 435 nm (22990 cm⁻¹) is due to 4 T₁g (F) → 4 T₁g (F).

Shibata¹⁸, Tsuchida¹⁹, Kuroya and Tsuchida²⁰, Sueda²¹,²² studied a number of complexes and noticed that three absorption bands occur in the complexes, which contain at least two negative ligands or groups in trans position, but are absent if the negative ligands are adjacent to each other. On the basis of these observations it is evident that complexes studied by the present author possess octahedral stereo-chemistry and have two negative succinimidate groups lying in the trans-position in propyl-, butyl- and amyl amine complexes.

Further Shibata and Urbain\textsuperscript{23} found with cobalt (II) complexes two bands, one being in the visible while the other near the ultraviolet region. These two absorption bands around 425 and 525 nm are associated with the transitions, \(4T_{1g}(F) \rightarrow 4A_{2g}(\delta_2)\) and \(4T_{1g}(F) \rightarrow 4T_{2g}(F)(\delta_1)\) respectively. The complexes with \(o\)-phenanthroline, ethylenediamine, propylenediamine and dimethylglyoxime worked by the present author show a sharp band near 425 nm (23530 cm\(^{-1}\)) while around 525 nm (19050 cm\(^{-1}\)) give a shoulder. Analogous to the observations referred to above it is apparent that these complexes possess an octahedral stereo-chemistry and Cis-configuration, which also supports the conclusion based on analytical data; colour and magnetic measurement studies.

The absorption spectra of the complexes of ammonia, 2-2 Dipyridylamine, 2:4:6 collidine show two bands at 327 nm (30,580 cm\(^{-1}\)), 560 nm (17,860 cm\(^{-1}\)); 295 nm (33,900 cm\(^{-1}\)), 380 nm (26,320 cm\(^{-1}\)) and 300 nm (33,333 cm\(^{-1}\)), 407 nm (24,570 cm\(^{-1}\)) respectively. The band at 30,580 cm\(^{-1}\), 33,900 cm\(^{-1}\) and 33,333 cm\(^{-1}\) may be considered to have arisen from charge transfer. The band around 17,860 cm\(^{-1}\) corresponds to \(4T_{1g}(F) \rightarrow 4A_{2g}(F)\) transition which is generally observed in the

\textsuperscript{23} Shibata and Urbain; Compt rend, 157, 593, 1914.
region 16,000 to 18,000 cm\(^{-1}\) and the band at 26,320 cm\(^{-1}\) and 24,570 cm\(^{-1}\) corresponds to \(4 \text{T}_{1g} (F) \rightarrow 4 \text{T}_{1g} (P)\) transition, usually observed in the region 20,000 cm\(^{-1}\) to 21,000 cm\(^{-1}\).\(^{24,25}\) The molar extinction coefficients reported for charge transfer bands also fall in the acceptable range of the order \(10^4\) lmol\(^{-1}\) cm\(^{-1}\) or greater.\(^{26,27}\)

Evidence of the mode of bonding of Cobalt (II) succinimidate complexes is provided by infra-red spectroscopy. The infra-red frequencies for these complexes are given with the analytical data (page 43-82). All complexes show absorption bands in the region 2900 - 3450 cm\(^{-1}\) and can be assigned to N'-H stretching vibration. An absorption band at 3400 cm\(^{-1}\) is due to the carbonyl frequency (\(>\text{C} = \text{O}\) group) which absorbs at 1700 cm\(^{-1}\). It is also an absorption frequency for N-H stretching vibrations.

The two carbonyl groups in the succinimidate ion have fixed orientation in space, and hence cannot co-ordinate with the

same metal ion. The absorption bands of carbonyl group in potassium succinimidate occurs at 1698 cm⁻¹. But in complexes this band occur in the region 1700 - 1750 cm⁻¹. The cause of this hypsochromic effect appears to be the electron density of nitrogen. The bands observed in the vicinity of 1290-1315 cm⁻¹ are due to the C-H bending vibration.

The bands in the region 1570 - 1670 cm⁻¹ can be assigned to N-H bending vibrations, and the band at ~ 673, ~ 690, and ~ 1310 cm⁻¹ to C-H bending vibration, while in the region 1000 - 1200 cm⁻¹ to C-N vibrations.

The non-electrolytic nature of the cobalt (II) succinimidate complexes shows that succinimidate ion neutralises the charge of the central metal ion as well as co-ordinates with the amine ligands. The succinimidate ion may co-ordinate with the central metal ion either through the negatively charged nitrogen or the oxygen of the two carbonyl groups. All these co-ordinating groups, however, cannot co-ordinate with the same metal ion because of the structural limitations. Gerrard²⁸ and various other workers²⁹-³⁴ have shown that the double bond


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character between carbon and oxygen is reduced when
coo-ordination occurs through the oxygen of the carbonyl group
and causes a shift of the carbonyl stretching frequency to
lower values.

Further, any change in the negatively charged nitrogen
of succinimidate ion will alter the molecular environment as
well as the frequency of the carbonyl group, even if it is
not co-ordinated. According to Lewis concept also there is
greater possibility of co-ordinating negatively charged
nitrogen atom than the oxygen of the carbonyl group.

Thus the analytical data, molar conductance, molecular
weight, spectral and magnetic studies as well as the colour of
the complexes (pink or orange) all confirm their octahedral
stereo-chemistry.

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36 Bailar, J.C.; Chemistry of Coordination Compounds, New York,
STRUCTURE OF COBALT (II) CHROMATE COMPLEXES

On the basis of analytical data the molecular formula of the cobalt (II) chromate complexes may be written as

\[ [\text{Co(NH}_3\text{)}_6] \text{CrO}_4; \quad [\text{Co(en)}_3 \text{CrO}_4; \quad [\text{Co(pn)}_3 \text{CrO}_4 \quad \text{and} \quad [\text{Co(EDTA)} \text{CrO}_4 \quad \text{(where en = ethylenediamine, pn = propylenediamine and EDTA = ethylenediamine tetra acetic acid). These complexes are soluble in water. The electrolytic conductance measurements of these complexes have been made in conductivity water and molar conductance value clearly indicates electrolytic nature of the complexes, falling in the range} \sim 120 \text{ ohm}^{-1} \text{ cm}^2. \]

The molecular weight measurements by cryoscopic method shows a depression in the freezing point two times greater than the expected value, which supports the 1:1 electrolytic nature of the complex.

From the yellow colour of the complexes, an octahedral stereo-chemistry may be expected for these complexes. The magnetic moments found by the present author for Cobalt (II) chromate complexes with ammonia, ethylenedi-, propylenedi-

observed for these high spin octahedral complexes are higher than the spin only value due to large orbital contribution arising out of orbitally degenerate ground state. Thus it may be inferred that these complexes are spin-free octahedral.

An electronic absorption study of these complexes shows two absorption bands around $\sim 275$ nm (36,360 cm$^{-1}$) and $\sim 370$ nm (27,030 cm$^{-1}$) with an extinction coefficient of the order $10^4$ 1 mol$^{-1}$ cm$^{-1}$. The absorption band around 36,360 cm$^{-1}$ extends over a range of wave length 260 nm to 270 nm continuously in the case of ethylenediamine and propylenediamine complexes, which suggests$^{38}$ the loose nature of bonding in the ground state of the complex.

The molar absorption coefficients fall in the range of charge transfer transition$^{39,40}$ (the transition occurring between molecular orbitals which are essentially centered on different atoms is called charge transfer transition). The CrO$_4^{2-}$ have no d-electrons, therefore, it is not possible to explain intense colour of these ions on the basis of d-d transitions.

The frequency of maximum absorbancy, \( \gamma_{\text{max}} \), in the case of charge transfer transition, often, but not necessarily occurs in the ultra-violet region. The two bands observed around 36,360 cm\(^{-1}\) and 27,030 cm\(^{-1}\) in these cases supports this hypothesis.

Four vibrational modes of vibration are possible in the case of chromate ion possessing Td symmetry. These four modes are assigned to \( \nu_6 (\text{Cr-O}) \), \( \delta (\text{O-Cr-O}) \), \( \nu_4 (\text{Cr-O}) \) and \( \delta (\text{O-Cr-O}) \). But only two out of these four are infra-red active. Bassi and Coworkers\(^{41}\) observed two absorption bands in ionic chromate ion at 884 cm\(^{-1}\) \( \nu_4 (\text{Cr-O}) \) vibration mode and at 366 cm\(^{-1}\) \( \nu_6 (\text{O-Cr-O}) \) vibration mode. The absorption band observed in cobalt (II) chromate complexes is at 890 cm\(^{-1}\) which supports the above study and thus it may be inferred that the chromate ion lies out of the sphere of the complex and also shows the ionic nature of the complex.

Absorption resulting from N-H stretching vibrations of amines\(^{42}\) lies in the region \( \sim 3570-3333 \text{ cm}^{-1} \). Thus the band at 3500 cm\(^{-1}\) can be assigned to N-H stretching vibration. The absorption in the regions 1658 - 1608 cm\(^{-1}\) and 2580 - 1494 cm\(^{-1}\)

caused by N-H bending vibrations. The band observed at \( \sim 3200 \text{ cm}^{-1} \) is due to a N-H stretching vibration and in the range 1000 - 1200 cm\(^{-1}\) due to C-N vibrations. The bands near \( \sim 1325, 1350 \) and 1400 cm\(^{-1}\) are \(-C-N\) vibration while at 1640 cm\(^{-1}\) is due to N-H bending (primary vibration).

Thus from the analytical data, magnetic measurements, conductivity and molecular weight measurements and spectral studies it may be inferred that these complexes possess octahedral spin-free stereo-chemistry.


STRUCTURE OF COBALT (II) PERCHLORATE COMPLEXES

The general molecular formula assigned to cobalt (II) perchlorate complexes on the basis of analytical data are

\[ \text{Co}(\text{Am})_n \text{ClO}_4^-_2 \] and \[ \text{Co}(\text{nP})_3 \text{ClO}_4^-_2 \], where Am represents ammonia, methyl- and ethylamine and nP, ethylenediamine and propylene diamine. The cobalt (II) perchlorate complexes with ammonia, methyl- and ethylamine are grey in colour and insoluble in water and various organic solvents, e.g., ethyl alcohol, methyl alcohol, acetone, chloroform, carbon tetrachloride, carbondisulphide and benzene. The grey colour and analytical data shows a tetrahedral stereo-chemistry for these complexes. The magnetic moments in the range 4.50 to 4.57 B.M. further support the tetrahedral cobalt (II) stereo-chemistry.

The complexes of ethylenediamine- and propylenediamine are yellow in colour and soluble in water. The molar conductance measurements studies clearly indicate that \[ \text{Co}(\text{nP})_3 \text{ClO}_4^-_2 \] is correctly viewed as a 1:2 electrolyte.

Molecular weight measurements by cryoscopic method give a depression of freezing point three times greater than the expected value if no dissociation took place. This also supports the molar conductance studies.

The absorption spectroscopic studies show two absorption bands in the ultra-violet region of very high extinction coefficient of the order of $10^4$ l mol$^{-1}$ cm$^{-1}$. Drago\textsuperscript{46} has also reported that the anion $\text{ClO}_4^{2-}$ shows a very intense band. The molar extinction coefficients for cobalt (II) perchlorate complex with ethylenediamine are 1980 l mol$^{-1}$ cm$^{-1}$ at 270 nm (37,040 cm$^{-1}$) and 1430 l mol$^{-1}$ cm$^{-1}$ at 350 nm (28,570 cm$^{-1}$) respectively and for propylenediamine complex 1860 l mol$^{-1}$ cm$^{-1}$ at 270 nm (37,040 cm$^{-1}$) and 1365 l mol$^{-1}$ cm$^{-1}$ at 350 nm (28,570 cm$^{-1}$) respectively.

The absorption bands for both the complexes occur at 270 nm and 350 nm. Both these bands lying in the ultra-violet region, with such a high extinction coefficient of the order of $10^4$ l mol$^{-1}$ cm$^{-1}$ can be assigned to charge transfer.

Gibson\textsuperscript{47} studied a series of complexes and observed the bands in the range 1050 - 1125 cm$^{-1}$ arising due to the presence

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of ionic perchlorate ion. In the present investigations the bands have been observed in the above mentioned range showing the presence of perchlorate ion out of the co-ordination sphere. The two modes (C-N stretching and γ NH) give rise to absorption at 1333 and 790 cm$^{-1}$. An increase in C-N frequency is observed on co-ordination. Thus an increase in C-N frequency on co-ordination has been observed (1333 → 1380 cm$^{-1}$) and the band at 790 cm$^{-1}$ is lowered to ~ 740 cm$^{-1}$. The band at ~ 845 cm$^{-1}$ can be assigned to γ (N-H) vibration. The bands observed at ~ 1650 and ~ 1410 cm$^{-1}$ are due to N-H stretching vibration and C-N vibration respectively, while at 3200 cm$^{-1}$ is also due to N-H stretching vibration.

All the above observations thus assign unambiguously an octahedral stereo-chemistry to the complexes.

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STRUCTURE OF COBALT (III) COMPLEXES

The general molecular formula derived from analytical data (from the percentages of metal, carbon, hydrogen, nitrogen and halogen) may be represented as $[\text{Co(MA)}_4(\text{Succ})_2]X$ or $[\text{Co(DA)}_2(\text{Succ})_2]X$, where MA represents monoamine like propyl-, amyl-, dimethyl-, diethylamine; DA, diamine, i.e., 2:2 dipyridyl, ethylenediamine, propylenediamine; $X$, halogens (Cl or I); and Succ, succinimidate ion. All these complexes show a co-ordination no. 6 and are stable at room temperature but decompose on heating. The complexes show a variety of colour, i.e., bluish-green, orange, black, brown or light pink.

The complexes with dimethyl-, propyl-, amyl-, ethylenedi-, propylenediamine have been found to be soluble in water, while only one isomer of each of diethylamine and 2:2 dipyridylamine were soluble in water, alcohol and acetone.

The two isomers obtained in the case of diethyl-, 2:2 dipyridyl-, propyl- and amylamine have been separated by dissolving the compound in absolute alcohol, filtering and evaporating to dryness. The complexes have been recrystallised from acetone.
The molar conductance measurement in water and molecular weight determination by cryoscopic measurement have enabled the author to know the nature of the electrolyte and the true molecular weight of the complexes. The molar conductance data observed for these complexes fall in the range accepted for 1:1 electrolyte, i.e., $100 \pm 15 \text{ ohm}^{-1} \text{ cm}^2$. It is, therefore, inferred that the complexes are 1:1 electrolytes.

The molecular weight determination by cryoscopic method shows a depression in freezing point two times greater than the calculated value which also supports the 1:1 electrolytic nature of the complexes.

The electronic configuration of cobalt (III) ion is $1s^2$, $2s^2 \ p^6$, $3s^2 \ p^6$, $d^6$. The number of $d$ electrons available in cobalt (III) ion is six, and hence the spin only value of the ion should be zero. 49

The magnetic moment data observed for these complexes clearly indicate that the complexes are diamagnetic in nature and possess an octahedral stereo-chemistry. The $1A_{1g}$ state, which originates in the high energy singlet states of the ion