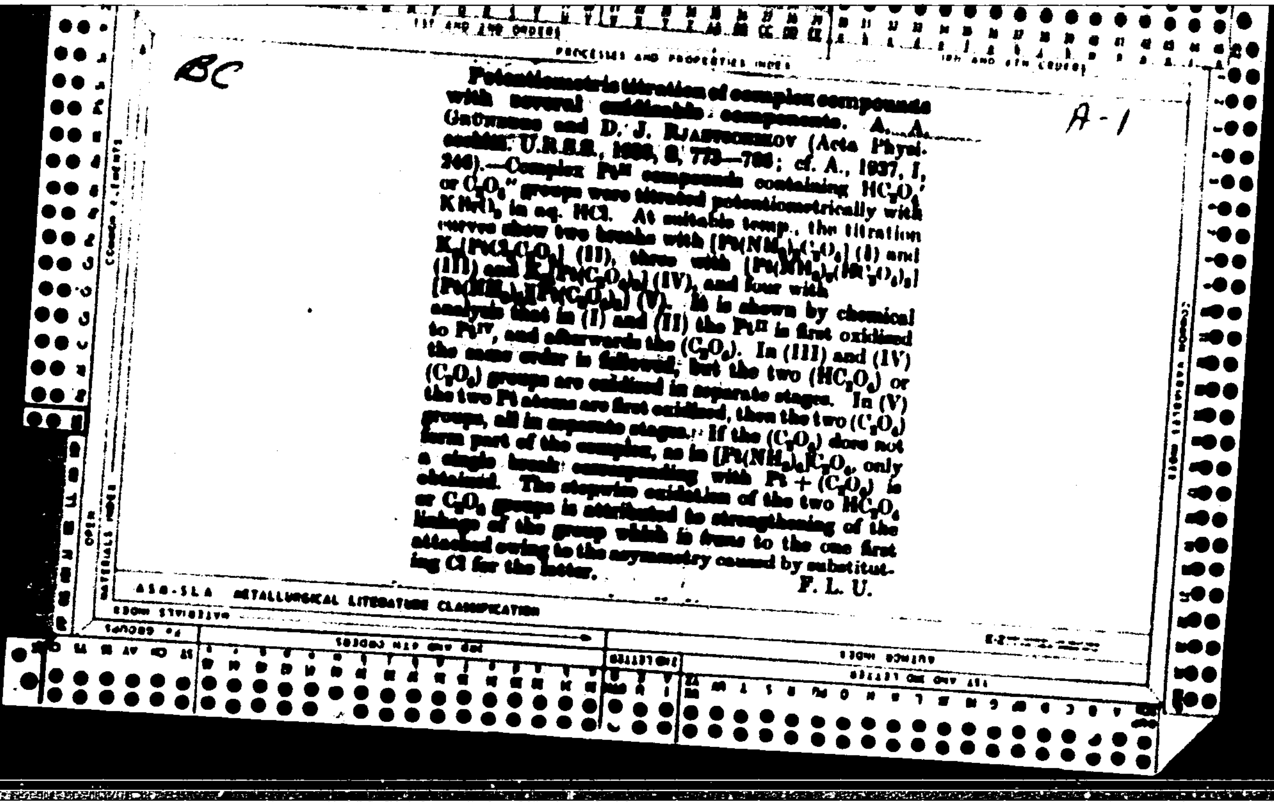
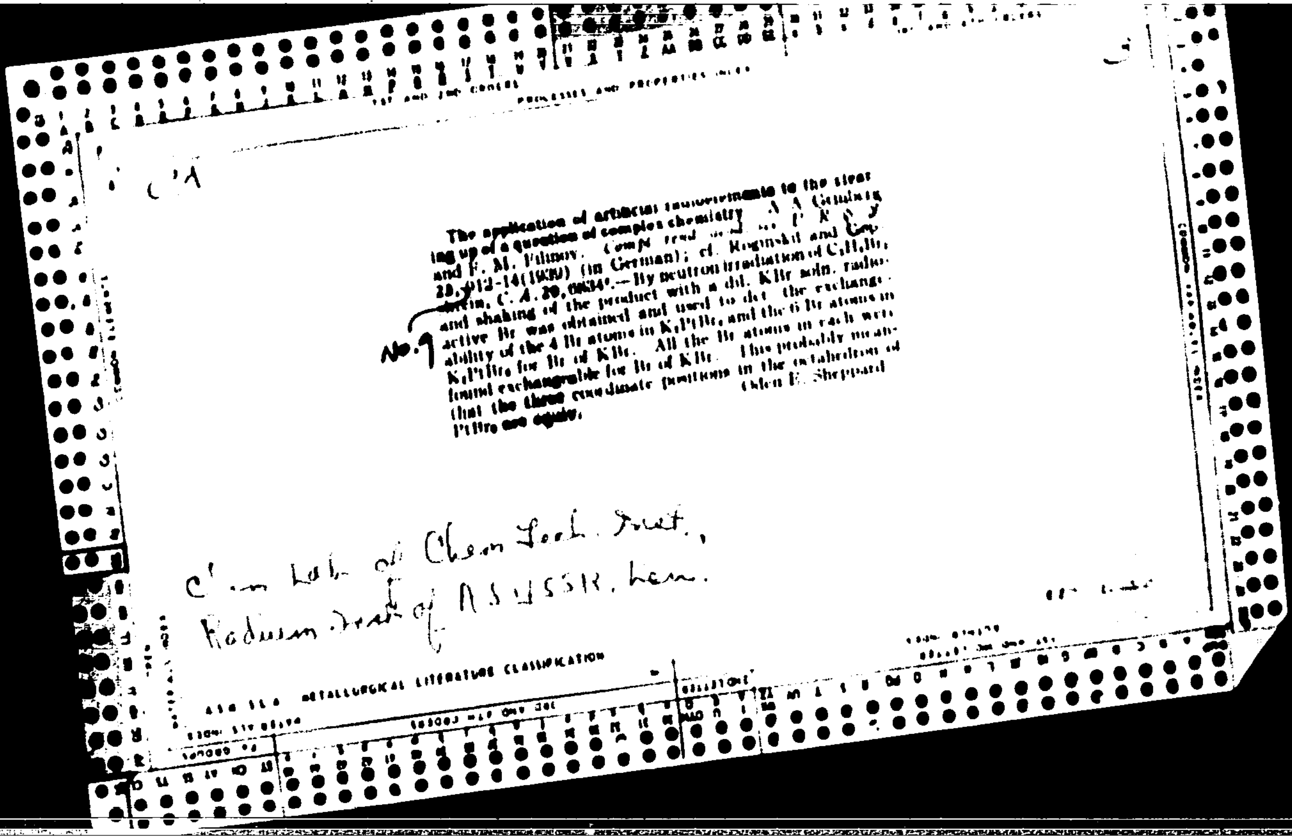


BC

A-1

Potentiometric titration of complex compounds with several oxidisable components. A. A. Grünberg and D. J. Rjabtschikov (Acta Physicochim. U.R.S.S., 1936, 5, 773—786; cf. A., 1937, I, 246).—Complex Pt^{II} compounds containing HC_2O_4' or C_2O_4'' groups were titrated potentiometrically with $KMnO_4$ in aq. HCl. At suitable temp., the titration curves show two breaks with $[Pt(NH_3)_2C_2O_4]$ (I) and $K_2[PtCl_2C_2O_4]$ (II), three with $[Pt(NH_3)_2(HC_2O_4)_2]$ (III) and $K_2[Pt(C_2O_4)_2]$ (IV), and four with $[Pt(NH_3)_4][Pt(C_2O_4)_2]$ (V). It is shown by chemical analysis that in (I) and (II) the Pt^{II} is first oxidised to Pt^{IV}, and afterwards the (C_2O_4). In (III) and (IV) the same order is followed, but the two (HC_2O_4) or (C_2O_4) groups are oxidised in separate stages. In (V) the two Pt atoms are first oxidised, then the two (C_2O_4) groups, all in separate stages. If the (C_2O_4) does not form part of the complex, as in $[Pt(NH_3)_4]C_2O_4$, only a single break corresponding with Pt + (C_2O_4) is obtained. The stepwise oxidation of the two HC_2O_4 or C_2O_4 groups is attributed to strengthening of the linkage of the group which is trans to the one first attacked owing to the asymmetry caused by substituting Cl for the latter.

F. L. U.



PROCESSES AND PROPERTIES INDEX

CA

No. 7

The application of artificial radioelements to the clearing up of a question of complex chemistry. A. A. Grinberg and F. M. Filinov. Compt. rend. acad. sci. U.R.S.S. 23, 912-14(1939) (in German); cf. Roginskii and Gopshtein, C. A. 30, 6634⁴.—By neutron irradiation of C_2H_5Br, and shaking of the product with a dil. KBr soln. radioactive Br was obtained and used to det. the exchangeability of the 4 Br atoms in K_2PtBr_4 and the 6 Br atoms in K_2PtBr_6 for Br of KBr. All the Br atoms in each were found exchangeable for Br of KBr. This probably means that the three coordinate positions in the octahedron of $PtBr_6$ are equiv. Glen E. Sheppard

Chem Lab. of Chem Tech. Inst., Radium Inst. of AS USSR, Len.

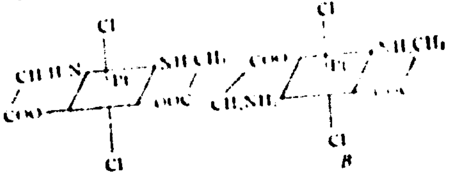
ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDER

PROCESSES AND PROPERTIES INDEX

6

The action of glycine on potassium chloroplatinate. A. A. Grinberg and I. M. Volshtein. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1941, 381-8 (in German 388-). Glycine (2.2 g.) in 30 cc. H_2O was treated, with heating, with 1.2 g. K_2PtCl_4. The mixt. was heated on a steam bath for 1.25-1.5 hrs. Immediately upon mixing, the soln. became almost red then faded to a greenish yellow. After the heating period the soln. was allowed to crystallize for several days, two fractions being collected. The 2 fractions had the same compn.: $PtGl_2Cl_2$ (Gl = H_2NCH_2COO). The total yield approached 45-50%, with approx. 10% being left in soln. The two fractions differ somewhat in their cryst. form and in chem. behavior. The 1st fraction (I) heated with concd. HCl dissolved very slowly on boiling with excess HCl, yielding on cooling yellow crystals of $Pt(GlH)_2Cl_4$. The 2nd (II) fraction heated with concd. HCl dissolved rapidly and did not crystallize on cooling. Reduction of I by K oxalate was slow and yielded *trans*-$PtGl_2$, while II reacted rapidly yielding *cis*-$PtGl_2$. The *cis* structure (*A*) of II and the *trans* structure (*B*) of I were further confirmed by comparison with prepns. made from samples known to be *trans*-$PtGl_2$ and *cis*-$PtGl_2$.



$Pt(GlH)_2Cl_4$ is apparently formed by breaking of the glycine complex ring with liberation of the COOH group and introduction of Cl atoms into the complex at the points of attachment of the COO groups. The product is a dibasic acid, which can be titrated. Addn. of $AgNO_3$ gives a yellow ppt., apparently of $Ag_2(PtGl_2Cl_4)$, which on treatment with HNO_3 yields AgCl and $PtGl_2Cl_4$.

G. M. Kosolapoff

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

CA 2

The properties of copper glycinate. A. A. Grinberg and Z. E. Gol'braikh. *J. Gen. Chem.* (U.S.S.R.) 11, [illegible]-45 (1941).—$(NH_2CH_2CO_2)_2Cu$ exists as needles (I) and blue platelets (II). Both are monohydrates, but II loses H_2O at 105° whereas I must be heated to 1[illegible]0° and then partly decomposes. The H_2O soly. of I at 25° is 0.[illegible] g. per 100 g. soln. and at 0° 0.[illegible] g. The corresponding solubilities of II are 0.[illegible] and 0.[illegible]. When solns. of I or mixts. of I and II are allowed to stand, the soly. falls to that of II. Rise in temp., stirring, and the presence of II hasten this change. No differences between I and II are found in cond. or chem. reactions. The compds. are probably geometrical isomers, and by analogy with the Pt and Pd analogs, the more stable II should be the trans form.

H. M. Leicester

ASD-SLA METALLURGICAL LITERATURE CLASSIFICATION [illegible] [illegible]

Application of artificial radioelements to the elucidation of problems of chemical complexes. A. A. Grinberg and P. M. Filinov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 453–455). Using radioactive Pt and Ir it has been shown that there is no exchange of central ion between $[PtCl_6]''$ and $[Pt(NH_3)_2Cl_4]$, $[IrCl_6]''$ and $[IrC_5H_5N)_2Cl_4]'$, and $[IrCl_6]'''$ and $[Ir(C_5H_5N)_2Cl_4]'$. The considerable difference in the activities of Pt and Ir after bombardment with neutrons suggests a simple method of determining traces of Ir in Pt. C. R. H.

GRINBERG, A. A.

"Oxidation of Geometric-Isomeric Platodiglycine," Dok. AN, 32, No. 1, 1941
(Dr., Lab. Chemistry, Medical Inst. im. I. P. Pavlov, Leningrad, -1941-.

PROCESSES AND PROPERTIES INDEX

8C

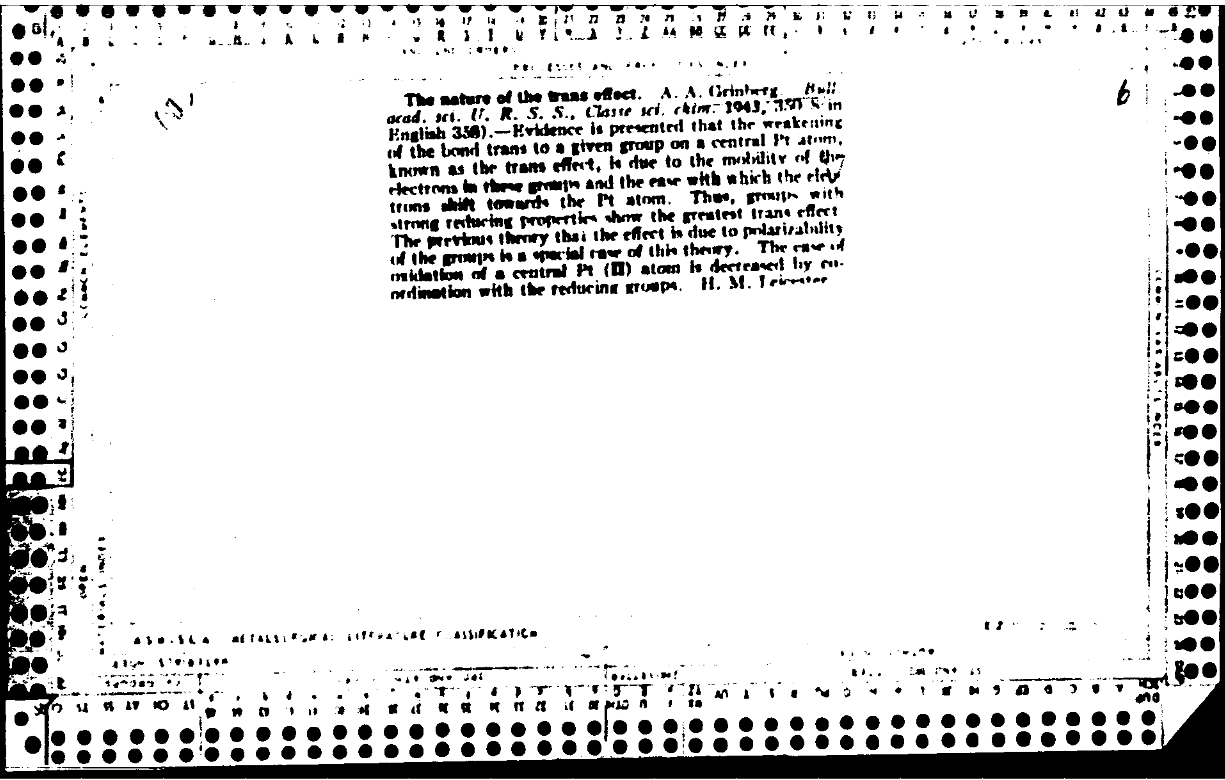
Nos 12,

Reduction-oxidation potentials of the metals of the platinum group. III. A. A. Grinberg and A. I. Schamsiev (*J. Gen. Chem. Russ.*, 1942, **12**, 55—72).—The prep. of various complex halogen compounds of Pd and Ir, and the determination of the reduction oxidation potentials of their solutions, are described. The systems investigated are: $K_2PdCl_6 \rightleftharpoons K_2PdCl_4$ (E_0 1·291 v. in n-NaCl at 25°), $K_2PdBr_6 \rightleftharpoons K_2PdBr_4$ (E_0 0·996 v. in n-KBr at 25°), $K_2PdI_6 \rightleftharpoons K_2PdI_4$ (E_0 0·482 v. in n-KI at 25°). The system $(NH_4)_2IrCl_6 \rightleftharpoons (NH_4)_3IrCl_6$ was fully investigated (E_0 0·966 v. in n-NaCl at 25°). Measurements of electrical conductivity of the solution, which rises rapidly to a max. and then falls slowly, suggest first a hydrolytic change $(NH_4)_3IrCl_6 + H_2O \rightarrow (NH_4)_2[IrCl_5H_2O] + NH_4Cl$, followed by oxidation $2(NH_4)_2[IrCl_5H_2O] + O + 2NH_4Cl \rightarrow 2(NH_4)_2IrCl_6 + 2NH_4OH$. The latter stage is demonstrated by chemical analysis.

I. L. W.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Oxidation-reduction potentials of the platinum compounds including organic amines and glycine. A. A. Grünberg and V. N. Lavrentiev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, [illegible], 203–205).—Oxidation-reduction potentials (E) at 25° of (a) $[Pt(NH_2R)_2Cl_4] + 2e \rightleftharpoons [Pt(NH_2R)_2Cl_2] + 2Cl'$ (*cis* and *trans*) (R = H, Et), (b) $[Pt(NH_2\cdot CH_3)_2Cl_4] + 2e \rightleftharpoons [Pt(NH_2\cdot CH_3)_2Cl_2] + 2Cl'$, and (c) $[Pt(NH_2\cdot CH_2\cdot CO_2H)_2Cl_4] + 2e \rightleftharpoons [Pt(NH_2\cdot CH_2\cdot CO_2H)_2Cl_2] + 2Cl'$ (*cis* and *trans*) in N-NaCl are > in N-HCl (cf. A., 1940, I, 296), by 26 and 20 mv. for the *cis* and *trans* systems respectively, which is about the same as for $[PtCl_6]'' + 2e \rightleftharpoons [PtCl_4]'' + 2Cl'$. The vals. of *E* for (a) R = Et > for (a) R = H > for (b). Exceptionally (c) has lower vals. of *E* which for the *cis* is greater by 18 mv. than for the *trans* system. F. R. G.



(3)

b

The nature of the trans effect. A. A. Grinberg. *Bull. acad. sci. U. R. S. S., Classe sci. chim.* 1943, 350-5 in English 358).—Evidence is presented that the weakening of the bond trans to a given group on a central Pt atom, known as the trans effect, is due to the mobility of the electrons in these groups and the ease with which the electrons shift towards the Pt atom. Thus, groups with strong reducing properties show the greatest trans effect. The previous theory that the effect is due to polarizability of the groups is a special case of this theory. The ease of oxidation of a central Pt (II) atom is decreased by coordination with the reducing groups. H. M. Leicester

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

6

The potentiometric method of determining the structure of coördinately polymeric complexes of Pt. A. A. Grinberg and N. N. Kats. No. 1 Bull. acad. sci. U. R. S. S., Classe sci. chim. 1948, 8-14 (English summary).—On the basis of oxidation-reduction potentials detd. previously (C. A. 36, 6153⁴) equil. consts. are calcd. for the oxidation of the following: $[Pt(NH_3)_4]^{++}$ (I) by $[PtCl_6]^{--}$ (II), $10^{4.07}$; $[Pt(NH_3)_3Cl]^+$ (III) by II, 10^{4}; $[Pt(NH_3)_2Cl_2]$ (IV) by II, $10^{0.00}$; $[PtNH_3Cl_3]^-$ by II, $10^{1.0}$; I by $[PtNH_3Cl_5]^-$ (V), $10^{4.10}$; III by V, $10^{1.11}$; IV by V, 10^{1}; I by $[Pt(NH_3)$[illegible]$]$ (VI), $10^{2.17}$, III by VI, $10^{0.73}$, and I by $[Pt(NH_3)_3Cl_3]^+$, $10^{1.4}$. From these values, the extent of formation of the products is calcd., and the theoretical curve is constructed for the oxidation of such compds. as $[Pt(NH_3)_4][PtCl_4]$ by $KBrO_3$ in HCl. The curves agree well with those detd. experimentally. Thus, the structure of a compd. of this type can be proved by comparing its theoretical and exptl. titration curves.

H.M. Leicester

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

Ca

1

Progress of general and inorganic chemistry in the U.S.S.R. during the past 25 years. A. A. Grinberg. *Uspekhi Khim.* 11, [illegible](1942).—[illegible] references, mostly to the Russian literature.
F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

GRINBERG, A. A.

"On the Interaction of the Joining of Divalent Platinum with Iodine," Zhur. Prik. Khim., 26, No. 11, 1943.

"New Method of Preparation of Monohydroxo-Derivatives of Tetravalent Platinum, Dok. A. N., 38, No. 7, 1943. [illegible]

3, 16.

Preparation of monohydroxo-derivatives of quadrivalent platinum. A. A. Grünberg and L. J. Michelis (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, [illegible], 209–210).—HOCl with K_2PtCl_4 yields $K_2[PtCl_4](OH)Cl$, with *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ yields $[Pt(NH_3)_2Cl_2](OH)Cl$, with $[Pt(NH_3)_4]Cl_2$ yields mainly $[Pt(NH_3)_4(OH)Cl]Cl_2$, and with $[Pt(NH_3)_4]SO_4$ yields $[Pt(NH_3)_4(OH)Cl]SO_4$. F. R. G.

CA

6

PROCESSES AND PROPERTIES INDEX

Interaction of salts of Pt metals with derivatives of H_3PO_3. I. Action of Et_3PO_3 and Et_2HPO_3 on K_2PtCl_4. A. A. Grinberg and A. D. Troitskaya. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1944, 178-81 (English summary).—Action of Et_3PO_3 on K_2PtCl_4 in aq. soln. yields as the primary product $[Pt(Et_3PO_3)_4]PtCl_4$ (I); the second product to sep. from the soln. is $[Pt(Et_2HPO_3)_2(Et_3PO_3)_2]$, formed from the action of K_2PtCl_4 on Et_2HPO_3 resulting from the partial hydrolysis of Et_3PO_3. I on prolonged boiling in $CHCl_3$ yields $[Pt(Et_3PO_3)_2Cl_2]$. The case of formation of the complex involving Et_2HPO_3 is evidence for the existence of two tautomeric forms of this ester (trivalent and quinquevalent P). G. M. Kosolapoff

No. 4

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

11

M

*The Determination of Quadrivalent Platinum by Visual Titration with Permanganate. A. A. Grinberg and Z. E. Gol'braikh (Zhur. Obshch. Khim., 1944, 14, (7/8), [illegible]. [In Russian.] It is possible to determine Pt^{IV} in the form of $PtCl_6^{2-}$ ion by titrating with $KMnO_4$, after reduction with CuCl and oxidation of excess CuCl by oxygen from the air. —N. A.

METALLURGICAL LITERATURE CLASSIFICATION

GRINBERG, ALEKSANDR ABRAMOVICH.

An introduction to the chemistry of complex compounds; textbook Moskva. Gos. nauchno-tekhn. i-d-vo khim. lit-ry, 1945. 366 p. (51-22310)

6

Complex compounds of platinum with phosphines and derivatives of phosphorous acid. A. A. Grinberg, Z. A. Razumova, and A. D. Troitskaya. *Bull. acad. sci. U.R.S.S., Classe sci. Chim.*, 3, 253-64 (1948).—Several new complex Pt compds. contg. PEt_3, $P(OEt)_3$, and $P(OH)(OEt)_2$ have been prepd. The following are described: $[Pt(PEt_3)_2(NH_3)_2][PtCl_4]$, $[Pt(PEt_3)_2en][PtCl_4]$, cis- and trans-$[Pt(PEt_3)_2(CS(NH_2)_2)_2]Br_2$, cis- and trans-$[Pt(PEt_3)_2Br_2]$, $[Pt(P(OEt)_3)_4][PtCl_4]$, $[Pt(P(OEt)_3)_2(NH_3)_2][PtCl_4]$, $[Pt(P(OEt)_3)_2(CS(NH_2)_2)_2]Cl_2$, $[Pt(OH.P(OEt)_2)_2(PO(OEt)_2)_2]$, $[Pt(P(OEt)_3)_2en][PtCl_4]$, their structure being detd. from the dipole moments and their syntheses from Pt compds. of known structure, and from their chem. behavior to reagents, e.g., ethylenediamine. PEt_3, $P(OEt)_3$, and $P(OEt)_2OH$ have a strong trans influence and, as with Jensen's phosphinic derivs., deviations from Peyrone and Jorgensens' rules are found. The rules for the behavior of the Pt amine salts are mostly reversed for compds. with Pt-P links; so also is the rule that cis compds. are more colored and melt at lower temp. than the corresponding trans isomers. B. A.

METALLURGICAL LITERATURE CLASSIFICATION

GRINBERG,

455. Potentiometric method for determination of total platinum and iridium. A. A. Grinberg, E. A. Maximjuk, and I. C. Putan (*Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **51**, 687—688).—Potentiometric titration with $KMnO_4$ and a H electrode gives vals. within ±1% for the Pt + Ir content of solutions containing 0·19—0·28 mg.-atom of Pt and 0·06—0·35 mg.-atom of Ir, after reduction of K_2PtCl_6 and $(NH_4)_2IrCl_6$ with Cu_2Cl_2 in hot HCl solution and keeping for 15—18 hr. in contact with air. L. J. J.

No.9

CA

Cupremetric titration of platinum and iridium. A. A. Grinberg and K. A. Makarovich. *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.* (*Ann. secteur platine, Inst. chim. gén.*) No. 20, 160-67(1947). —The method is an adaptation of the Muller and Tanaka method (C.A. 20, 3311). Quadrivalent Pt and quadrivalent Ir were titrated separately and together with CuCl potentiometrically. Quadrivalent Pt was detd. in a soln. acidified to 0.05 N HCl and kept at 70°. The av. Pt content of a series of solns. contg. 40.15% Pt (detd. gravimetrically) was found potentiometrically to be 40.08%. Equally good results were obtained in the presence of Pt^{++}, Pd^{++}, and Rh^{+++}. Quadrivalent Ir was detd. in solns. acidified to 0.1 N HCl and kept at 80°. Ir^{4+} was detd. by this method also in the presence of Ir^{3+}, Pd^{2+}, and Rh^{3+}. In detg. the sum of Pt^{4+} and Ir^{4+}, the nature of the titration curve depended on the temp., acidity, and the relative quantities of Pt and Ir. For a mol. ratio of $K_2PtCl_6:(NH_4)_2IrCl_6 = 0.5$-2, the temp. should be 70 ± 5° and the initial acidity up to 0.3 N HCl. By controlling the temp. and acidity of the soln. the titration curve can have one break for Pt and Ir or 2 breaks, the 1st occurring after the reduction of Ir and the 2nd after the reduction of Pt. M. Hosch

GRINBERG, A. A.

FA 27/49T38

USSR/Chemistry - Platinum Compounds Sep/Oct 48
Chemistry - Ammonia

"Acid Properties of Ammoniates and Aminates of Tetravalent Platinum," A. A. Grinberg, Kh. I. Gil'dengershel', Leningrad Tech Inst imeni Lensovet, 14 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5

Introduces new data which details acid characteristics of ammonia and ethylenediamine molecules in complex compositions of tetravalent platinum. Submitted 15 Oct 47.

27/49T38

PROCESSES AND PROPERTIES INDEX

Isomeric thiourea derivatives of bivalent platinum. A. A. Grinberg and Z. A. Razumova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) **18**, 282-5(1948).—Contrary to the prediction of Kurnakov's rule, action of $CS(NH_2)_2$ (th) on cis-$[PtI_2(PEt_3)_2]$ resulted not in substitution of all 4 coordinants, to give the expected $[Pt(th)_4]I_2$, but in the cis-$[Pt(th)_2(PEt_3)_2]I_2$, even with th in a 2-3-fold excess over the amt. necessary for 4 th. 0.2 g. th in 6 ml. H_2O per 0.2 g. cis-iodide, gave a white ppt. of $[Pt(PEt_3)_2(th)_2]I_2$, soly. 0.40-0.42 g. per 100 g. soln. With trans-$[PtI_2(PEt_3)_2]$, is obtained a white ppt. of the same analytical compn. but of distinctly different soly., 0.23-0.24 g. per 100 g. soln., at 20°. This difference proves that the 2 products are actually cis-trans isomers. The difference is even greater in the case of the bromides. With 0.8 g. th in 24 ml. H_2O, and 0.7 g. trans-$[PtBr_2(PEt_3)_2]$, soln. is slow and requires heating and stirring; the white product, trans-$[Pt(PEt_3)_2(th)_2]Br_2$, has a soly. of 0.097 g. per 100 g. soln. at 26°. With cis-$[PtBr_2(PEt_3)_2]$ soln. takes place readily in the cold, and the cis product, of the same analytical compn. as before, has a soly. of 2.45 g. per 100 g. soln. N. Thon

METALLURGICAL LITERATURE CLASSIFICATION

GRINBERG, A. A.

FA 19/49T25

USSR/Chemistry - Solubility
Chemistry - Solutions
Aug 48

"The Reaction of an Added Component on the Solubility of Material in a Mixed Solution," A. A. Grinberg, Ye. P. Zemlyakova, Chair Inorg Chem, Leningrad Chem Phar Inst and Chair of Gen Chem, Leningrad Tech Inst imeni Lensovet, 10½ pp

"Zhur Obshch Khimii" Vol XVIII (LXXX), No 8

Confirmed phenomenon (previously described by Wright) of increased solubility of type KX inorganic salts in 50% aqueous alcohol due to

[redacted] 19/49T25

USSR/Chemistry - Solubility (Contd) Aug 48

addition to benzene. Shows this phenomenon takes place not only for binary electrolytes but for salts of other types and also for organic substances readily soluble in water. Shows that effect of additional component can be generalized: It is not confined to particular case of alcohol-water systems and does not necessarily result in increased solubility. Effect should be observed on any combinations of two solvents, and its sign (increase or decrease of solubility) depends on interrelation of properties of solute, solvent and additives. Submitted 18 Apr 47.

[redacted] 19/49T25

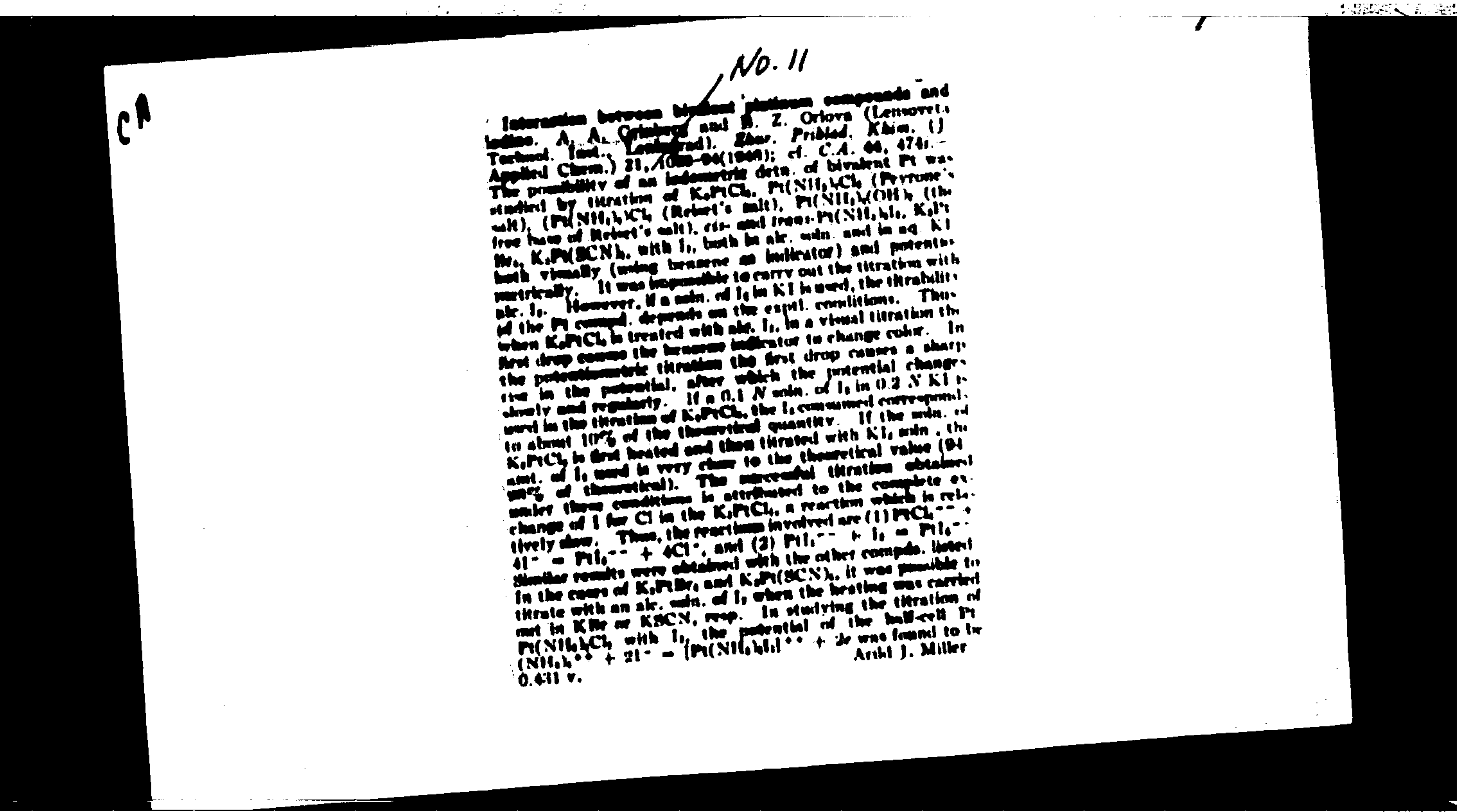
PROCESSES AND PROPERTIES INDEX

2

The refraction of inorganic sulfur compounds. A. A. Grinberg (Lensovet Technol. Inst., Leningrad). *Zhur. Priklad. Khim.* (J. Applied Chem.) 21, 686-9(1948)(in Russian).—The ionic refractions *R* calcd. by Spacu and Popper (*C.A.* 32, 71; 33, 481, 9074) for CN^-, CNS^-, $CNSe^-$, SO_4^{--}, SO_3^{--}, HS^-, $S_2O_3^{--}$, and $S_2O_6^{--}$ from measurements on the K and Na salts, are erroneous owing to adoption of a wrong value for the ion Cl^- and consequently also for K^+ (from KCl). With the correct value 9.07 for Cl^- (according to Fajans), instead of Eisenlohr's 5.967 (valid only for org. Cl), *R* for K^+ becomes = 2.26 instead of [illegible], and the measurements of S. and P. lead to the following correct values of *R*: CN^- 8.633, SCN^- 17.[illegible], SO_4^{--} 14.[illegible], SO_3^{--} 13.2[illegible], HS^- 13.[illegible], $S_2O_3^{--}$ 17.114, $S_2O_6^{--}$ 41.1[illegible]. From SCN^-, one finds for S, with Eisenlohr's increments for C (2.418) and for nitrile N (3.070), R_S = 12.101, fairly close to R_0 of free S^{--}. Subtraction of the *R* value of SO_3^{--} from that of $S_2O_3^{--}$ gives for the outer S, R_0 = 3.725; calcn. by way of SO_4^{--}, R_0 = [illegible], i.e. in both cases far below R_0 for free S^{--} (not less than 18). This militates against the formulation $O_3S^+\langle^{O-}_{S^{--}}$, and is consistent only with a central S^{++} and an outer neutral S, i.e. the thiosulfate ion should be represented as a compd. of SO_3^{--} with S. Tentative estn. of *R* for neutral S, on the basis of $SH^-/OH^- \sim 2.7$ and $H_2S/H_2O \sim 2.6$, gives for S^{--}, R_0 = 18.9, and for neutral S, R_0 = 5.3, i.e. close to the value derived from $S_2O_3^{--}$ which thus would corroborate the above representation of that ion. For the $S_2O_6^{--}$ ion, *R* is much higher than twice the *R* value for SO_3^{--}; the loss of 2 electrons in the formation $2SO_3^{--} \rightarrow S_2O_6^{--} + 2e$ should reduce *R* rather than increase it. The high *R* of $S_2O_6^{--}$ can be due only to presence of the highly refractive S^{--}. If the $S_2O_6^{--}$ ion is formulated (after Mendeleev) SO_3-S_2-SO_3, and the middle S_2 is considered as a combination $S.S^{--}$, *R* can be calcd. by $2\,SO_4^{--} - 2O^{--} + S^{--} + S = (2 \times 14.84) - (2 \times 3.70) + 18 + 5.3 = 45.6$, as against the exptl. 41.19.

N. Thon

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



CA

No. 11

Interaction between bivalent platinum compounds and iodine. A. A. Grinberg and B. Z. Orlova (Lensovet Technol. Inst., Leningrad). *Zhur. Priklad. Khim.* (J. Applied Chem.) 21, 1088-94(1948); cf. *C.A.* 44, 474i.—The possibility of an iodometric detn. of bivalent Pt was studied by titration of K_2PtCl_4, $Pt(NH_3)_2Cl_2$ (Peyrone's salt), $[Pt(NH_3)_4]Cl_2$ (Reiset's salt), $Pt(NH_3)_2(OH)_2$ (the free base of Reiset's salt), *cis*- and *trans*-$Pt(NH_3)_2I_2$, K_2PtBr_4, $K_2Pt(SCN)_4$, with I_2, both in alc. soln. and in aq. KI, both visually (using benzene as indicator) and potentiometrically. It was impossible to carry out the titration with alc. I_2. However, if a soln. of I_2 in KI is used, the titrability of the Pt compd. depends on the exptl. conditions. Thus when K_2PtCl_4 is treated with alc. I_2, in a visual titration the first drop causes the benzene indicator to change color. In the potentiometric titration the first drop causes a sharp rise in the potential, after which the potential changes slowly and regularly. If a 0.1 *N* soln. of I_2 in 0.2 *N* KI is used in the titration of K_2PtCl_4, the I_2 consumed corresponds to about 10% of the theoretical quantity. If the soln. of K_2PtCl_4 is first heated and then titrated with KI_3 soln., the amt. of I_2 used is very close to the theoretical value (94-99% of theoretical). The successful titration obtained under these conditions is attributed to the complete exchange of I for Cl in the K_2PtCl_4, a reaction which is relatively slow. Thus, the reactions involved are (1) $PtCl_4^{--} + 4I^- = PtI_4^{--} + 4Cl^-$, and (2) $PtI_4^{--} + I_2 = PtI_6^{--}$. Similar results were obtained with the other compds. listed. In the cases of K_2PtBr_4 and $K_2Pt(SCN)_4$, it was possible to titrate with an alc. soln. of I_2 when the heating was carried out in KBr or KSCN, resp. In studying the titration of $Pt(NH_3)_4Cl_2$ with I_2, the potential of the half-cell $Pt(NH_3)_4^{++} + 2I^- = [Pt(NH_3)_4I_2]^{++} + 2e$ was found to be 0.431 v. Arthl J. Miller

CA

no. 5,

Stability of complex compounds and exchange reactions. A. A. Grinberg and L. K. Nikol'skaya. *Zhur. Priklad. Khim.* (J. Applied Chem.) **22**, 642-3(1949).—(Summary of a lecture.) (1) The tendency to complex formation is measured by the change of free energy, ΔF, in the process of formation of the hydrated complex from the hydrated simple ions. For the complexes $[HgX_4]$, the values of ΔF, for $X = Cl, Br, I, CN$, are 21.8, 20.5, 41.3, and 58.5 kcal/mole, resp. For $[PtCl_4]$ and $[PtBr_4]$, $\Delta F = 21.8$ and ~ 25 kcal/mole, resp. The sequence $Cl < Br < I < CN$ holds also for complexes of Pd^{II}. (2) The condition for the presence of complexes in soln. is $\Delta F > 3\ RT/2$. Only above this "thermal threshold" can there be an equil. between undissocd. complexes and their dissocn. products. By $\Delta F = -RT \ln K = -1.36 \log K$, the Ostwald const at the threshold is 2.2×10^{-1}. This threshold is the natural limit sepg. systems with an equil. between undissocd. and dissocd. forms (weak electrolytes) and systems without actual undissocd. forms but only interionic forces (strong electrolytes). (3) Geometric isomerism is possible only in the absence of a rapid exchange between the central ion in the complex and the free ions in the soln. (4) The rate of the exchange reaction $[PtX_4]^{--} + X^*$ decreases in the order $X = CN > I > Br > Cl$, i.e. exchange is fastest in the thermodynamically most stable system; this is linked with the phenomenon of trans influence. The observed absence of an exchange $[Fe(CN)_6] + CN^*$ is also linked with the smaller trans-effect in Fe complexes. N. Thon

CA

6

New method of preparation of hexammine complexes of quadrivalent platinum. A. A. Grinberg and Kh. I. Gil'dengershel. *Zhur. Priklad. Khim.* (J. Applied Chem.) 22, 1053-8(1949).—Complete exchange of all 6 coördinate groups in $[\mathrm{Pt}e_4\mathrm{Cl}_2]\mathrm{Cl}_2$ (I) (where $e = \mathrm{EtNH_2}$) for $\mathrm{NH_3}$ groups was obtained by heat soln. of an aq. soln. of I with solid $(\mathrm{NH_4})_2\mathrm{SO_4}$, the light-yellow ppt., treated with $\mathrm{NH_4OH}$ and heated 15-20 min., turns into a fine white ppt. of compn. very near to $[\mathrm{Pt(NH_3)_6}](\mathrm{SO_4})_2$ (II) but with an admixt. of some Cl. II is dissolved by careful dropwise addn. of 30% NaOH, and the soln. is pptd. with the theoretical amt. of $\mathrm{BaCl_2}$ in a small vol. of $\mathrm{H_2O}$. From the filtrate, excess concd. HCl ppts. white crystals of $[\mathrm{Pt(NH_3)_6}]\mathrm{Cl_4.H_2O}$ (III). The sequence of reactions is I + $2(\mathrm{NH_4})_2\mathrm{SO_4} + 2\mathrm{NH_3} \rightarrow$ II + $4\mathrm{EtNH_3Cl}$; 2 II + $2\mathrm{NaOH} \rightarrow [\mathrm{Pt(NH_3)_5NH_2}]_2(\mathrm{SO_4})_3 + \mathrm{Na_2SO_4} + 2\mathrm{H_2O}$; $[\mathrm{Pt(NH_3)_5NH_2}]_2(\mathrm{SO_4})_3 + \mathrm{Na_2SO_4} + 4\mathrm{BaCl_2} \rightarrow 4\mathrm{BaSO_4} + 2[\mathrm{Pt(NH_3)_5NH_2}]\mathrm{Cl_3} + 2\mathrm{NaCl}$; $[\mathrm{Pt(NH_3)_5NH_2}]\mathrm{Cl_3} + \mathrm{HCl} \rightarrow$ III. The initial I was obtained by the action of $\mathrm{Cl_2}$ on a soln. of $[\mathrm{Pt}e_4]\mathrm{Cl_2}$ acidified with HCl, or by the action of free $\mathrm{EtNH_2}$ on an alc. soln. of $\mathrm{H_2PtCl_6}$, giving $[\mathrm{Pt}e_4]\mathrm{Cl_2}$, and then, with $\mathrm{Cl_2}$ in the presence of HCl, I. An alternative synthesis consists in dissolving $\mathrm{K_2PtCl_4}$ in an aq. $\mathrm{EtNH_2}$ soln., this results in the formation of $[\mathrm{Pt}e_4]\mathrm{Cl_2}$, which can be identified by the pink $[\mathrm{Pt}e_4][\mathrm{PtCl_4}]$. From this soln., acidified with concd. $\mathrm{H_2SO_4}$, a stream of $\mathrm{Cl_2}$ ppts. yellow $[\mathrm{Pt}e_4\mathrm{Cl_2}](\mathrm{HSO_4})_2$, which can be converted into II by the action of $(\mathrm{NH_4})_2\mathrm{SO_4} + \mathrm{NH_3}$, and then into III as above. This method gives somewhat better yields with respect to the initial $\mathrm{K_2PtCl_4}$, about 18% of the theory.

N. Thon

GRINBERG, A. A.

"Oxidation-Reduction Potentials of Complex Platinum Ammoniates and Aminates," Zhur. Prik. Khim., 22, No. 5, 1949.

CA

6

Interaction between potassium chloroplatinite and the isomeric aminobenzoic acids. A. A. Grinberg and S. S. Kats (Acad. Sci. U.S.S.R.). Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 248-52(1950). The product of the reaction between K_2PtCl_4 (1 g. in 10 ml. H_2O) and o-$NH_2C_6H_4CO_2H$ (1.32 g. in 100 ml. H_2O), corresponding to a mol. ratio 1:4, carried out on a water bath in a stream of CO_2, is a mixt. of $[PtCl_2(NH_2C_6H_4CO_2H)_2]$ and the cyclic $[Pt(NH_2C_6H_4CO_2)_2]$. These 2 compds. were sepd. by alkali, which titrates only the 1st. Reactions with m- and with p-$NH_2C_6H_4CO_2H$ give only $[PtCl_2(NH_2C_6H_4CO_2H)_2]$. By reaction with $CS(NH_2)_2$, the complex with the para acid was shown to have the cis configuration. On heating to 200-10°, the ortho complex evolves CO_2, in contrast to the meta and para complexes. Whereas this behavior of the ortho and meta complexes coincides with that of the free o- and m-$NH_2C_6H_4CO_2H$, the para complex differs from the free p-$NH_2C_6H_4CO_2H$, which evolves CO_2 at as low as 215°. N. Thon

GRINBERG, A. A.

"Introduction to the Chemistry of Complex Compounds," by A. A. Grinberg, published by State Scientific-Technical Publishers of Chemical Literature, Leningrad-Moscow, 1951

B-76030

B/R

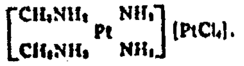
7849*. Problems of the Stability of Complex Compounds and of Exchange Reactions. (In Russian.) A. A. Grinberg and L. E. Nikol'skaia. *Zhurnal Prikladnoi Khimii*, v. 24, Sept. 1951, p. 893-901.

Theoretical and experimental study. 24 ref.

GRINBERG, A.A.

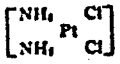
5

A new synthesis of isomer compounds having the composition $Pt(CH_3NH_2)_2Cl_2$. A. A. Grinberg and Kh. I. Gil'dengershel (Lensovet Te[illegible]d). *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.* 26, 115-23(1951).—Treatment of K_2PtCl_4 with $AcONH_3Me$ *cis*-$[Pt(NH_2Me)_2Cl_2]$. The structure was proved by Kurnakov's thiourea action, and by formation of



$$\begin{bmatrix} CH_3NH_2 & & NH_3 \\ & Pt & \\ CH_3NH_2 & & NH_3 \end{bmatrix}[PtCl_4].$$

By dissolving



$$\begin{bmatrix} NH_3 & & Cl \\ & Pt & \\ NH_3 & & Cl \end{bmatrix}$$

in $MeNH_2$ and then treating with HCl, *trans*-$[Pt(CH_3NH_2)_2Cl_2]$ was produced. The structure of this salt was proved by the formation of a colorless soln. in thiourea and by the formation of

$$\begin{bmatrix} CH_3NH_2 & & NH_3 \\ & Pt & \\ NH_3 & & CH_3NH_2 \end{bmatrix}[PtCl_4].$$

J. R. Behrman

CA

2

The periodic law of D. I. Mendeleev and the stability of complex compounds. A. A. Grinberg and K. B. Yatsimirskii. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1952, 211-17.—The tendency to complex formation is characterized quantitatively by the energies of formation of the gaseous complex ions, and by the instability const. K of the complex; the latter magnitude actually expresses the difference of the stability of the complex ion and of the corresponding aquo ion. From a thermochem. cycle involving the formation of a complex ion $[MA_n]^{++}$ from $M^{++} + nA$, the heat is $\Delta H = (W_1 - W_2) + (L_1 - L_2) + n(\lambda_1 - \lambda_2)$, where W_1 and W_2 are the energies of addn. of H_2O and of A, resp., to the gaseous M^{++}, L_1 and L_2 are the heats of hydration of $[MA_n]^{++}$ and $[M(H_2O)_n]^{++}$, resp., and λ_1 and λ_2 the heat of evapn. of H_2O and of hydration of A, resp. The latter term being const. for reactions of one type, and the middle term approx. const., $\Delta H \approx (W_1 - W_2) + C$ (const.), and $RT \ln K \approx (W_1 - W_2) + C'$ (const.). This gives the relation between the 2 characteristics of the tendency to complex formation. This relation is verified by data for $[Mg(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, $[Ni(NH_3)_6]^{++}$, $[Co\ en_3]^{++}$, $[Ni\ en_3]^{++}$, and $[Zn\ en]^{++}$. In application to ions with an inert-gas structure of the outer electron shell, but different charge and radius, this leads to the conclusion that the stability of complexes increases from left to right in the period and decreases from top to bottom in the groups of the periodic system. For ions with 18-electron shells, the complex stability ought to decrease with increasing at. no. in the groups if the bond is predominantly ionic; with predominantly covalent bonding, elements of the 6th period should form particularly stable complexes. As a result of the 2 antagonistic factors, the heat of formation of gaseous complex ions within a subgroup may pass through a min.; examples are, for complex ions $[M(NH_3)_2]^{+}$, M = Cu 131, Ag 104, Au 160 kcal./mole, and for ions $[M(NH_3)_4]^{++}$, M = Zn 300, Cd 311, Hg 376 kcal./mole. The same is found for the free-energy change $\Delta F = RT \ln K$ of formation of complex ions in aq. soln. The more pronounced the covalent character of the bond, the more marked is the increase of the stability (ΔF) of the complex ions from top to bottom; this is illustrated by comparison of ΔF for complex chlorides, bromides, and iodides, the latter showing the most marked change of ΔF from Cu to Au or from Zn to Hg, and the chlorides the least marked. In series of complex ions formed by central ions with the same charge, but with different outer-electron shell structures, the complex sta-

GRINBERG, A.A.; DOBROBORSKAYA, A.I.; SHAGISULTANOVA, G.A.

Isomery of dinitrodibromoplatoates. Izv.AN SSSR. Otd.khim.nauk no.6: 968-971 N-D '53. (MLRA 6:12)

1. Radiyevyy institut im. V.G.Khlopina Akademii nauk SSSR i Tekhnologicheskiy institut im. Leningradskogo soveta.

(Platinum compounds)

GRINBERG, A.A.

Mechanism of formation of potassium chloroplatinite from thechloroplatinite.
(MLRA 6:3)
Zhur. Priklad. Khim. 26, 224-5 '53.
(CA 47 no.21:11061 '53)

1. Lensovet Technol. Inst., Leningrad.

GRINBERG, A.A.; SIMONOVA, L.K.

Derivation of palladium acetylacetonate. Zhur.prikl.khim. 26 no.8:880-882 Ag '53. (MLRA 6:8)

1. Leningradskiy tekhnologicheskiy institut im. Lensoveta. 2. Leningradskiy tekhnologicheskiy institut im. Molotova. (Palladium organic compounds)

GRINBERG, A. A.

14

New method for determining nitrogen in stable ammoniates of platinum and cobalt. A. A. Grinberg and L. K. Simonova (Lensovet Technol. Inst., Leningrad). *Zhur. Priklad. Khim.* 26, 1080-1(1953). —Ammonia (and perhaps other forms of combined N) in Pt and Co complexes can easily be detd. by means of an illustrated app. in which the ammoniate is mixed with a large excess of dil. $FeSO_4$ soln. and NaOH added. The soln. is then distd. 45 min. into a known vol. of standard H_2SO_4 soln. The complex is reduced to metal and the liberated NH_3 is absorbed by the acid, the excess of which is finally titrated. J. W. Lowsberg, Jr.

③

GRINBERG, A.A.

USSR.

✓The potentiometric titration of bivalent iron, bivalent platinum, and trivalent iridium in the presence of one another. A. A. Grinberg, N. B. Karpenko, and E. A. Maksimyuk. [redacted] Khim. 26, 1105-13(1953); J. Appl. Chem. U.S.S.R. 26, 1047-55(1953)(Engl. translation). —A soln. contg. Fe^{++}, Ir^{3+}, and Pt^{++} was titrated potentiometrically with $KMnO_4$. Two discontinuities were observed on the potentiometric curve corresponding to the transition $Fe^{++} \rightarrow Fe^{3+}$ and $Ir^{3+} \rightarrow Ir^{4+}$. Part of the Pt reaction is accounted for in the Fe transition and the rest in the Ir transition. The amt. in each case is detd. by the concn. of the Pt in the soln. being titrated. J. R. L.

[illegible]RG, A. A.

Structure of dichlorobistriphenylphosphineplatinum. A.
A. Grinberg and Z. A. Razumova. *Zhur. Priklad. Khim.*
27, 105-6(1954).—The structure of $[Pt(Ph_3P)_2Cl_2]$ (I) (cf.
Jensen, *C.A.* 31, 3753^{3}; G., R. and Troitskaya, *C.A.* 43,
4172*g*) was examd. I was prepd. by the action of aq.
K_2PtCl_4 on alc. Ph_3P with heating and a 1:2 molar ratio of
reactants; 1.5 g. Ph_3P in 12 ml. hot EtOH was treated with
a hot soln. of 1.2 g. K_2PtCl_4 in 12 ml. H_2O and the mixt.
was shaken further 20 hrs. to insure completion of reaction.
The ppt. was washed with hot H_2O, hot EtOH, and Et_2O,
giving 75% yield of the pure I, insol. in org. solvents, de-
comp. 308°. I (0.3 g.) mixed with 20 ml. H_2O was treated
with large excess of $(CH_2NH_2)_2$ and heated and shaken for
a long time leading to gradual soln. The soln. was filtered,
cooled, and added to a filtered concd. aq. soln. of 0.3 g.
K_2PtCl_4, yielding a pink ppt., which was filtered off; this
amounted to 0.4 g. (95%) $[Pt(Ph_3P)_2en][PtCl_4]$ (II).
Thus the reaction utilizes equimolar amounts of the re-
actants and the initial I must have the cis configuration.
The reaction with K_2PtCl_4 thus can be formulated as:
$[Pt(Ph_3P)_2en]Cl_2 + K_2PtCl_4 \rightarrow 2KCl + II$. It was previ-
ously shown that Et_3P shows a strong trans effect, the same
being true of phosphites. In the present series, Ph_3P also
shows a strong trans effect. Thus II treated with concd.
HCl and heated, dissolves slowly and the pink ppt. is then
replaced by a white ppt. while the soln. acquires the color
of $PtCl_4^{--}$. The dried ppt., m. 305°, is I. Such ready
cleavage of the diamine cycle can be explained only by a
strong trans effect of the Ph_3P group. G. M. Kosolapoff

NA

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V.(Moscow); YATSIMIRSKIY, K.B. (Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIALKOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow); GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A. (Leningrad); VOL'KENSHTEYN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow); PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M. (Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow); BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTEYN, A.M.(Moscow) CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Izv.Sekt.plat.i blag.met. no.28: 56-126 '54. (MLRA 7:9)
(Compounds, Complex) (Platinum)

GRIMBERG, A.A.

5

4020 AEC-tr-2435((Pt. 2) (p. 145-52))
INVESTIGATION OF THE STRUCTURE AND REACTIONS OF COMPLEX COMPOUNDS BY THE METHOD OF LABELED ATOMS. A. A. Grimberg. p. 145-52 of CONFERENCE OF THE ACADEMY OF SCIENCES OF THE USSR ON THE PEACEFUL USES OF ATOMIC ENERGY, JULY 1-5, 1955. SESSION OF THE DIVISION OF CHEMICAL SCIENCE. (Translation). 8p.

This paper was originally abstracted from the Russian and appeared in Nuclear Science Abstracts as NSA 9-7714.

RM

GRINBERG, A.A.

7714

STRUCTURE AND REACTIONS OF COMPLEX COMPOUNDS.
CH A. A. Grinberg. p.238-50 in Meetings of the Division of Chemical Sciences. Session of the Academy of Sciences of the U.S.S.R. on the Peaceful Use of Atomic Energy. July 1-5, 1955. Moscow, Publishing House of the Academy of Sciences of the U.S.S.R., 1955. 378p. (In Russian)

A short review of the works in this field is given. Major attention is paid to the exchange and substitution reactions. The following conclusions were made: The application of tracers makes it possible to verify and establish the stereochemical conceptions of coordination chemistry in a new manner. The same method permits a more profound insight into the mechanism of different reactions of complex compounds; the processes of exchange and substitution in the inner coordination sphere may proceed in different ways. The isotope exchange $[PtBr_4]^{2-}$ under the conditions studied proceeds via aquo-ion species. The possibility of extrapolation of such a mechanism over $[PtX_4]^{2-}$ compounds with other ligands requires experimental proof in each case; the lifetime of the metal-ligand bond may differ widely for various stable complexes; and the exchange rate of coordinated ligands is not necessarily determined by the thermodynamic stability of the complex in the sense of ionic dissociation. (auth)

Grinberg, A.

5000

3

Chem

The mechanism of reactions of complex compounds. A. A. Grinberg, L. E. Nikol'skaya, and G. A. Shagisultanova. *Voprosy Khim. Kinetiki, Kataliza i Reaktsionnoi Sposobnosti, Akad. Nauk S.S.S.R.* 1955, 633-43.—Work on the mechanism of reactions of complex compds. is reviewed, and the results obtained by G. and published in a no. of papers are summarized. The isotope-exchange velocity in complex ions must be favored by factors that help in reaching the complex-ion dissocn. equil. and by factors that reduce the mutual repulsion of particles that enter into exchange.

W. M. Sternberg

BM

GRINBERG, A.A.

4.

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The exchange kinetics in complex platinum bromides. A. A. Grinberg and G. A. Shagisultanova. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1955, 981-7; cf. *C.A.* 50, 10494*f*.—Isotopic exchange of Br in $K_2[PtBr_4]$ and $K_2[PtBr_6]$ was studied in aq. solns. Dependence of the exchange on concn. of the complex, concn. of Br^-, age of solns., temp., and illumination were detd. Activation energy for the exchange was calcd. to be 4–10 kcal. for $[PtBr_4]^{--}$ and ~ 17 kcal. for $[PtBr_6]^{--}$. The exchange mechanisms are different for the 2 ions; in the case of $[PtBr_4]^{--}$ it occurs through the intermediary aquo ions, whereas for $[PtBr_6]^{--}$ it depends on oxidation reduction equil. The results obtained show that the rate of exchange is not detd. by the stability consts. of the complex ions. A. L. Popov

RMK

GRINBERG, A.A.

AID P - 1572

Subject : USSR/Chemistry

Card 1/1 Pub. 152 - 2/21

Authors : Grinberg, A. A., Kozlova, L. I., Nikol'skaya, L. Ye., and Shagisultanova, G. A.

Title : Exchange reactions in platinum complexes

Periodical : Zhur. prikl. khim., <u>28</u>, no.1, 7-11, 1955

Abstract : Experimental measurements of the rates of exchange reactions showed that the exchange rate of iodine in $K_2 [PtI_6]$ is higher than that of chlorine in $K_2 [PtCl_6]$. A method for the preparation of $K_2 [Pt(NO_2)_2Br_2]$ is given. One table, 2 references (Russian: 1927-51)

Institution: None

Submitted : Je 26, 1953

Grinberg, A. A.

CH

Reactions of glutamic acid and aspartic acid with potassium chloroplatinate(II). A. A. Grinberg and N. N. Kats (Lensovet Technol. ~~Inst., Leningrad~~). *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.* No. 29, 37-44(1955).—Glutamic acid (0.7 g.) added to 0.5 g. of K_2PtCl_4 in 10 ml. water, and heated for 46 min. on a steam bath, gave silvery white Pt diglutamate (I) crystals. To obtain a pure product, the vol. of the soln. must be kept const. during the crystn. A test with ethylenediamine confirmed that I consists predominantly of trans form. Reaction in concd. HCl with thiourea showed that some of the cis form was present. Platinum diaspartate (II) was prepd. in 20% yield by a similar method. At a concn. of 2.5×10^{-4} moles/l. the elec. cond. of I was 89 ohm^{-1} $cm.^2$ and of II 129.2 ohm^{-1} $cm.^2$ This agrees well with the accepted coordination formulas.

A. P. [illegible]

①

GRINBERG, A.A.

USSR/Chemistry - Synthesis

Card 1/1 Pub. 22 - 25/49

Authors : Grinberg, A. A., Memb. Corresp., Acad. of Sc., USSR, and Gil'dengershel', Kh. I.

Title : The mechanism of the new systhesis of hexammines of tetravalent Pt

Periodical : Dok. AN SSSR 101/3, 491-493, Mar 21, 1955

Abstract : In explaining the mechansim of the new method of synthesizing hexammines of tetravalent Pt the authors point out that the intra-complex bound ethylamine molecules in the $Ptl_4Cl_2\ Cl_2$ compound become sponified into ammonia which remains in bond with the Pt and ethyl alcohol which remains in the solution. Experiments showed that only the intraspherelly bound ethylamine is subject to sponification and not the ethylamine which was separated from the complex as result of substitution reaction. The process of conversion of ethylamine into ethyl alcohol is described. One USSR reference (1949).

Institution : The Lensoviet Technological Institute, Leningrad

Submitted : October 15, 1954

Grinberg, A.A

USSR/ Chemistry - Reaction processes

Card 1/1 Pub. 22 - 21/47

Authors : Grinberg, A. A., Memb. Corresp., Acad. of Sc., USSR; Nikol'skaya, L. Ye.; and Shagisultanova, G. A.

Title : The mechanism of displacement reaction in the internal sphere of complex compounds

Periodical : Dok. AN SSSR 101/6, 1059-1060, Apr. 21, 1955

Abstract : A new effect is described which, as it appears, offers definite proof in favor of a reaction mechanism utilizing the intermediate reaction between the complex ion and the solvent as a basis. The new effect is explained as the rate of isotopic exchange in relation to the increase in complex solution, i. e., the rate of exchange depends upon the time interval which expired from the moment the aqueous solution of the complex was prepared and the realization of the exchange with various addenda including the marked atom. In other words, the exchange occurs through intermediate formation of aquo-ions. Four references: 3 USSR and 1 USA (1939-1954).

Institution : .....

Submitted : December 1, 1954

Grinberg, A. A.

GRINBERG, A. A.

Forms of existence of phosphorous acid and its derivatives. A. A. Grinberg (Lensovet Technol. Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 105, 1256-7(1955). Theoretical discussion of the structure of H_3PO_3. Although (EtO)₃P forms a complex with bivalent Pt and (EtO)₂POH (EtO)₃P forms a complex with (Trudy Leningrad. Tekhnol. react. with K_2PtCl_4 on boiling no reaction could be Inst. 1950, 39, 39, 16-) Thus, although $(EtO)_3P$ has an induced with H_3PO_3. Thus, the free acid does not, and its structure unshared electron pair, the free acid does not, and its structure is $(HO)_2P(O)H$. The use of radioactive tracers is suggested for detn. of tautomerism in $(RO)_2POH$. A complex of type $PtCl_2 \cdot 2PCl_3$ on treatment with H_2O should yield $Cl_2Pt[P(OH)_3]_2$, without rupture of the coordination link. Under these conditions the free acid cannot tautomerize into P^V form, since the 4th coordination location is already occupied by Pt; this is viewed as a possible method for formation of the form $P(OH)_3$ under special conditions.

G. M. Kosolapoff

GRINBERG, A.A.

3000

The effect of the outer-sphere anions on the nature of substitution in the inner sphere of complex compounds. A. A. Grinberg and Kh. I. Gil'dengershel. Doklady Akad. Nauk S.S.S.R. 108, 250-8(1956); cf. C.A. 44, 4741; 49, 12173f.—Attempts were made to substitute PO_4^{---} for SO_4^{--} in the hexammine $[Pt(NH_3)_6]Cl_4 \cdot H_2O$ prepn. described in the preceding communication, because of the difficulty in eliminating SO_4^{--} as $BaSO_4$. However, the substitution of $NH_3 + (NH_4)_2HPO_4$ for $NH_3 + (NH_4)_2SO_4$ in the earlier synthesis from $[Pt(NH_3)_4Cl_2]Cl_2$ produced $[Pt(NH_3)_5Cl]Cl_3$ instead of the hexammine, and no weighable amt. of any solid substance was recovered when starting with $[Pt(CH_3NH_2)_4Cl_2]Cl_2$. On addn. of NH_3 or NaOH to the soln. obtained with the first ammine, $[Pt(NH_3)_4NH_2Cl]Cl_2$ was obtained. The results emphasize the effects of the outer ion on substitution reactions in the cation inner sphere, and show that different substitution products can be obtained under the influence of different outer-sphere anions.

W. M. Sternberg

GRINBERG, A.A.; BELOUSOV, Ye.A.

Exchange reactions in complex iridium compounds. Dokl.
AN SSSR 111 no.3:599-600 N '56. (MLRA 10:2)

1. Chlen-korrespondent Akademii nauk SSSR. (for Grinberg).
(Iridium compounds) (Compounds, Complex)

GRINBERG, A.A.

5

Physical-chemical properties of oxalates of quadrivalent uranium and thorium. A. A. Grinberg and G. I. Petrzhak.

[illegible]

MT

GRINBERG, A.A.; PTITSYN, B.V.; TEKSTER, Ye.N.

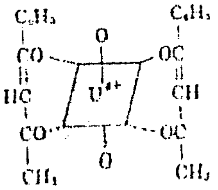
Physical and chemical properties of the aqueous solutions of complex uranyl oxalates. Trudy Radiev.inst.AN SSSR 7:74-86 '56. (MLRA 10:5)
(Uranyl oxalates)

GRINBERG, A.A.

Distr: 4E4j/4E3d

7 7 5 2

Uranyl benzoyl- and acetylacetonates. A. A. Grinberg and A. D. Troitskaya. *Trudy Radievogo Inst. im. V. G. Khlopina* 7, 6-13(1956).—On the basis of the structure proposed for UO_2^{++} and measurements of the dipole moment of the benzoylacetonate complex in benzene (3.12 D.) and CCl_4 (3.00 D.) the following structure is proposed for uranyl benzoylacetonate. The dipole moment found for uranyl acetylacetonate in benzene (6.12 D.) does not agree with a *trans* form of the uranyl group, however. G. Melnyk



GRINBERG, A.A.

Preparation of uranium hexacarbonyl. A. A. Grinberg, B. V. Ptitsyn, F. M. Filinov, and V. N. Lavrent'ev. *Trudy Radievogo Inst. im. V. G. Khlopina, Khim. i Geokhim.* 7, 14-16(1956).—The hexacarbonyls of W, Mo, and Cr can be prepd. by the Hieber and Romberg method (C.A. 29, 2467*), but synthesis of uranium hexacarbonyl in the same manner is impossible. Such compd. probably does not exist. In this case some conclusions can be drawn about the structure of the 7th period of the periodic table. Elements of at. nos. 89-103 should occupy the same relative positions as the lanthanides, and elements of at. nos. 104-118 should occupy the same relative positions as elements 72-80.

G. Melnyk

MT

GRINBERG, A. A.

7 27

Oxalate compounds of quadrivalent uranium. A. A. Grinberg and G. I. Petrzhak. *Trudy Radievogo Inst. im. V. G. Khlopina, Khim. i Geokhim.* 7, 17-40(1956).—High resistance of quadrivalent uranium oxalate to air oxidation was the reason of many investigations. The hydrated K salt $K_4[U(C_2O_4)_4].5H_2O$ was prepd. The Ba salt was prepd. by $K_4[U(C_2O_4)_4] + 2BaCl_2 = Ba_2[U(C_2O_4)_4] + 4KCl$ to give the heptahydrate that after some time lost a mol. of water to form the hexahydrate. The octahydrate of the Pb salt and the heptahydrate of the Cd salt were obtained in an analogous manner. Ca^{++} reacts with $K_4[U(C_2O_4)_4]$ to yield ppts. of $U(C_2O_4)_2$ and CaC_2O_4. Magnetic susceptibility studies of $U(C_2O_4)_2$ and K, Ba, and Cd salts of $H_4[U(C_2O_4)_4]$ indicate 2 unpaired electrons. The absorption spectrum of $K_4[U(C_2O_4)_4].5H_2O$ has max. 490.0, [illegible], and 695.5 mμ, and the complex salt shows predominate character of ion bonding. G. Mehl

GRINBERG, A.A.

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√ **9020*** Problem of the Interinfluence of Groups in the Inner Sphere of Complex Compounds. K voprosu o vzaimnom vliianii grupp vo vnutrennei sfere kompleksnykh soedinenii. (Russian.) A. A. Grinberg and A. I. Dobroborskaia. *Zhurnal Neorganicheskoi Khimii*, v. 1, no. 1, 1956, p. 42-47.

Laboratory proof of one theory of *trans*-influence; consideration of *cis*-influence; problems of isometry. Variants of substitution processes in isometric dinitrodiammines. Table. 3 ref.

Chem

PM

GRINBERG, A. A.

"Investigation of the Structure and Transformations of Complex Compounds by the Tracer Atom Method," a report presented at the USSR Conference on Application of Tracer Atom Methods in Chemistry of Complex Compounds, Kiev, 5-8 October 1955, Zhur. Neorgan. Khim., 1, No.2, 1956

Above conference was described in an article by Z. A. SHEK.

GRINBERG, A. A.

3

Chem

The exchange of acidic ligands in K_2PdX_4-type compounds. A. A. Grinberg, L. E. Nikol'skaya, and N. V. Kiseleva. *Zhur. Neorg. Khim.* 1, 229-4(1956).—The $Cl^-_{(aq.)}$-$PdCl_4^{--}{}_{(aq.)}$ and $Br^-_{(aq.)}$-$PdBr_4^{--}{}_{(aq.)}$ exchanges were studied by radioactive tracer technique with Cl^{36} and Br^{82} isotopes, resp. In $5.5 \times 10^{-3}M$ solns. exchange was complete in 5 min. in case of the Br salt, and was somewhat slower for the Cl salt. This rapid rate of exchange (as compared with that of Pt complexes) is due to the rapid hydrolysis of the Pd salts, rather than to differences in dissocn. consts. A contributing factor may also lie in the tendency of Pd^{++} to bond with ligands in addn. to the ones required by its coördination no. A. I. Popov

GRinberg, A.A.

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21

The effect of the outer-sphere anions on the nature of substitution in the inner sphere of complex compounds. A. A. Grinberg and Kh. I. Gil'dengershel. *Proc. Acad. Sci. U.S.S.R., Sect. Chem.* 108, 233-6(1956)(English translation).—See *C.A.* 51, 928f. B. M. R.

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GRINBERG, A.A.

4

Study of the strength of bases of the type $[Pt(NH_3)_4](OH)_2$. I. The stability of $[Pt(thio)_4]Cl_2$ in ~~neutral and alkaline~~ solutions and the strength of the base $[Pt(thio)_4](OH)_2$. A. A. Grinberg and A. I. Stetsenko. *Zhur. Neorg.* ~~*Khim.* 1, 2849-60~~ (1956).—Because of hydrolysis $[Pt(thio)_4]Cl_2$ (I) (thio = thiourea) has an acid reaction in soln. and the pH of this soln. can be used to det. the strength of the base $[Pt(thio)_4](OH)_2$ (II). Upon standing an aq. soln. of I becomes more acid owing to the displacement of the thiourea group in the complex by OH^-. II can be prepd. by rapidly adding an equiv. amt. of base to a 0.001*M* soln. of I in a satd. soln. of thiourea. The base can be titrated with 0.1*N* HCl. The titration curves give the following values for the dissocn. consts.: $K_1 \approx 10^{-4} - 10^{-6}$; $K_2 \approx 10^{-9} - 10^{-10}$.

J. Rovtar Leach

MT

Grinberg, A. A.

G-1

Category: USSR/Analytical Chemistry - General Questions.

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 30924

Author : Grinberg A.A., Dobroborskaya A. I.
Inst : Not given
Title : Volumetric Determination of Iron, Platinum and Iridium in the Presence of One Another

Orig Pub: Zh. neorgan. khimii, 1956, 1, No 10, 2360-2367

Abstract: For the analysis of the system Fe^{2+}, $[PtCl_4]^{2-}$ and $[IrCl_6]^{3-}$, $Ce(SO_4)_2$ was used as the oxidizing agent. The sample of $K_2[PtCl_4]$ (0.05 to 0.015 g) was dissolved in 20-25 ml water, and to this solution were added 10 ml of approximately 0.1 N solution of Mohr's salt, 20 ml of 25% H_2SO_4 and 10 ml H_3PO_4 (specific gravity 1.5). The resulting solution was titrated, at 18-20°, with a solution of $Ce(SO_4)_2$, in the presence of 4-5 drops of a solution of diphenylamine, until the color of the solution changed to bluish-violet. It was found that the presence of $K_2[PtCl_4]$ and replacement of H_2SO_4 by HCl do not

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Category: USSR/Analytical Chemistry - General Questions. G-1

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 30924

affect the results of titration of Fe^{2+} with a solution of $Ce(SO_4)_2$. On potentiometric titration the end point of titration of Fe^{2+} is sharp; oxidation of $[PtCl_4]^{2-}$ begins after completion of the oxidation of Fe^{2+}. Presence of H_3PO_4 or of KH_2PO_4 in the solution does not interfere. For the determination of $[IrCl_6]^{3-}$ the titration is carried out in sulfuric acid solution (about 15% H_2SO_4); $[IrCl_6]^{2-}$ does not interfere. To determine the sum Pt + Ir in the presence of Fe the samples of $K_2[PtCl_6]$ and $(NH_4)_2[IrCl_6]$ were dissolved in about 20 ml water with addition of 20 ml H_2SO_4 (2 N); solution of $NH_4Fe(SO_4)_2.12H_2O$ was combined with a solution of CuCl, the mixture was added to the heated solution under study, aliquot portions were taken after 20 hours, in one portion the Fe^{2+} content was determined by titration with a solution of $Ce(SO_4)_2$ in the presence of H_2SO_4, H_3PO_4 and diphenylamine, while in the other portion the sum of Pt + Ir was determined by potentiometric titration with a solution of $KMnO_4$. It was found that on oxidation

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Category: USSR/Analytical Chemistry - General Questions. G-1

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 30924

of $K_2[PtCl_6]$ with a solution of $Ce(SO_4)_2$ as well as with a solution of $KMnO_4$ there is formed $K_2[PtCl_4(OH)_2]$ and that in solutions of the latter there takes place the equilibrium: $2K_2[PtCl_4(OH)_2] \rightleftarrows K_2[PtCl_6] + 2K_2[PtCl_2(OH)_4]$.

Card : 3/3

[illegible], A., [illegible], [illegible], [illegible], [illegible],

"Research on the Oxalates of Uranium (IV) and Thorium," a paper submitted at the 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 July 1957.

[illegible] and KOMKUCHKIN, M., [illegible]

"On the Kinetics and the Exchange and Substitution Mechanism of Coordinated Groups in Complex Compounds," a paper submitted at the 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 July 57.

Grinberg, A. A

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2

Extraction of streptomycin and vitamin B_{12} from streptomycin mother liquor. B. P. Bruns, M. V. Vittikh, A. A. Grinberg, S. M. Mamiofe, V. V. Matveev, S. I. Pavlov, K. B. Pashkov, A. D. Prokof'ev, B. N. [illegible], E. B. Savitskaya, K. M. Saldadze, M. A. [illegible], A. A. Kunin, and D. I. Savelov. U.S.S.R. 106,431, July 25, 1957. The extn. is accomplished with the aid of cation-exchange resins (I), e.g. copolymers of Me methacrylate and divinylbenzene sapond. with alk. solns. The mother liquor is first passed through a H form of I contg. 1.6% divinylbenzene to ext. vitamin B_{12}. The acid soln. is neutralized and passed through a Na form of I contg. 2.6% divinylbenzene to ext. the streptomycin. M. [illegible]

GRINBERG, A. A.

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Kinetics of the reaction of ammonia[27] with potassium chloroplatinite[2] and with Koss salt. A. A. Grinberg and Yu. N. Kukushkin. *Zhur. Neorg. Khim.* 2, 100-11(1957).—The rate of the reaction of NH_3 with K_2PtCl_4 and $K[PtNH_3Cl_3]$ was studied with freshly prepd. samples as well as with aged samples (before mixing with NH_3 the solns. were maintained at 25° for 135-50 min.). In all cases the reaction changes its character with time. For freshly prepd. K_2PtCl_4 the process is characterized by a slow increase in the rate coeff. during the first 30 min. Then the process undergoes a significant rate of increase. The rate of this second stage is characterized by the coeff. 2.0×10^{-3}. An analogous phenomenon was observed for the freshly prepd. Koss salt.

J. Rovtar Leach

GRINBERG, A.A.; KUKUSHKIN, Yu.N.

Kinetics of the hydrolysis of certain complex compounds of bivalent platinum. Zhur. neorg. khim. 2 10:2360-2367 O '57. (MIRA 11:3)
(Platinum compounds) (Hydrolysis)

GRINBERG, A.A.; BORZAKOVA, S.S.

Phenomena of thiourea exchange in complex compounds of bivalent platinum. Zhur. neorg. khim. 2 10:2368-2370 O '57. (MIRA 11:3)
(Platinum compounds) (Urea)

GRINBERG, A.A.

27 7

✓**Slightly soluble compounds of quadrivalent uranium obtained with the aid of rongalite.** A. A. Grinberg, L. E. Nikol'skaya, G. I. Petrzhak, B. V. Ptitsyn, and F. M. Filinov (Radium Inst., Leningrad). *Zhur. Anal. Khim.* 12, 92-4(1957).—Sexivalent U taken as $UO_2(NO_3)_2$ was reduced to the quadrivalent form by rongalite in acid soln. The reduction was carried out in the presence of $H_2C_2O_4$ so that the oxalate pptd. The reaction was carried out in HNO_3 of final concn. 1*N*, in the presence of $H_2C_2O_4$ 10% excess of theoretical value using for each mol. U 1 mol. rongalite plus 7-10% excess. With this procedure the soln. contained no more U than detd. by the soly. of the oxalate. Under similar conditions U was also pptd. as UF_4.

—[illegible]

GRINBERG, A.A.

Determination of nitrogen in complex compounds. A. A. Grinberg and L. K. Simonova. *Zhur. Priklad. Khim.* ~~30, 160-2~~(1957); cf. *C.A.* 48, 51??h.—The method for the detn. of N previously described (*loc. cit.*) was extended to complex amines which either boil at low temps. or can be steam distd. such as $[Pt(PhCH_2NH_2)_2(NH_3)_2]Cl_2$. In complexes which do not possess these properties the N of the NH_3 only can be detd. by this method and then the total by Dumas' method. In this group are included dichlorodiammineethanolamineplatinum, [illegible], and $[Pt(NH_3)AcO]NO_3$. I. Bencowitz

Chem

GRINBERG, A.A.

GRINBERG, A.A.

5(4)
AUTHORS: Vasil'yev, V. P., Korableva, V. D., Yatsimirskiy, K. B. SOV/153-58-3-30/30

TITLE: Conference Discussion on the Methods of Investigating the Complex Formation in Solutions (Soveshchaniye-diskussiya po metodam izucheniya kompleksoobrazovaniya v rastvorakh)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 3, pp 173 - 174 (USSR)

ABSTRACT: From February 18 to 21, 1958 a conference discussion took place at the town of Ivanovo; it dealt with the subjects mentioned in the title. It was called on a decision of the VIIth All-Union Conference on the Chemistry of Complex Formations. More than 200 persons attended the conference, among them 103 delegates from various towns of the USSR. At the conference methods of determining the composition of the complexes in solutions were discussed, as well as the methods of calculating the instability constants according to experimental data and problems concerning the influence of the solvent upon the processes of complex formation.

. . . . In the lecture by A. K. Babko and M. M. Tananayko, "Physical and Chemical Analysis of the Systems With 3 Colored Complexes in the Solution", the results of a systematic investigation in copper-quinoline-salicylate, as well as in copper-pyridine-salicylate systems by means of the optical method were dealt with. In the lecture by Ya. A. Fialkov the idea of a further investigation of the complex formation processes in solutions was developed. Besides the determination of the composition and stability of the complexes also the physical and chemical properties, the chemical nature and the structure of the complex compounds must be investigated . . . . . .

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I. I. Alekseyeva and K. B. Yatsimirskiy in their lecture "Investigation of the Polymerisation of Iso-Poly Acids in Solutions" mentioned experimental results of the investigation of the polymerisation in solutions of molybdic acid. The authors proved that especially the molybdic acid within a certain range of the pH values and the concentrations exists as a number of compounds that can be expressed by an overall formula $MoO_4(HMoO_4)^{n-2}$. In the lecture by N. V. Aksel'rud and V. B. Spivakovskiy investigation results on basic salts taking into account the complex formation in solutions by means of the potentiometric method were mentioned for systems with zinc, cadmium and indium. In the evaluation of their results the authors employed the method of the table difference. The calculation of the consecutive constants was carried out according to the interpolation formula by Newton. N. A. Chamalevskiy held a lecture on "pH Measurement Method of the Solutions in Combination With the System Analysis of the Solubility Diagram of the System Cu^{2+}-HCl - H_2O in Investigating Complex Copper Compounds in Saturated Solutions". It was found that the substance at the bottom of the liquid is more basic than the solution; furthermore, the increased acidity of the solution from the viewpoint of the formation of hydroxy-chloro complexes in the solution was explained. V. I. Kuznetsov opened the discussion with his lecture; he pointed out the necessity of utilizing the concepts worked out in the investigations of the polymerisation in organic chemistry in the chemistry of polynuclear complexes. A. A. Grinberg thinks that the new approach of the hydrolysis

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investigation as developed by the Scandinavian school is of high value. He also pointed to the necessity of studying the kinetics of the polymerization process and a quantitative determination of the strength of the polymers. A. K. Babko pointed out that the study of the polymer structure was necessary. N. P. Komar' mentioned in his lecture that the rather widely spread polymerization type according to the scheme "nucleus + chain members" is not obtained in all cases. The following scientists took part in the discussion: V. E. Tolmachev, A. V. Ablov, I. S. Mustafin, I. V. Tananayev and K. B. Yatsimirskiy. A. K. Babko then discussed in his lecture "Methods of Determining the Dissociation Constant of the Complex Groups in Solutions" the main principles of determining the instability constants. N. P. Komar' discussed in his lecture "Calculation Methods of the Instability Constants of the Complex Compounds According to Experimental Data" the possibilities of using the known calculation methods of the instability constants for various cases of the complex formation in solution. If several mononuclear complexes are formed the displacement method by Abegg and Bodlaender (completed by

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A. K. Babko) cannot be recommended for the calculation of the instability constant. The lecturer discussed the dissolution methods of the polynomials proposed by B'yerrum, Leden, Rossotti, Scatchard, Edsolley and other authors. The constants calculated in this way are not very accurate. It was proved that the method of successive approximations can lead to wrong conclusions as to the chemical processes taking place in the system investigated. The most probable value of the physical constants can be obtained by the method of the least squares. B. V. Ptitsyn, Ye. N. Tekster and L. I. Vinogradova described the determination methods of the instability constants of the oxalate complexes of niobium, uranium and iron which are based on the investigation of the equilibrium displacement of the complex formation by silver ions. N. K. Bol'shakova, I. V. Tananayev and G. S. Savchenko held a lecture on "The Role of the Time Factor in the Investigation of the Complex Formation". In the discussion on the lectures A. A. Grinberg mentioned that due to the slow adjustment of the equilibria the methods discussed of determining the instability constants (palladium and cobalt

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complexes) can often not be employed. A. V. Ablov pointed out the necessity of devising direct methods of proving the existence of intermediate forms in a step-wise complex formation. K. B. Yatsimirskiy mentioned that the instability constants of slowly dissociating complexes can be calculated from thermochemical data. L. P. Adamovich, A. M. Golub among others took part in the discussion on the lectures. A. K. Babko requested inclusion in the next conference on the chemistry of complex compounds a lecture in which various calculation methods of the instability constants should be discussed by the example of actual cases. This should clarify to which divergencies of the values of the constants different methods of evaluating the experimental data can lead. N. P. Komar' stressed that in the determination of the instability constants all chemical equilibria should be taken into account that render complex the complex formation process in the solution, especially the hydrolysis processes of the central ion and the addendum. In the lecture delivered by V. M. Peshkova and A. P. Zozulya "Application of the Distribution Method to the Investigation of the Stability Constants

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of Some Thorium Complex Compounds" results obtained from the experimental investigation of the distribution of thorium compounds in the systems: acetylacetone - benzene - water, and 2-oxy-1,4,-naphthoquinone - chloroform - water were given. From these data the instability constants of the thorium complexes with acetyl-acetone and 2-oxy-1,4-naphthoquinone were calculated. I. V. Tananayev, G. S. Savchenko and Ye. V. Goncharov held a lecture on the application of the solubility method in the determination of the stability of complex compounds in solutions. In this lecture also other methods of investigating complex formation processes in the solution were discussed (pH measurement, measurement of the optical density, as well as of the heat of mixing). B. D. Berezin held a lecture on the "Application of the Solubility Method in Studying the Phthalocyanine Complexes of Metals". He used the determined quantitative characteristics of the reaction of the transition of the phthalocyanides of cobalt, nickel, copper and zinc, as well as of the free phthalocyanine into the sulfuric acid solution for the theoretical reasoning, and as an experimental proof of the existence of

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π-bonds in the complexes investigated. These characteristics also served him as a proof of new electronic formulae of phthalocyanine and its complex derivatives. In the lecture delivered by I. L. Krupatkin on "The Method of the Two Solvents as a Method of Investigating the Formation and Properties of Organic Complexes" it was proved that this method makes it possible to determine the number of complexes formed in the system, their composition and relative stability. V. I. Kuznetsov, A. K. Babko, N. P. Komar', I. S. Mustafin and Ya. I. Tur'yan took part in this discussion. In the lecture delivered by A. A. Grinberg and S. P. Kiseleva on the complex palladium compounds (II) with a coordination number above four it was proved that in the case of a large chlorine and bromine ion excess complexes with the coordination number 5 are formed. The instability constants of these complexes were estimated. L. P. Adamovich mentioned a new manipulation in the spectrophotometric investigation of the complex compounds that can be used in systems with the formation (or predomination) of one single complex. This method makes it possible to determine the composition and instability constant

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of the complex. In the lecture delivered by K. B. Yatsimirskiy and V. D. Korableva the application of the theory of crystalline fields for the determination of the composition and structure of the chloride complexes of cobalt, nickel and copper according to the absorption spectra of these complexes was discussed. It was proved that in a hydrochloric acid concentration above 5 mole/liter in the solution there exists an equilibrium between the tetrahedric and octahedric form of the cobalt chloro complexes. Yu. P. Nazarenko proved in his lecture "The Application of Radioactive Isotopes in the Investigation of the Solvation Equilibrium in Solutions of Complex Compounds" the possibility of using data on the isotope exchange to clarify the structure of the complex and mechanism of the hydration processes. V. Klimov mentioned in his lecture the use of radioactive isotopes in the study of tin and antimony complexes in non-aqueous solutions. A. V. Ablov, V. E. Tolmachev, V. I. Kuznetsov and A. M. Golub took part in the discussion of the lectures. The usefulness of employing the theory of the crystalline fields in explaining the results obtained from the absorption spectra of the com-

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plex compounds was stressed. In the lecture delivered by I. A. Shek on "The Investigation of the Complex Formation by the Method of the Dielectric Permeability and the Polarization" the principles of the methods mentioned were presented. This method was employed for investigating the compounds of the type of the "affiliation" products. The lecture delivered by I. A. Shek and Ye. Ye. Kriss "Employing the Method of the Dielectric Constant for Investigating Complex Compounds of the Type of Crystal Solvates in Solutions" dealt with the investigation of the solvates of lanthanum and cerium chlorides with ketones, as well as with the study of the compounds formed in heterogeneous systems with tributyl phosphate and nitric acid. V. F. Toropova gave in her lecture "The Polarographic Method of Investigating the Complex Formation in Solutions" a survey of the applications of the polarographic method in the study of the complex compounds, and illustrated several fine characteristic features of this method. In the lecture delivered by T. N. Sumarokova "The Cryoscopic Method of Investigating the Complex Formation Reactions" a survey of

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the possibilities of the cryoscopic method was given, and its applicability in the study of several complex compounds of stannic chloride with organic substances was proved. A. M. Golub described the results of his investigations of thiocyanate complexes of several metals. A vivid discussion took place on the lectures held. Ya. A. Fialkov and Yu. Ya. Fialkov considered the cryoscopic method of investigating complex compounds to be of considerable value. K. B. Yatsimirskiy pointed out that the publication of the surveys on individual methods of investigating the complex formation reactions would be desired; this concerns especially the polarographic method. The cryoscopic method should be brought to a level that makes the calculation of the equilibrium constants of the processes to be investigated possible. The problem of the method of evaluating the experimental results becomes more and more important. Many scientists use the instability constants without taking into account the way in which they had been obtained. The calculation methods employed by A. M. Golub are one step back, as compared to those employed at present. In his lecture N. P. Komar' pointed out the extremely great importance of the mathematical

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evaluation of the results obtained, as well as of the plotting of curves. A. K. Babko suggested selecting one or two systems that are experimentally well investigated, and to evaluate the results obtained according to different methods so that it is possible to check and evaluate them. Ya. I. Tur'yan took part in the discussion. Ya. A. Fialkov discussed in his lecture "The Effect of the Solvent on the Complex Formation Process as Well as on the State of Equilibrium in the Solutions of Complex Compounds" the influence exerted by the solvents upon the molecular state, upon the solvation of the system components, upon the stabilization of the complexes formed in the system, upon the step-wise dissociation of the complexes and upon a number of other processes. The influence exercised by the dielectric constant upon the complex formation process was discussed. It was concluded that a direct relation does not exist, and that the chemical nature of the solvent must be taken into account. A. V. Abiev and L. V. Nazarova held a lecture on "The Spectroscopic Investigation of Nickel Cobalt 'Pyridinates' in Various Solvents". The instability constants of the complexes were determined and it was proved that the

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Conference Discussion on the Methods of Investigating the Complex Formation in Solutions

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stability of the 'pyridinates' is changed in dependence on the solvent. Ya. I. Tur'yan in his lecture "The Influence of the Solvent Upon the Composition and Stability of Complex Ions" discussed the polarographic investigation method of the chloride and thiocyanate complexes of lead in aqueous ethanol solutions at different content of the non-aqueous solvent and at a constant ionic strength. A step-wise character of the complex formation was found as well as the instability constants of the complexes. The influence of the dielectric constant of the solution on the stability of the investigated complexes was proved. In the lecture by V. P. Vasil'yev on the "Investigation of Aquo Complexes in Mixed Solvents" the main attention was devoted to the necessity of the qualitative recording of the solvation effects in the complex formation. The applicability of the polarographic method in the determination of the composition and stability of the aquo complexes in mixed solvents was proved and experimental material on the thermodynamics of the dissociation of the cadmium-aquo complexes in aqueous ethanol solutions was mentioned. V. S. Tolmachev, V. I. Kuznetsov

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and I. V. Tananayev stressed in their lectures the necessity of a more complete and general investigation of the solvation processes. A. K. Babko and A. M. Golub pointed out the great importance of the investigations of the complex formation equilibria in non-aqueous solutions, and made several critical comments on the lecture by Ya. I. Tur'yan. The following scientists took part in this discussion: L. P. Adamovich, O. I. Khotyanovskiy, A. P. Moskvin and A. G. Mustafayev. At the final meeting of the conference A. A. Grinberg, Corresponding Member, AS USSR, said in his speech that such a conference was very urgent. A detailed discussion of the determination methods of the composition of the complexes, as well as of the method used in the study of the quantitative characteristics of the stepwise complex formation was extremely useful for all who attended this conference.

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[illegible]

GRINBERG, A.A.

78-1-36/43

AUTHOR: Grinberg, A. A.

TITLE: On the Importance of Complex Compounds for Radiochemistry (O znachenii kompleksnykh soyedineniy radiokhimii).

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 1, pp. 195-203 (USSR).

ABSTRACT: The article deals with the abovementioned questions only in general outline, the use of complex compounds for the obtaining of preparations of a high specific activity and for the separation of isotopes was not taken into account.
The first part deals with the state of radio-elements in the solution. Besides other examples, the difference of uranium- and thorium-oxalate and the separation of the thorium-isotope UX from uranium is given.
The next chapter deals with coprecipitation and complex-formation. Coprecipitation develops by adsorption or incorporation into the crystal lattice. A lower limiting concentration below which the radio-element is not built in, exists frequently, but not always, for "abnormal" formation of mixed crystals.
In the third part the author deals with the formation of complexes and processes of extraction. The rules governing the extraction are derived and some recent extraction solvents are enumerated.

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On the Importance of Complex Compounds for Radiochemistry. 78-1-36/43

In the last chapter, dealing with chromatography and formation of complexes, the author limits himself to a discussion of description. A table of the constants of stability of various alkaline-earth-complexes is reproduced from the work of Martell-Calvin (Kel'vin): Chemistry of the Metal Chelate Compounds. There are 1 table, and 3o references, 21 of which are Slavic.

SUBMITTED: August 2, 1957.

AVAILABLE: Library of Congress.

Card 2/2

GRINBERG, A.A.

AUTHORS: Grinberg, A. A., Petrzhak, G. I., Yevteyev, L. I. 78-1-37/43

TITLE: **Studies in the Chemistry of Uranium- and Thorium-Oxalates**
(**Issledovaniya** po khimii oksalatov urana i toriya).

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 1, pp. 204-211
(USSR).

ABSTRACT: After a brief survey of literature the authors find that according to reference 6, the formulae of uranium oxalate (IV) and its derivates should be doubled. Since these conceptions were not in mutual accordance with the theory of coordination and since they were not based on any physico-chemical data, the authors charged themselves with supplying this necessity.

Complex uranium oxalates. A salt $(UC_2O_4)_2 \cdot 2K_2C_2O_4 \cdot 5H_2O$ was produced. Barium salt, as well as new representatives of this series of compounds: lead-, cadmium-, and calcium-salts were isolated by double-exchange-reactions. The two latter representatives of the uranium-IV-derivates are "abnormal" red-violet colored. The molecular conductivity of the water solutions of the potassium salts was investigated for proving the coordination-structure of the oxalates of uranium

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Studies in the Chemistry of Uranium- and 78-2-37/43
Thorium-Oxalates.

salts. Respective measurements prove that the potassium salt is a 5-ion-electrolyte which decays according to the scheme:

$K_4/U\ (C_2O_4)_4) \rightleftarrows 4K + /U\ (C_2O_4)_4/^{4-}$. Previous test results - which were precisely determined meanwhile - together with data from literature for other 5-ion-electrolytes are shown in table 1. Since the pH of the potassium salt solutions hardly deviates from the pH of the water (figure 1) at the beginning, the authors, taking account of the conductivity concluded that the coordination number of uranium in potassium salt is equal to 8. Probable equations of the interaction of the $[U\ (C_2O_4)_4]^{4-}$ -ion with water are set up and the further dissociation of the aquo-ions is explained. The pH consequently decreases in the course of time. The constants of stability of the afore-mentioned ions are evaluated (according to reference 12) and a value of the order 10^{-4} is obtained by potentiometric titration with HCl. The known salt $U_2(C_2O_4)_2.K_2C_2O_4.8H_2O$ precipitates with this titration (after adding 1 mol HCl). The production of mixed salts was achieved with cerium and lanthanium (according to reference 13).

Card 2/4 There are metastable phases which gradually decay in the solution and enrich the deposit with rare earths. For clarifying the character of linkage in the complex oxalates of uranium, the magnetic properties of some salts were investigated and absorption curves of the potassium salt were plotted. It results from table 2 that in all cases the magnetic moment depends on 2 unpaired electrons. Further it was proved that the violet barium salt, just as the green tetravalent one, contains uranium. The curves in figure 2 show the absorption of the potassium salt in the visible (luminous) region of the spectrum. Its solutions have a maximum absorption in 3 ranges: with the wavelength of 490,0, 560,0 and 659,5 mμ. The tetravalent state of uranium as part of the complex ion does not greatly differ from other known derivatives of the tetravalent uranium. These data - in view of the magnetic properties - allow to state that the two unpaired electrons of uranium (IV) are not included in the formation of the co-valent bonds.

Comparison of the properties of $U(C_2O_4)_2 \cdot 6H_2O$ and $Th(C_2O_4)_2 \cdot 6H_2O$.

The authors elaborated 2 new methods of production for the oxalate of tetravalent uranium: 1) based upon an electrolytic reduction of $UO_2(C_2O_4)$ in presence of a surplus of oxalic acid. 2) by the action

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Studies in the Chemistry of Uranium- and
Thorium-Oxalates.

of rongalite on uranyl salts in an acid solution in presence of necessary surplus of oxalic acid. The molecular conductivity and the pH of the $U(C_2O_4)_2.6H_2O$ resulting from the 1st method, the water solubility (comparing for $Th(C_2O_4)_2.6H_2O$) and the solubility in acqueous solutions of various acids were investigated and a potentiometric titration with permanganate in a H_2SO_4-milieu was carried out. 2 potential differences occur with the titration (figure 3): a) with the oxidation of U^{IV}in U^{VI}, b) at the end of the oxidation of the oxalate-groups. It was found that $U(C_2O_4)_2.6H_2O$ and $Th(C_2O_4)_2.6H_2O$ behave quite different in water solutions. The much greater of the acidity of uranium salt, compared with thorium salt was confirmed by the action of gaseous pyridine on the two hexahydrates. The acid properties of uranium salt are finally confirmed by a much less solubility in diluted acids than in water. The difference in the properties of acidity between the derivates of U(IV)- and Th(IV) can be explained by the relation of the ion-radii.
There are 4 figures, 2 tables, and 19 references, 7 of which are Slavic.

SUBMITTED. April 29, 1957.
AVAILABLE. Library of Congress.
Card 4/4

GRINBERG, A.A.

[illegible]-3-5-17/32

AUTHORS: Grinberg, A. A., Gil'dengershel', Kh. I., [illegible], V. V.

TITLE: II. On the Effect of Anions of the Outer Sphere Upon the Nature of Substitution Within the Inner Sphere of Complex Compounds (II. O vliyanii anionov vneshney sfery na kharakter zameshcheniya vo vnutrenney sfere kompleksnykh soyedineniy)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5, pp 1162 - 1165 (USSR)

ABSTRACT: The interaction between the isomeric diamines of tetravalent platinum and ammonia in the presence of sulfate- and phosphate ions was investigated. The results showed that in the presence of SO_4^{2-} and PO_4^{3-} different products were obtained. Upon the action of ammonia upon $[(Pt\ NH_3)_5Cl]^{3+}$, hydroxypentamine forms in the presence of SO_4^{2-}. In the presence of PO_4^{3-} chloropentamine forms. By means of these experiments,

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II. On the Effect of Anions Within the Outer Sphere Upon the Nature of Substitution Within the Inner Sphere of Complex Compounds

it is proved that the anions SO_4^{2-} and PO_4^{3-} direct the reaction into the **inner sphere.** . CrO_4^{2-} also has the same effect upon the above-mentioned ammonia-cis or-trans $\left[(Pt\ NH_3)_5Cl\right]^{3+}$ system. From the obtained results, it can be seen that in the presence of SO_4-ions and CrO_4-ions the **substitution** process within the **inner sphere** is very profound. The last chlorine atom is displaced by hydroxide. The results showed that the anions within the **outer sphere** of a complex can cause a certain loosening in the anions of the **inner sphere** of a complex. There are 8 references, 7 of which are Soviet.

SUBMITTED: May 16, 1957
AVAILABLE: Library of Congress
Card 2/2

1. **Complex** compounds--Substitution reactions--Effects of anions

AUTHORS: Grinberg, A. A., Kukushkin, Yu. N. 78-3-6-6/30

TITLE: On the Production of Cossa Salt (K voprosu o poluchenii soli kossa)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6, pp. 1312-1314 (USSR)

ABSTRACT: Kinetic investigations of the reaction of $K_2[PtCl_4]$ and $K[PtNH_3.Cl_3]$ with ammonia were performed. The smaller yield of $K[PtNH_3.Cl_3]$ due to the direct action of ammonia on $K_2[PtCl_4]$ was discussed. 46 % of the Cossa salt which can be produced theoretically were obtained by the Lebedinskiy-Golovnya method.
It was found that the greatest yield of Cossa salt in the calculated equivalent amount can be obtained in the boiling Peyrone salt - cis $[Pt(NH_3)_2Cl_2]$ with KCl and acetic acid. There are 8 references, 6 of which are Soviet.

SUBMITTED: October 27, 1957

AVAILABLE: Library of Congress

Card 1/1 1. Chemistry 2. Salt--Production

78-3-6-7/30

AUTHORS: Grinberg, A. A., In'kova, Ye. N.

TITLE: On the Mechanism of the Synthesis of Hexamine Platinum-(IV) (K voprosu o mekhanizme sinteza geksammina chetyrekhvalentnoy platiny)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6, pp. 1315-1325 (USSR)

ABSTRACT: It was found that in the synthesis of hexamine platinum-(IV) a reduction of platinum-(IV) occurs in platinum-(II) if $[PtEt_4Cl_2](HSO_4)_2$, NH_4OH and $(NH_4)SO_4$ are used as initial components.
Experiments were carried out for the explanation of the action of various oxidizing and reducing agents on the hexamine reactions. On this occasion it was found that in the presence of potassium permanganate, manganese sulfate and H_2O_2 in the reaction medium hexamine formation does not take place. However, the yield of hexamine is 80 - 90% in the presence of chlorine as oxidizing agent in the reaction medium. This reaction is of special interest for the explanation of the mechanism of formation of platinum hexamines. The mechanism consists in repeated oxidation and reduction

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On the Mechanism of the Synthesis of Hexamine Platinum-(IV) 78-3-6-7/30

of platinum. Instead of gaseous chlorine a frshly prepared solution of NaOCl can be used as oxidizing agent.
Also the action of the quantity of the ammonia introduced into the solution was investigated and it was found that at higher concentration of ammonia in the solution favorable conditions for the production of platinum hexamine exist.
The yield of hexamine is increased by the introduction of small quantities of cobalt-(II)-salts into the reaction mixture.
There are 9 tables and 12 references, 10 of which are Soviet.

SUBMITTED: October 26, 1957

AVAILABLE: Library of Congress

1. Hexamine platinum--Synthesis

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SOV/78-3-8-16/48

AUTHORS: Grinberg, A. A., Kukushkin, Yu. N.

TITLE: Kinetic Investigations of Some Complex Compounds of Bivalent Platinum (Kineticheskiye issledovaniya nekotorykh kompleksnykh soyedineniy dvukhvalentnoy platiny). On the Mutual Influence of Coordination Groups (O vzaimnom vliyanii koordinirovannykh grupp)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 8, pp. 1810-1817 (USSR)

ABSTRACT: The kinetics of the interaction of ammonia with $[Pt(NH_3)_3Cl]Cl$ and $K[PtPyCl_3]$, as well as the kinetics of the interaction of pyridine with $K_2[PtCl_4]$, $K[PtPyCl_3]$ and $K[PtNH_3Cl_3]$ were investigated. It was shown that in the compounds $K_2[PtCl_4]$, $K[PtNH_3Cl_3]$, trans-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]$ the velocity of interaction of the complexes with NH_3- and OH- groups increases from $K_2[PtCl_4]$ to trans-$[Pt(NH_3)_2Cl_2]$, and then decreases to $[Pt(NH_3)_3Cl]Cl$. This

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Kinetic Investigations of Some Complex Compounds SOV/78-3-8-16/48
of Bivalent Platinum. On the Mutual Influence of Coordination Groups

dependence of the velocity of interaction is based on the cis-effect of the NH_3- molecules on the coordination group $Cl-Pt^{2+}-Cl$.
Based on the comparative investigations of the velocity of interaction of pyridine in $K_2[PtCl_4]$ and $K[PtPyCl_3]$ it was found that also pyridine can exert a cis-effect. The cis-effect of pyridine in the system investigated is greater than the cis-effect of ammonia.
There are 4 figures, 1 table, and 17 references, 11 of which are Soviet.

SUBMITTED: December 12, 1957

Card 2/2

AUTHORS: Grinberg, A. A., Shagisultanova, G. A. SOV/78-3-10-11/35

TITLE: The Question of Geometrical Isomerism of Dinitro-Dibromo Platinum Compounds (K voprosu o geometricheskoy izomerii dinitrodibromoplatoatov)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 10, pp 2289-2294 (USSR)

ABSTRACT: The compound $K_2[Pt(NO_2)_2Br_2]$ was produced by interaction of $K_2[Pt(NO_2)_4]$ with HBr. This compound is enriched with cis-isomers. Lemon-colored preparations are produced in the interaction of $K_2[PtBr_4]$ and $K_2[Pt(NO_2)_4]$. The preparation produced by interaction of $K_2[Pt(NO_2)_4]$ and HBr, has an orange color. The yellow and orange form of $K_2[Pt(NO_2)_2Br_2]$ differ not only in color, but also in solubility in 96% ethyl alcohol, in electric conductivity and in the pH-values of their diluted aqueous solutions. The solubility of the yellow modification is 0,138 g/100 ml in 96% alcohol, that of the orange modification is 0,179 g/100 ml (at 25°C).

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The Question of Geometrical Isomerism of Dinitro-Dibromo Platinum Compounds

The aqueous solution of the yellow modification has a pH-value of 5,10, that of the orange modification has an initial pH-value of 4,65, and one of 3,97 after three hours. Various products are obtained in the interaction of the yellow and the orange modification with ammonia. Dinitro-diammino platinum compounds are produced in the interaction of ammonia with the yellow modification, and cis-dinitro-diammino platinum compounds are obtained from the interaction of ammonia with the orange modification. There are 6 references, 6 of which are Soviet.

SUBMITTED: July 17, 1957

Card 2/2

AUTHORS: Grinberg, A. A., Shikheyeva, L. V. SOV/78-3-11-12/23

TITLE: The Oxidation of Complex Titanium Oxalates in the Potentiometric Titration (Okislitel'noye potentsiometricheskoye titrovaniye kompleksnykh oksalatov titana)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 11, pp 2491 - 2495 (USSR)

ABSTRACT: The oxidation of the compounds $K_2[TiO(C_2O_4)_2] \cdot 2H_2O$, $K[Ti(C_2O_4)_2] \cdot 2H_2O$ and $[Pt(NH_3)_4][TiO(C_2O_4)_2] \cdot 2H_2O$ was investigated. The method of the synthesis of the above mentioned compounds was given. The potentiometric titration of these compounds with $KMnO_4$ was carried out at 35-70°C and a potentiometric titration curve was plotted. The curve of $K_2[TiO(C_2O_4)_2] \cdot 2H_2O$ was investigated in dependence on the acidity of the solution; it showed a jump which corresponds to the oxidation of the oxalate group. The potentiometric titration curve of the compound $K[Ti(C_2O_4)_2] \cdot 2H_2O$ has two jumps. The oxidation of the

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compound $K_2[TiO(C_2O_4)_2] \cdot 2H_2O$ proceeds according to the following scheme:
$5K_2[TiO(C_2O_4)_2] + 4KMnO_4 + 16H_2SO_4 = 4MnSO_4 + 5TiOSO_4 + 20.CO_2 + 7K_2SO_4 + 16H_2O$. The first stage of the oxidation of $K[Ti(C_2O_4)_2] \cdot 2H_2O$ is the following:
$5K[Ti(C_2O_4)_2] + KMnO_4 + 4H_2SO_4 + H_2O \rightarrow MnSO_4 + 5H_2[TiO(C_2O_4)_2] + 3K_2SO_4$. The gross-reaction of the oxidation of $[Pt(NH_3)_4][TiO(C_2O_4)_2] \cdot 2H_2O$ at 55°C proceeds according to the following scheme:
$5[Pt(NH_3)_4][TiO(C_2O_4)] + 6KMnO_4 + 19H_2SO_4 = 6MnSO_4 + 5[Pt(NH_3)_4(OH)_2]SO_4 + 20.CO_2 + 5TiOSO_4 + 3K_2SO_4 + 14H_2O$. The results show that no separation of the titrated oxalate groups takes place in the complex oxalate compounds of the trivalent and tetravalent titanium. A gradual oxidation of the oxalate groups was found only in the complex

The Oxidation of Complex Titanium Oxalates in the Potentiometric Titration

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compounds with platinum. There are 3 figures and 10 references, 8 of which are Soviet.

SUBMITTED: July 18, 1957

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SOV/78-3-12-1/36

AUTHOR: Grinberg, A. A.

TITLE: Filipp Mikhaylovich Filinov (Obituary Notice)(Filipp Mikhaylovich Filinov (Nekrolog))

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12, pp 2593-2596 (USSR)

ABSTRACT: The well-known Soviet inorganic chemist F. M. Filinov died on November 10, 1956. Since 1932 Filinov had worked in the field of inorganic chemistry and especially in regard to the chemistry of the complex compounds. His first investigations in this direction were those on the dihydroxy platinates and on the isomeric salts $[Pt(NH_3)_4][PtCl_4 \cdot (OH)_2]$ and $[Pt(NH_3)_4 \cdot (OH)_2][PtCl_4]$. This second compound was synthesized for the first time by Filinov. His dissertation in 1939 dealt with the migration processes in complex compounds of platinum. In 1939-1941 Filinov worked with A. A. Grinberg in investigating the transformations in complex compounds by using radioactive isotopes. F. M. Filinov was also active in developing analytic techniques for the noble metals using radioactive indicators. In regard to biochemical problems, he worked out in great

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Filipp Mikhaylovich Filinov (Obituary Notice)

detail means of investigating hemoglobin using radioactive isotopes. Filinov was especially active in the Leningrad Technological Institute, Chair for the Chemistry of the Rare and Radioactive Elements. F. M. Filinov became professor in 1956. There are 11 Soviet references.

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GRINBERG, A.A.; PETRZHAK, G.I.; NIKOL'SKAYA, L.Ye.; PTITSYN, B.V.; FILINOV, F.M. [deceased]

New means of preparing tetravalent uranium derivatives. Trudy Radiev.inst.AN SSSR. 8:166-169 '58. (MIRA 12:2)
(Uranium compounds)