

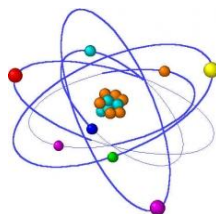
ZAPOROZHYE STATE MEDICAL UNIVERSITY

Kaplaushenko A.G., Pryakhin O.R., Varinskiy B.A., Iurchenko I.A.,
Shcherbak M.A., Samelyuk Yu.G., Kucheryavyi Yu.N., Hulina Yu.S.



COORDINATION COMPOUNDS

*Teaching and methodical manual
for foreign student*



Zaporozhye, 2016

ЗАПОРІЗЬКИЙ ДЕРЖАВНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

Каплаушенко А.Г., Пряхін О.Р., Варинський Б.О., Юрченко І.О.,

Щербак М.О., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

КОМПЛЕКСНІ СПОЛУКИ

Навчально-методичний посібник

для студентів англomовної форми навчання

Запоріжжя, 2016

UDC 54-3(075,8)=111
BBC 24.1/.7я73
C77

Authors:

Каплаушенко А.Г., Прыахін О.Р., Варинський В.А., Іурченко І.А.,
Щербак М.А., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

Reviewers:

Парченко В.В., Dr.hab., Professor of the Department of Toxicology and
Inorganic Chemistry, Zaporozhье State Medical University;

Гладишев В.В., Dr.hab, Professor, Head of the Department of Medicinal
Preparations Technology, Zaporozhье State Medical University.

Coordination compounds: teaching and methodical manual for foreign
students / A.G. Kaplaushenko, O.R. Pryakhin, B.A. Varinskiy [et al.]. – 2nd ed.,
updated and suppl. – Zaporozhье, 2016. – 70 p.

Автори:

Каплаушенко А.Г., Пряхін О.Р., Варинський В.А., Юрченко І.О.,
Щербак М.О., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

Рецензенти:

Парченко В.В., професор кафедри токсикологічної та неорганічної хімії
Запорізького державного медичного університету, д. фарм. н.

Гладишев В.В., зав. кафедри технології ліків Запорізького державного
медичного університету, д.фарм.н.

Комплексні сполуки: навчально-методичний посібник / А.Г.
Каплаушенко, О.Р. Пряхін, В.А. Варинський [та ін.]. – 2ге вид., оновл. та
доповн. – Запоріжжя, 2016. – 70 с.

Навчальний посібник розглянуто та затверджено:

Цикловою методичною комісією з фармацевтичних дисциплін
(протокол №__ від _____р.),
Центральною методичною радою ЗДМУ
(протокол №__ від _____р.)

CONTENTS

1. Preface.....	5
2. Introduction.....	7
3. Concise theoretical material.....	9
4. Questions for self-training.....	29
5. Tasks.....	30
6. The standard answers.....	31
7. Experimental part.....	33
8. Tests.....	44
9. References.....	58

PREFACE

Medicinal Chemistry is one of the most rapidly developing areas within the discipline of Chemistry, both globally and locally. It is the study of the design, biochemical effects, regulatory and ethical aspects of drugs for the treatment of disease.

The aim of this discipline is to produce graduates with an appropriate background in biology and pharmacology, built upon a strong chemistry foundation.

Methodical recommendation of Medicinal Chemistry is designed to equip students with strong grounding in biological and chemical technique which is relevant to the pharmaceutical world.

The discipline gives an in-depth coverage of the chemical techniques required and relates these to the relevant pharmacology, anatomy, biochemistry and molecular biology.

The whole course of Medical chemistry which consists of ten topics is studied by students-physicians during the first year. Lecturer staff of department has prepared an educational and methodical recommendation in which the theoretical material is stated in the concise and available form.

The distribution of material on each of ten topics that are studied is set according to training program, the thematic plan of lectures and practical training.

The material of each topic is stated in such way that performance of practical work and the solution of situational tasks are preceded by theoretical part in which questions of medicine and biological value and also connection with other disciplines (biological chemistry, normal physiology, pathophysiology and others) are included.

Offered laboratory works and situational tasks will give students the chance to understand theoretical material fully and to use this knowledge in practice.

The experience of teaching medical chemistry shows that it is not always possible to coordinate an order of laboratory works realization with sequence of lecture course statement. That is why students usually have to prepare for practical work performance independently before the lesson. Therefore the theoretical part (in which the necessary volume of knowledge for conscious performance of experiment is given) precedes to each section of these Methodical recommendations.

Increasing of level of seminar and laboratory works is reached by use of such forms of occupations which open and consolidate theoretical knowledge, train scientific thinking, develop creative initiative and impart skills of handling devices and chemicals, chemical ware.

The structures, figures and schemes are clear and easy to follow and color is used well, highlighting main points without being distracting.

Chapters are helpfully signposted throughout, informing the reader how topics are related, which is especially important in such a multidisciplinary subject.

Topics are also presented clearly and with a logical progression culminating in the main points, questions and reading sections at the beginning of each chapter.

An assortment of case studies is provided and the authors work through each one in great detail, giving an overall perspective on the science.

Finally, very useful and informative appendices and a glossary are provided together with a comprehensive index that is good enough to rival any search engine!

There are many books that describe medicinal chemistry and its uses, but these methodological recommendations present medicinal chemistry and its related topics in a clear, informative and interesting way that really demonstrates the application and impact of this fundamental subject in society.

INTRODUCTION

Purpose: to summarize the knowledge about the structure, nomenclature and properties of coordination compounds, their use in medical practice, to introduce on the bioligands, to study their biological role, as well as the implementation of the basic of coordination compounds in living organisms.

Targets:

- to learn the basics of the theory of Werner;
- to examine the overall performance of complex compounds;
- to explain the basic chemical properties;
- to explore an overview of d-elements and their basic chemical properties;
- to study of the biological role and application of major complex compounds of d-elements;
- to learn how to of perform typical analytical reactions on ions of d-elements I-VII groups;
- to master the complexometric titration method;
- to learn how to assess the reliability of the results;
- to learn the test material on the topic.

The student should know:

- D.I. Mendeleev's Periodic law;
- the structure of the atom, the types of chemical bonds and the concept of a valency;
- the structure of electron levels of d-elements;
- the theory of the structure of complex compounds;
- the basic concepts (valence, coordination number);
- the classification of complex compounds;
- the complex compounds to induce their stability constants and instability;
- the application of complex compounds in medicine and pharmacy.

The student should be able to:

- correctly use scales and chemical vessels;
- use measuring glassware and burettes;

- determine the quantitative content of metal ions in solution and carry out appropriate calculations;
- to conduct qualitative reaction using complex compounds.

CONCISE THEORETICAL MATERIAL

Properties of complex compounds allow for their application in medicine and pharmacy.

Many complex compounds have biological activity (Co^{2+} -ion is complexing agent in a molecule of vitamin B_{12} , compound of platinum - *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has antineoplastic effect). Currently available new drugs from plants, used for dissolving kidney stones, bladder stones.

Complexation in biological systems ensures certain physiological functions, for example phthalocyanine complex of iron(II) hemoglobin ensures oxygen transport to the tissues of the body.

Permanent exchange of substances to the environment enables to the body maintain a certain level of concentration of the compounds involved in the equilibrium of the complexation processes, providing metal-ligand homeostasis.

In addition, complex compounds are used in chemical analysis to detect and separate elements, for the dissolution of the precipitates, as quantitative method of the cation determination (complexometry).

This systems have great importance to reduce the hardness of the water.

The basic positions of complex compounds, their classification, nomenclature, chemical and physical properties and behavior in aqueous solutions should be discussed due to the large number of complex compounds.

1 A. Werner's Coordination theory. The composition of coordination compounds.

For the first time, structure and properties of coordination compounds of A. Werner was described in coordination theory (1893), which was based on the theory of spatial structure and the theory of electrolytic dissociation.

The basic positions of the A. Werner's Coordination theory are:

1. The most of the elements have two types of valence:

- Primary Valence: elements of compounds of the first order, such as HCl , H_2O , SO_2 , SO_3 and H_2SO_4 , etc.

- Non-Valence: saturation of the secondary Valence is a base for formation of compounds of the highest order, for example, NH_4Br , $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$. Such compounds are referred to complex compounds.

2. Each element (especially d-elements) intend to saturate both the primary and secondary valence.

3. Coordination compounds have centric structure. That is all the groups that are included in their composition are distributed around the atom (ion) - complexing agent (the central atom).

According to this theory, complex compounds are compounds of the highest order, which are formed by the compounds of the first order (CO , NH_3 and H_2O , NO).

2. Stereochemistry

Stereochemistry, a subdiscipline of chemistry, involves the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation. An important branch of stereochemistry is the study of chiral molecules.

Stereochemistry is also known as 3D chemistry because the prefix "stereo-" means "three-dimensionality".

The study of stereochemistry focuses on stereoisomers and spans the entire spectrum of organic, inorganic, biological, physical and especially supramolecular chemistry. Stereochemistry includes methods for determining and describing these relationships; the effect on the physical or biological properties these relationships impart upon the molecules in question, and the manner in which these relationships influence the reactivity of the molecules in question (dynamic stereochemistry).

Complex compounds are compounds formed by the joining of several ions or molecules with one or more ions or molecules with the help of donor-acceptor bonds.

Molecule of complex compounds consists of a central atom (ion - complexing agent, which occupies a central place) and ions or molecules directly related to complexing agent - ligands.

3. Schematic structure of complex compounds with complex cation:



The inner coordination sphere of the complex, a complex cation:



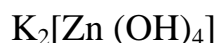
The external coordination sphere is Cl^- (chloride-ion)

The complexing agent is Ag^+ (silver-ion)

The ligands are NH_3 (ammonia molecules are monodentate)

The central atom (coordination number = 2).

4. Schematic structure of complex compounds with complex anion:



The inner coordination sphere of the complex, a complex anion:



The external coordination sphere is K^+ (potassium-ion).

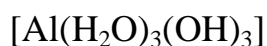
The complexing agent is Zn^{2+} (zinc-ion).

The ligands are OH^- (hydroxide ions, monodentate).

The central atom (coordination number = 4)

5. Schematic structure of the neutral complex (complex without the outer sphere): $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3]$

The inner coordination sphere, neutral complex



The complexing agent is Al^{3+} (aluminium-ion).

The ligands are OH^- , H_2O (molecules are monodentate)

(coordination number = 6)

The ion-complexing agent and ligands form the inner sphere. It is a complex ion. The outer sphere formed by ions of opposite sign. The inner coordination sphere formula of complex compounds is represented in the brackets. For example, in a molecule of diamminesilver (I) chloride $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ ion Ag^+ is complexing agent, the molecules of NH_3 are ligands, Cl^- ions form the outer sphere.

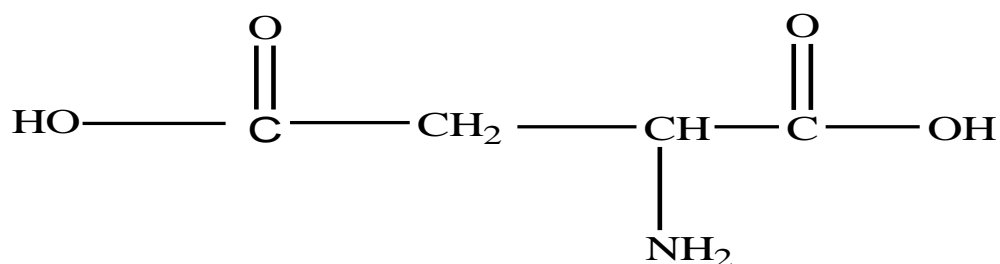
The complexing agents can be positively charged metal ions that have free electron cell (Fe^{2+} , Co^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Ag^+ , Hg^{2+}) and atoms of non-metals with positive oxidation number (Si^{4+} , P^{5+}).

The ligands can be anions (CN^- , NO_2^- , F^- , Cl^- , Br^- , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_4^{2-}$), polar molecules (H_2O , NH_3 , CO , NO) and some organic compounds.

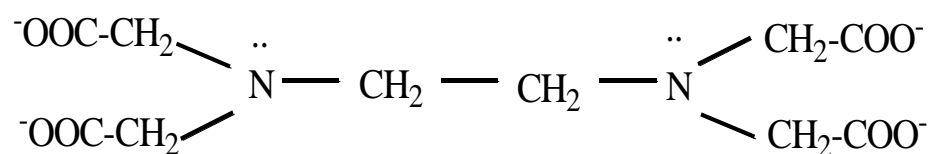
There are mono-, bi-, tri-, and polydentate ligands (lat. dentatus -with teeth). Examples of monodentate (simple, monovalent) ligands are molecules of NH_3 , H_2O , CO , NO ; ions: OH^- , NO_3^- , NO_2^- , F^- , Cl^- , Br^- , I^- , etc. Monodentate ligands are joined with a complexing agent using a single bond.

Bidentate ligands, e.g. anions of diprotic acids: SO_4^{2-} , SO_3^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, ethylenediamine molecule $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ (abbreviated - en) and most of the amino acids react with two complexing agents.

The tridentate ligands include aspartic (2-aminobutandioic) acid:



The polydentate ligands include polyaminopolycarbonic acids, such as edetate-ion, EDTA anion (anion of ethylenediaminetetraacetateacid):



Bi-and polydentate ligands to form with the atom (ion)-complexing agent cyclic complexes, which are also known as chelate or chelates (from Greek Shelate-claw), because the structure of these compounds like claws, which would take over as ligands of metal ions.

This cycle can be formed by coordination bonds (Figure 2.1 a) ionic bonds (fig. 2.1.b) or mixed bonds, i.e. coordination and ionic bonds simultaneously (fig. 2.1.c). In the latter case, the compounds are called intracomplex.

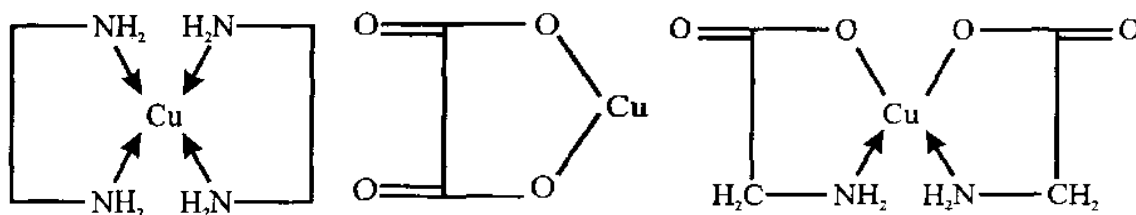


Fig. 2.1 and fig. 2.1. b fig. 2.1.c. Some complex compounds

The compounds' formulas have arrows showing coordination bonds, dashes showing covalent bonds (general electron pairs between atoms are joined). The ionic bonds marked by same dashes is an electrostatic attraction between the charged particles.

The ligands bonded to the central atom by covalent bond formed with donor-acceptor mechanism (coordination).

The complexing agent is characterized by the coordination number (c.n.). The number that shows how many simple (monodentate) ligands are coordinated around the central atom, or you can say otherwise, c.n. is number of links, by which ligands are joined with complexing agent. It depends on the

nature of complexing agent and ligands, and usually twice the absolute value of its oxidation state.

The ligands are donors of electron pairs.

The central atom is acceptor. In the majority of complex-forming agents coordination numbers are 2, 4, 6.

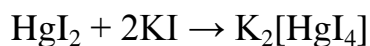
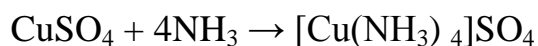
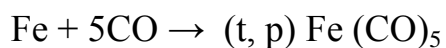
The possible values of coordination numbers for some complex-forming agents:

Coordination number	2	4	4 or 6	6
Complexing Agents	Ag ⁺ Au ⁺ Cu ⁺	Au ³⁺ Hg ²⁺ Pb ²⁺ Pt ²⁺ Sn ²⁺	Cd ²⁺ Co ²⁺ Cu ²⁺ Ni ²⁺ Zn ²⁺ Sc ³⁺	Al ³⁺ Co ³⁺ Cr ³⁺ Fe ²⁺ Fe ³⁺ Mn ²⁺ Ni ³⁺ Pd ⁴⁺ Pt ⁴⁺ Sn ⁴⁺

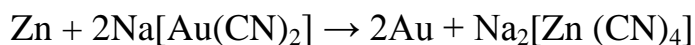
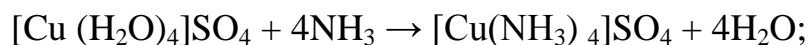
5. Methods of obtaining of coordination compounds

Coordination compounds are formed by conventional chemical reactions.

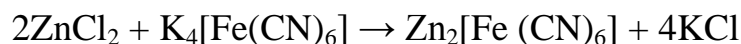
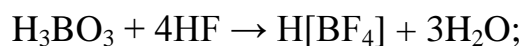
1. The addition reaction:



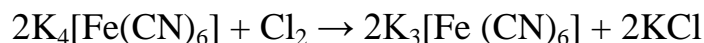
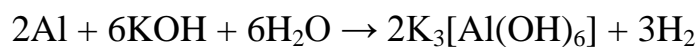
2. The reaction of the substitution:



3. The exchange reaction:



4. The redox reactions:



6. Classification of complex compounds

Currently, there are several classifications of complex compounds.

1. Classification on the nature of the ligands

The basis of this classification is the nature of the ligands of complexing agent:

Acidocomplexes (from latin acidum - acid) ligands are the residues of acids: CN^- , Cl^- , Br^- , I^- , for example $\text{H}[\text{AuCl}_4]$, $\text{K}_2[\text{HgI}_4]$, the residues of many organic acids: oxalate ion $\text{C}_2\text{O}_4^{2-}$, aminopolycarbonic acid residues, etc.;

Amminecomplexes. The ligands are molecules of ammonia NH_3 , for example, $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$, $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$;

Aquacomplexes. The ligands are water molecules: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cu}(\text{H}_2\text{O})_4](\text{NO}_3)_2$;

Hydroxocomplexes. The ligands are hydroxide ions: $\text{K}_3[\text{Co}(\text{OH})_6]$;

Carbonyl complexes. The ligands are CO molecules: $[\text{Ni}(\text{CO})_4]$, $[\text{Cr}(\text{CO})_6]$.

The inner sphere may be acid residues and neutral groups, for example: $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$. Such complexes are mixed.

The most common ligands:

Types of ligand	Chemical formula	The name of the ligand
Negative ions	CH_3COO^-	acetato-
	$\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$	the fluoro -, chloro- bromo-, iodo-
	OH^-	hydroxo-
	CN^-	cyano-
	SCN^-	thiocyano, tiocianato-
	NO_2^-	nitro-
	NO_3^-	nitrato-
	SO_4^{2-}	sulphato-
	SO_3^{2-}	sulphito-
	S^{2-}	thio-, sulphido-
	S_2^{2-}	disulphido-
	O_2^{2-}	peroxo-
Positive ions	NH_4^+	ammonium-
	OH_3^+	hydroxoniy-
Neutral molecules	NH_3	ammine-
	CO	carbonyl-
	H_2O	Aqua-
	NO	nitrosyl-
	$\text{N}(\text{CH}_3)_3$	trimethylamine-
Chelateformation particles	$\text{C}_2\text{O}_4^{2-}$	oxalate-
	$\text{NH}_2\text{-CH}_2\text{-COO}^-$	glicinato-
	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	ethylenediamine-

Chelation-complexes are complexes in which the metal atom-complexing agent is associated with organic ligands in several relationships. The complexing agent and ligands form loops, the strength of which is change due to Chugaev's rule (most stable of these compounds contain in the inner sphere of five- or six-membered rings).

The ligands are characterized by denticity - ability to form multiple coordination bonds with ions-complexing agent. There are monodentate and polydentate ligands. The coordination number is equal to the number of monodentate ligands coordinating by the central atom. For example, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the coordination number is 4. Due to NH_3 (ammonia) is monodentate ligand, and 4 molecules of ammonia are filled 4 places around central atom (Cu^{2+}).

7. The nomenclature of complex compounds

The name of the complex compounds are composed as follows:

Name the ligands first, in alphabetical order, then the central atom or ion. Name of the complex is written in one word. Neutral ligands called without changes; in the names of negatively charged ligands add «o» to the end. Greek prefixes are used to designate the number of each type of ligand in the complex ion, e.g. di-, tri- and tetra-.

Name of complexing agent depends on the charge of the complex. For neutral and cationic – English name of the cation. For the anionic complex - the Latin suffix «ate». Indicate the degree of oxidation of complexing agent using Roman numerals in parentheses.

Examples of names of the ligand: Aqua - H_2O , NH_3 - ammine, CO - carbon monoxide, NO - nitrosyl, OH^- - hydroxo, CN^- - cyano, NO^{2-} , SO_3^{2-} - nitro-, carbonato-, sulphito-, SO_4^{2-} - sulphato-, Cl^- -chloro-.

For Example:

$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ Diamminesilver(I) chloride;

$[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ Tetraamminecopper(II) hydroxide;

$[\text{Al}(\text{H}_2\text{O})_5\text{OH}]\text{Cl}_2$ Hydroxopentaaquaaluminium(III) chloride;

$[\text{Pt}(\text{H}_2\text{O})_3\text{OH}]\text{NO}_3$ Hydroxotriaquaplatinum(II) nitrate;

$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$ Carbonatotetramminecobalt(III) chloride;

$[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ Hexaaquaaluminium(III) chloride.

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

$[Cr(H_2O)_3F_3]$ -trifluorotriaquachromium(III).

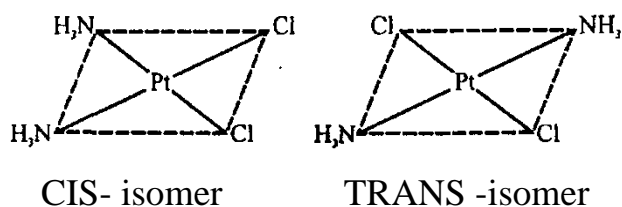
8. Isomerism of the complex compounds

Isomerism is a phenomenon, when substances have the same qualitative and quantitative composition, but have a different structure, and hence different properties.

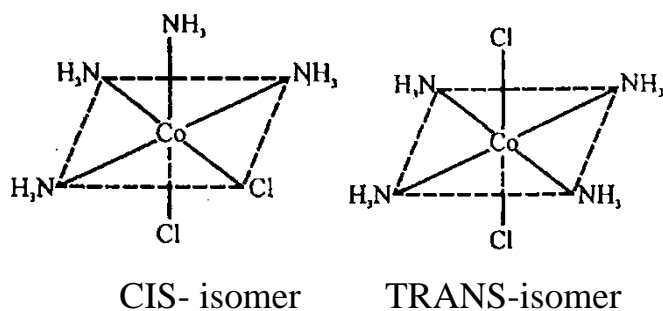
There are geometric, optical, hydrated, ionization, coordination, etc. types of isomerism of complex compounds.

Geometric (spatial) isomerism is common for complex compounds with different (heterogeneous) ligands. The geometric isomers have different placement of inhomogeneous ligands in a complex which has square-planar or octahedral structure.

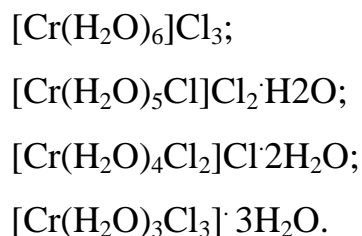
For example, for the complex $[Pt(NH_3)_2Cl_2]$ with square-planar structure, there are two geometric isomers (CIS-andTRANS-isomers), which explains the difference of their properties (different color, dipole moment, reactivity):



CIS (cis) refers to one side, close; and TRANS-(trans)-on different sides. For complex $[Co(NH_3)_4Cl_2]$ is octahedral structure of geometrical isomers can be shown schematically:

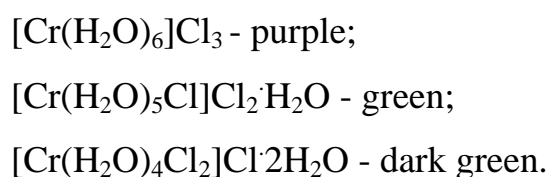


Hydrate isomers are substances which have the same composition, but is different allocation of molecules of the solvent between the internal and external spheres of complex compounds. For example, crystalline hydrate corresponds to four $6\text{H}_2\text{O} \cdot \text{CrCl}_3$ isomer:

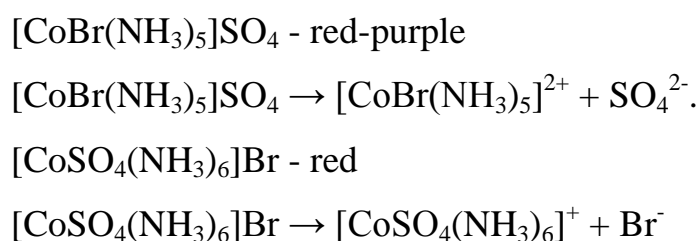


All isomers have different colour.

So:



Ionization isomers are substances which have the same composition, but is determined by the different distribution of charged ligands between internal and external spheres of the complex. These isomers are also distinguished by colour:



Coordination isomerism. When both positive and negative ions of a salt are complex ions and the two isomers differ in the distribution of ligands

between the cation and the anion occurs coordination isomerism. For example
[Co(NH₃)₆][Cr(CN)₆] and [Cr(NH₃)₆][Co(CN)₆]



That is, this type of isomerism is possible for compounds composed of two or more systems, and complexing agent exchange their ligands.

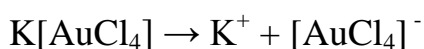
9. Properties of coordination compounds.

Complex compounds are involved in various chemical reactions-substitution, exchange, isomerization, redox processes.

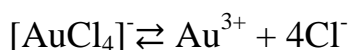
1. Stability of the complex compounds in solutions.

Neutral complexes (coordination compounds with no external coordination sphere) are non-electrolytes, i.e. does not dissociate in the aqueous solutions on ions.

Complex compounds with complex ion (cation or anion) dissociate in aqueous solutions on internal and external coordination spheres. This dissociation of complex compounds is called the primary. It is almost completely. There are complex compounds that have external coordination sphere, dissociate in aqueous solutions as strong electrolytes. For example, [Cu(NH₃)₄]SO₄, K[AuCl₄] such as simple salt dissociation:

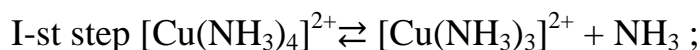


In turn complex ion is also capable to dissociate as electrolyte, but weak or middle force, that is, reversible (secondary dissociation): [Cu(NH₃)₄]²⁺ ⇌ Cu²⁺ + 4NH₃

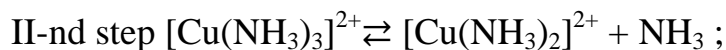


The number of stages depends on the number of ligands in the complex. Each step of the complex ion dissociation is characterized by equilibrium constant, called stepwise dissociation constant of the complex ion, or step

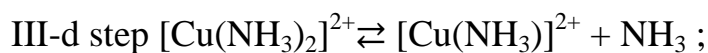
constant instability, for example:



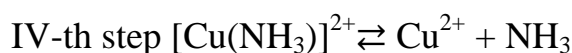
$$K_{inst1} = \frac{[\text{Cu}(\text{NH}_3)_3]^{2+} \cdot [\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_4]^{2+}}$$



$$K_{inst2} = \frac{[\text{Cu}(\text{NH}_3)_2]^{2+} \cdot [\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_3]^{2+}}$$



$$K_{inst3} = \frac{[\text{Cu}(\text{NH}_3)]^{2+} \cdot [\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_2]^{2+}}$$

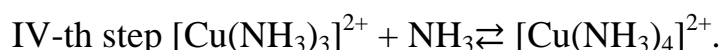
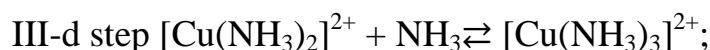
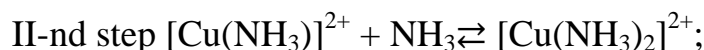


$$K_{inst4} = \frac{[\text{Cu}^{2+}] \cdot [\text{NH}_3]}{[\text{Cu}(\text{NH}_3)]^{2+}}$$

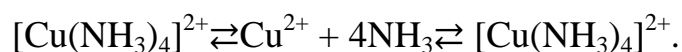
It is often used in the new chemical and biochemical literature the inverse of the dissociation constant (unstable) complex, which is called the constant of the complex formation, or a stability constant, and indicate β :

$$K_{st} = \beta = \frac{1}{K_{inst}}$$

The stability constant characterizes the equilibrium process of formation of a complex that also happens speed. For example, the formation of the complex of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, you can show the following equations:



Each stage corresponds to a certain value of the stability constant (or β). The General equation of complex formation is



The mathematical expression of the common constants of formation (stability) of the complex, as in the case of the general constant instability, can be presented by the formula:

$$K_{st} = \frac{1}{K_{inst}} = \beta_1 \cdot \beta_2 \cdot \beta_3 \cdot \beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}] \cdot [NH_3]^4} = \frac{1}{2,1 \cdot 10^{-13}} = 4,8 \cdot 10^{12}$$

where

$[Cu(NH_3)_4]^{2+}$, $[Cu^{2+}]$, $[NH_3]^4$ is equilibrium molar concentrations of the complex ion, complexing agent and ligands, respectively.

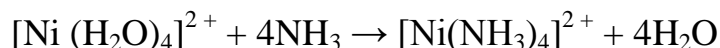
Constant instability of some complex ions in aqueous solutions at 25°C

The scheme of the complex ion dissociation	Instability constant, K_{inst}
$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$	$9.3 \cdot 10^{-8}$
$[Ag(NO_2)_2]^- \rightleftharpoons Ag^+ + 2NO_2^-$	$1.8 \cdot 10^{-3}$
$[Ag(S_2O_3)_2]^{3-} \rightleftharpoons Ag^+ + 2S_2O_3^{2-}$	$1.1 \cdot 10^{-13}$
$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$	$1.1 \cdot 10^{-21}$
$[HgCl_4]^{2-} \rightleftharpoons Hg^{2+} + 4Cl^-$	$8.5 \cdot 10^{-16}$
$[HgBr_4]^{2-} \rightleftharpoons Hg^{2+} + 4Br^-$	$1.0 \cdot 10^{-21}$
$[HgI_4]^{2-} \rightleftharpoons Hg^{2+} + 4I^-$	$1.5 \cdot 10^{-30}$
$[Hg(CN)_4]^{2-} \rightleftharpoons Hg^{2+} + 4CN^-$	$4.0 \cdot 10^{-42}$
$[Cd(NH_3)_4]^{2+} \rightleftharpoons Cd^{2+} + 4NH_3$	$7.6 \cdot 10^{-8}$
$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$	$7.8 \cdot 10^{-18}$
$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$	$2.1 \cdot 10^{-13}$
$[Cu(CN)_4]^{2-} \rightleftharpoons Cu^{2+} + 4CN^-$	$5.0 \cdot 10^{-31}$
$[Ni(NH_3)_6]^{2+} \rightleftharpoons Ni^{2+} + 6NH_3$	$1.9 \cdot 10^{-9}$

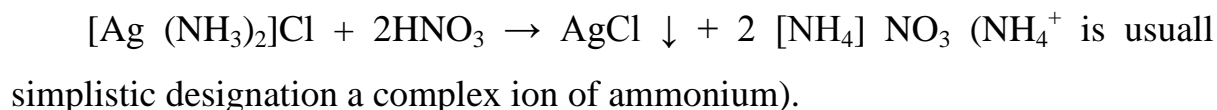
The table shows that the most stable ion is $[\text{Hg}(\text{CN})_4]^{2-}$, and less stable ion is $[\text{Ag}(\text{NO}_2)_2]^-$.

The value of K_{inst} is the basis for the reactions of substitution of ligands in a complex compounds. The ligand that forms stable complexes, able to replace other ligands.

So, for example, the reaction of ammonia with aquacomplex of nickel produce amminecomplex of nickel by the equation:

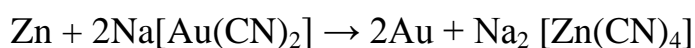
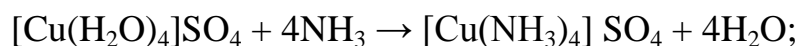


In the reaction of complex compound $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, ions of hydrogen of nitric acid react with ammonia molecules to produce a strong ammonium ion, which can show the equation:



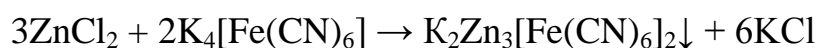
As noted above, complex compounds participate in various chemical reactions, such as substitution, exchange, isomerization, ox/red processes. Here are some examples:

1. Reactions of substitution of ligands in a complex ion internal coordination sphere:



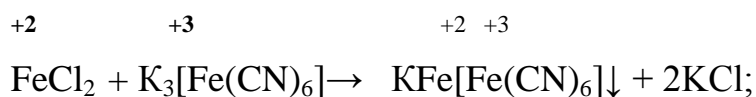
2. Exchange reactions. Exchange reactions of complex compounds often find application in analytical chemistry for the qualitative detection of certain ions.

For example, detection of the Zn^{2+} cation with hexacyanoferrate(II) potassium (yellow blood salt). As a result of the reaction a white sediment hexacyanoferrate(II) potassium zinc formation can be shown by equation:

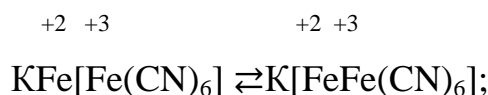


Reactions of Turnbull blue and the Prussian blue formation is used for detection of the the cations Fe^{2+} and Fe^{3+} , respectively. It is proved that

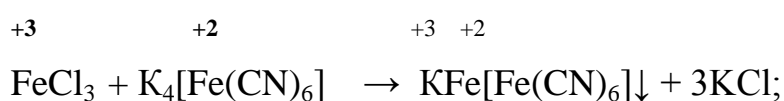
Prussian blue and Turnbull blue are identical in composition, as a result of the reaction they appear as dark blue precipitation:



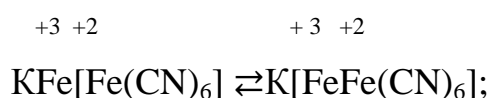
Potassium hexacyanoferrate(III) Turnbull blue



potassium hexacyanoferrate(II, III)



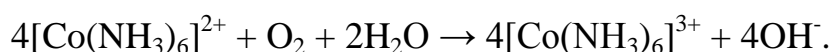
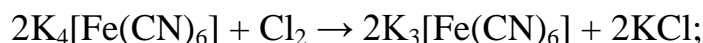
Potassium hexacyanoferrate(II) Prussian blue



potassium hexacyanoferrate(II, III)



3. Redox reactions:



10. The complexation in biological systems

Complexation in biological systems leads to the execution of several physiological functions. For example, the hemoglobin is a complex protein molecule which contains four polypeptide chains associated with the prosthetic group - heme. Heme is porphyrin complex of iron(II). (Fig. 2.2. and Fig. 2.3.)

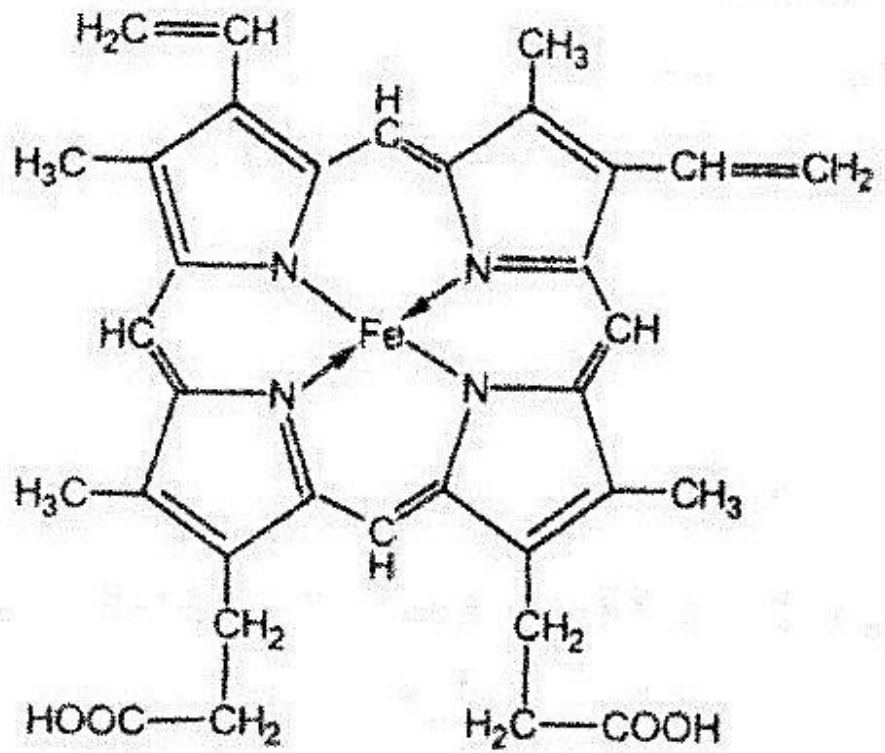


Fig. 2.2. Fe^{2+} porphyrin complex (HEM).

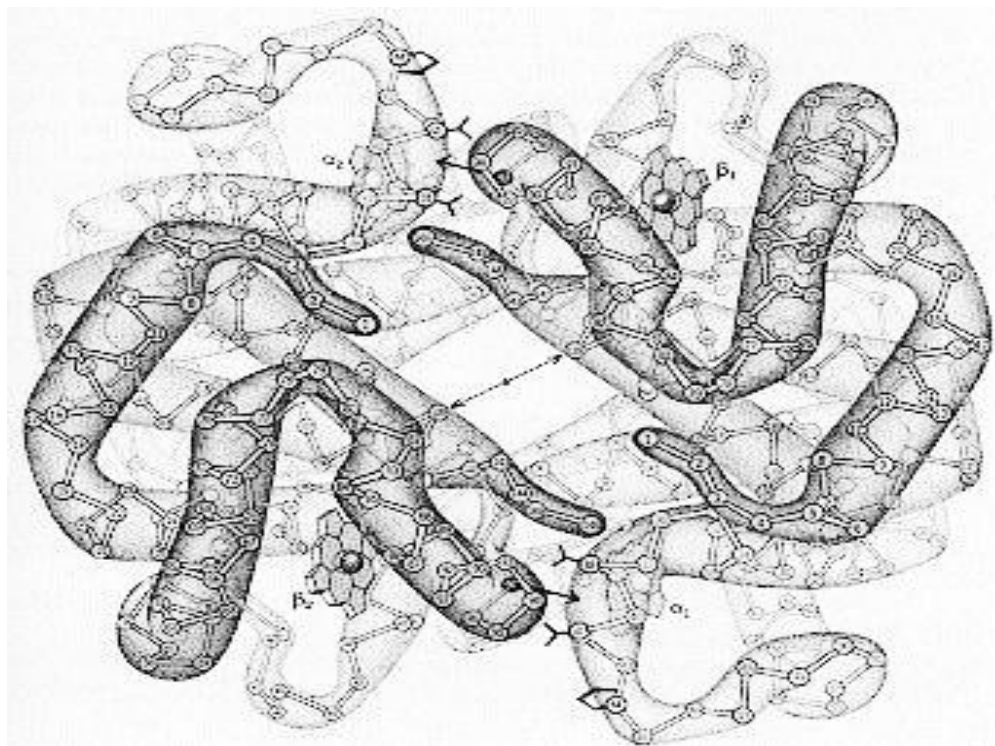


Fig. 2.3. Hemoglobin building.

Peculiarities in the structure of hemoglobin cause of important ability to bind oxygen and transfer it from the lungs to the tissues. Myoglobin has a structure like the hemoglobin, it is another iron containing protein. It is a tank of oxygen in the muscles, releasing it during muscle activity.

The green pigment of plants is the chlorophyll. It is also porphyrin complex, but magnesium cation is acting as complexing agent.

Vitamin B₁₂(cyanocobalamine) is used in medical practice as an antianemic remedy, complexing agents of the molecule is Co²⁺.

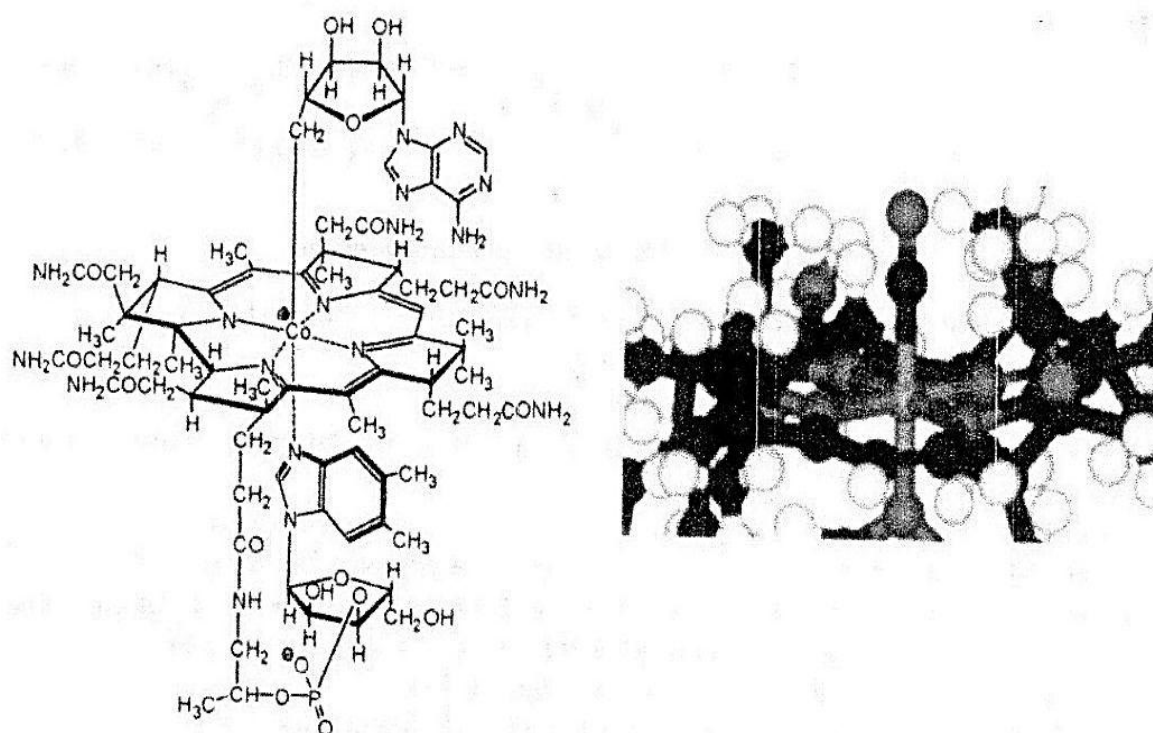
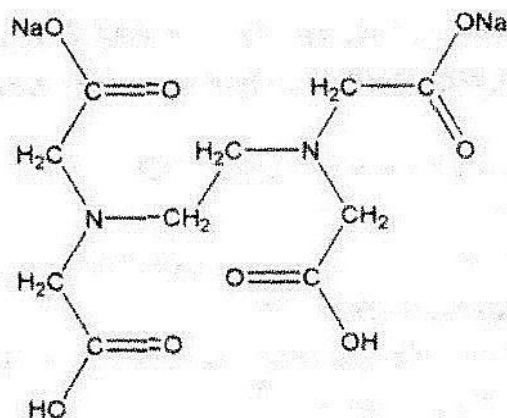
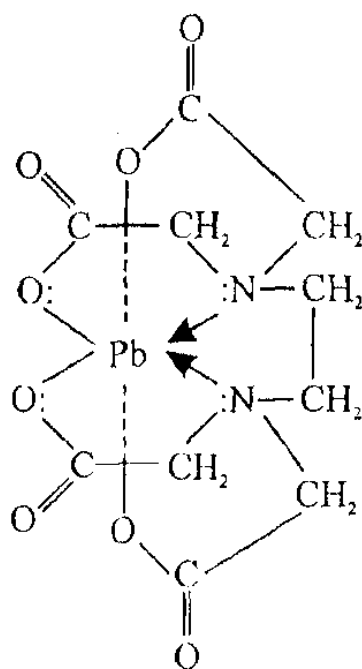


Fig. 2.5. Vitamin B₁₂

Organic compounds, derivatives of aminopolycarbonic acids are used for treatment by chelating during the poisoning by heavy metals. Widely used Trilon-B (EDTA, disodium ethylenediaminetetraacetate).



Preparations based on sodium edetate (Trilon B) apply in case of poisoning by salts of heavy metals by linking and removing them from the body. The mechanism of such preparations action is based on the ability of sodium edetate to form chelate complexes with metals. For example, complex producing with the ions of lead Pb^{2+} has the following structure:



11. The concept of the metal-ligand homeostasis.

Processes based on the formation and destruction of biocomplexes, consisting of cations of various biometals and bioligands such as amino acids, peptides, porphyrins, etc. are constantly going in living systems. Constant exchange of substances with the environment allows the body to maintain a

certain level of concentration of substances involved in the equilibrium processes of complexation, providing the state of the so-called metal-ligand homeostasis.

Characteristic set of equilibrium processes metal-bioligand that is determined by the stability of the formed complexes and concentration in the internal environment of the forms of metal ions and bioligands, exists for each biometal.

The metal-ligand balance of iron(II) and iron (III) cations is the most studied in the bound state (as part of biocomplexes, such as myoglobin and hemoglobin, cytochromes, ferritin, transferrin, ferredoxin and metalloenzymes, such as catalase and peroxidase. Each of these biologically active substances performs the organism specific function. Therefore, the condition for the normal functioning of many bio-complexes of iron there is a certain concentration of these ions in the blood. Violation total balance leads to pathological state, such as siderosis (iron excess state) or anemia (iron deficit state).

Thus, chelating agents are widely used in medical practice for treatment of metal excess or metal deficit states associated with metabolic disorders in the body.

Scientific search, introduction into medical practice and use of drugs, which action is based on the formation of chelates between metal ions and complexones is called chelatotherapy.

QUESTIONS FOR SELF-TRAINING

1. Coordination theory of A. Werner. The definition of complex compounds, examples.
2. The structure of coordination compounds. Denticity.
3. Classification and nomenclature of complex compounds.
4. Specific examples to explain the types of isomerism of complex compounds (geometrical, optical, solvate, ionization, coordination).
5. The relative stability of the complexes. Instability constant. Chelatometric titration. Chelating agents.
6. The biological role of complex compounds. Application in medicine and pharmacy.
7. Complexation in biological systems.
8. What are ion-complexing agent, ligands, coordination number and oxidation state of the central atom in the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$?
9. Write coordination formula of iron complex compound if empirical formula is $3\text{KCN} \times \text{Fe}(\text{CN})_3$. Coordination number of iron(III) is six. To name the compound.
10. Write an expression of instability constant for compound $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$.
11. Calculate the concentration of ions of Cd^{2+} in the 0.01 M solution of $\text{K}_2[\text{Cd}(\text{CN})_4]$ containing in excess 1 mol of potassium cyanide ($K_{\text{inst}}=1.4 \times 10^{-10}$).
12. The silver nitrate was precipitated only 1/4 of chloride ions of $\text{PtCl}_3 \times 3\text{NH}_3$ complex compound. Write coordination formulas of both salt.

TASKS

1. What are ion-complexing agents, ligands, coordination number and oxidation state of the central atom in complex ions $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^{2+}$, $[\text{FeF}_6]^{3-}$, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$.

2. Write formulas of the complex compounds of cobalt based on empirical formula composition: $\text{CoCl}_3 \times 3\text{NH}_3 \times \text{H}_2\text{O}$, $3\text{NaNO}_2 \times \text{Co}(\text{NO}_2)_3$, $2\text{KNO}_2 \times \text{NH}_3 \times \text{Co}(\text{NO}_2)_3$, $\text{KCN} \times \text{Co}(\text{CN})_3 \times 2\text{H}_2\text{O}$, $\text{CoCl}_3 \times 4\text{H}_2\text{O}$. The coordination number of cobalt(III) is the six. Write the equations of dissociation of these compounds.

3. What is the oxidation states of the complexing agents of the compounds: $\text{Na}_3[\text{Co}(\text{CN})_6]$, $[\text{Pb}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$, $\text{H}_2[\text{PtCl}_4(\text{OH})_2]$, $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$, $[\text{Cu}(\text{H}_2\text{O})_4](\text{NO}_3)_2$.

4. Write an expression of instability constants for complex compounds: $\text{Na}_3[\text{Al}(\text{OH})_6]$, $\text{Zn}_2[\text{Fe}(\text{CN})_6]$, $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$, $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, $\text{H}_2[\text{CoCl}_4]$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}_2$, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$, $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$.

5. The silver nitrate react with the solution of complex $\text{CoCl}_3 \times 6\text{NH}_3$. It was precipitated all of the chloride ions. The silver nitrate was precipitated only 2/3 of chloride ions of $\text{CoCl}_3 \times \text{NO}$ complex compound. Write coordination formulas of both salts, equations of the dissociation and expression of instability constants of complex ions.

6. Create formulas of the complex compounds: sodium dithiosulfatoargentate(I), thiocyanatopentaamminecobalt(II) nitrate, potassium dihydroxochloroplatinate(IV), potassium trioxalatomanganate(III), potassium bromopentanitroferrate(III).

7. Calculate the concentration of Ag^+ -ions of 0.01 M solutions $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ and $\text{K}[\text{Ag}(\text{CN})_2]$ (value of K_{inst} respectively 5.8×10^{-8} and $1,4 \times 10^{-21}$).

8. Calculate the concentration of Hg^{2+} ions in 0.01 M solution of $\text{K}_2[\text{Hg}(\text{CN})_2]$ containing excess of 1 mol of NaCN ($K_{\text{inst}} = 4 \times 10^{-42}$).

THE STANDARD ANSWERS

Example # 1.

What are ion-complexing agent, ligands, coordination number and oxidation state of the central atom in the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$?

Solution.

Complexing agents in the complex ion is Cu^{2+} , ligands are NH_3 . Ligands are monodentate, each creates one bond with the central atom, the coordination number is 4. The oxidation of the central atom is determined based on charge ligands. The total charge of the ammonia molecule is equal to zero hence the oxidation state of the central atom is equal to +2.

Example # 2.

Write coordination formula of iron complex compound if empirical formula is $3\text{KCN} \times \text{Fe}(\text{CN})_3$. Coordination number of iron(III) is six. To name the compound.

Solution.

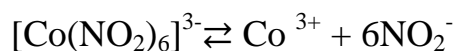
$\text{K}_3[\text{Fe}(\text{CN})_6]$ - potassium hexacyanoferrate(III).

Example # 3.

Write an expression of instability constant for compound $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$.

Solution.

Secondary dissociation of the equation:



Instability constant describes secondary dissociation and has an expression:

$$K_{\text{inst}} = \frac{[\text{Co}^{3+}][\text{NO}_2^-]^6}{[[\text{Co}(\text{NO}_2)_6]^{3-}]}$$

Example # 4.

Calculate the concentration of ions of Cd^{2+} in the 0.01 M solution of $\text{K}_2[\text{Cd}(\text{CN})_4]$ containing in excess 1 mol of potassium cyanide ($K_{\text{inst}} = 1.4 \times 10^{-10}$).

Solution.

Complex salt $K_2[Cd(CN)_4]$ dissociates at the first stage as a strong electrolyte:



Therefore, the concentration of ions $[Cd(CN)_4]^{2-}$ in the solution is equal to the concentration of salt (0.01 mol). Secondary dissociation is characterized by constant instability and runs very slightly, so the concentration of CN^- - ions in solution can be assumed equal to the concentration of cyanide-ions due to the presence in salt solution KCN, i.e. 1 mol. Then:

$$K_{\text{нект}} = \frac{[Cd^{2+}][CN^-]^-}{[[Cd(CN)_4]^{2-}]}$$

$$1,4 \times 10^{-19} = \frac{[Cd^{2+}] \times 1^4}{0,01}$$

where $[Cd^{2+}] = 1,4 \times 10^{-21}$ mol/L.

Answer: the concentration of ions $Cd^{2+} = 1,4 \times 10^{-21}$ mol/L.

Example # 5.

The silver nitrate was precipitated only 1/4 of chloride ions of $PtCl_3 \times 3NH_3$ complex compound. Write coordination formulas of both salt.

Solution.

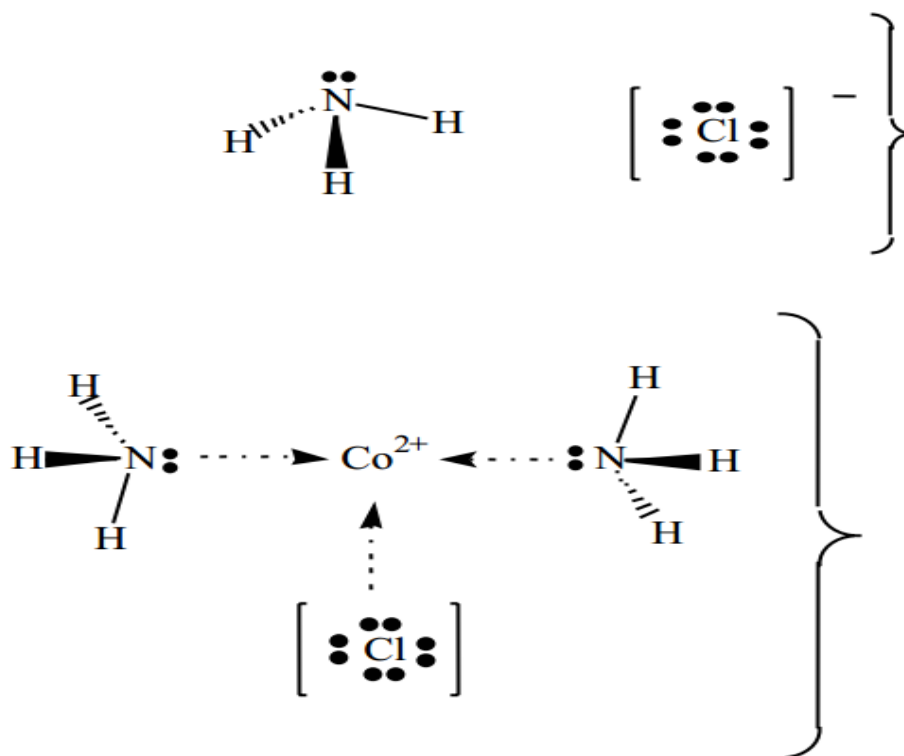
The silver nitrate $AgNO_3$ may precipitate only chloride-ions of the external sphere, so in the external sphere is only 1/4 of the chloride ions. Compound has the formula $[Pt(NH_3)_3Cl_3]Cl$.

EXPERIMENTAL PART

Laboratory work: Synthesis of a Coordination Compound

Introduction

This experiment serves as an introduction to the area of synthetic chemistry – and more specifically, to inorganic synthesis. You are going to make some new chemical bonds as you synthesize a large molecule from smaller ones! You will be synthesizing a coordination compound. The bonds in coordination compounds are two-electron bonds (like covalent bonds), but both electrons come from the ligand (a Lewis base with an unpaired electron pair). The metal ion serves as a Lewis acid (an electron-deficient species which can use its empty orbitals for the bond). The pictures below show the ligands we will be using and a representation of the bonding in a coordination complex.



These entities can function as ligands since they possess lone (nonbonding) pairs of electrons.

Lewis bases can approach and subsequently "coordinate" to transition metal cations via the participation of nonbonding electron pairs. Electron deficient transition metal cations are strong Lewis acids.

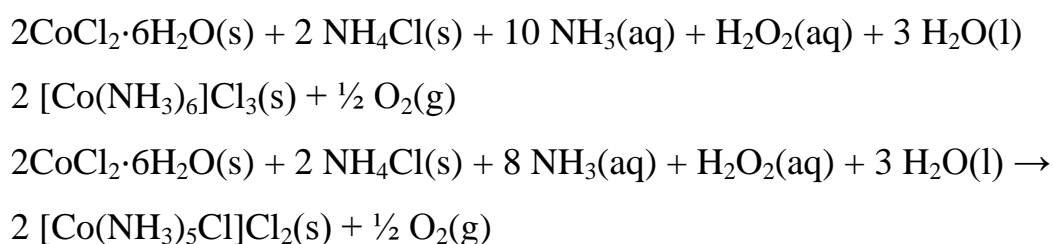
You will have the opportunity to synthesize one of two possible coordination complexes in this experiment. One molecule is named hexaamminecobalt(III) chloride. Its formula is written $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

The other molecule is named pentaamminechlorocobalt(III) chloride. Its formula is written $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

The ammonia and chloride ligands of these complexes use lone pairs of electrons to form bonds with the cobalt cation. The coordination number for the cobalt in both products is six and these cations are octahedral, as predicted by VSEPR theory.

The cobalt ion ends up having a charge of 3+; each chloride ion is 1-, and the ammonia ligands are neutral, so $[\text{Co}(\text{NH}_3)_6]$ has a net 3+ charge and $[\text{Co}(\text{NH}_3)_5\text{Cl}]$ has a net 2+ charge. These complex cations crystallize from solution as chloride salts.

The overall reactions for the syntheses of these salts are very similar:



Notice that cobalt(II) chloride is hygroscopic and is available as the hydrate: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The dot in this formula implies a strong association between the cobalt(II) chloride and the water molecules. This is not a chemical bond, but a result of water being incorporated into the crystal structure of CoCl_2 (in a very specific way!) as the solid forms. The 6 does indicate the stoichiometric relationship between the components of this material: there are 6

water molecules in the crystal for every Co atom and every two Cl atoms. As you follow the procedure, keep complete records of your observations in your laboratory notebook. Record what your eyes, ears, and nose detect! (But don't inhale the fumes above or stick your ear into the reaction vessel – that's dangerous!) Often in syntheses small things can go slightly wrong which alter the reaction in some way. Accurate notes that describe each step of a protocol as it was actually implemented, and the observed result each step along the way, help document where a procedure has gone awry. Your laboratory score for this experiment will be primarily based on the quality of your "running account:" your summary of what you did and what you observed throughout the synthesis. Be sure to write down what you did, after you do it, rather than writing down what you will do in your lab book.

Synthesis A: Preparation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

1. Set up a hot water bath on your hotplate, using a 1000 mL beaker containing 200 mL of deionized water. Turn the hotplate on at its minimum setting. Turn on your VWR digital thermometer, and place the probe in the water. Set the body of the thermometer up on the center console of the lab bench, so that the cord does not get scorched.

2. Select a clean 250 mL beaker with gradations (volume marks) from your lab drawer. This will be your "reaction beaker". Inspect it carefully for cracks or other signs of damage. It will be heated, so we want to make sure it is sound. If none of the beakers available to you are both clean and marked with approximate volumes, please ask for one.

3. Weigh 10.0 ± 0.2 g of ammonium chloride (NH_4Cl) directly into your 250 mL reaction beaker, using a top-loading balance. Record the exact amount used (to the precision limit of the top-loading balance).

4. Add 40. mL of deionized water to your reaction beaker and stir until most of the the solid ammonium chloride dissolves.

5. Weigh 8.0 ± 0.2 g of cobalt (II) chloride hexahydrate directly into your reaction flask. Record the exact amount added (to the precision limit of the top-loading balance).

6. Stir the reaction mixture until most of the solids dissolve.

7. IN THE HOOD, add 40. mL of 15 M ammonia, pumping slowly and smoothly so that none spatters. CAUTION: This is a concentrated basic reagent with a strong odor. Stir your reaction mixture with your stirring rod for about thirty seconds.

8. Add approximately 0.8 g of activated charcoal. Transfer this directly from the reagent bottle into your reaction beaker. Try to avoid spilling, as this stuff makes a mess. If you spill any, clean it up immediately with a wet paper towel, before it stains someone's clothes, lab book, etc. The activated charcoal serves as a catalyst for the reaction that forms the bonds between NH_3 and Co. Conveniently, it also catalyzes the transformation of Co^{2+} into Co^{3+} by the H_2O_2 !

9. IN THE HOOD, add 50. mL of 10% mass H_2O_2 one pump at a time, stirring between each pump. CAUTION: Be careful to not spill or spatter this reagent on your skin: use gloves. There will be some effervescence as oxygen gas is evolved. Remain in the hood and keep stirring until all the bubbling stops. The purpose of the hydrogen peroxide (H_2O_2) is to convert the cobalt from Co^{2+} to Co^{3+} .

10. Once all bubbling has stopped, place your 250 mL reaction beaker in your 1000mL hot water bath, which should be at roughly 60°C . If all is going well, your reaction mixture volume should be 135 ± 5 mL, and your solution should be almost deep maroon in color.

11. Leave the reaction beaker in the water bath for 30-40 minutes, while maintaining the temperature of the water bath between 50°C and 70°C . Stir periodically, avoiding the fumes above the reaction beaker when you do.

13. After at least 30. minutes, remove your 250 mL reaction beaker from the water bath. It is safest to do this with your hand, rather than to attempt to use the beaker tongs.

14. Set up a cold water bath, using a 400 ml beaker containing 150 ml of cool tap water. Cool the reaction beaker in the cold water bath for 2 minutes. Then transfer it to one of the ice baths in the sinks, stirring occasionally as it cools. This helps promote crystallization. (Use a CheckTemp 1 digital thermometer probe placed directly in the reaction mixture to monitor the temperature. Keep your reaction beaker in the ice bath until the temperature reads less than 10°C when the reaction mixture is stirred.)

15. Set up a Büchner funnel apparatus. Filter the mixture using #1 filter paper moistened with deionized water. You don't have to get all the solid out of your reaction beaker, or clean the reaction beaker, as you'll be pouring the precipitate (solid) right back into the reaction beaker. Pull air through the solid in the funnel for at least a minute, to dry it out.

16. Turn off the vacuum. Release the vacuum on the sidearm flask by twisting off the vacuum hose as you pull gently. Rotate the filter cup of the Büchner funnel to free it from the rest of the apparatus.

17. Knock or scrape the contents of the filter cup, including the filter paper, back into your 250 mL reaction beaker. You do not need to clean or rinse your reaction beaker.

18. Rinse the filter cup with deionized water from your squirt bottle, into the reaction beaker.

19. Pick up the filter paper with the plastic tweezers provided. Use your squirt bottle, filled with deionized water, to rinse all the colored cobalt compound off of the filter paper. (It's Ok if some black material remains on the filter.)

20. Discard the used filter paper in the trash, unless it is still colored.

21. Discard the filtrate (liquid) into the aqueous cobalt waste container.

22. Using your squirt bottle, rinse down the sides of the reaction beaker and your stirring rod into the reaction beaker. Add deionized water to your reaction beaker until the total solution volume is approximately 100 mL, as indicated by the gradations on the beaker.

23. IN THE HOOD, add 5 mL of 12 M HCl, and stir. CAUTION: 12 M HCl a concentrated acidic reagent with a choking odor.

24. Heat the mixture to boiling directly on your hot plate while stirring to dissolve the crystals. DO NOT ATTEMPT TO MEASURE THE TEMPERATURE. You may set the hotplate to 10, provided you stir frequently. (Otherwise, don't exceed 6.)

25. Rinse the suction flask with deionized water and reassemble your Büchner funnel. (You can do this while waiting for the previous step). You don't need to clean the filter cup.

26. Turn off the hotplate. Holding the reaction beaker securely with a pair of beaker tongs, pour the hot reaction mixture, a little at a time, onto the moistened filter paper in the Buchner funnel apparatus, under suction. This removes the charcoal. If the filtration stops, ask for help, and do not add more liquid! Squirt deionized water at any colored material remaining in the reaction flask, and pour the resulting colored water out into the funnel. Stop rinsing when no color remains, even if some black material is left behind.

27. The filtrate should be orange, and it contains the dissolved product. Do not discard it!

28. Wipe any residual carbon out of the reaction beaker with a paper towel. Wipe any residual carbon off of your stirring rod as well. Rinse the reaction beaker with hot tap water and then with de-ionized water. You don't need to dry it completely.

29. Transfer your filtrate to the cleaned out 250-mL reaction beaker. Swirl the sidearm flask just before transferring portions of the liquid: try to transfer any solid present in the flask into the reaction beaker. However, do not add any water to the system: don't rinse!

30. IN A HOOD, add 15 mL 12 M HCl to your reaction beaker, and stir.
CAUTION: This is a concentrated acidic reagent with a choking odor.

31. Place your reaction beaker in the ice bath in the sink. Stir the reaction mixture as it cools. Continue to stir and cool the mixture until its temperature has been below 10° C for at least 5 minutes. You can carry out the next step while you wait.

32. Clean the filter cup of your filtering apparatus. Unless the used filter paper in your funnel has a color (other than black), throw the used filter paper (with the carbon black on it) into the trash, using your scoopula to scrape it out. Wipe out any remaining carbon with a moist paper towel. Do this over another paper towel, because the bottom of the filter cup may have a yellow Co compound on it. Reassemble the filtering apparatus. Before you put it in and wet it, determine the mass of the filter paper you will use in the next step. Use a top-loading balance, making the determination to ± 0.01 g. 6

33. Filter the cold precipitated product suspension by pouring it onto the moistened filter paper while the suction is on. To transfer as much of your product as possible, stir the reaction mixture with your stirring rod just before you pour out the portions, and pour pretty quickly, a little at a time. Some product will remain in the reaction beaker – don't attempt to rinse it out, or you will dissolve away some of your product!

34. Draw air through the crystals for five minutes.

35. Weigh a clean, dry watchglass to ± 0.01 g on a top-loading balance.

36. Transfer the crystals and your filter paper to the watchglass by “burping” the vacuum hose, removing the filter cup, and inverting the filter cup onto the watchglass. You may have to tap or thump the filter cup a few times to get the product to fall out.

37. Place your emptied filter cup into the solids collection bin in the hood. Please do not attempt to clean it.

38. Rinse your reaction beaker with the minimum amount of water from your squirt bottle needed to dissolve all remaining yellow product. Pour the cobalt-contaminated (colored) water into the filter flask.

39. With it still in the filter flask, rinse down the white, funnel-shaped portion of your Büchner funnel into the sidearm flask, using your squirt bottle and stir bar to scrape and wash off any solid material. Get all the color off both the funnel and your stirring rod.

40. If your filtrate is only faintly colored, pour it down the sink. If it does have a distinct color (and it may), pour it into the aqueous cobalt waste jug.

41. Put the watchglass in your drawer to dry.

42. Clean up, following your instructor's directions.

43. Next laboratory period, you'll weigh your product to determine your synthetic yield.

Synthesis B: Preparation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

1. Set up a hot water bath on your hotplate, using a 1000 mL beaker containing 200 mL of deionized water. Turn the hotplate on and set it to power level 2. Turn on your VWR digital thermometer, and place the probe in the water. Set the body of the thermometer up on the center console of the lab bench, so that the cord does not get scorched.

2. Select a clean 250 mL beaker with gradations (volume marks) from your lab drawer. This will be your “reaction beaker”. Inspect it carefully for cracks or other signs of damage. It will be heated, so we want to make sure it is sound. If none of the beakers available to you are both clean and marked with approximate volumes, please ask for one.

3. Weigh 4.0 ± 0.1 g of ammonium chloride (NH_4Cl) directly into your 250 mL reaction beaker, using a top-loading balance. Record the exact amount used (to the precision limit of the top-loading balance).

4. IN THE HOOD, slowly add 25 mL of 15 M ammonia. Stir to dissolve the NH_4Cl . CAUTION: This is a concentrated basic reagent with a strong odor.

5. Weigh 8.0 ± 0.2 g of cobalt (II) chloride hexahydrate directly into your reaction flask. Record the exact amount added (to the precision limit of the top-loading balance). IN A HOOD, stir the solution until the solid chunks of cobalt (II) chloride hexahydrate are dissolved and can no longer be seen from underneath. A tan slurry in a deep red to brown liquid should result.

6. IN THE HOOD, add 20 mL of 10% mass H_2O_2 one pump at a time, stirring between each pump. CAUTION: This reagent can cause severe skin burns. Be careful to not spill or spatter this reagent on your skin and use gloves when handling it. There will be some effervescence as oxygen gas is evolved. The solution will get hot as the reaction proceeds. Remain in the hood and keep stirring until all the bubbling stops. Use your stirring rod to insure that any tan material on the walls of the beaker comes into contact with the hydrogen peroxide solution. The purpose of the hydrogen peroxide (H_2O_2) is to convert the cobalt from Co^{2+} to Co^{3+} .

7. IN THE HOOD, stirring between each addition, add 25 mL of 12 M HCl, 5 mL at a time. White dust will form above your beaker, but don't freak. (Ammonium chloride dust is produced as HCl reacts with the ammonia escaping from your reaction mixture.) CAUTION: Hydrochloric Acid is a concentrated acidic reagent with a choking odor.

8. Heat the mixture in your hot water bath on the hotplate to 75° - 85°C for 30 minutes. Stir periodically, avoiding the fumes above the reaction beaker when you do. Your reaction 8 beaker should contain a deep purple solid in a beautiful indigo solution, with both colors changing somewhat as you stir and heat.

9. Remove the beaker from the water bath after at least 30 minutes have passed. Keep the water bath on the hotplate: it will be needed again later.

10. Cool the beaker to room temperature in a cool water bath, consisting of a 400 ml beaker filled with approximately 150 ml of cool water. Once the beaker is no longer hot, transfer it to an ice bath. Keep it there until its temperature drops below 10°C, as measured with a Check Temp 1 digital thermometer placed in the reaction mixture.

11. Set up a Büchner funnel apparatus. Place a piece of #1 filter paper in the Büchner funnel. Moisten the filter paper with deionized water. Using suction, filter the mixture through the filter paper. You don't have to get all of the solid out of your reaction beaker, or clean the reaction beaker, as you'll be pouring the precipitate (solid) right back into the reaction beaker. Pull air through the solid in the funnel for at least a minute, to dry it out.

12. Turn off the vacuum. Release the vacuum on the sidearm flask by twisting off the vacuum hose as you pull gently. Rotate the filter cup of the Büchner funnel to free it from the rest of the apparatus.

13. Knock or scrape the contents of the filter cup, including the filter paper, back into your 250 mL reaction beaker. You do not need to clean or rinse your reaction beaker.

14. Rinse the filter cup with deionized water from your squirt bottle, into the reaction beaker.

15. Pick up the filter paper with the plastic tweezers provided. Use your squirt bottle, filled with deionized water, to rinse all the colored cobalt compound off of the filter paper.

16. Discard the used filter paper in the trash, unless it is still colored.

17. Discard the filtrate (liquid) in the aqueous cobalt waste container.

18. Using your squirt bottle, rinse down the sides of the reaction beaker and your stirring rod into the reaction beaker. Add deionized water to your reaction beaker until the total solution volume is approximately 35 mL, as indicated by the gradations on the beaker.

19. IN THE HOOD, add 25 mL of 15 M ammonia directly to the reaction flask, and stir.

20. IN THE HOOD add 60 mL of 12 M HCl directly to the reaction beaker.

21. Heat the solution to 80-85°C in your hot water bath for thirty minutes.

22. Cool your reaction beaker in the cool water bath (400 mL beaker) for 2 minutes. Then transfer it to one of the ice baths in the sinks, stirring occasionally as it cools. This helps promote crystallization. (As before, use a CheckTemp 1 digital thermometer in the reaction mixture to monitor the temperature.)

23. Before you put it in and wet it, determine the mass of the filter paper you will use in the next step. Use a top-loading balance, making the determination to ± 0.01 g.

24. Reassemble your Büchner funnel apparatus. (You do not need to rinse out the sidearm flask.) Filter the cold precipitated product suspension by pouring it onto the moistened filter paper while the suction is on. To transfer as much of your product as possible, stir the reaction mixture with your stirring rod just before you pour out the portions, and pour pretty quickly, a little at a

time. Some product will remain in the reaction beaker – don't attempt to rinse it out, or you will dissolve away some of your product!

25. Draw air through the crystals for five minutes.

26. Weigh a clean, dry watchglass to ± 0.01 g on a top loading balance.

27. Turn off the suction, and release the vacuum by “burping” the hose: while twisting, pull on the vacuum hose to remove it from the sidearm flask, then stick it back on.

28. Transfer the crystals and your filter paper to the watchglass by inverting the filter cup onto the watchglass. You may have to tap or thump the filter cup a few times to get the product to fall out.

29. Place your emptied filter cup into the solids collection bin in the hood. Please do not attempt to clean it.

30. Rinse your reaction beaker with the minimum amount of water from your squirt bottle needed to dissolve all remaining yellow product. Pour the cobalt-contaminated (colored) water into the filter flask.

31. With it still in the filter flask, rinse the white, funnel-shaped portion of your Büchner funnel into the sidearm flask, using your squirt bottle and stir bar to scrape and wash off any solid material. Get all the color off both the funnel and your stirring rod.

32. If your filtrate is only faintly colored, pour it down the sink. If it does have a distinct color (and it may), pour it into the aqueous cobalt waste jug.

33. Put the watchglass in your drawer to dry.

34. Clean up, following your instructor's directions.

35. Next laboratory period, you'll weigh your product to determine your synthetic yield.

TESTS

Molar conductivity of solution of compound is 0. Choose it compound from list:

- a) $[\text{Pt}(\text{NH}_3)_6] \text{Cl}_4$
- b) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2] \text{Cl}_2$
- c) $*[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$
- d) $\text{PtCl}_4 \cdot 2\text{KCl}$
- e) $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$

Molar conductivity of solution of compound is 0. Choose it compound from list:

- a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- b) $*[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
- c) $\text{CoCl}_3 \cdot \text{KCl}$
- d) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
- e) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Molar conductivity of solution of compound is 0. Choose it compound from list:

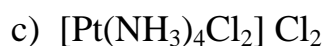
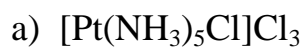
- a) $*[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$
- b) $\text{CoCl}_2 \cdot \text{KCl}$
- c) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$
- d) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$
- e) $\text{CoCl}_2 \cdot \text{NaCl}$

Molar conductivity of solution of compound is 0. Choose it compound from list:

- a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- b) $*[\text{Ni}(\text{CO})_4]$
- c) $[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$



What compound has highest molar conductivity?



Choose complex biochemical active compound.

a) Ribose

b) Ascorbic acid

c) Glucose

d) Vitamin B₁

e) *Vitamin B₁₂

Choose complex biochemical active compound.

a) Desoxyribose

b) Fructose

c) Ascorbic acid

d) *Hem

e) Vitamin B₂

Choose complex biochemical active compound.

a) Nicotinic acid

- b) Ascorbic acid
- c) Vitamin B₆
- d) Lactose
- e) *Chlorophyll

Choose formula of complex compound:

- a) (CuOH)₂CO₃
- b) CaClOCl
- c) KAl(SO₄)₂
- d) PtCl₄*2KCl
- e) *K₄[Fe(CN)₆]

Choose formula of complex compound:

- a) K₂Cr₂O₇
- b) Sr(HS)Cl
- c) NaTl(NO₃)₂
- d) *[Cu(NH₃)₄]Cl₂

How many chloride-ions in [Pt(NH₃)₂Cl₄] can react with AgNO₃:

- a) 4
- b) 3
- c) 2
- d) *0

How many chloride-ions in [Pt(NH₃)₄Cl₂] Cl₂ can react with AgNO₃:

- a) 3

- b) 4
- c) 0
- d) 1
- e) *2

How many chloride-ions in $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3] \text{Cl}$ can react with AgNO_3 :

- a) 4
- b) 3
- c) 0
- d) 2
- e) *1

How many chloride-ions in $[\text{Pt}(\text{NH}_3)_4\text{Cl}] \text{Cl}_3$ can react with AgNO_3 :

- a) 1
- b) 2
- c) 4
- d) 0
- e) *3

How many chloride-ions in $[\text{Pt}(\text{NH}_3)_6] \text{Cl}_4$ can react with AgNO_3 :

- a) 3
- b) 1
- c) 0
- d) *4
- e) 2

How many chloride-ions in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ can react with AgNO_3 :

- a) 1
- b) 2
- c) 4
- d) *3
- e) 0

How many chloride-ions in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$ can react with AgNO_3 :

- a) 1
- b) *2
- c) 4
- d) 3
- e) 0

How many chloride-ions in $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ can react with AgNO_3 :

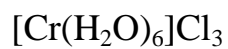
- a) 1
- b) 4
- c) 3
- d) 0
- e) *2

How many chloride-ions in $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$ can react with AgNO_3 :

- a) 4
- b) 0
- c) 3
- d) 2

e) *1

How many molecules of water easy to evaporate from compound:



a) 4

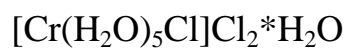
b) 6

c) 1

d) *0

e) 2

How many molecules of water easy to evaporate from compound:



a) *1

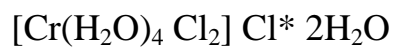
b) 4

c) 2

d) 0

e) 6

How many molecules of water easy to evaporate from compound:



a) 4

b) 5

c) 6

d) 1

e) *2

Choose complexing agent of compound:

$K[Pt(NH_3)_2Cl_4]$:

- a) K^+
- b) NH_3
- c) Cl^-
- d) $*Pt^{4+}$
- e) Pt^{2+}

Choose complexing agent of compound:

- a) $[Cu(NH_3)_4]SO_4$
- b) NH_3
- c) SO_4^{2-}
- d) Cu^+
- e) $[Cu(NH_3)_4]^{2+}$
- f) $*Cu^{2+}$

Choose complexing agent of compound:

- a) $[Co(NH_3)_5Cl]NO_3$
- b) $[Co(NH_3)^{2+}$
- c) Cl^-
- d) Co^{3+}
- e) NH_3
- f) $*Co^{2+}$

Choose complexing agent of compound:

- a) $[Ni(NH_3)_6]SO_4$

- b) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- c) SO_4^{2-}
- d) H
- e) NH_3
- f) $^*\text{Ni}^{2+}$

Choose complexing agent of compound:

- a) $\text{K}_2[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]$
- b) $[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{2-}$
- c) NO^{2-}
- d) $^*\text{Co}^{2+}$
- e) K^+
- f) NH_3

Formula of compound is $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$ Choose formula of ligand:

- a) NO^{3-}
- b) $[\text{Ag}(\text{NH}_3)_2]^+$
- c) $^*\text{NH}_3$
- d) Ag^+

Formula of compound is $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$. Choose formula of ligand:

- a) Cu^+
- b) Cu^{2+}
- c) SO_4^{2-}
- d) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$
- e) $^*\text{H}_2\text{O}$

Formula of compound is $K_4[Fe(CN)_5Cl]$. Choose ions of outer coordination sphere.

- a) $[Fe(CN)_5Cl]^{4+}$
- b) Cl^-
- c) $*K^+$
- d) Absent
- e) CN^-

Formula of compound is $[Co(NH_3)_5(NO_2)]Cl_2$. Choose ions of outer coordination sphere.

- a) $[Co(NH_3)_5]^{3+}$
- b) $*Cl^-$
- c) Absent
- d) Co^{3+}
- e) $[Co(NH_3)_5(NO_2)]^{2+}$

Formula of compound is $K_3[Co(NO_2)_5Cl]$ Choose ions of outer coordination sphere:

- a) $[Co(NO_2)_5Cl]^{3-}$
- b) $*K^+$
- c) Co^{3+}
- d) Absent
- e) Cl^-

Formula of compound is $(\text{NH}_4)_2[\text{Pt}(\text{OH})_2\text{Cl}_4]$. Choose ions of outer coordination sphere:

- a) $[\text{Pt}(\text{OH})_2\text{Cl}_4]^{2+}$
- b) Pt^{4+}
- c) OH^-
- d) Absent
- e) $^*\text{NH}_4^+$

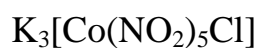
Formula of compound is $[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_3]$ Choose ions of outer coordination sphere:

- a) NH_3
- b) Cl^-
- c) Co^{3+}
- d) $^*\text{Absent}$
- e) NO_2^-

Formula of compound is $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$. Choose inner coordination sphere:

- a) NO_2
- b) Cl^-
- c) Co^{3+}
- d) NH_3
- e) $^*[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$

Formula of compound is



Choose inner coordination sphere:

- a) Cl^-
- b) K^+
- c) Co^{3+}
- d) NO^{2-}
- e) $*[\text{Co}(\text{NO}_2)_5\text{Cl}]^{3-}$

Formula of compound is $\text{K}_4[\text{Fe}(\text{CN})_5\text{Cl}]$. Choose inner coordination sphere:

- a) Cl^-
- b) Fe^{2+}
- c) K^+
- d) $*[\text{Fe}(\text{CN})_5\text{Cl}]^{4-}$
- e) CN^-

Formula of compound is $(\text{NH}_4)_2[\text{Pt}(\text{OH})_2\text{Cl}_4]$. Choose inner coordination sphere:

- a) Cl^-
- b) NH_4^+
- c) Pt^{4+}
- d) OH^-
- e) $*[\text{Pt}(\text{OH})_2\text{Cl}_4]^{2-}$

Formula of compound is $[\text{Co}(\text{NO}_2)_2\text{Cl}(\text{NH}_3)_3]$. Choose inner coordination sphere:

- a) Co^{3+}
- b) Cl^-

- c) NH_3
- d) NO^{2-}
- e) $*[\text{Co}(\text{NO}_2)_2\text{Cl}(\text{NH}_3)_3]$

What ligand is monodentate?

- a) $\text{C}_2\text{O}_4^{2-}$
- b) SO_3^{2-}
- c) SO_4^{2-}
- d) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$
- e) $*\text{Cl}^-$

What ligand is monodentate?

- a) $\text{B}_4\text{O}_7^{2-}$
- b) SO_4^{2-}
- c) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$
- d) PO_4^{3-}
- e) $*\text{NH}_3$

What ligand is bidentate?

- a) CN^-
- b) NO^{2-}
- c) NH_3
- d) H_2O
- e) $*\text{C}_2\text{O}_4^{2-}$

What ligand is bidentate?

- a) Br^-
- b) Cl^-
- c) F^-
- d) CN^-
- e) $^*\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

Choose formula of aquacomplex:

- a) $\text{MgSO}_4 \cdot \text{H}_2\text{O}$
- b) $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- c) $\text{NaCl} \cdot 2\text{H}_2\text{O}$
- d) $^*[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$
- e) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

What size of most stable cycles of chelates?

- a) 3 and 4
- b) 4 and 5
- c) 3 and 7
- d) *5 and 6
- e) 7 and 8

What central ion in molecule of hem?

- a) Fe^{3+}
- b) Cu^{2+}
- c) Cr^{3+}
- d) Co^{2+}
- e) $^*\text{Fe}^{2+}$

What central ion in molecule of vitamin B₁₂?

- a) Cr³⁺
- b) Cu²⁺
- c) *Co²⁺
- d) Fe²⁺
- e) Fe³⁺

What central ion in molecule of chlorophyll?

- a) Co²⁺
- b) Fe³⁺
- c) Fe²⁺
- d) Cr³⁺
- e) *Mg²⁺

Choose chelate molecules:

- a) Ribose, desoxyribose
- b) Maltose, sucrose
- c) *Chlorophyll, vitamin B₁₂, hem
- d) Glucose, fructose, lactose
- e) DNA, RNA

Choose formula of potassium pentacyanoammineferrate (III):

- a) K[Fe(CN)₃(NH₃)₃]
- b) K₂[Fe(CN)₄(NH₃)₂]
- c) K₄[Fe(CN)₆]

- d) $K_3[Fe(CN)_6]$
- e) $*K_3[Fe(CN)_5NH_3]$

Choose formula of ammonium dihydroxotetrachloroplatinate (IV):

- a) $(NH_4)_2[Pt(OH)_5Cl]$
- b) $(NH_4)_2[Pt(OH)_4Cl_2]$
- c) $(NH_4)_2[Pt(OH)Cl_5]$
- d) $(NH_4)_2[Pt(OH)_3Cl_3]$
- e) $*(NH_4)_2[Pt(OH)_2Cl_4]$

Choose name of the compound $[Cr(H_2O)_3F_3]$

- a) potassiumdiaquatetrafluorochromate (III)
- b) monochlorotetraquachromium
- c) monofluorotetraquachromium
- d) tetrafluorodiaquachromium
- e) $*trifluotriaquachromium$ (III)

Choose name of the compound $[Pt(NH_3)_4Cl_2](NO_3)_2$:

- a) dinitrotetrammineplatinum (IV) chloride
- b) potassiumpentachloroammineplatinate (IV)
- c) tetrachlorodiammineplatinum(IV)
- d) monochloropentammineplatinum(IV) nitrate
- e) $*dichlorotetraammineplatinum(IV)$ nitrate

Choose more stable complex compound:

- a) $[Cu(CN)_2]^-$ $K_{inst} = 1 * 10^{-16}$

- b) $[\text{Ag}(\text{NO}_2)_2]^-$ $K_{\text{inst}} = 1,3 \cdot 10^{-3}$
- c) $[\text{Ag}(\text{NH}_3)_2]^+$ $K_{\text{inst}} = 6,8 \cdot 10^{-8}$
- d) $[\text{Ag}(\text{S}_2\text{O}_3)]^{3-}$ $K_{\text{inst}} = 1 \cdot 10^{-13}$
- e) $*[\text{Ag}(\text{CN})_2]^-$ $K_{\text{inst}} = 1 \cdot 10^{-21}$

Choose less stable complex compound:

- a) $[\text{HgCl}_4]^{2-}$ $K_{\text{inst}} = 6 \cdot 10^{-17}$
- b) $[\text{Ni}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 4,8 \cdot 10^{-8}$
- c) $[\text{Cd}(\text{CN})_4]^{2-}$ $K_{\text{inst}} = 1,4 \cdot 10^{-17}$
- d) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 4,56 \cdot 10^{-14}$
- e) $*[\text{Cd}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 2,5 \cdot 10^{-7}$

Choose less stable complex compound:

- a) $*[\text{HgCl}_4]^{2-}$ $K_{\text{inst}} = 6 \cdot 10^{-1}$
- b) $[\text{Ni}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 4,8 \cdot 10^{-8}$
- c) $[\text{Cd}(\text{CN})_4]^{2-}$ $K_{\text{inst}} = 1,4 \cdot 10^{-17}$
- d) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 4,56 \cdot 10^{-14}$
- e) $[\text{Cd}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 2,5 \cdot 10^{-7}$

The electron configuration of a Ni^{2+} ion is:

- a) $[\text{Ar}]4s^23d^8$
- b) $[\text{Ar}]4s^23d^6$
- c) $*[\text{Ar}]3d^8$
- d) $[\text{Ar}]3d^6$

The Fe^{3+} ion has _____ electrons in 3d orbitals.

- a) 6
- b) *5
- c) 4
- d) 3
- e) 2

The Fe^{2+} ion has _____ electrons in 3d orbitals.

- a) 6
- b) 5
- c) *4
- d) 3
- e) 2

Choose less stable complex compound:

- a) $[\text{HgCl}_4]^{2-}$ $K_{\text{inst}} = 6 \cdot 10^{-17}$
- b) $[\text{Ni}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 4,8 \cdot 10^{-8}$
- c) $*[\text{Cd}(\text{CN})_4]^{2-}$ $K_{\text{inst}} = 1,4 \cdot 10^{-2}$
- d) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 4,56 \cdot 10^{-14}$
- e) $[\text{Cd}(\text{NH}_3)_4]^{2+}$ $K_{\text{inst}} = 2,5 \cdot 10^{-7}$

A ligand is:

- a) a molecule or ion that has at least one lone pair of electrons
- b) a nucleophile
- c) a Lewis base
- d) part of a coordination compound
- e) *All of the above

In $\text{K}[\text{Cu}(\text{CN})_2]$, how many 3d electrons does the copper ion have?

- a) *10
- b) 9
- c) 8
- d) 7
- e) 6

Which of the following is a bidentate ligand?

- a) cyanide ion
- b) nitrite ion
- c) ammonia
- d) thiocyanate ion
- e) *ethylenediamine

The correct chemical formula for tetraamminecopper(II) chloride is:

- a) $[\text{Cu}(\text{NH}_3)_4\text{Cl}]$
- b) * $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$
- c) $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_3$
- d) $[\text{Cu}(\text{NH}_3)_4]\text{Cl}$
- e) $[\text{Cu}(\text{NH}_3)]\text{Cl}_4$

The best name for $\text{K}[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{CN})_2]$ is:

- a) *potassium diamminedichlorodicyanochromate(III)
- b) potassium diamminedichlorodicyanochromium(III)
- c) potassium diamminedichlorochromatium(III) cyanide

- d) potassium diamminedichlorochromate(II) cyanide
- e) potassium diamminedichlorodicyanochromate(II)

Which of the following species could exist as a pair of isomers?

- a) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$
- b) $[\text{Fe}(\text{CN})_6]^{3-}$
- c) $*[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
- d) $[\text{Pt}(\text{en})\text{Cl}_2]$
- e) $[\text{Pt}(\text{NH}_3)\text{Br}_3]^-$

Which of the following ligands is most likely to form a high spin octahedral complex with cobalt(II)?

- a) CN^-
- b) NO_2^-
- c) $*\text{I}^-$
- d) CO
- e) En

In the complex ion ML_6^{n+} , M^{n+} has four d electrons and L is a weak field ligand. According to crystal field theory, the magnetic properties of this complex ion correspond to the presence of how many unpaired electrons?

- a) 0
- b) 1
- c) 2
- d) 3
- e) *4

Why are phosphates being eliminated from detergents?

- a) Detergents with phosphates are less efficient cleansers.
- b) By chelating Ca^{2+} ions, the phosphates allow more efficient cleansing
- c) Phosphates are important plant nutrients which increase algae growth and deplete oxygen
- d) None of the above.

The magnitude of crystal field splitting has a direct effect on the color of complex ions.

- a) True
- b) False

Place the ligands, CN^- , Br^- , H_2O , and OH^- in order from least to greatest according to their ability to split the orbital energy level

- a) CN^- , OH^- , H_2O , Br^-
- b) Br^- , OH^- , H_2O , CN^-
- c) Br^- , H_2O , CN^- , OH^-
- d) None of the above

Coordination compounds are useful in:

- a) biological organisms because of their color
- b) industry due to their magnetic properties
- c) biological organisms as ligand transporters
- d) none of the above

The electron configuration of a Ni atom is:

- a) $[\text{Ar}]4s^23d^8$
- b) $[\text{Ar}]3d^{10}$
- c) $1s^22s^22p^63s^23p^64s^23d^8$
- d) A and B
- e) B and C
- f) *A and C

The Zn^{2+} ion has _____ electrons in 3d orbitals.

- a) *10
- b) 8
- c) 6
- d) 4
- e) 2

The Al^{3+} ion has _____ electrons in 3d orbitals.

- a) *6
- b) 8
- c) 5
- d) 4
- e) 2

The charge on the central metal ion in $[\text{Cr}(\text{NH}_3)_4(\text{CO}_3)]^+$ is

- a) -1
- b) 0
- c) 1

d) *3

e) 5

The correct formula for diamminedichloroethylenediaminecobalt(III) bromide is

a) $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]\text{Br}_2$.

b) $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]\text{Br}$.

c) $*[\text{CoCl}_2(\text{en})_2(\text{NH}_3)_2] \text{Br}_2$.

d) $[\text{CoCl}_2(\text{en})_2(\text{NH}_3)_2]\text{Br}$.

e) $[\text{CoCl}(\text{en})(\text{NH}_3)_2]\text{Br}$.

Which of the following coordination compounds is incorrectly named?

a) $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$, dichlorobisethylenediamineplatinum(IV) chloride

b) $[\text{Co}(\text{NH}_3)_4\text{Br}_2]_2[\text{ZnCl}_4]$, tetraamminedibromocobalt(III) tetrachlorozincate

c) $*[\text{Pt}(\text{NH}_3)_2]\text{Cl}_2$ diamminedichloroplatinate(II)

d) $\text{Fe}[\text{PtCl}_4]$, iron(II) tetrachloroplatinate(II)

e) $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$, hexaamminecobalt(III) bromide

Which of the following ions is paramagnetic?

a) Sc^{3+}

b) Ti^{4+}

c) Mn^{7+}

d) $*\text{Ni}^{2+}$

e) V^{5+}

Which of the following ions is least likely to form colored complex ions?

- a) $*\text{Zn}^{2+}$
- b) Mn^{2+}
- c) Fe^{3+}
- d) Cu^{2+}
- e) Cr^{3+}

Which of the following octahedral complexes should have the largest crystal field splitting energy?

- a) $[\text{Cr}(\text{NH}_3)]^{3+}$
- b) $[\text{CrF}_6]^{3-}$
- c) $[\text{Cr}(\text{H}_2\text{O})]^{3+}$
- d) $*[\text{Cr}(\text{CN})_6]^{3-}$
- e) $[\text{CrCl}_6]^{3-}$

In the complex ion $[\text{Cr}(\text{NH}_3)_6]^{3+}$, how many unpaired electrons are there ?

- a) 1
- b) 2
- c) *3
- d) 4
- e) 5

CN^- is a strong field ligand, whereas Cl^- is usually a weak field ligand. Which of the following octahedral complexes has no unpaired electrons?

- a) $[\text{NiCl}_6]^{4-}$
- b) $*[\text{Zn}(\text{CN})_6]^{4-}$



BASIC REFERENCES

1. Medical chemistry: educational and methodical recommendations / A.G. Kaplaushenko, I.A. Iurchenko, B.A. Varinskiy, M.A. Shcherbak, Yu.N. Kucheryavyi. – Zaporozhye, 2014. – 263 p.
2. Medical chemistry: textbook for students of higher medical educational institutions of the III-IV accreditation levels / V.A. Kalibabchuk, V.I. Halynska, V.I., Hryshchenko [et al.]. – Kyiv : Medicine Publishing, 2010. - 223 p.
3. Fundamentals of Medicinal Chemistry / Gareth Thomas, John Wiley & Sons – First Edition. – December, 2003. – 285 p.
4. An Introduction to Medicinal Chemistry / Graham L. Patrick. – Oxford University Press – 4th Edition. – October, 2009. – 776 p.

SUPPORTING REFERENCES

1. Principles of Bioinorganic Chemistry/ Stephen J. Lippard, Jeremy M. Berg, University Science book, 2005, 411 p.
2. Biological Inorganic Chemistry: Structure and Reactivity 1st Edition. Harry B. Gray, Edward I. Stiefel, Joan Selverstone Valentine, Ivano Bertini. University Science book, 2007, 731 p.
3. Biological Inorganic Chemistry, Second Edition: A New Introduction to Molecular Structure and Function 2nd Edition. Robert R. Crichton . Elsevier. 2012, 447 p.
4. Foye's Principles of Medicinal Chemistry 7th Edition. David A. Williams. Lippincott Williams & Wilkins, 2013. 1500 p.
5. Principles of Colloid and Surface Chemistry, Third Edition, Revised and Expanded (Undergraduate Chemistry: A Series of Textbooks) 3rd Edition. Paul C. Hiemenz, Raj Rajagopalan. Taylor & Francis. 1997, 650 p.
6. Physical Chemistry, 9th Edition 9th Edition. Peter Atkins , Julio de Paula. Oxford University Press. 2010. 959 p.
7. Handbook of Surface and Colloid Chemistry, Fourth Edition. K. S. Birdi. CRC Press. 2015. 708 p.