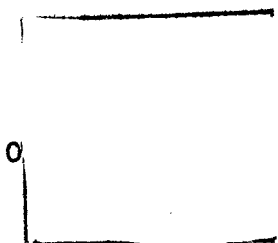


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20 May 1960

EIGHTH ALL-UNION CONFERENCE ON THE CHEMISTRY OF COMPLEX COMPOUNDS

- USSR -

By Z. A. Sheka

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## FOREWORD

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EIGHTH ALL-UNION CONFERENCE ON THE CHEMISTRY OF COMPLEX COMPOUNDS

[Following is a translation of an article by Z. A. Sheka in the Russian language periodical Zhurnal Neorganicheskoy Khimii (Journal of Inorganic Chemistry), Vol. IV, No. 11, Moscow, November 1959, pages 2647-2654.]

The VIII All-Union Conference on the Chemistry of Complex Compounds was held in Kiev in May 1959, which was attended by approximately 600 chemists, including 300 chemists from 27 cities in the Soviet Union, as well as Czech and Polish chemists. A total of 97 papers were presented and discussed at the conference.

Work at the conference was conducted in 3 sections, which studied complex compounds in solution, the structure and stability of complex compounds, the preparation and properties of complexes formed by a number of metals of the platinum group, cobalt, rare and rare earth elements, heteropoly acids, and the composition and structure of crystalline complex compounds.

The conference was opened by I. I. Chernyayev, chairman of the Organization Committee.

Problems concerned with a study of complex compounds, associated with chemical problems of the 7-Year Plan, were examined by V. I. Spitsyn, who pointed out the role played by complex compounds in the manufacture of semiconductors (ferromagnetic and piezoelectric compounds, such as Rochelle salt and materials having similar properties), in radiochemical studies, in the production of pure metals (extraction and chromatographic methods), in hydroelectrometallurgy, in the production of binding materials, in the synthesis of catalysts used in the production of high polymers, and in the application of complex-forming compounds, including water softening and ore concentration.

The problems and the results of a study of complex formation in solutions were described in a number of papers.

A. K. Babko (Kiev), in his paper entitled "Study of Complex Formation in Solutions of Three-Component Systems", showed that, in systems containing a metal cation, an electronegative addend and an organic base, compounds are formed, which are closely related in their properties to intracomplex compounds, although a chelate-type bond is absent. Compounds of a new type, containing one addend and two different central ions, have been isolated and studied. The complex tin-iron - dimethyl glyoxime, characterized by a high stability, is such a type of compound.

The same problem was described in a paper read by M. M. Tananayko (Kiev), which presented the results of a study of ternary compounds of copper, cobalt and iron rhodanides with pyridine and quinoline.

A number of reports described the results of a study of complex formation between metal ions and ethylene diamine tetraacetic acid ( $H_4Ac$ ), namely the paper by G. S. Savchenko, I. V. Tananayeva and Ye. V. Goncharova (Moscow) on "Study of the Complex Formation of Aluminum, Gallium and Indium Ions With Ethylene Diamine Tetraacetic Acid in Solution by the Method of Physical-Chemical Analysis", the paper by B. P. Nikol'skiy, A. M. Trofimov, and N. B. Vysokooostrovskaya (Leningrad) on "Complex Formation of Radium, Barium and Potassium in Ethylene Diamine Tetraacetic Acid Solutions", and the paper of L. I. Martynenko and A. I. Kameneva (Moscow) on "Mechanism of Complex Formation During the Ion-Exchange Separation of Rare Earth Elements With Ethylene Diamine Tetraacetic Acid". In the first paper, it was shown that, by measuring the electric conductivity and pH of solutions by means of spectrophotometric methods, the reaction leading to the formation of complexes of  $H_4Ac$  with aluminum, gallium and indium takes place in three stages; the formation of complex ions is reflected in diagrams in the form of sharply expressed singular points. In the second paper, the complex formation of barium and radium was studied by the ion-exchange method on a KU-2 ionite; the anionic complexes of radium and barium with  $H_4Ac$  were determined and the instability constants were established; potassium does not form any complex anions with  $H_4Ac$  in noticeable amounts.

B. P. Nikol'skiy, V. V. Pal'chevskiy and R. G. Gorbunova (Leningrad) in a paper describing complex formation in inorganic oxidation reduction systems, made use of pH measurements in studying complex formation in a system containing the ions  $Fe^{3+}$ ,  $Fe^{2+}$  and  $CH_3COO^-$ , and determined the product of staggered instability constants for the complex iron compounds formed.

I. Koryta (Prague) reported on the velocities of formation of certain cyclic compounds.

I. V. Pyatnitskiy (Kiev), in a paper describing the stability in solutions of metal and hydroxy acid complexes, showed that, within the limits of the groups listed in the periodic system, the stability of complexes decreases as the radii of the complex-forming cations increase, while within the limits of the periods, the stability increases as the charge of the cation increases. The stability of complexes formed by a metal and various hydroxy acids is determined by the structure of the acid. In an alkaline medium, trioxylglutaric acid complexes are the most stable, and complexes of tartaric, malic and citric acids are less stable. In acid solutions, citric acid forms the most stable complexes.

Compounds of aluminum and zinc with various hydroxy acids were also reported by A. V. Pavlinova and A. Ye. Protsenko (Chernovtsy) Reactions leading to the formation of aluminum and zinc complexes with

tartaric, citric, trioxylglutaric and saccharic acids were studied by the potentiometric and refractometric methods, and also by measurements of the electric conductivity.

The paper presented by Ya. D. Fridman (Frunze) was devoted to a study of equilibria in solutions of mixed compounds of copper, silver, mercury, lead, cadmium, antimony, bismuth and other metals. The author comes to the conclusion that many mixed complexes possess a greater stability, as compared to uniform complex compounds.

A. A. Vlchek (Prague) read a paper describing the application of polarography in the study of complex compounds.

P. K. Migal' and N. Kh. Grinberg (Kishinev) reported on the study of the composition and stability of aquocomplexes of metal ions.

A lively discussion followed the presentation of reports describing the application of chromatographic methods in studying complex compounds in solution.

The paper read by D. I. Ryabchikov, A. N. Yermakov, V. K. Belyayeva and I. N. Marov (Moscow) presented an evaluation of the possible application of ion exchange in studying complex compounds of multicharge ions, on hand of an example showing the complex formation of zirconium and hafnium with a number of mono- and dibasic organic oxyacids. The ion exchange method was also used by Z. A. Sheka and Ye. Ye. Kriss (Kiev) in determining complex compounds in systems consisting of nitric acid and nitrates of rare earth elements. R. M. Dranitskaya, A. A. Morozov, Ye. K. Tsuguy and A. I. Gavril'chenko (Odessa) reported on the possible separation of the green and violet modifications of chromium sulfate, after their absorption by KU-1 and SVS cationites followed by elution with hydrochloric and sulfuric acids of various concentration. B. N. Laskorin (Moscow) reported on new and practically important methods for separating barium and radium, zirconium and hafnium, and also aluminum and gallium. It was shown that the selection of complex-forming compounds is of great importance in the chromatographic separation of these metal pairs.

A report on the study of the condition of molybdenum (VI) and zirconium (IV) in acid solutions, performed by the electric migration and ion-exchange chromatographic methods, was presented by B. I. Nabivanets (Kiev). The pH areas and the conditions required for the presence of polymeric anionic forms of molybdic acid, of molybdenum and zirconium cations of low ionic weight, and of anionic chloride and sulfate complexes were established.

A great deal of attention was devoted to the application of various physical methods in studying the structure of complex compounds. A paper read by M. Ye. Dyatkina (Moscow) examined problems concerned with magnetic properties, absorption spectra, stability and stereochemistry of complex compounds in the light of the crystalline field theory ("ligand" field). The incorrect nature of the conclusions based on the assumption of a purely electric nature of the crystalline field is shown, and a case is listed in which the crystalline field theory cannot

be used for explaining the formation of aromatic metal complexes and compounds of transition elements with unsaturated molecules, which can be described within the framework of the molecular orbit method.

The application of the theory of crystalline fields in determining the structure and the geometrical configuration of complexes on the basis of optical and thermodynamic data was described by K. B. Yatsimirskiy (Ivanovo). The author pointed out that in a number of ions  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ , the thermodynamic characteristics (heat of formation, free energy) of many processes (complex formation, formation of a crystalline lattice, of a solvate, etc.) can be expressed by a general equation of the type:

$$\varphi = \alpha N + p \Delta E + \text{const},$$

where  $\varphi$  is the thermodynamic characteristic,  $\alpha N$  is a magnitude determined by the covalence rate of the bond ( $\alpha$  is the characteristic of the addend,  $N$  is the order number of the element in the periodic table),  $p$  is a structural characteristic, depending upon the distribution of electrons in a field of a specific symmetry,  $\Delta E$  is the difference between two basic energy levels in the ion.

The paper read by V. I. Belovaya and Ya. K. Syrkin (Moscow), entitled "Susceptibility and Structure of Complex Compounds of Nickel, Iron, Osmium and Ruthenium", noted the advantages and disadvantages of the "ligand" (?) field theory in explaining the magnetic properties of complexes. During the description of experimental data, the agreement between magnetic and X-ray structural studies was noted.

The report presented by V. N. Tolmachev, L. N. Sorbukhova and G. G. Lomakina (Khar'kov) on the interaction between the absorption spectra of complex compounds and their stability described the effect exerted by the nature of the chemical bond in complexes upon their absorption spectra and magnetic properties. It was noted that it is indispensable to take into account solvation processes occurring in solution during a study of the interrelation between the physical-chemical characteristics of complex compounds and their stability.

G. B. Bokiya, M. N. Lyashenko and V. I. Sokol (Moscow) read a paper on the "Coordinate Refractions of Complex Palladium, Rhodium and Iridium Compounds". A number of complex palladium, rhodium and iridium compounds were synthesized, their stability and dispersion of refraction factors were determined, and the molecular refractions of these compounds and a number of coordinate refractions were calculated. It was shown that the coordinate refraction is determined mainly by the type of addend, and to a considerably lesser extent, by the central atom.

In a paper entitled "Structure of Complex Compounds of Co, Ni, Cu, and Pt of the  $MeA_2X_2$  Type", presented by M. A. Poray-Koshits, G. N. Tishchenko and L. O. Atovmyan (Moscow), it was noted that a common characteristic, from a crystallochemical standpoint, of elements belonging to the first transition period is an octaedral coordination of  $Me^{II}$ ,

a chain linkage of  $\text{Me}^{\text{II}}$  atoms with each other through acid residues, in which two types of chain packing are possible, the selection of which is determined by the geometrical configuration of addends A and X. The individuality of transition metals is expressed in a change of individual distances between the metal and the addend, and as a result, in distortions of the basic packing pattern. The report presented a detailed analysis of the structure of crystals  $\text{CoPy}_2(\text{NCS})_2$  and  $\text{CuPy}_2(\text{NCS})_2$ . Coordination isomerism, characteristic for  $\text{CoA}_2\text{X}_2$  compounds, was studied on hand of an example involving  $\alpha$  and  $\beta$  -  $\text{CoPy}_2\text{Cl}_2$ . As an example of compounds, which may have both an ordered (coordinated) as well as a disordered (uncoordinated) structure, the structure of  $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$  was examined.

M. I. Usanovich (Alma-Ata), in a paper entitled "Complex Formation in the System  $\text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{CH}_3\text{COOH} - \text{H}_2\text{O}$ ", showed that the properties of studied ternary systems are influenced by complex acid-base interactions, which are aggravated by autocomplex formation in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The reduction of the specific electric conductivity of acids and their mixtures upon addition of water is explained as being due to a great mobility of autocomplex ions in sulfuric and nitric acid.

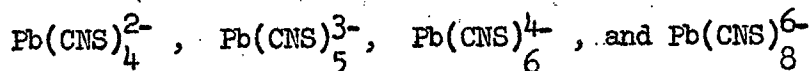
D. S. Bystrov, V. N. Filimonov and A. N. Terenin (Leningrad) described the results of a study of the infra-red absorption spectra of molecular compounds formed by a number of unsaturated hydrocarbons and organic molecules, containing O, N and S atoms, with  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{SnCl}_4$ ,  $\text{SbCl}_5$  and certain other metal halides, which are typical aprotic acids. On the basis of the data obtained, it was possible to solve the problem concerning the structure of certain molecular compounds and the point of addition of the halides to the organic molecules.

A number of reports was devoted to the study of complex formation processes in nonaqueous solutions and in aqueous-organic media. Such reports include the study conducted by Ya. A. Fialkov and Z. A. Fokina (Kiev) on "Complex Formation Between Gallium Trichloride and Chlorides of Certain Other Elements in Nonaqueous Systems", in which complex formation is investigated by various methods in the following systems:  $\text{GaCl}_3 - \text{C}_6\text{H}_5\text{NO}_2$ ,  $\text{GaCl}_3 - \text{KCl} - \text{C}_6\text{H}_5\text{NO}_2$ ,  $\text{GaCl}_3 - \text{JCl} - \text{C}_6\text{H}_5\text{NO}_2$ ,  $\text{GaCl}_3 - \text{PCl}_5$ ,  $\text{GaCl}_3 - \text{PCl}_5 - \text{C}_6\text{H}_5\text{NO}_2$ .

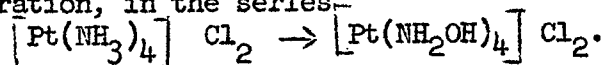
T. N. Sumarokova, E. Sh. Yarmukhamedova and I. G. Litvyak (Alma-Ata) reported on the interaction of tin (IV) halides with amines and amino acids in various solvents ( $\text{CCl}_3\text{COOH}$ ,  $\text{CH}_2\text{ClCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{NO}_2$ ). New complex compounds of  $\text{SnCl}_4$  with amino acids and amines were isolated.

In a paper entitled "On the Thermochemistry of Aquo- and Solvo-complexes", V. P. Vasil'yev (Ivanovo) showed the great effect exerted by the solvent on the change of thermodynamic functions during complex formation in solution. On the basis of data showing the heats of dilution and mixing in alcohol and aqueous-alcohol solutions, it was possible to calculate the heats associated with a change in the composition of solvate ionic shells during the transition from a mixed or

nonaqueous solvent to water. New data on the participation of water in equilibria of complex formation in solutions were presented by L. L. Shevchenko (Kiev). A paper read by A. M. Golub, L. I. Romanenko and V. M. Samoylenko (Kiev) listed the conditions necessary for the formation of complex lead ions with rhodanide ions of the following composition:



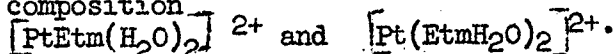
A large group of papers was devoted to the examination of new data on complex compounds of platinum and of platinum group metals. I. I. Chernyayev, L. A. Nazarova and V. S. Orlova (Moscow) in their paper "On Platinum Pentamines", presented data on the preparation and properties of a large number of new compounds, namely iodopentamines of quadrivalent platinum and their derivatives. By making use of the high trans-activity of iodine, it was possible to obtain such derivatives as iodopentamine platinonitrate, platinocarbonate, platinosulfate and nitropentamine. In the papers of A. A. Grinberg and A. I. Dobroborskaya (Leningrad) on "The Problem of the Detection of Cis-Platino-Diamines in Trans-Isomers and of Trans-Platino-Diamines in Cis-Isomers", and in the paper of A. A. Grinberg and A. I. Stetsenko on "Acid-Basic Properties of Compounds of  $\text{Pt}^{2+}$  With Hydroxylamine", the sensitivity of the potassium iodide and phenolphthalein reaction for the detection of cis-diamines was established experimentally and was theoretically substantiated. Conditions allowing the determination of a cis-isomer in trans-isomers and of a trans-isomer were established. Data are presented, which deal with a study of changes in acid-basic properties, conducted by means of a potentiometric titration, in the series-



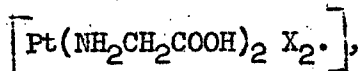
The acid dissociation constants of cis- and trans isomers of  $\left[ \text{Pt}(\text{NH}_3)_2 (\text{NH}_2\text{OH})_2 \right] \text{Cl}_2$  were calculated.

The paper read by A. D. Troitskaya (Kazan') presented experimental data, which confirm the explanation given by A. A. Grinberg concerning the transactivity of coordinated substituents in connection with their reducing properties during the reaction of potassium platinitate with tricyanoalkyl phosphites.

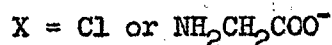
Kh. I. Gil'dengershel' (Leningrad) reported on the acid properties of aquoions having the composition



L. M. Volshteyn (Dnepropetrovsk) showed that, during the formation of intracomplex compounds containing two cycles, the process involving the closing of cycles from corresponding non-cyclic compounds takes place in a step-by-step manner. The conversion of non-cyclic compounds of the type

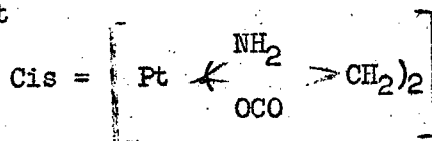


where

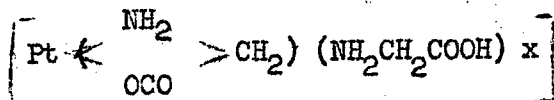




into an intramolecular salt



could be broken up into 2 stages. It was possible to effect the individual isolation of intermediate reaction products, such as:



whereby each of these products contains only one cycle.

A. V. Babayeva and O. N. Yevstaf'yeva (Moscow) reported the results of a study of infra-red spectra of ammonia-containing complex compounds of di- and tetravalent platinum. The effect of the composition of the coordination sphere and of the configuration of the complex compound molecule upon the frequency of the deformation (strain) oscillations of ammonia was studied. In the paper read by S. V. Bukhovets (Leningrad), it was pointed out that divalent platinum salts, upon reacting with acetylene under various conditions, yield amorphous and unstable compounds which explode on heating; monosubstituted acetylene derivatives decomposed without exploding to give metallic platinum; disubstituted acetylenes enter into the internal sphere of the complex, yielding crystalline and relatively stable compounds.

S. S. Batsanov and Ye. D. Ruchkin (Novosibirsk) reported a new form of geometrical isomerism in platinum compounds, designated by the authors as square-coordinate isomerism. The paper read by A. A. Babushkin, L. A. Gribov and A. D. Gel'man (Moscow) described a detailed analysis of infra-red spectra of complex compounds of platinum with ethylene and propylene. It was shown that the double bond C = C in ethylene and propylene, upon entering into the internal sphere of the platinum atom, is transformed into an ordinary bond, whereby the bond strength between the platinum and the carbon atoms is equal in magnitude to the stability of an ordinary covalent bond. I. I. Chernyayev and A. G. Mayorova (Moscow) read a paper entitled "Thiosulfate Complex Compounds of Rhodium", in which methods for preparing such multinuclear compounds are described, and their composition and properties are established. N. K. Pshenitsyn, S. I. Ginzburg and L. G. Sal'skaya (Moscow) reported the synthesis of a number of complex phosphates and sulfates of iridium with the following cations:  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{C}_9\text{H}_{14}\text{N}^+$ .

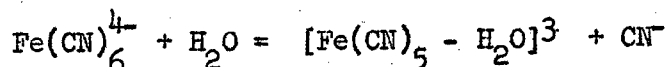
O. Ye. Zvyagintsev and S. M. Starostin (Moscow) reported on the behavior of water in acidocomplex nitroso compounds of ruthenium. The behavior of water, entering into the composition of the complex, differs according to the nature of the solvent; in organic solvents, the water in the compound acts as a common addend, while in aqueous solutions, a rapid proton dissociation of water entering into the complex is observed.

A number of reports were concerned with the study of complex cobalt compounds. A. V. Ablov (Kishinev) read a paper entitled "The Trans Influence of Substituents in Complex Compounds of Trivalent Cobalt With Dimethyl Glyoxime", and another paper in collaboration with A. Ya. Sychev entitled "Kinetics of Hydration of Halogeno-Bis-Dimethylglyoximoaquocobalt". Constants of the hydration velocity of  $[\text{Co}(\text{H}_2\text{O})_4(\text{DH})_2\text{Hal}]$  were determined, and the activation energies of the hydration reaction were calculated. The hydration velocity decreases in the series chloro-bromo-, iodo-bis-dimethylglyoximoaquocobalt. The unusual sequence of hydration velocities in halo-geno-bisdimethylglyoximoaquocobalt is apparently related to the presence of a water molecule in the internal coordination sphere. V. A. Golovnya and L. A. Kokh (Moscow) reported on carbonate complex compounds of trivalent cobalt. It was shown that, when sodium cobaltihexanitrite reacts with sodium bicarbonate, a monocarbonate  $[\text{Co}(\text{NO}_2)_4\text{CO}_3]^{3-}$  is formed according to the trans-influence rule, and then a dicarbonate, while a cobaltitricarbonate is formed in the presence of a considerable excess of sodium bicarbonate. The reaction involving the formation of dinitro diamino carbonate from Erdman's salt was studied, and the rule of the trans-effect was found to be applicable to this reaction. A paper entitled "Reactions of Pyridine-Containing Complex Compounds of Divalent Cobalt and Nickel" was presented by A. V. Bahayeva and I. B. Baranovskiy (Moscow). New compounds were synthesized, containing both different acidic substituents and different amines in a coordination form. Complex compounds of cobalt and nickel were also reported by P. V. Gogorishvili, M. G. Karkarashvili and M. G. Tskitishvili (Tbilisi) in a paper entitled "Complex Compounds of Cobalt and Nickel With Ethylene Diamine, Hydrazine and Acid Hydrazides". The authors found that the trans-activity of the  $\text{NO}_2$  group is always greater than the trans-activity of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{N}_2\text{H}_4$ . A. N. Sergeyeva and K. N. Mikhaevich (L'vov) reported the results of the synthesis of sulfur-containing complex cobalt cyanides of the type  $\text{K}_4[\text{Co}(\text{CN})_3\text{S}_2] \cdot 6\text{H}_2\text{O}$ . The solubility, electric conductivity, pH values of aqueous solutions and the molecular weight of this compound were studied, and its crystalloptical characteristic was given. When this compound is subjected to the action of mineral acids, a complex acid  $\text{H}_4[\text{Co}(\text{CN})_3\text{S}_2]$  is formed. Difficult soluble salts of this acid, such as the Mn, Fe, Co, Ni, Cu, Zn and other metal salts, were isolated. I. B. Khakham and I. M. Reybel' (Kishinev) reported on the study of conditions necessary for the formation of dinuclear cobalt ammoniates, belonging to the decamine- $\mu$ -peroxodicobalti series, in solution. N. I. Lobanov and O.S. Konovalenko (Kishinev) presented a large volume of experimental data on the synthesis of bromates, periodates and polybromides of cobaltiamines.

Several reports were concerned with the study of complex compounds of copper, zinc and other nonferrous metals. Yan Gazho (Bratislava) reported on the synthesis and properties of  $\alpha$ - and  $\beta$ - $\text{Cu}(\text{NH}_3)_2\text{X}_2$  (where X = Cl or Br), performed for the purpose of studying

the mutual effect exerted by addends in complex divalent copper compounds depending upon their method of preparation. The compounds were prepared in a non-aqueous (acetone) medium and by dry methods. The compounds were recrystallized from a concentrated aqueous solution of  $\text{NH}_4\text{Br}$ . It was found that the structure of the compounds obtained in this manner depends on their method of preparation.  $\alpha$ - and  $\beta$ - $\text{Cu}(\text{NH}_3)_2\text{X}_2$  were obtained, the properties of which are not connected with the existence of cis- and trans-isomers. V. V. Udovenko and M. V. Artemenko (Kiev) reported the interaction of copper chloride and copper hydroxide with monoethanolamine; a relationship was established between the composition of the complexes and the ratio of the components and the nature of the solvent. G. A. Popovich and A. V. Ablov (Kishinev) presented extensive data on the synthesis of double triple copper tartrates (with alkali metal tartrates), having an isomorphic structure and a complex anion of the probable composition  $[\text{Cu}_2(\text{C}_4\text{H}_4\text{O}_6)_3]$ . I. L. Kukhtevich (Dnepropetrovsk) reported on the chemical stability of  $\alpha$ - and  $\beta$ -copper and zinc pheophytinates.

A number of reports included experimental and theoretical data concerned with complex compounds of individual metals and metalloids. Thus, M. N. Orlova and K. B. Yatsimirskiy (Ivanovo) reported on the kinetics and mechanism of reactions



in the presence of gold salts and a considerable excess of hexacyanoferroate, which follows a kinetic equation of the first order in regard to the concentration of gold, which is not bound in the cyanide complex. A sensitive method for the determination of gold was developed on this basis, and a reaction mechanism was suggested. B. V. Ptitsyn, L. I. Vinogradov and L. L. Getskina (Leningrad) presented a characteristic of a citrate-silver electrode and determined its application range during the determination of instability constants of complex citrates. In a paper entitled "Complex Compounds of Beryllium", A. V. Novoselova, K. M. Semenenko, N. Ya. Turova and A. I. Grigor'yev (Moscow) showed that in the formation of complex compounds of beryllium oxyacetate or oxypropionate with  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_2$  and  $\text{C}_4\text{H}_9\text{NH}_2$ , the predominant reaction is an addition reaction of the type  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6 \cdot n\text{X}$ . The beryllium oxyacetate molecule has four gaps (hollows), as a result of which cavities are present in the crystalline lattice of this salt, which explain the ability of beryllium oxyacetate or oxypropionate to form inclusion compounds. L. P. Adamovich, I. I. Timofeyeva, and B. V. Yutsis (Khar'kov) studied aurintricarbonic acid and its reaction products with its reaction products with beryllium. The authors established the composition of the reaction product (1:1), determined the instability constant, which exhibited a high stability in a wide concentration range, and found that this system is of analytical interest during visual determinations. S. N. Avakyan (Yerevan) reported on

methods for obtaining mixed diamine complex compounds of cadmium chloride and bromide, and described the properties of pyridine-aniline and pyridine-ammonia complexes. The paper presented by M. S. Novakovskiy and M. G. Mushkina (Khar'kov) was devoted to the study of the formation of cadmium pyrophosphate complexes at various pH values. The composition and instability constants were determined by the emf measurement method. G. Vanag, E. Gudrinietse and A. Ievin'sh (Riga) reported on complex compounds of arylazo- $\beta$ -diketones. Arylazo- $\beta$ -diketones, obtained from ortho-oxyaromatic amines, form complexes of 1:1 composition with divalent metals (Cu, Cd, Co, Ni). With the same metals, arylazo- $\beta$ -diketones, which do not contain a hydroxyl group in the aromatic nucleus, form complexes with a 2:1 Me composition. Complexes of arylazo- $\beta$ -diketones are adsorbed on fabrics and can be used as metal-containing azo dyes.

Complex boron compounds were described in 2 papers. I. G. Ryss (Dnepropetrovsk) showed that the hydrolysis of coordination compounds of boron fluoride with a number of amines takes place as a reaction of the first order. The activation energy of the hydrolysis of these compounds increases when the pH of the basic dissociation of the amine decreases, while the entropy of the activation increases proportionately to the activation energy of the hydrolysis. V. I. Mikheyeva and V. Yu. Markina (Moscow) showed that under the action of nitrogen-containing bases, tetraborane may be decomposed, whereby  $BH_3$  groups are split off and more complex radicals  $B_3H_7$  and  $H_2B_4$  are formed. Under the action of pyridine and trimethyl amine, solid substances are obtained, having the composition  $B_2H_4NC_5H_5$  and presumably  $[BH(CH_3)_3]_n$ .

B. Yezhovskaya-Tshebyatovskaya and Ya. Danovskaya (Vroclav) reported on complex rhenium compounds of the lowest valence order. Previously, the formation of a complex rhenium cyanide, obtained by reduction of oxycyanorhenite in a potassium cyanide solution, had been established by means of a polarographic and coulometric method. The monovalency of rhenium was established by a potentiometric method. In a complex with  $\alpha$ -pyridyl, rhenium is present in the anion in the form of a monovalent element. A paper entitled "Structure and Stability of Vanadium Complexes" was presented by B. Yezhovskaya-Tshebyatovskaya and L. Paydovskiy (Broclav). The authors studied trinuclear complex vanadium compounds, obtained by them for the first time, having the composition  $VAc_6(OH)_2X.yH_2O$  (Ac - fatty acid residue, X - organic or inorganic acid residue). Magnetic studies showed that these compounds have a system of 3 nuclei. The formation constants of the complexes were determined.

F. Ya. Kul'ba and V. Ye. Mironov (Leningrad) studied the solubility of the rhodanide and of halides of monovalent thallium in aqueous solutions of the same alkali metal salts. The instability constants of complex cations in the presence of various cations were determined. The nature of alkali and alkaline earth metal ions exerts a noticeable effect on the process of formation of these complexes.

A. M. Zharnovskiy (Odessa) reported on the thermal stability of bromothallates of metals belonging to the first and second group in the periodic system. Anhydrous tetrabromothallates of divalent metals belong to straight series, according to the nature of the effect exerted by the external environment on the thermal stability of complex anions. In the case of tetrabromothallates of monovalent metals, a reverse nature of the effect exerted by ions of the external environment is observed. V. F. Toropova (Kazan') reported on the composition and stability of thiosemicarbazide complexes of mercury, silver, cadmium and nickel, and of cadmium and nickel semicarbazide complexes. The instability constants of these compounds were determined, on the basis of which conclusions were drawn on the nature of bonds and structure of the studied compounds.

V. G. Tronev, G. K. Babeshkina, A. S. Kotel'nikova, Myao Tsishen' (Moscow) reported a number of new data on "labile" and "inert" complex compounds of di-, tri- and tetravalent rhenium. V. A. Nazarenko (Odessa) reported on complex compounds of germanium with ortho-diphenols and ortho-oxyquinones.

A number of papers were devoted to the study of complex compounds of rare earth elements and their utilization for purposes of separation. A review paper by Ya. A. Fialkov, entitled "Rare Earth Elements as Complex-Forming Compounds", presented by Yu. Ya. Fialkov, was read at the plenary session. A paper presented by Ya. A. Fialkov and V. I. Yermolenko (Kiev) described the results obtained in a study of the formation of a compound consisting of a rare earth element and salicylic acid, depending upon the pH and the concentration of the salicylate ion.

N. V. Aksel'rud (Kiev) reported on basic chlorides and hydroxides of rare earth elements, precipitated from aqueous solutions. A number of generalizations concerned with the study of the composition and properties of these compounds were presented. A paper read by S. I. Yakubson and N. A. Kostromina (Kiev) described the results obtained with the aid of a potentiometric, conductometric and polarimetric research method, as well as data on ion transfer in systems containing lanthanum, cerium, neodymium, samarium, yttrium, gadolinium and ytterbium chlorides and gluconic acid.

V. A. Golovnya and L. A. Pospelova (Moscow) synthesized a large number of sulfate and carbonate complexes of tri- and tetravalent cerium, and showed that sulfate and carbonate ions can occupy not only two, but even one, coordination point in the internal sphere. L. A. Alekseyenko and V. V. Serebrennikov (Tomsk) described problems dealing with the connection between the complex formation of rare earth elements and the solubility of their compounds, and with the complex formation in aqueous systems of a lanthanide iodide and iodine. In studying the latter system, the formation of polyiodides was observed, and it was established that the stability of polyiodides is reduced when the order number of the lanthanide cations located in the external sphere increases (decrease in radii).

N. Ye. Brezhneva, V. I. Levin and M. G. Panova (Moscow) reported on a study of complex formation of yttrium with ortho-oxyquinoline by the extraction method.

L. S. Serdyuk and G. P. Fedorova (Dnepropetrovsk) studied the reaction involving the formation of a complex by the Stil'bazo reagent and yttrium, used in the colorimetric determination of yttrium.

The same cycle of research work also includes studies of complex compounds of rare elements and certain actinides. O. A. Osipov and Yu. B. Kletenik (Rostov on the Don) studied the electric and thermal properties and also conducted cryoscopic research on a number of complex compounds formed by zirconium halides with complex esters of monobasic acids. The formation of complex compounds of the type  $ZrHal_4RCCOOR_1$  and  $ZrHal_4.2RCCOOR_1$  is accompanied by a high thermal effect and a sharp increase in polarity (dipole moment). Complex compounds were isolated, their properties were studied, and the dipole moments were determined. I. A. Sheka and K. F. Karlysheva (Kiev) studied the composition of zirconium and hafnium cupferronates, obtained from hydrochloric, nitric, sulfuric and hydrofluoric acid solutions. In a hydrofluoric acid medium, when the concentration of the acid ranges from 0.1 to 5N, cupferronates of the composition  $Me(C_6H_5N_2O_2)_4$  are obtained. Cupferronates precipitated from other media have a variable composition. The solubility of cupferronates in sulfuric, hydrochloric, nitric and hydrofluoric acids was determined. Oxalic acid complexes of aluminum, titanium and zirconium were also reported by L. I. Dubovenko (Kiev). The gradual dissociation constants of oxalate complexes of zirconium and zirconyl ions were calculated.

A. I. Volkova and T. Ye. Get'man (Kiev) studied titanium salicylate complexes.

I. I. Chernyayev and a group of associates studied uniform complex uranyl compounds containing carbonate, oxalate and sulfate groups, as well as mixed compounds containing the same addends. Uranyl-rhodanide complexes and uranyl compounds with nitrogen-containing molecules were also investigated. These compounds were isolated in an individually pure state and were studied in aqueous solutions by physical-chemical analysis methods. V. M. Vdovenko, A. A. Lipovskiy and S. A. Nikitina (Leningrad) reported on the formation of a complex trichlorodiuranyl compound, which was investigated by the authors during the extraction of uranium with tributyl phosphate from hydrochloric acid solutions. The spectroscopic study of the solvation of uranyl nitrate in organic solvents was described in a paper by V. V. Vdovenko and D. N. Suglobov (Leningrad). M. P. Mefod'yeva (Moscow) reported on a study of the complex formation of neptunyl with acetate ions. The synthesis and the study of the physical-chemical properties of certain acidocomplex compounds of uranium (IV) and cerium were described by V. A. Golovnya and G. T. Bolotova (Moscow).

A paper by I. V. Tananayev and Lu Chzhao-da (Moscow), entitled "On Complex Thorium Fluorides", described the results of a systematic study of the system  $\text{Th}(\text{NO}_3)_4 - \text{NaF} - \text{H}_2\text{O}$  at low concentrations of  $\text{Th}(\text{NO}_3)_4$ . The isolated solid phases were subjected to a thermographic and an X-ray diffraction study. It was shown that interaction in the above system depends on the ratio between the initial concentrations of NaF and  $\text{Th}(\text{NO}_3)_4$ . In case of an equimolar ratio, ions  $\text{ThF}_3^+$ , and in part  $\text{ThF}_2^{2+}$ , are formed in solution. In case NaF is present in a large excess, precipitates of  $\text{ThF}_{3,8} \cdot \text{X}_{0,2}$  ( $\text{X} = \text{NO}_3^-$  or  $\text{OH}^-$ ) are formed, followed by the formation of normal thorium fluoride, and in case of a large excess of NaF, the compound  $\text{NaThF}_5 \cdot \text{H}_2\text{O}$  is formed.

Problems concerned with a study of hetero polycompounds, which aroused a lively exchange of opinion, played a prominent role in the work of the conference. A paper by V. I. Spitsyn, entitled "On the Problem of the Basicity of Hetero Polyacids and on the Nature of So-Called Highly Substituted Salts", listed the results of a study involving the interaction of small amounts of bases with the normal salts of certain hetero polyacids. It was shown that already a slight increase in the pH results in the formation of unsaturated hetero polyanions and in the splitting off of a portion of the addends in the internal sphere, instead of the formation of highly substituted salts, as was stated in a number of articles published by various authors. A. A. Babushkin, G. V. Yukhnevich, I. D. Kolli and V. I. Spitsyn (Moscow) reported on the spectroscopic study of the effect exerted by water upon the structure of potassium silicotungstate and on the nature of the bond between water and the anion. The infra-red absorption spectra of various hydrates of cis-potassium silicotungstate were investigated, as well as the spectrum of a fully dehydrated sample. The authors assume that in potassium silicotungstate, water is present in two forms: as chemically combined water, in the form of the hydroxyl  $\text{W} - \text{OH} \dots$ , and as water of crystallization, surrounding the anion and connected with the anion by hydrogen bonds. V. I. Spitsyn, Ye. A. Torchenkova and G. G. Stepanova reported on the study of certain rare earth salts of ceriomolybdic acid.

A paper of A. K. Babko and Yu. F. Shkaravskiy (Kiev) was devoted to the study of the extraction of hetero polyacids. On the basis of solubility data of phosphomolybdic and silicomolybdic acids in water and in isobutanol, and also on the basis of the distribution between these solvents under various conditions, the authors came to the conclusion that these compounds undergo polymerisation in concentrated aqueous solutions. Optimum conditions are given for the separation of silicomolybdic and phosphomolybdic acids by extraction with mixed solvents.

Ye. Ya. Rode and M. M. Ivanova (Moscow) reported on the physical-chemical study of germanium hetero polycompounds. The authors synthesized and studied germaniumtungstic and germaniummolybdic hetero polyacids, and the alkali metal salts of these acids, by using methods of

physical-chemical analysis. In a crystalline state, the above hetero polyacids are tetrabasic acids, which is in accord with the theoretical structure of these compounds. A paper by Ye. A. Nikitina and N. A. Tsvetkov (Moscow), entitled "Research in the Field of Isomeric  $\alpha$ - and  $\beta$ -Luteophosphotungstates", reported a new accelerated method for synthesizing ammonium  $\alpha$ - and  $\beta$ -luteophosphotungstates; the paper also described the preparation of free  $\beta$ -luteophosphotungstic acid and its sodium salts of various degrees of substitution, and the properties of the various compounds obtained.

At the final session, A. A. Grinberg reported on the conference on coordination chemistry, held in April 1959 in London, where the Soviet Union was represented by A. A. Grinberg and V. I. Spitsyn.

The resolution adopted at the conference noted that "in recent years, the importance of complex compounds has noticeably increased in view of their greater use in the production of nuclear fuel and auxiliary materials used in the atomic energy industry, in the preparation of high-purity compounds used in semiconductor technology, in the manufacture of ferromagnetic and peizoelectric compounds, and as catalysts in processes involving the synthesis of high polymer compounds, in the extraction of nonferrous, rare and noble metals from the corresponding ores and in the extraction of some of these metals in hydro-metallurgical processes, in carrying out extraction and ion exchange processes which are being introduced on a wide scale in various branches of technology, and in other fields of modern technology, biology, medicine, etc."

The conference also noted the considerable increase in the volume of studies concerned with the theory of the chemical structure, the reaction mechanism and the methods of application of complex compounds in the USSR, which was reflected in the reports and in the numerous communications presented during the conference, as well as the greater number of personnel engaged in studying the chemistry of complex compounds, and the greater scope of research work.

At the same time, the opinion was expressed at the conference that the development of theoretical work on the nature of chemical bonds present in complex compounds is lagging behind the requirements imposed by practical applications. The synthesis of new types of complex compounds is not being conducted on a sufficiently wide scale.

Modern physical research methods are used on a limited scale. The number of published monographs and reviews devoted to the chemistry of complex compounds is small.

The conference believes that the principal trends in the field of research on the chemistry of complex compounds during the coming years should be the following ones:

a. Work involving the synthesis and the extensive study of the properties of new types of complex compounds, which could be used in the preparation of high polymers, semiconductor materials, as catalysts in technically important processes and in the preparation of other compounds required for technical, defense, medical and other purposes.



b. Work involving the study of the properties of known complex compounds, aimed at finding among them compounds with semiconductor properties, as well as piezoelectric materials and other valuable products which could be used in modern technology.

c. The expansion of work presently in progress on the theory of the structure and reaction mechanisms of complex compounds, including the application for this purpose, in addition to methods being used at the present time, of new physical methods such as the use of paramagnetic resonance, neutronography, radiation effects, etc.

d. Work involving the extensive study of the properties of complex compounds in solution, aimed at developing a theory and obtaining data necessary for a practical application in the fields of hydro-metallurgy, chemical engineering and analytical chemistry.

e. Studies involving the application of wave mechanics in theoretical work on the nature of the chemical bond in complex compounds, and in clarifying the possible synthesis of new types of compounds.

f. Studies on the crystallochemistry of complex compounds, conducted with the aid of modern technical computer equipment.

In order to enable chemists engaged in the study of complex compounds to successfully fulfill their tasks, the conference issued the following directives:

a. To request the Division of Chemical Sciences of the Academy of Sciences USSR to include the problem entitled "Preparation, Study of the Structure and Properties, and Application of Complex Compounds" among the leading problems in the chemical field, and to set up a council for handling the problem of planning and coordinating studies in this field.

b. To organize the next (Ninth) Conference on the Chemistry of Complex Compounds in 1962. The Organization Committee will be entrusted with the determination of the location and the date on which this conference will take place.

c. It is suggested that limited conferences devoted to specific problems on the chemistry of complex compounds be convened prior to 1962.

d. It is considered advisable to publish monographs, handbooks and reviews dealing with individual problems of the chemistry of complex compounds, including translations and photo copies of foreign works.

e. It is indispensable that individual Soviet scientists participate on a permanent basis in the organization and work of international conferences on the chemistry of complex compounds.