History of Modern Coordination Chemistry

- **1798**: Tassart (France) discovers $CoCl_3$ in aqueous ammonia gives a pink "salt" with the composition of $CoN_6H_{18}Cl_3 = CoCl_3(NH_3)_6$.
- **Over the next 50 years**: Numerous series of related cobalt, iridium and platinum complexes were prepared (see below). The nature of these inorganic species remained a mystery.

Semi-empirical formula	Colour	Original name	Equivalents of AgCl precipitated upon Ag^+ addition (Blomstrand)	Number of ions (+ve or –ve) predicted from conductivity measurements (Werner)
$CoCl_3(NH_3)_6$	**Yellow**	Luteocobaltic	3	4
$CoCl_3(NH_3)_5$	**Purple**	Purpureocobaltic	2	3
$CoCl_3(NH_3)_4$	**Green**[1]	Praseocobaltic	1	2
$CoCl_3(NH_3)_4$	**Violet**[1]	Violeocobaltic	1	2
$CoCl_3(NH_3)_3$	**Orange**	-	0	0

1. This compound has two isomers. One is green (*trans*-isomer) and the other is violet (*cis*-isomer).

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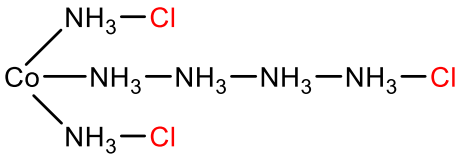
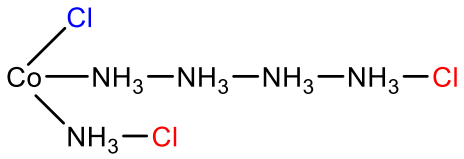
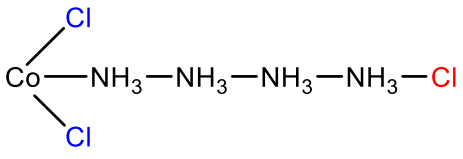
1862: Blomstrand (Sweden) suggested these structures:



$CoCl_3(NH_3)_6$



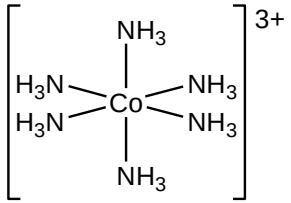
$CoCl_3(NH_3)_5$



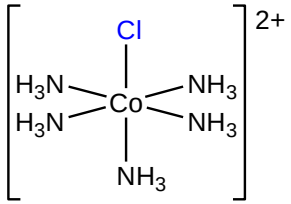
$CoCl_3(NH_3)_4$

1892: Werner (Germany) proposed a different interpretation based on careful conductivity measurements:

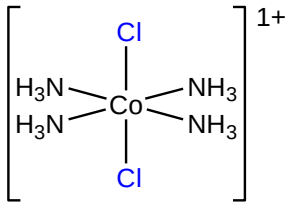
$CoCl_3(NH_3)_6$ =
$[Co(NH_3)_6]Cl_3$ =



$CoCl_3(NH_3)_5$ =
$[CoCl(NH_3)_5]Cl_2$ =

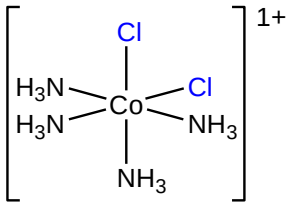


$CoCl_3(NH_3)_4$ =
$[CoCl_2(NH_3)_4]Cl$ =



trans

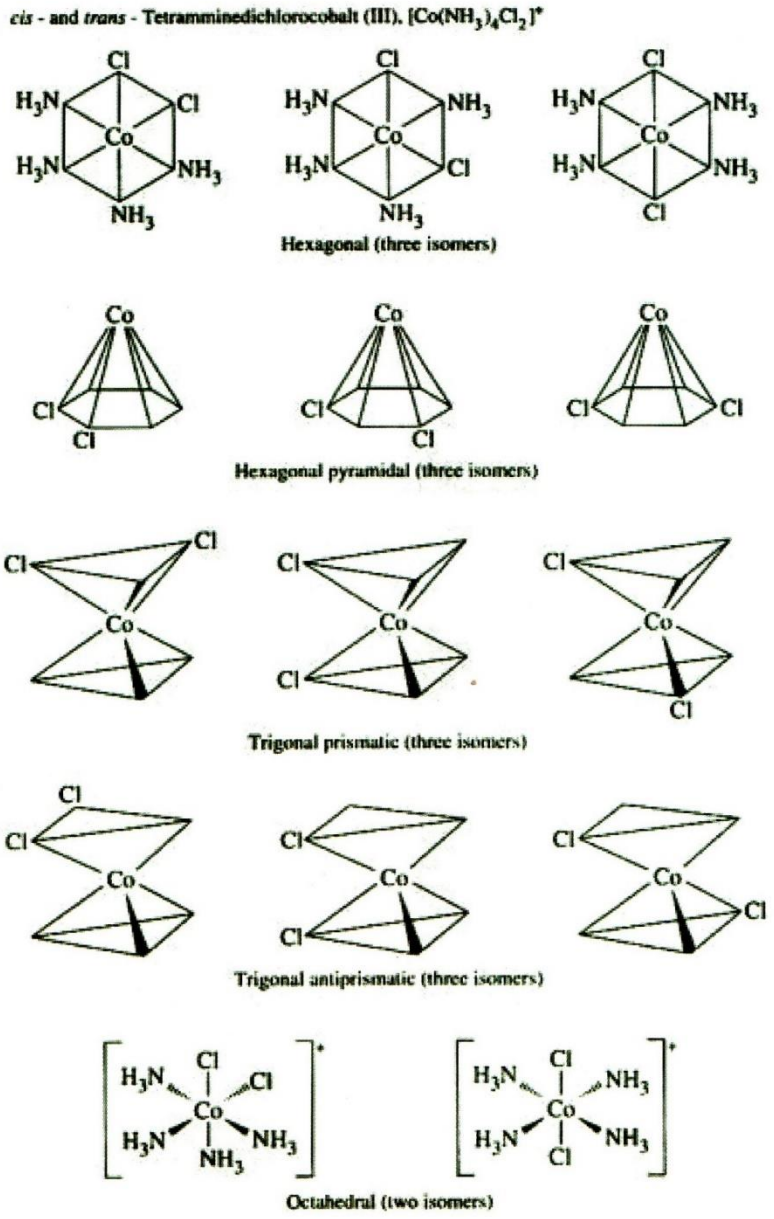
or



cis

Alfred Werner

History of Modern Coordination Chemistry



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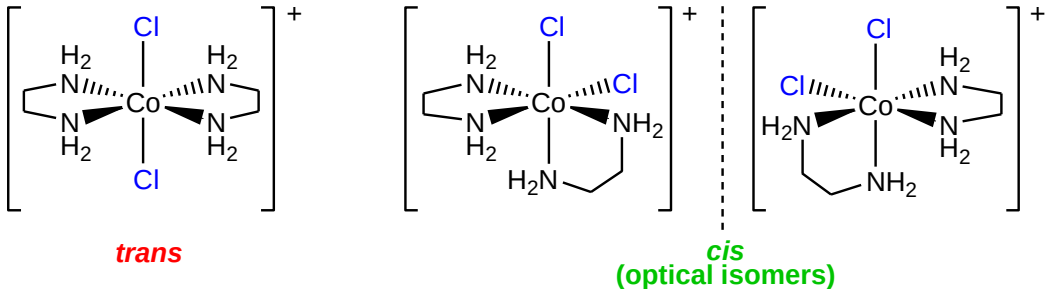
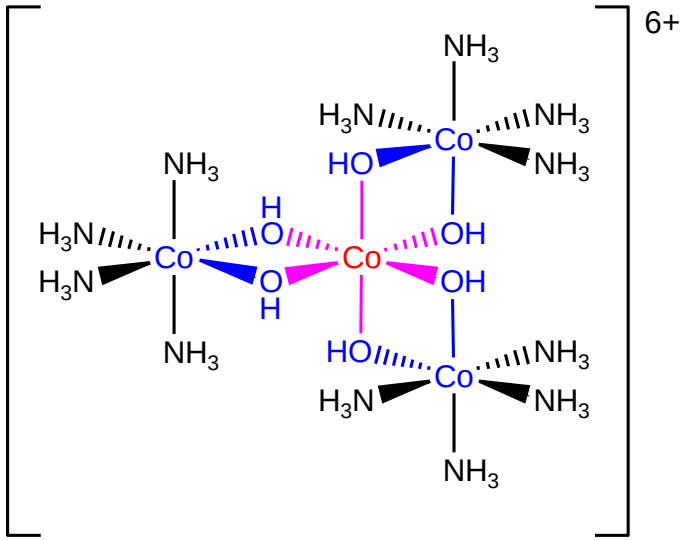
- In order to persuade his toughest critics Werner prepared the following chiral complex, the *cis* isomer of which is chiral, and thus, has two optical isomers.



- The two optical isomers were separate and specific optical rotation measured.
- Blomstrand insisted he was correct, and that the optical activity of the compounds was due to the carbon atoms.
- Werner aims to prepare the first optically active octahedral complex that does not contain carbon.
- **1913**: Werner received Nobel Prize.
- **1914**: Werner resolves the optical isomers of the first optically active compound that does not contain carbon.



Conductivities of Coordination Compounds

Formula	conductivity [$W^{-1}cm^2mol^{-1}$]	Electrolytes	Werner formulation
$PtCl_4 \cdot 2NH_3$	4	0	$[Pt(NH_3)_2Cl_4]$ (trans)
$PtCl_4 \cdot 2NH_3$	7	0	$[Pt(NH_3)_2Cl_4]$ (cis)
NaCl	124	1 : 1	-
$PtCl_4 \cdot 3NH_3$	97	1 : 1	$[Pt(NH_3)_3Cl_3]Cl$
$PtCl_4 \cdot NH_3 \cdot KCl$	107	1 : 1	$K[Pt(NH_3)Cl_5]$
$CaCl_2$	261	1 : 2	-
$CoCl_3 \cdot 5NH_3$	261	1 : 2	$[Co(NH_3)_5Cl]Cl_2$
$CoBr_3 \cdot 5NH_3$	258	1 : 2	$[Co(NH_3)_5Br]Br_2$
$CrCl_3 \cdot 5NH_3$	260	1 : 2	$[Cr(NH_3)_5Cl]Cl_2$
$CrBr_3 \cdot 5NH_3$	280	1 : 2	$[Cr(NH_3)_5Br]Br_2$
$PtCl_4 \cdot 4NH_3$	229	1 : 2	$[Pt(NH_3)_4Cl_2]Cl_2$
$PtCl_4 \cdot 2KCl$	257	2 : 1	$K_2[PtCl_6]$
$LaCl_3$	394	1 : 3	-
$CoCl_3$	408	1 : 3	-
$CoCl_3 \cdot 6NH_3$	432	1 : 3	$[Co(NH_3)_6]Cl_3$
$CoBr_3 \cdot 6NH_3$	427	1 : 3	$[Co(NH_3)_6]Br_3$
$CrCl_3 \cdot 6NH_3$	442	1 : 3	$[Cr(NH_3)_6]Cl_3$
$PtCl_4 \cdot 5NH_3$	404	1 : 3	$[Pt(NH_3)_5Cl]Cl_3$
$PtCl_4 \cdot 6NH_3$	523	1 : 4	$[Pt(NH_3)_6]Cl_4$