Verification of Werner's Theory

(1) Conductivity Measurement

The molar conductivity of an ionic compound depends on:

(i) The concentration of solute.

(ii) The number of charges on the species which are formed on dissolution.

Molar conductivity relates to a 1 M solution and thus the concentration factor is removed. As the number of charges increases, the molar conductivity of the complexes also increases. The total no. of charges on the species formed when the complex is dissolved, can be deducted by comparison of its molar conductivity with that of known simple ionic compound. The molar conductivity measurement of cobalt/ammonia/chlorine complexes suggest structures similar to Werner's Theory.

Table: Number of charges related to Werner structures.

	Charges	Primary valency ionizable chlorines	Secondary valency
$[Co(NH_3)_6]^{3+}$ $3Cl^-$	6	3	$6NH_3 = 6$
$[Co(NH_3)_5Cl]^{2+}$ $2Cl^-$	4	2	$5NH_3 + 1Cl^- = 6$
$[Co(NH_3)_4Cl_2]^+$ Cl^-	2	1	$4NH_3 + 2Cl^- = 6$

(2) Cryoscopic Measurement

The freezing point of a liquid is lowered when a non volatile chemical substance is dissolved in it. Cryoscopic measurements involve measuring how much the freezing point is lowered. The depression of freezing point obtained depends on the number of particles present. Larger no. of ions cause a greater amount of depression in freezing point. Cryoscopic measurements can be used to find if a molecule dissociates, and how many ions are formed. If a molecule dissociates into two ions it will give twice the expected depression for a single particle. If three ions are formed this will give three times the expected depression. Thus:

$LiCl \rightarrow Li^+ + Cl^-$ (2 particles) (2 charges)

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$ (3 particles) (4 charges)

$LaCl_3 \rightarrow La^{3+} + 3Cl^-$ (4 particles) (6 charges)

The number of particles formed from a complex molecule determines the size of the depression of freezing point. Note that the number of particles formed may be different from the total number of charges which can be obtained from conductivity measurements. The two types of information can be used together to establish the structure.

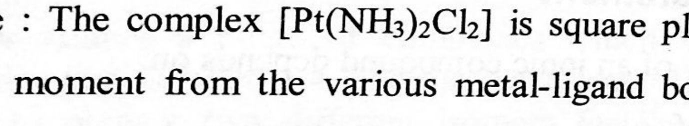
Molar conductivities and cryscopic measurements for chromium (III) complexes involving ammonia molecules and chloride ions, for example, helps in demarcating the coordination sphere from ionization sphere

Table : Elucidation of structure on the basis of molar conductivity and cryoscopic measurements.

Compound	Molar conductivity	Cryoscopic measurements	Structure
$CrCl_3 \cdot 6NH_3$	6 charges	4 particles	$[Cr(NH_3)_6]^{3+} + 3Cl^-$
$CrCl_3 \cdot 5NH_3$	4 charges	3 particles	$[Cr(NH_3)_5Cl]^{2+} + 2Cl^-$
$CrCl_3 \cdot 4NH_3$	2 charges	2 particles	$[Cr(NH_3)_4Cl_2]^+ + Cl^-$
$CrCl_3 \cdot 3NH_3$	0 charge	1 particle	$[Cr(NH_3)_3Cl_3]$

(3) Dipole moment Measurement

Dipole moment measurement may also give structural information but only for non-ionic complexes. For example : The complex $[Pt(NH_3)_2Cl_2]$ is square planar and can exist as *cis* or *trans* forms. The dipole moment from the various metal-ligand bonds cancel out in the trans forms. However, a finite dipole moment is given by the *cis* forms.



Cis– *Trans–*