Inorganic and Physical Chemistry Department
General and Inorganic Chemistry

Coordination compounds

In specialty 226 Pharmacy, industry pharmacy

Ye.Ya.Levitin,
Doctor of Pharmaceutical Sciences, Professor

Plan

1. **Basic theses of the theory of coordination compounds**
2. **Coordination number**
3. **Ligands**
4. **Classification of coordination compounds**
5. **The Nomenclature of Coordination Compounds**
6. **Electrolytic Dissociation of Complex Ions in Solutions**
7. **Isomerism of Coordination Compounds**
8. **Bonding in Complex Ions – Valence Bond Theory**

Actuality of theme

Coordination compounds are of great importance in analytical chemistry, medicine and pharmacy.

Aim: to study the structure and properties of coordination compounds for the purpose of using these positions in the study of other pharmaceutical disciplines

Specific goals:

- Classify of coordination compounds .
- Use tabular data of $K_{\text{instab.}}$ to determine the stability of coordination compounds.
- Understand the structure of coordination compounds.

Theoretical questions for independent work

Hemoglobin and chlorophyll as an example of a coordination compounds.

Bibliographical Guidance

General and inorganic chemistry: Textbook for students of higher schools Ye.Ya.Levitin, I.O.Vedernikova.– Kharkiv:Publishing House of NUPH :Golden Pages, 2009. – 360 p.

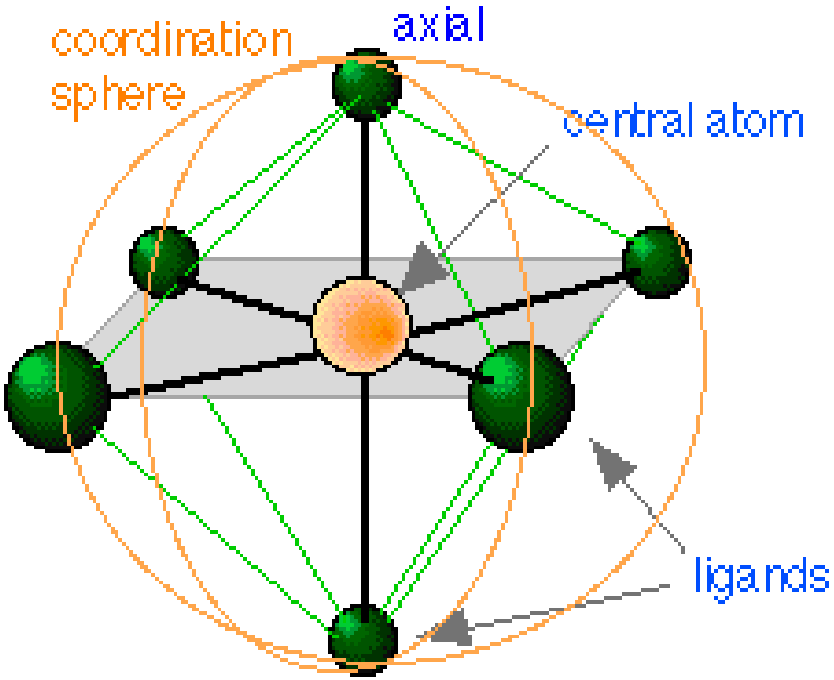
Laboratory Practicum in General and inorganic chemistry.I module/ Ye.Ya.Levitin, I.O.Vedernikova et al.– Kharkiv,2020. – 106 p.

General and inorganic chemistry:The lecture courses for the students of pharmaceutical universities. I Module / Ye.Ya.Levitin, I.O.Vedernikova et al.– Kharkiv: NUPH Publishers, 2020. – 123 p.

The collection of theoretical questions and tests in inorganic chemistry:for the students of higher school. / Ye.Ya.Levitin, I.O.Vedernikova.– Kharkiv: NUPH Publishers, 2007. – 76 p.

Basic theses of the theory of coordination compounds

The coordination compounds are named complex compounds, forming a complex ion, which consists of a **central ion** with a number of other molecules or ions surrounding it (**ligands**), capable to independent existence in solution and in a crystal.



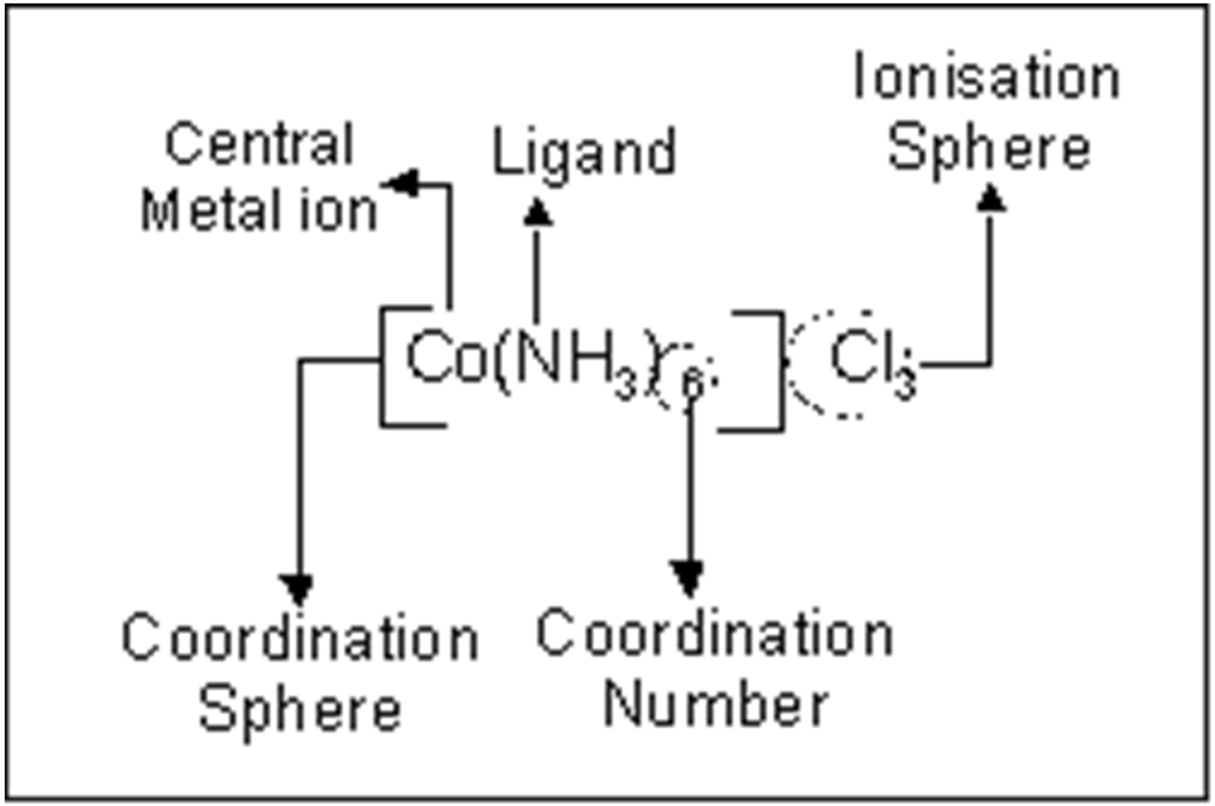
Central ion is a atom or ion, which has free vacant atomic orbitals (acceptor of electron pairs). The most common central ions are ***d*-family** elements of periodic system.

Ligands are ions or molecules with one or more electron pairs that can form bonding by donor-acceptor mechanism with a central ions (donor of electron pairs).

The combination of a central metal ion and its ligands is called a **complex ion**, and a neutral compound containing complex ion where ligands are found is called the inside **coordination sphere**.

The ions, which were not including in coordination sphere, make **external (outside) sphere** of complex compound. The coordination sphere is separated from external by square brackets.

$$CoCl_{3(s)} + 6NH_3 \rightarrow [Co(NH_3)_6]Cl_3$$



Founder of Coordination Theory, 1893

Alfred Werner(1866-1919), Switzerland

Nobel Prize in Chemistry, 1913

Coordination number is the number of ligands attached to the central atom/ion.

$[Ag(NH_3)_2]Cl$ $K[BiI_4]$ $Na_3[Al(OH)_6]$

In accordance with Werner’s rule of thumb coordination number of the central atom is usually two times greater than the absolute value of its oxidation state.

Coordination number	**2**	**4**	**6**
Central ions	Cu^+, Ag^+, Au^+	Cu^{2+}, Hg^{2+}, Au^{3+}, Pb^{2+}, Pt^{2+}, Sn^{2+}, Zn^{2+}	Fe^{2+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Al^{3+}, Pt^{4+}, Sn^{4+}

Charge of the complex ion is equal to the algebraic sum of the charges central atom and ligands. Complex molecule is electrically neutral.

Dentate of the ligand is the number of places that a ligand may occupy.

Monodentate		**Bidentate**
Neutral molecules	Negative ions	
CO carbonyl- NH_3 amine- H_2O aqua-	F^- fluoro- Cl^- chloro- Br^- bromo- OH^- hydroxo- CN^- cyano- NO_2^- nitro- NO_3^- nitrato- NCS^- thiocynato- CH_3COO^- acetato- $S_2O_3^{2-}$ thiosulfato	CO_3^{2-} carbonato- $C_2O_4^{2-}$ oxalato - SO_4^{2-} sulphato- N_2H_4 hydrazine - $H_2NCH_2CH_2NH_2$ (En) – ethylenediamine-

Example 1

Calculate the oxidation number and coordination number of central ion, the charge of the complex ion $Na_3[Ag(S_2O_3)_2]$.

$Na_3[Ag(S_2O_3)_2]$

$1+ \times 3 = 3+$ $[\quad]^{3-}$

the charge of outside sphere the charge of inside sphere

The silver oxidation number +1, one ligand thiosulphato has the charge 2–, two ligands have the charge 4– but $S_2O_3^{2-}$ is monodentate and coordination number of central ion is 2.

Classification of coordination compounds

1. Depending on the charge of the complex ion *coordination compounds* are divided into three parts:

Cationic	$[Ag(NH_3)_2]^+ Cl$
Anionic	$K_4[Fe(CN)_6]^{4-}$
Neutral	$[Fe(CO)_5]^0$, $[Pt(NH_3)_2Cl_2]^0$

2. Depending on the structure of the outer sphere *coordination compounds* are divided into:

Complex acids	$H[AuCl_4]$
Complex bases	$[Cu(NH_3)_4](OH)_2$
Complex salts	$[Zn(NH_3)_4]SO_4$, $K_3[Fe(CN)_6]$
Nonelectrolytes	$[Pt(NH_3)_2Cl_2]$

3. By the nature of the ligands:

Aquacomplex	$[Al(H_2O)_6]Cl_3$
Ammoniates	$[Cu(NH_3)_4]SO_4$
Acidocomplexes	$Na_2[Hg(CN)_4]$
Hydroxocomplexes	$Na_3[Al(OH)_6]$
Mixed complex compounds	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

The Nomenclature of Coordination Compounds

- ✓ Cations are named before anions.
- ✓ For a complex ion or neutral complex, the names of the ligands are given first, followed by the name of the central ion.
- ✓ In naming ligands an “o” ending is used for anions (chloro-, cyano-).
- ✓ If a ligands is a neutral molecule, the unmodified name of the molecule is used (H_2O – aqua, NH_3 – ammine)
- ✓ The Greek prefixes mono = 1, di = 2, tri = 3, tetra = 4, penta = 5, gexa = 6 are used to designate the number of ligands of a given type. For example, “dichloro” signifies two Cl^- ions as ligands.
- ✓ Ligands are named in alphabetical order.

- ✓ The oxidation state of the central metal ion in a complex cation is denoted by a Roman numeral placed in parentheses the name of the ion. The ion $[Co(NH_3)_6]^{3+}$, for example, is called hexaamminecobalt (III) ion.
- ✓ In complex anions the oxidation state of the central ion is modified to carry an “ate” ending. The ion $[Al(OH)_6]^{3-}$ is called the hexa hydroxoaluminate (III) ion. For the following metals the English name is replaced by the Latin name, to which the “ ate” ending is added: **iron – ferrate; tin – stannate; lead – plumbate; copper – cuprate; silver – argentate; gold – aurate.** Thus, $[CuCl_4]^{2-}$ is tetrachlorocuprate (II) ion.

What is the name of the following compounds?

$[Ag(NH_3)_2]Cl$ – diammineargentum (I) chloride.

$[CoBr(NH_3)_5]SO_4$ – pentaamminebromocobaltum (III) sulphate.

$K_3[Fe(CN)_6]$ – potassium hexacyanoferrate (III).

$Na_3[Co(C_2O_4)_3]$ – sodium trioxalatocobaltate (III).

$[Pt(NH_3)_2Cl_2]$ – diamminedichloroplatinum (II).

What is the formula of the compound pentaaquachlorochromium (III) chloride?

The central metal ion is Cr^{3+}. There are one Cl^{-} ion and five H_2O molecules as ligands. The complex ion carries a net change of +2. Two Cl^{-} ions are required outside the coordination sphere to neutralize this charge. The formula of the coordination compound is $[Cr(H_2O)_5Cl]Cl_2$.

Electrolytic Dissociation of Complex Ions in Solutions

Distinguish initial and secondary dissociation of complex ions.

Initial dissociation – dissociation of coordination compounds on a complex ion and ions of external sphere. It dissociates as strong electrolytes:

$$[Ag(NH_3)_2]Cl \rightarrow [Ag(NH_3)_2]^+ + Cl^-$$

Complex ions are exposed to secondary dissociation:

$$[Ag(NH_3)_2]^+ \leftrightarrows [Ag(NH_3)]^+ + NH_3$$

$$[Ag(NH_3)]^+ \leftrightarrows Ag^+ + NH_3$$

Total process: $[Ag(NH_3)_2]^+ \leftrightarrows Ag^+ + 2NH_3$

The constant of equilibrium is called a **dissociation constant, K_D,** or an **instability constant, K_i**.

General constant of instability:

$$[Ag(NH_3)_2]^+ \leftrightarrows Ag^+ + 2NH_3$$

$$K_{i_{gen.}} = \frac{[Ag^+][NH_3]^2}{[[Ag(NH_3)_2]^+]}$$

$$K_{i_{gen.}} = K_{i_1} \cdot K_{i_2}$$

The value of a constant of instability of a complex ion depends on its nature and from temperature.

Than less the value K_i, the internal sphere of complex ions is durable.

Using values of constants of instability, which are given in the table, it is possible to predict a direction of course of reactions in solutions of complex ions.

Constants of instability for several complex ions at 25 °C

$[Ag(NH_3)_2]^+ \leftrightarrows Ag^+ + 2NH_3$	9.3×10^{-8}
$[Ag(S_2O_3)_2]^{3-} \leftrightarrows Ag^+ + 2S_2O_3{}^{2-}$	2.5×10^{-14}
$[Ag(CN)_2]^- \leftrightarrows Ag^+ + 2CN^-$	8.0×10^{-22}
$[Au(CN)_2]^- \leftrightarrows Au^+ + 2CN^-$	5.0×10^{-39}
$[AuCl_4]^- \leftrightarrows Au^{3+} + 4Cl^-$	5.0×10^{-22}
$[Cd(NH_3)_4]^{2+} \leftrightarrows Cd^{2+} + 4NH_3$	7.6×10^{-8}
$[Cd(CN)_4]^{2-} \leftrightarrows Cd^{2+} + 4CN^-$	1.4×10^{-19}
$[Co(NH_3)_6]^{3+} \leftrightarrows Co^{3+} + 6NH_3$	3.1×10^{-33}
$[Cu(NH_3)_4]^{2+} \leftrightarrows Cu^{2+} + 4NH_3$	2.1×10^{-13}
$[Fe(CN)_6]^{4-} \leftrightarrows Fe^{2+} + 6CN^-$	1.0×10^{-24}
$[Fe(CN)_6]^{3-} \leftrightarrows Fe^{3+} + 6CN^-$	1.0×10^{-31}
$[HgCl_4]^{2-} \leftrightarrows Hg^{2+} + 4Cl^-$	8.5×10^{-16}
$[HgBr_4]^{2-} \leftrightarrows Hg^{2+} + 4Br^-$	1.0×10^{-21}
$[HgI_4]^{2-} \leftrightarrows Hg^{2+} + 4I^-$	1.5×10^{-30}
$[Hg(CN)_4]^{2-} \leftrightarrows Hg^{2+} + 4CN^-$	4.0×10^{-42}

Example 2

At addition of solution KI to a solution $K_2[HgCl_4]$ is formed new stronger complex $K_2[HgI_4]$, which constant of instability is much less, than at an initial complex is formed

$$K_2[HgCl_4] + 4KI \leftrightarrows K_2[HgI_4] + 4KCl$$

$$K_i = 8.5 \times 10^{-16} \gg K_i = 1.5 \times 10^{-30}$$

Example 3

At addition Na_2S to a solution $Na_3[Ag(S_2O_3)_2]$, last collapses, as is formed slightly soluble in water Ag_2S:

$$2Na_3[Ag(S_2O_3)_2] + Na_2S \leftrightarrows Ag_2S_{(s)} + 4Na_2S_2O_3$$

$$K_i = 2.5 \times 10^{-14} \qquad K_{sp} = 1.5 \times 10^{-30}$$

$$K_i[Ag(S_2O_3)_2]^{3-} \gg K_{sp}Ag_2S$$

Isomerism of Coordination Compounds

The phenomenon when substances have identical qualitative and quantitative composition, but have various a structures so, and various properties, is named **isomerism.**

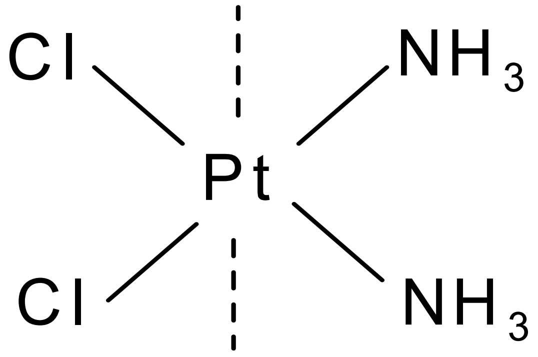
Two or more species having the same composition but different structures and properties are said to be **isomers.**

Distinguish **geometric, hydrated, ionization, coordination isomerism.**

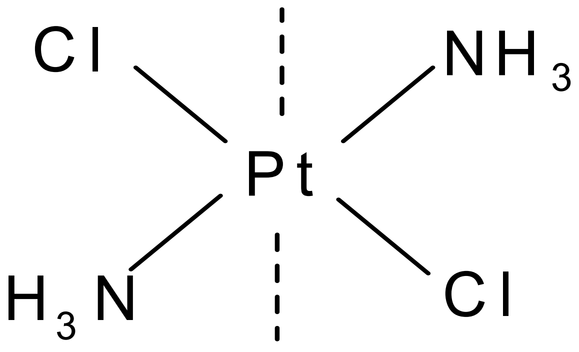
Geometrical (*cis-trance*) isomerism is caused by various position of ligands be relative each other.

For example,

Diamminedichloroplatinum (II) $[Pt(NH_3)_2Cl_2]$:



cis-



trance-

Cis-$[Pt(NH_3)_2Cl_2]$ slows growth of malignant tumors, and trance-isomer has not antitumor activity.

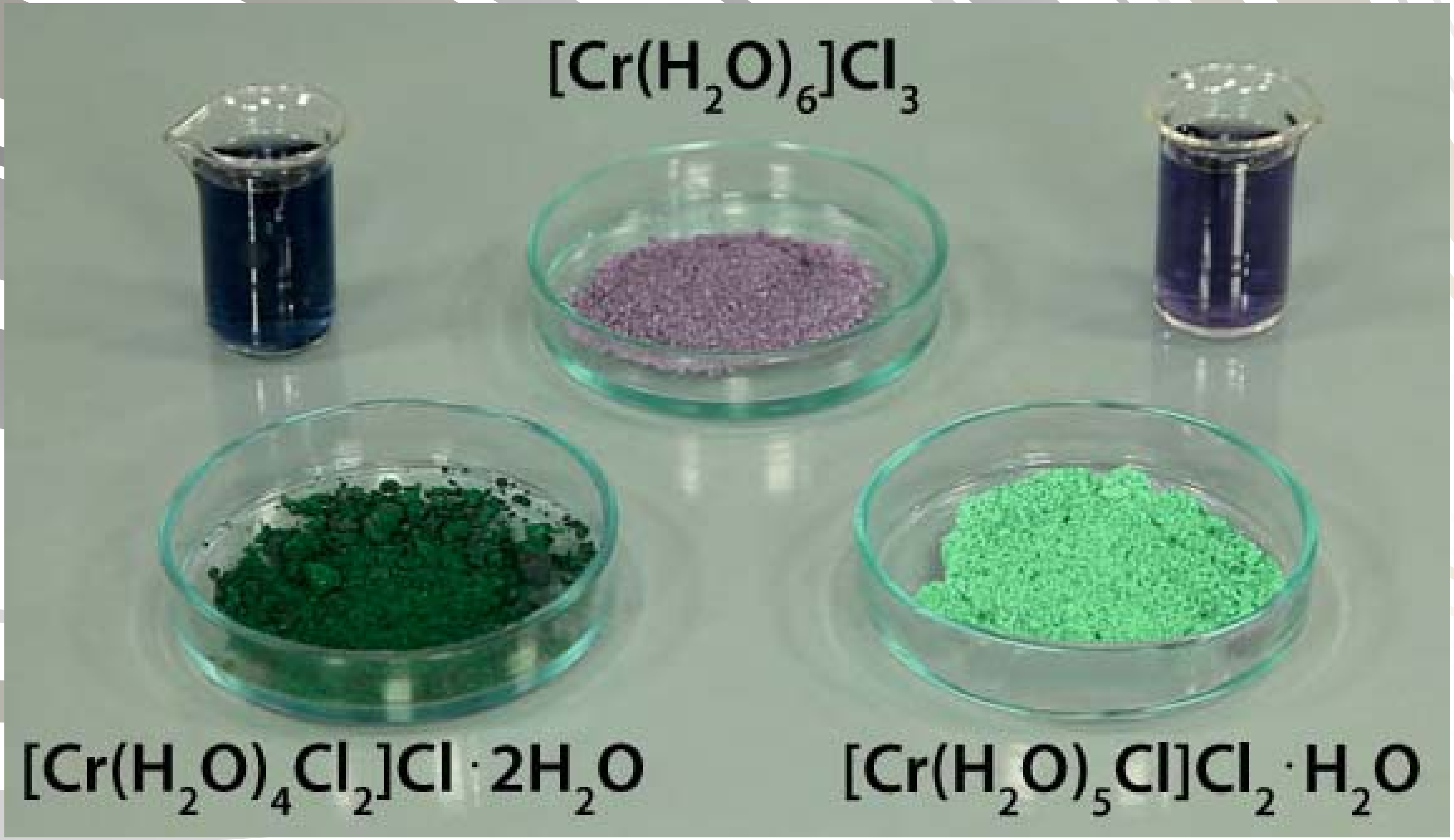
Hydrated Isomerism is caused by unequal distribution of molecules of water between coordination and external spheres of coordination compounds. Some examples of hydrated isomerism are aquacomplex cations of chromium (III). Experimentally established of three compounds of structure $CrCl_3 \cdot 6H_2O$ which differ coloring and electro conductivity.

Some coordination compounds of Cr^{3+} and their colors

$[Cr(OH_2)_6]Cl_3$,	$[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$	$[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$
violet	blue-green	green

Hydrated Isomerism

$CrCl_3 \cdot 6H_2O$



Ionization Isomerism is caused by unequal distribution of ions of the acid rests between coordination and external spheres of coordination compounds.

$[Co(NH_3)_5Br]SO_4$

pentaamminebromo-
cobalt(III) sulphate

$[Co(NH_3)_5SO_4]Br$

pentaamminesulphato-
cobalt(III) bromide

Coordination Isomerism is caused by an exchange of ligands of two central ions.

$[Co(NH_3)_6][Cr(CN)_6]$ $[Cr(NH_3)_6][Co(CN)_6]$

Bonding in Complex Ions – Valence Bond Theory

According to a method of valence bond theory a ligand is a species having an atoms capable of donation an electron pairs to a central metal ion in the coordination sphere. Empty orbitals of central metal are acceptors electron pairs.

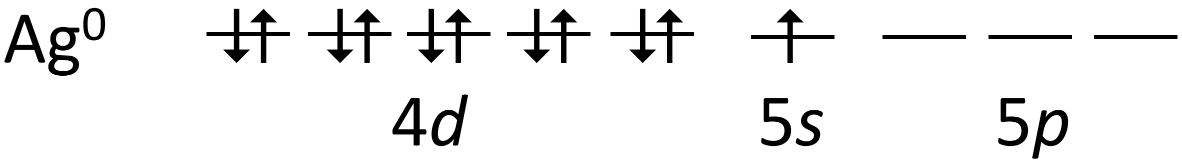
Electronic pairs of ligands influence on valence electrons central metal. On a degree of influence on valence electrons central metal ligands place in **spectrochemical series**:

$CN^- > CO > NO_2^- >$	$En > NH_3 > SCN^- >$	$H_2O >$	$OH^- > F^- > Cl^- > Br^- > I^-$
Strong field	Ligands of average force		Weak field
Couple electrons of central metal		Do not couple electrons of central metal	

Consider the formation of complex ion $[Ag(NH_3)_2]^+$

Atom of silver has next short hand electronic configuration of the valence electrons: Ag [Kr] $4d^{10}5s^1$

In the central ion silver has charge +1 and an atom of silver lose one 5*s* electrons: Ag [Kr] $4d^{10}5s^0$

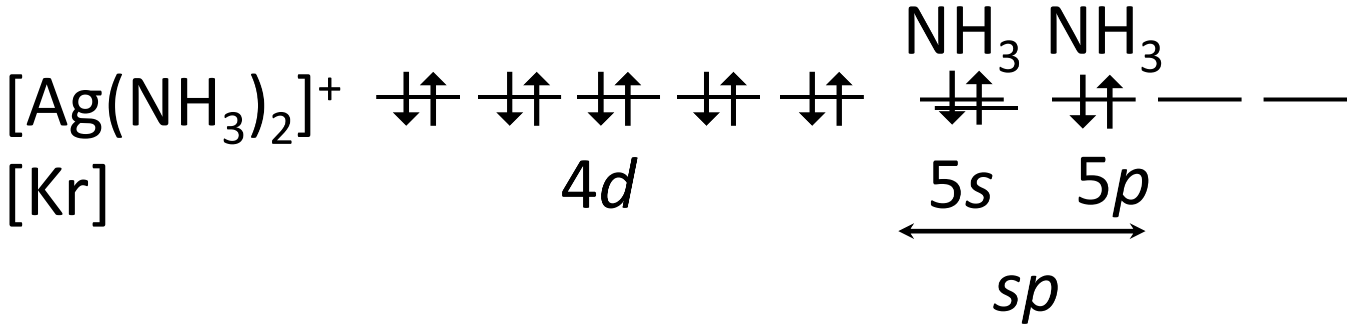


Consider the formation of complex ion $[Ag(NH_3)_2]^+$

Atom of silver has next shortened electronic configuration of the valence electrons: Ag [Kr] $4d^{10}5s^1$

In the central ion silver has charge +1 and an atom of silver lose one 5s electrons: Ag [Kr] $4d^{10}5s^0$

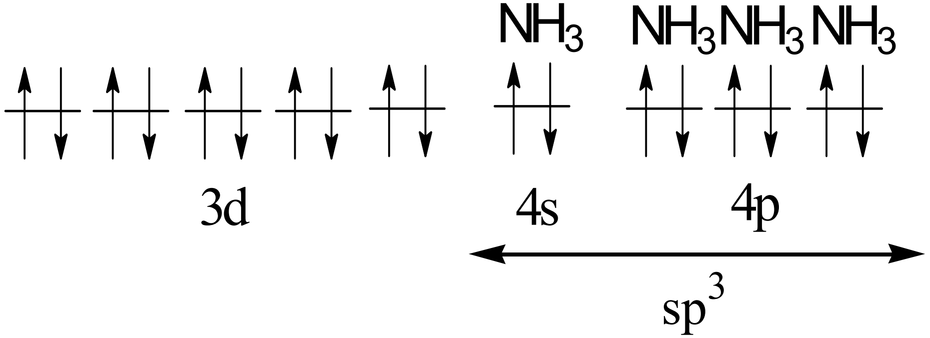
Molecules NH_3 are ligands of **average force** and therefore couple electrons of central metals. Ten electrons of central metal are place on three 4*d* orbitals.



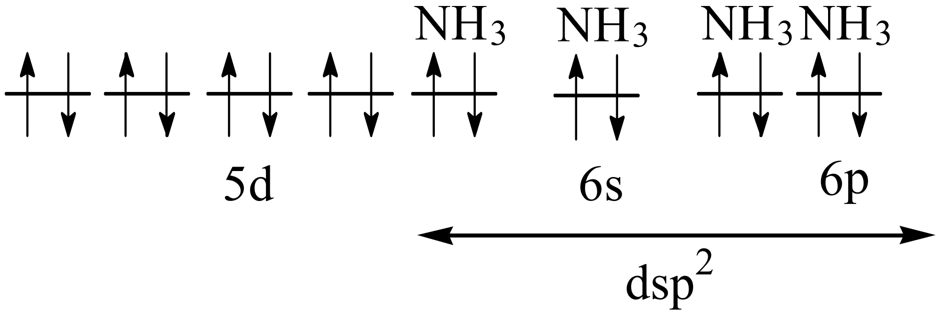
A scheme consistent with the formula and structure of the complex ion $[Ag(NH_3)_2]^+$ involves the hybridization of one 5*s* orbitals with a one 5*p* orbitals.

Two additional hybridization schemes are given on the examples for the tetrahedral (*sp*^{3}-hybridization) $[Zn(NH_3)_4]^{2+}$, the square planar (*dsp*^{2}-hybridization $[Pt(NH_3)_4]^{2+}$ respectively.

$[Zn(NH_3)_4]^{2+}$
[Ar]



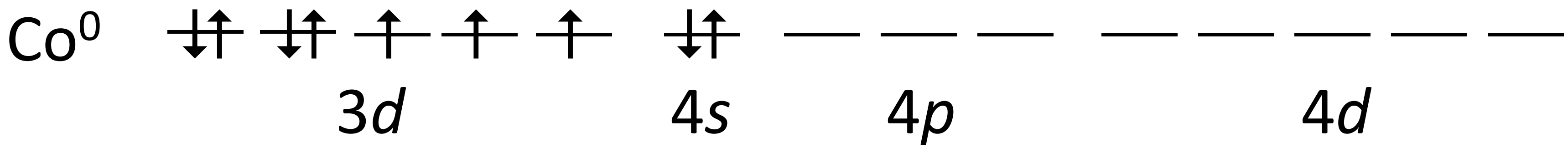
$[Pt(NH_3)_4]^{2+}$
[Xe]$4f^{14}$



Taking into account spectrochemical series of ligands, we'll consider formation of complex ion $[Co(NH_3)_6]^{3+}$.

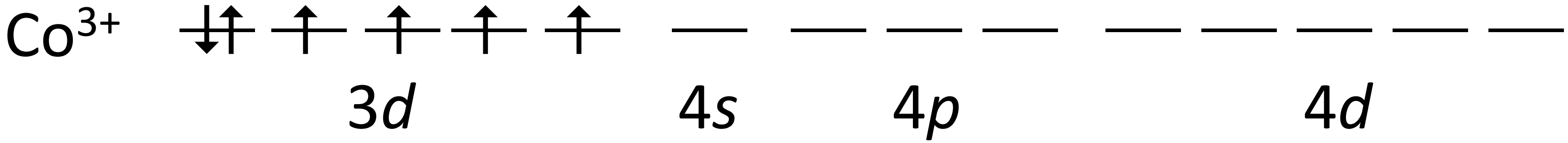
Cobalt has next shortened electronic configuration of valence electrons:

$$Co\ [Ar]\ 3d^74s^2$$



An atom of cobalt has two electrons in its 4s orbitals and seven electrons in the 3*d* electronic sublevel.

In that complex ion an atom of cobalt lose two 4s electrons and one 3d electron to form the ion Co^{3+}:



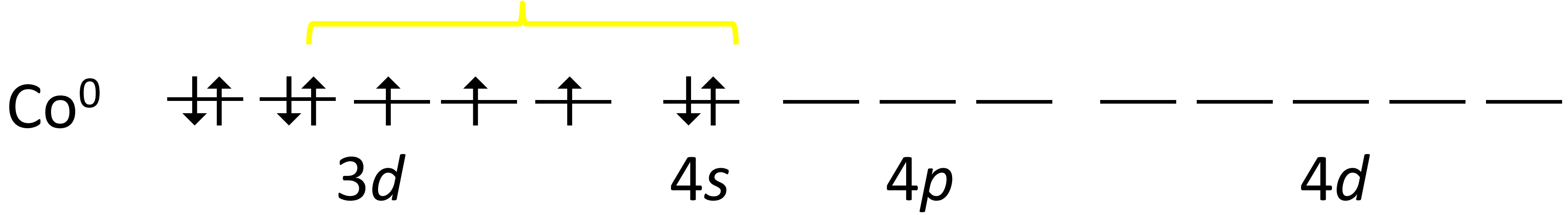
Molecules NH_3 are ligands of **average force** and therefore couple electrons of central metals. Six electrons of central metal are place on three 3*d* orbitals.

$CN^- > CO > NO_2^- >$	En > **NH_3** > $SCN^- >$	$H_2O >$	$OH^- > F^- > Cl^- > Br^- > I^-$
Strong field	**Ligands of average force**		Weak field
Couple electrons of central metal		Do not couple electrons of central metal	

METOD OF VB

$[Co^{+3}F_6]^{3-}$ $[Co^{+3}(NH_3)_6]^{3+}$

Co^0 [Ar] $3d^74s^24p^0$



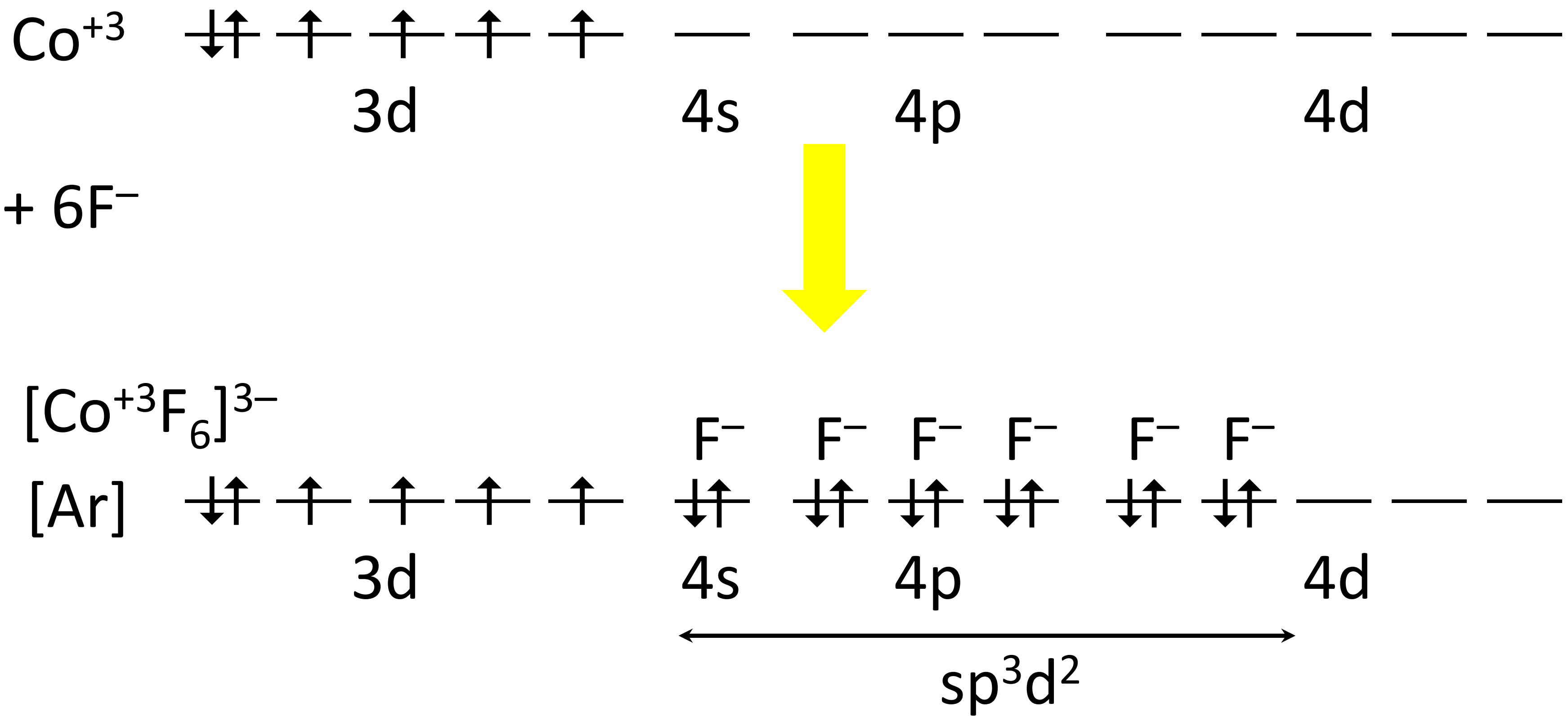
$-3\bar{e}$

Co^{+3} [Ar] $3d^64s^04p^0$

METOD OF VB

$[Co^{+3}F_6]^{3-}$

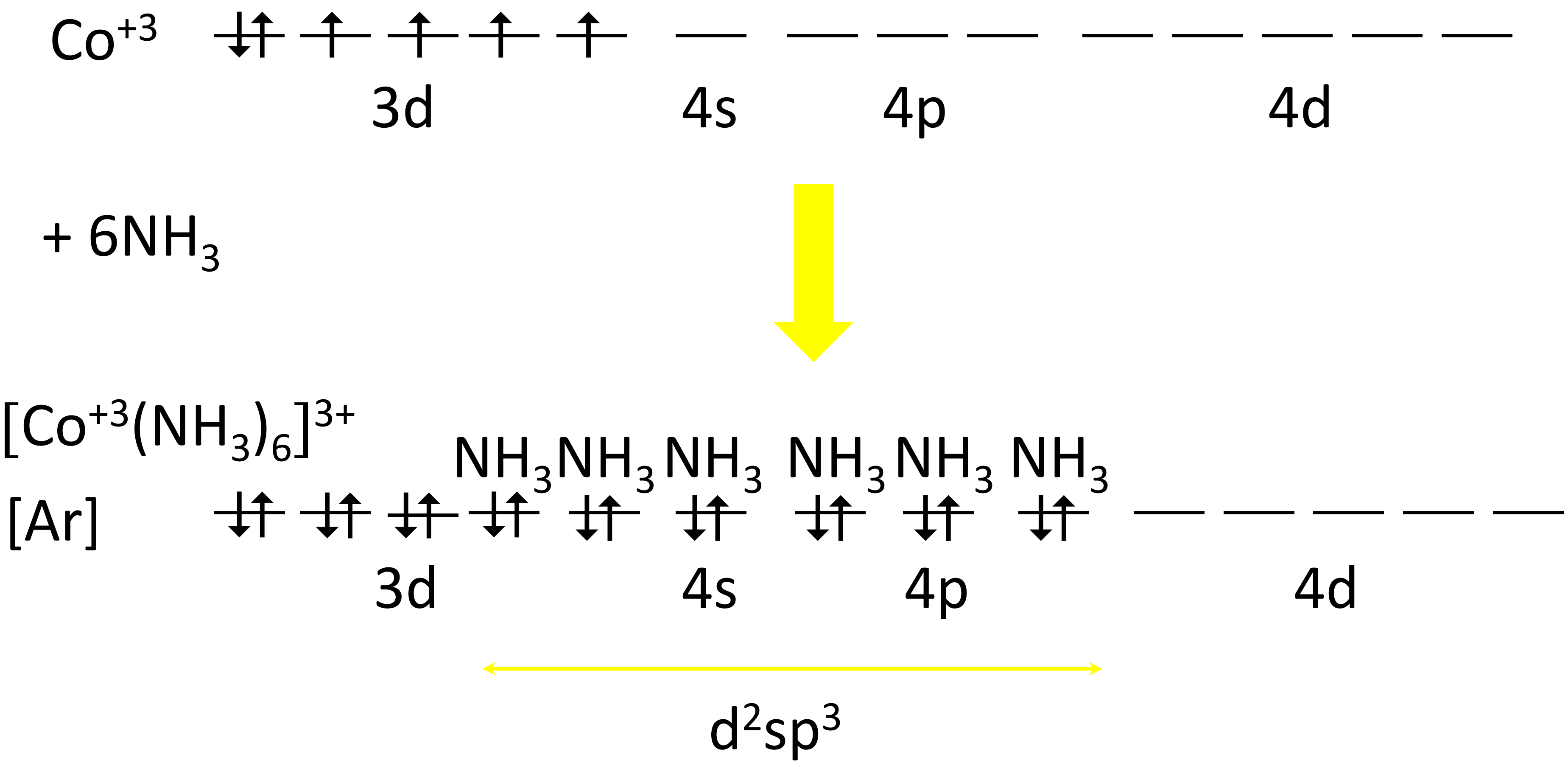
Co^{+3} [Ar] $3d^64s^04p^0$



The complex ion is called an outer orbital complex. It is **paramagnetic** “high spin” complex.

METOD OF VB

$[Co^{+3}(NH_3)_6]^{3+}$



Co^{+3}

3d 4s 4p 4d

$+ 6NH_3$

$[Co^{+3}(NH_3)_6]^{3+}$

[Ar]

NH_3 NH_3 NH_3 NH_3 NH_3 NH_3

3d 4s 4p 4d

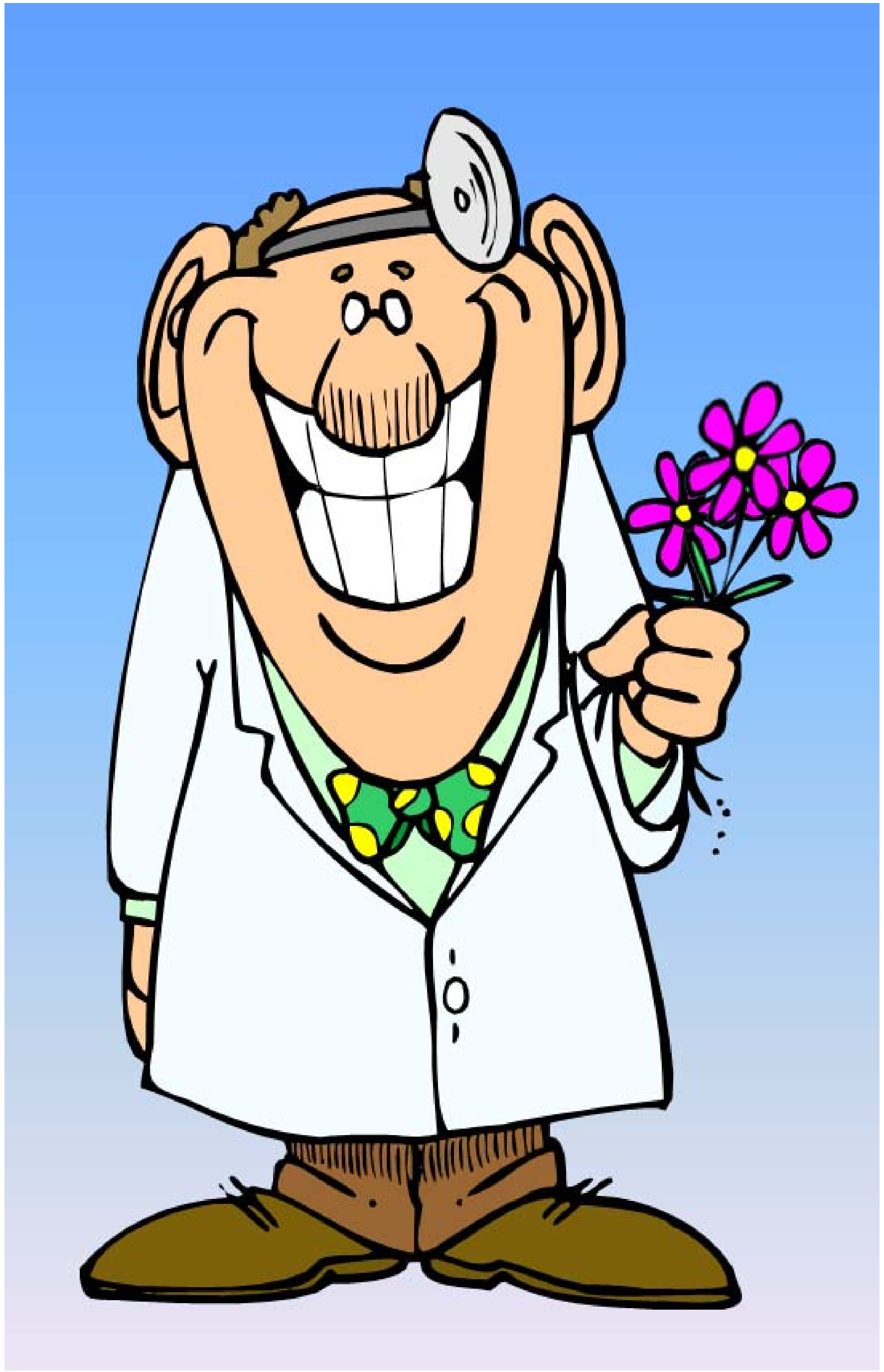
d^2sp^3

The complex ion $[Co(NH_3)_6]^{3+}$ is **diamagnetic** “low spin” complex, because all electrons are paired.

Unpaired electrons act as tiny magnets; if a substance that contains unpaired electrons is placed near an external magnet, it will undergo an attraction that tends to draw it into the field.

Such substances are said to be ***paramagnetic***, and the degree of paramagnetism is directly proportional to the number of unpaired electrons in the molecule.

Magnetic studies have played an especially prominent role in determining how electrons are distributed among the various orbitals in transition metal complexes.



Thank you
for
attention!