INTRODUCTION

The stereochemistry of metal complexes has attracted the attention of scientists working in the field. It is general observation that with a slight change in the mode of preparation of the metal complex entirely different type of complex species may be formed\(^1\). It, therefore becomes necessary to know about the type of species, that is formed following different preparation procedures. In past, some methods viz. X-ray diffraction analysis, dipole moment studies, IR studies etc. on Cis-Trans isomers of metal complexes have been used for the purpose of analysis\(^2\), but these methods suffer from various complications\(^3\).

Fortunately Crow and Westwood\(^4\) have suggested a polarographic method for such type of analysis. In our laboratory cis-trans isomers of \([\text{Pt(NH}_3\text{)}(\text{NO}_2\text{)}\text{Cl}_2]\)\(^7\) have been studied polarographically\(^5\). Encouraged by previous results the authors have undertaken the work...
of qualitative and quantitative, polarographic/voltammetric analysis of some Cis-Trans complexes of Platinum(II), Cobalt(II) and Chromium(III).

The results of which have been discussed in this chapter.

To analyse such systems, DC polarography, Differential Pulse Polarography and Cyclic Voltammetry have been used by the author. The systems undertaken for the study are Cis-Trans isomers of 

1. $\left[\text{Pt(NH}_3\right]_2\text{Cl}_2]$;  
2. $\left[\text{Co(NH}_3\right]_4\text{Cl}_2]$;  
3. $\left[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$; and  
4. $\left[\text{Co(NH}_3\right]_4\text{Cl}_2]\text{Cl}$.

THE TRANS EFFECTS AND ITS EXPLANATION

THE TRANS EFFECT

Ligands can be arranged in a series depending on the relative magnitude of the trans effect, which they exert. Certain ligands labilize (susceptible to substitution) groups in the trans-position. Various ligands may be compared as to their abilities in this respect. In the following list, the ligands are listed in the order of decreasing trans-effect.

$$\text{CN}^- > \text{C}_2\text{H}_4 > \text{CO} > \text{NO}_2^- > \text{SC(NH}_2\right]_2 > \text{R}_2\text{S} \sim \text{PR}_3$$
$$\sim \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- \sim \text{NH}_3 > \text{OH}^- > \text{H}_2\text{O}.$$

For example the reaction of the tetrachloroplatinate(II) ion with two molecules of ammonia. After one molecule of ammonia has reacted, there are two kinds of chloride ions remaining in the complex, those which are trans to each other, and that which is trans to ammonia. Chloride is more trans-directing than ammonia, and so the chlorides which are trans to each other are labilized more than the chloride which is trans to ammonia. Hence, it is
one of these labilized chlorides which is next displaced forming Cis- \([\text{Pt(NH}_3\text{)}_2\text{Cl}_2]\).

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array}
\xrightarrow{\text{NH}_3}
\begin{array}{c}
\text{Pt} \\
\text{Cl} \\
\text{NH}_3 \\
\text{Cl}
\end{array}
\xrightarrow{\text{NH}_3}
\begin{array}{c}
\text{Pt} \\
\text{Cl} \\
\text{NH}_3 \\
\text{Cl}
\end{array}
\xrightarrow{\downarrow}
\begin{array}{c}
\text{Pt} \\
\text{NH}_3
\end{array}
\text{Cis- } [\text{Pt(NH}_3\text{)}_2\text{Cl}_2]
\]

The reaction of the tetraamine platinum(II) ion with two moles of chloride ions, after the displacement of one ammonia molecule, there remain two ammonia trans to each other and the ammonia trans to the chloride. The latter ammonia molecule is labilized by the chloride and is the next to be displaced, forming trans- \([\text{Pt(NH}_3\text{)}_2\text{Cl}_2]\).

\[
\begin{array}{c}
\text{NH}_3 \\
\text{Pt} \\
\text{NH}_3
\end{array}
\xrightarrow{\text{Cl}^-}
\begin{array}{c}
\text{NH}_3 \\
\text{Pt} \\
\text{Cl}
\end{array}
\xrightarrow{\text{Cl}^-}
\begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{NH}_3
\end{array}
\xrightarrow{\downarrow}
\begin{array}{c}
\text{NH}_3 \\
\text{Pt} \\
\text{Cl}
\end{array}
\text{Trans- } [\text{Pt(NH}_3\text{)}_2\text{Cl}_2]
\]

**AN EXPLANATION TO THE TRANS-EFFECT**

Substitution reactions of Pt(II)-complexes are bimolecular. It is reasonable that the entering group approaches the complex from one side of the plane over the group to be replaced. In the activated complex the leaving group will have moved down so that a trigonal bipyramid arrangement is achieved.
The ligands with the largest trans-effects are just those which have vacant orbitals suitable for forming π bonds. The d-orbital of platinum, which would be used in π-bonding to ligand. It has four lobes in a plane perpendicular to that of the original complex\textsuperscript{10}, as shown in figure 4.5. The two lobes directed towards the positions occupied by Y and C' in the activated complex\textsuperscript{9}. The activated complex will be stabilized by a reduction in the density of d electrons at these positions. This exactly happens when the d electrons are used in bonding to ligand A\textsuperscript{9}. The stronger is the double bonding, the lower is the electron density in the critical directions and the more trans-directing is the ligand.

Fig. 4.5 - $d_{xz}$ or $d_{yz}$ orbital of a Pt(II) complex.

**SURVEY OF LITERATURE**

The polarographic technique can be successfully employed for the identification of Cis-Trans isomers of metal complexes. Crow and Westwood\textsuperscript{11,12} have prepared the Cis-Trans isomers of Rhodium(III) and cobaltic ions separately and got two distinct waves for the two forms of the complex. The Cis-Trans isomers of Platinum(II) complex of the type $[\text{Pt(NH}_3\text{)}(\text{NO}_2\text{)}\text{Cl}_2]^-$ were prepared\textsuperscript{13} and their polarograms recorded\textsuperscript{14}. 
Cis-Trans isomerism is also found in certain compounds containing bidentate (chelate) groups. Because of steric factors chelate groups occupy cis positions only. On the other hand, when two bidentate groups are present, the other two groups may be arranged, cis or trans to each other.

Hexacovalent coordination compounds of the types $MX_2Y_2Z_2^-$, $M(AA)_2X_2^-$, $M(AA)(BB)X_2^-$, $M(AA)X_2YZ^-$, and so on possess certain isomeric forms unique in that they may be resolved into optical antipodes. For example $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ has been found to exist in two forms, one is green and the other is violet. Certainly one of these must correspond to a trans-configuration for the chlorides and the other to a cis-configuration. It has been unequivocally demonstrated that the violet form is the cis-isomer, because when it is treated, with a solution of ammonium d-α-bromo camphor-$\alpha$-sulfonate, it crystallizes out as a salt, which when treated with hydrochloric acid, yields optically active $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$.\(^{16}\)

Two isomers of dichlorobis (ethylenediamine) chromium(III) chloride are known. The reactions used to assign the cis-configuration to the violet form and the trans-configuration to the green form\(^{17}\) it is possible to prepare at least two isomers of trimethylborazine $B_3N_3H_3(CH_3)_3$. One isomer, with a boiling point of 133°C and a melting point of -7.5°C, may be prepared by heating a mixture of trimethyl-ammonium chloride and lithium borohydride\(^{18}\). The other isomer with a boiling point of 129°C and a melting point of 31.5°C may be prepared by heating a mixture of boron-trimethyl and borazine\(^{19}\).
The only preparation of a π-allylplatinum complex besides from the generally applicable reaction of a metal halide with an allyl Grignard reagent is the reduction of an allyl chloride-\(\text{PtCl}_2\) mixture with tin(II) chloride\(^{20}\). Tetrahydrofuran is purified by distillation from LiAlH\(_4\)\(^{21}\).

Tetrakis (allylchloro)[platinum(II)] is an air-stable, yellow solid which is insoluble in organic solvents. It reacts with Na[C\(_3\)H\(_5\)] to give \([\text{C} \_3\text{H} \_5\text{Pt(C} \_3\text{H} \_5\text{)}]^{22}\). Triphenylphosphine converts it into (π-allyl) bis (triphenylphosphine) platinum(II) chloride, \([(\pi \cdot \text{C} \_3\text{H} \_5\text{)}\text{Pt(PPH} \_3\text{)}\_2\text{Cl}]\). The tetramer has a cyclic structure as determined by G. Raper and W.S. McDonald\(^{23}\). Each platinum atom is bonded to two bridging chloride ligands as well as to two bridging allyl ligands.

Early interesting but wholly unsuccessful explanations were offered by Blomstrand Jorgensen, and others\(^{24,25}\). Modern theory may be traced to the work of Alfred Werner\(^{25}\), to whom complete credit must be given not only for advancing a correct explanation for the characteristics of these compounds, Werner had completed the revolutionary paper\(^{25}\) which summarized these views on structures and properties and opened an entirely new field for investigation.

Transfer of Werner's general views to an electronic basis is due largely to Sidgwick\(^{26}\) and Lowry\(^{27}\), Werner's primary valencies were regarded as amounting to electron pair sharing. Thus ions such as \([\text{Co(en)}(\text{NO}_2\text{)}\text{Cl}]^+\) and \([\text{Co(en)}(\text{C}_2\text{O}_4\text{)}\text{Cl}_2]\) should theoretically at least, exist in Cis and Trans forms.
The Cis-Trans isomers of \( \text{[Cr(H}_2\text{O)}_4\text{Cl}_2 \text{]}^+ \)

When 1-cis-[Co en\(_2\text{Cl}_2 \text{]}^+ \) is heated in methanol solution with radiochloride (Cl\(^-\)) both trans- [Co en\(_2\text{Cl}_2 \text{]}^+ \) and di-Cis-[Co en\(_2\text{ClCl} \text{]}^+ \) are formed according to first-order rate laws\(^{28}\). Eventually, practically all the cis- [Co en\(_2\text{ClCl} \text{]}^+ \) is converted to trans- [Co en\(_2\text{ClCl} \text{]}^+ \). The experimental activation energy for the formation of the trans-isomer is greater than that for the formation of the di-cis-isomer.

When a bidentate group is replaced by two monodentate groups, such groups may be assumed to enter cis to each other. Rearrangement to the more symmetrical and therefore more generally stable, trans configuration can then occur. Both cis and trans forms being capable of isolation.

Werner resolved the cis- [Co(en)\(_2\text{Cl}_2 \text{]}^+ \) (violeo) and cis-[Co(en)\(_2\text{(NO}_2\text{)}_2 \text{]}^+ \) (flavo) ions. Ions of the types \([M\text{en}_3]^n\) where \(M = \text{Co(III)}, \text{Cr(III)}, \text{Pt(IV)}, \text{Rh(III)}, \text{Ir(III)}, \text{Zn(II)}, \text{Cd(II)}\) and \(M\text(C}_2\text{O}_4\text)_3^{+n-6}\) [where \(M = \text{Co(III)}, \text{Cr(III)}, \text{Rh(III)}, \text{Ir(III)}, \text{Pt(IV)}\)] may be cited as other examples. As illustrative of the general technique involved, reference may be made to the use of \(d\)-\(L\)-bromocamphor-\(\alpha\)-sulfonate in the resolution of Cis-[Co(en)\(_2\text{Cl}_2 \text{]}^+\)^{29}.

Selective adsorption of d or l forms on inert optically active materials such as quartz\(^{30}\) and differences in the rates with
which certain diastereoisomers react with a few coordinating agents$^{31}$, have yielded partial resolutions but have not proved to be extremely effective.

The addition of coordinated groups sometimes gives polynuclear halides. Thus a series of compounds of general formula $\text{PtCl}_2\cdot A$, where $A = \text{PR}_3, \text{AsR}_3, \text{Co}, \text{C}_2\text{H}_4, \text{PCl}_3, \text{P(OCH}_3)_3$, etc. has been characterized$^{32}$. Shinkai$^{33}$ and Coworkers have studied photoresponsive macrocyclic systems in which trans isomers were isomerized by UV light to the cis isomers. The cis isomers were isomerized thermally and, in some cases also by visible light to the trans isomers, the interconversion being completely reversible.

Structures$^{34}$ and spectral properties of some Bis(β-diketonoato) Copper(II) - Diazole Complexes and 1:1, 1:2 and 1:3 adducts of bis (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(II) and 4-methyl-1H-pyrazole have been reported in the literature.

Voltammetric$^{35}$ investigation on the response mechanism of the ion-selective electrodes based on the polymer modified with poly (oxyethylene) derivatives in acetonitrile have been studied by T. Nakamura et al.

Synthesis$^{36}$ and characterization$^{37}$ of Pd(II) and Pt(II) complexes$^{38}$ containing monodentate phosphorus donating or chelating 2-dimethylphosphinopyridine ($\text{PMe}_2\text{py}$)$^{39}$ have been reported in the literature.
Peptidyl-prolyl Cis-Trans Isomerase activity of Cyclophilin has been studied by one-dimensional H nuclear magnetic resonance spectroscopy by Victor and coworkers\textsuperscript{40}. Cis-Trans\textsuperscript{41} isomerization of thioindigo derivatives adsorbed on silica gel modified with octadecyl groups has been reported.

**EXPERIMENTAL AND PREPARATIONS**

**EXPERIMENTAL**

AnalaR/BDH grade chemicals were used for the investigations. All the solutions were prepared in double distilled water. All the polarograms/voltammograms were recorded at room temperature (30±1°C). Cis-Trans isomers of the following complexes i.e.
1. [Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}] ;
2. [Co(NH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2}] ;
3. [Cr(en)\textsubscript{2}Cl\textsubscript{2}]Cl ;
4. [Co(NH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2}]Cl were prepared as under\textsuperscript{42-45}.

**PREPARATION OF CIS\TRANS ISOMERS AND THE ANALYTE FOR POLAROGRAPHIC / VOLTAMMETRIC STUDIES**

1. (i) Cis-[Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}] was prepared\textsuperscript{42} by mixing 5 ml (0.01 M) H\textsubscript{2}PtCl\textsubscript{6} + 10 ml (0.01 M) ammonia. The Cis form, so formed, was converted into analyte for polarographic / voltammetric analysis by adding to it 25 ml (2M) KCl, the volume was made to 100 ml.

(ii) Trans-[Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}] was prepared by adding 5 ml (0.01 M) H\textsubscript{2}PtCl\textsubscript{6} + 20 ml (0.01 M) ammonia and treating the above solution with 10 ml (0.01 M) HCl, the trans form so formed was converted into analyte as above.
2. (i) Cis-[Co(NH$_3$)$_4$Cl$_2$] was prepared$^{43}$ by mixing 5 ml (0.01 M) CoCO$_3$ to 20 ml (0.01 M) NH$_3$ and 10 ml (0.01 M) HCl, the cis form so formed, was converted into analyte for polarographic analysis by adding 25 ml (2 M) KCl and the volume was made to 100 ml.

(ii) Trans-[Co(NH$_3$)$_4$Cl$_2$] was formed by boiling the above solution for sometime and the analyte was prepared as above.

3. (i) Cis-[Cr(en)$_2$Cl$_2$]Cl violet coloured cis isomer was prepared$^{44}$ by mixing 5 ml (0.01 M) CrCl$_3$ + 10 ml (0.01 M) ethylenediamine, the cis form so formed was converted into analyte using 25 ml (2 M) KCl as supporting electrolyte and making the volume to 100 ml.

(ii) Trans-[Cr(en)$_2$Cl$_2$]Cl green coloured trans form was prepared by evaporating cis form with mercury(II) chloride and the analyte was prepared as above.

4. (i) Cis-[Co(NH$_3$)$_4$Cl$_2$]Cl was prepared$^{45}$ by mixing 5 ml (0.01 M) CoCl$_2$ + 20 ml (0.01 M) NH$_3$, the cis form so formed was converted into analyte by adding 25 ml (2 M) KCl, the volume was made to 100 ml for polarographic/voltammetric analysis.

(ii) Trans-[Co(NH$_3$)$_4$Cl$_2$]Cl was prepared by slowly adding conc. HCl to the Cis-[Co(NH$_3$)$_4$Cl$_2$]Cl solution.

The Cis-Trans isomer of dichlorobis ethylenediamine chromium(III) chloride were distinguishable with naked eye. The cis form
produced violet coloured solution whereas trans form produced green coloured solution. All other Cis-Trans isomers understudy were colourless.

Test solutions for polarographic/voltammetric analysis were prepared in 0.5 M overall concentration of KCl as supporting electrolyte. The pH of the test solution was recorded on a pH meter. Pure nitrogen gas was bubbled through the test solution for 15 minutes before recording the polarogram.

RESULTS AND DISCUSSION

It is observed that the voltammetric behaviour of cis and trans isomers of each system gives well defined polarographic reduction waves separately at different potentials, which enables the use of DC Polarography, Differential Pulse Polarography and Cyclic Voltammetry for their qualitative as well as quantitative analysis.

Figures 4.1 to 4.4 show the DCP, DPP and Cyclic Voltammograms of the Cis-Trans isomers of the four complexes understudy. The half wave potentials/peak potentials and also diffusion currents/peak currents for the Cis-Trans isomers understudy have been depicted in Table 4.1. It clearly shows that in each case the cis isomer is reduced at a relatively lower negative potentials and accordingly the diffusion current has a lower value for each of the cis form as compared to its trans counterpart. An explanation for the reduction of cis isomer at a relatively lower negative potential as compared to its trans form may be given on the basis of simple
Table 4.1: Voltammetric Parameters for Cis-Trans Complexes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>COMPLEX</th>
<th>DCP $-E_{1/2}$ V vs SCE</th>
<th>DPP $-E_p$ V vs SCE</th>
<th>Cyclic Voltammetry (V)</th>
<th>DCP $I_d$ Value</th>
<th>DPP $I_p$ Value</th>
<th>Cyclic Voltammetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cis form</td>
<td>Trans form</td>
<td>Cis form</td>
<td>Trans form</td>
<td>Cis $-E_C$</td>
<td>Cis $-E_A$</td>
</tr>
<tr>
<td>1.</td>
<td>[Pt(NH$_3$)$_2$Cl$_2$]</td>
<td>1.30</td>
<td>1.35</td>
<td>1.32</td>
<td>1.37</td>
<td>1.39</td>
<td>1.37</td>
</tr>
<tr>
<td>2.</td>
<td>[Co(NH$_3$)$_4$Cl$_2$]</td>
<td>1.15</td>
<td>1.20</td>
<td>1.21</td>
<td>1.31</td>
<td>1.21</td>
<td>1.21</td>
</tr>
<tr>
<td>3.</td>
<td>[Cr(en)$_2$Cl$_2$]Cl</td>
<td>1.55</td>
<td>1.60</td>
<td>1.60</td>
<td>1.60</td>
<td>1.66</td>
<td>1.66</td>
</tr>
<tr>
<td>4.</td>
<td>[Co(NH$_3$)$_4$Cl$_2$]Cl</td>
<td>1.10</td>
<td>1.15</td>
<td>1.16</td>
<td>1.26</td>
<td>1.15</td>
<td>1.08</td>
</tr>
</tbody>
</table>

$E_{1/2}$, $E_p$, $E_C$ and $E_A$ are half wave potential, peak potential, peak potentials for cathodic and anodic peaks respectively.

$i_d$, $I_p$, $I_C$ and $I_A$ are diffusion current, peak current, peak currents for cathodic and anodic peaks respectively.
**FIG: 4.1 A, B, C** are direct current polarograms (DCP), Differential Pulse polarograms (DPP) and cyclic voltammograms (CV) for 1.0 mM Cis-$\left[\text{Pt}\left(\text{NH}_3\right)_2\text{Cl}_2\right]$ complex in 1.0 M KCl.

**FIG: 4.1 B, a', b', c'** The corresponding trans-$\left[\text{Pt}\left(\text{NH}_3\right)_2\text{Cl}_2\right]$ polarograms/voltammograms.
FIG 4.2.A, b, c are direct current polarograms (DCP) differential pulse polarograms (DPP) and cyclic voltammograms for 1.0 mM Cis-[Co(NH$_3$)$_4$Cl$_2$] complex in 1.0 M KCl.

FIG 4.2.A, a, b, c’ The corresponding trans-[Co(NH$_3$)$_4$Cl$_2$] polarograms/voltammograms.
FIG. 43A. a, b, c are direct current polarograms (DCP) differential pulse polarograms (DPP) and cyclic voltammograms (CV) for 1.0 mM cis- \([\text{Cr} (\text{en})_2 \text{Cl}_2] \text{Cl}\) complex in 1.0 M KCl.

FIG. 43B. a', b', c' The corresponding trans- \([\text{Cr} (\text{en})_2 \text{Cl}_2] \text{Cl}\) polarograms/voltammograms.

For a and a':
- X axis = 500 mV/cm
- Y axis = 200 mV/cm

For b, b' and c, c':
- X axis = 500 mV/cm
- Y axis = 100 mV/cm

PH = 6.96 AT 30°C

INITIAL APPLIED VOLTAGE = -135V vs SCE
SENSITIVITY = 10 µA/V
FIG:4.4A. a, b, c are direct current polarograms (DCP) differential pulse polarograms (DPP) and cyclic voltammograms (CV) for 1.0 mM cis-[Co(NH₃)₄Cl₂]Cl complex in 1.0 M KCl.

FIG:4.4B. a', b', c' The corresponding trans-[Co(NH₃)₄Cl₂]Cl polarograms/voltammograms.
electrostatic argument that the preferred orientation of the cis complex is due to the large internal dipole at a positive surface.

It has also been observed that the diffusion current is proportional to the concentration of each of the Cis-Trans forms which was confirmed by performing polarographic/voltammetric studies on these complexes using their different concentrations, thus enabling their quantitative determination.
REFERENCES


15. (AA) and (BB) represent bidentate ligands, i.e. ligands, such as ethylenediamine, which may coordinate to a metal atom at two adjacent positions.


