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# SOME NEW ANALYTICAL REACTIONS OF THE PLATINUM METALS

By S. C. Ogburn, Jr.[1]

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## Introduction

The six elements, ruthenium, rhodium, palladium, osmium, iridium and platinum, familiarily known as the "platinum group," have been a source of many investigations, but in regard to a critical study of their analytical reactions with a view of effecting their successive gravimetric separation, relatively little has been accomplished. Their close analogy with each other and the remarkable manner in which the relations of each to chemical reagents are controlled by the presence of the others give rise to many difficulties in their detection and separation. The ability of certain of the metals, particularly palladium and platinum, to form coördinated, or "inner," salts has aided materially in this effort. Such inorganic salts as the metallic carbonyls, double cyanides and double nitrites, and the organic glyoximes are well known. The application of the latter type has been demonstrated by Tschugaeff,[2] Wunder and Thüringer[3] and Feigl and Christiani-Kronwald.[4]

The insolubility of basic organic derivatives of the metals with alkaloids, pyridine, quinoline and certain aliphatic amines has been utilized by other investigators in effecting their precipitation. Chief among these have

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[1] This paper is constructed from a thesis entitled, "The Analytical Reactions, and a Scheme for the Separation, of the Platinum Metals," presented to the faculty of the Graduate School of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Tschugaeff, *Ber.*, **41**, 1678 (1908).

[3] Wunder and Thüringer, *Ann. chim. anal.*, **17**, 201 (1912); *Z. anal. Chem.*, **52**, 737 (1913).

[4] Feigl and Christiani-Kronwald, *ibid.*, **65**, 341 (1925).

been Hesse,[5] Gutbier,[6] Charonnat,[7] Delépine,[8] Gutbier and Woernle,[9] and Schleicher, Henkel and Spies.[10] There have also been found several miscellaneous compounds that are, under certain conditions, useful as analytical reagents for one or more of the metals. Prominent examples have been contributed by Erdmann and Makowka,[11] separating palladium with acetylene gas; Schmidt,[12] separating palladium with $\alpha$-nitroso-$\beta$-naphthol; Vivario and Wagenaar,[13] also Cole,[14] separating platinum and iridium with hexamethylenetetramine, and Bargellini and Bellucci,[15] separating platinum and palladium with 8-hydroxyquinoline.

In the case of the basic compounds, the metal, in acid solution, unites to form salts or addition products which are more or less insoluble, but with most other types, especially the organic ones, the structural constitution of the precipitate is quite complex, the different types forming products whose structures are peculiar to that type. With hydroxyquinolines, the condition $=C-O-M-N=$ (where M is one metallic equivalent and in which the ring is closed by a secondary valence) must be met. Of the two types of glyoximes, only the *syn* form is capable of forming metallic complex salts,[2] and as Lowry[16] has shown, this precipitation "depends upon the formation of complexes in which the electrons in the outer shell of the metal are made up to the number present in the next inert gas by a process of sharing electrons with coördinated groups."

The purpose of this paper is (A) to present a study of the reactions of typical classes of organic and inorganic compounds on solutions of the platinum metals and (B) to deduct some relationship between the constitution of the type of compound used and its power of precipitating the individual metals, with an ultimate view of finding compounds which will precipitate each of the metals in the presence of the others—thus insuring their selective gravimetric separation.

## Experimental Part

Chloride solutions of the six metals, each containing approximately 3 mg. of the metal per cc. were prepared as follows.

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[5] Hesse, *Ann.*, **207**, 309 (1881).

[6] Gutbier, *Ber.*, **56B**, 1008 (1923).

[7] Charonnat, *Compt. rend.*, **178**, 1423 (1924).

[8] Delépine, *ibid.*, **152**, 1390, 1589 (1911); **175**, 1075, 1211, 1408 (1922); **176**, 445 (1923).

[9] Gutbier and Woernle, *Ber.*, **39**, 2716, 4134 (1906).

[10] Schleicher, Henkel and Spies, *J. prakt. Chem.*, **105**, 31 (1922).

[11] Erdmann and Makowka, *Ber.*, **37**, 2694 (1904); *Z. anal. Chem.*, **46**, 125 (1907).

[12] Schmidt, *Z. anorg. Chem.*, **80**, 335 (1913).

[13] Vivario and Wagenaar, *Pharm. Weekblad*, **54**, 157 (1917).

[14] Cole, *Phillippine J. Sci.*, **22**, 63 (1923).

[15] Bargellini and Bellucci, *Gazz. chim. ital.*, **53**, 605 (1923).

[16] Lowry, *J. Soc. Chem. Ind.*, **42**, 316, 462 (1923).

**Ruthenium.**—Ruthenium trichloride was obtained by dissolving the pure, distilled ruthenium tetroxide in concd. hydrochloric acid and diluting with water. It yielded a clear red to red-brown solution.

**Rhodium.**—Sodium chlororhodite was obtained by dissolving the pure salt[17] in water containing a few drops of hydrochloric acid. It yielded a clear rose solution.

**Palladium.**—Palladium dichloride was obtained by dissolving the pure salt[17] in hot water acidulated with hydrochloric acid. It yielded a clear, brownish-red solution.

**Osmium.**—Two solutions were used, potassium osmate, $K_2OsO_4$ and potassium chloro-osmate, $K_2OsCl_6$. They were used, either separately or together, as is indicated in Tables I and II. The former was made by dissolving the salt[17] in water acidulated with hydrochloric acid. In later experiments, when this supply was exhausted, the salt was prepared by treating a potassium hydroxide solution of distilled osmium tetroxide with alcohol. The crystals obtained were dissolved in water acidulated with hydrochloric acid. This yielded a clear rose solution, which on standing several months, slightly decomposed and changed to pale yellow. The potassium chloro-osmate was made by dissolving the salt in water acidulated with hydrochloric acid, boiling being necessary to effect solution. In later experiments, when this supply was exhausted, the salt was prepared by repeatedly evaporating a hydrochloric acid solution of osmium tetroxide with a saturated solution of potassium chloride. The crystals obtained were dissolved in water acidulated with hydrochloric acid and yielded a pale yellow solution.

**Iridium.**—Sodium chloro-iridate was obtained by dissolving the pure salt[17] in hot water containing a few drops of hydrochloric acid; it yielded a clear red solution.

**Platinum.**—Chloroplatinic acid was obtained by dissolving pure platinum sponge in dilute aqua regia and successively evaporating the solution with concd. hydrochloric acid to remove nitrogen oxides and to prevent the formation of the nitrosoplatinum compound. It was then diluted with water, yielding a clear rose solution, which on further dilution, changed to orange.

Five-cc. samples of each of these solutions were then used in the study of their reaction towards 33 typical inorganic and nearly 90 organic compounds selected from the various classes and including those known to react with these metals. These tests were carried out at room temperature, but if no visible reaction was noted, the temperature was gradually raised to the boiling point. As the solution of each metal possesses a definite color, a lightening in color of the solution upon treatment with a reagent offers an indication that a reaction has taken place and in every

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[17] Kindly furnished by Baker and Co., Newark, N. J.

TABLE I

REACTIONS WITH INORGANIC REAGENTS

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| Acetylene gas, on sat. the soln. and warming | 1 (*h*), Brown | 1 (*h*), Black | 3, Brown | Blue, then green soln. (*d*), 1 (*h*) | ...... | ...... |
| Ammonium chloride, satd. soln. on warming | (*b*) | (*b*) | ...... | Black-violet soln. (*d*), 1 (*h*) Black | (*b*) | 3, 2 (*a*), Yellow |
| Ammonium chloride and potass. ferrocyanide | ...... | ...... | ...... | Blue, then violet soln. (*d*) | ...... | ...... |
| Ammonium hydroxide concd. on warming | 2, Black | 2, Yellow | 1 (*i*), Yellow | ...... | ...... | ...... |
| Ammonium hydroxide and sodium thiosulfate | Rose-violet soln. (*c*) | Light green soln. (*c*) | Green soln. (*c*) | Orange soln. (*c*) | Green soln. | Yellow-green soln. |
| Ammonium sulfide on warming | 3, 2 (*h*), Black | 3, 2 (*c*), Red-brown | 3, Black | 3, Black | 2 (*g*), Brown | 3, 2 (*c*) (*g*), Red-brown |
| Cobalt pentammines, roseo and purpureo | 2, Orange | 2, Buff | ...... | ...... | 2, Buff | 2, Orange-brown |
| Hydrazine hydrate concd. aq. soln. | ...... | 3, 2 (*c*), Black | 3, 2 (*c*), Black | Green soln., (*c*) | ...... | 3, 2 (*c*), Black |
| Hydrazine hydrochloride, concd. aq. soln. | Yellow soln. | 3, (*c*) (*a*) (*j*), Black | 2 (*c*), Black | 1 (*h*), Black | ...... | 1 (*h*), Brown |
| Hydrazine sulfate, soln. alk. with NaOH | 3, 2 (*c*), Brown-black | 3, 2, Black (*c*) | 3, 2 (*c*), Black | Violet soln. and black, (*d*) | 1 (*h*), White | 3, 2 (*c*), Black |
| Hydrogen sulfide at 80°C. | Blue soln. and 3, 2 (*c*) (*h*), brown | 3, Black | 3, Black | 3, Black | (3, 2), (*c*), Brownish | 3, Brown-black |
| Hydroxylamine sulfate, satd. aq. soln. | ...... | ...... | 3, 2 (*c*), Black | ...... | Yellow soln., (*c*) | 2 (*h*), Black |
| Mercuric cyanide, concd. aq. soln. | (1) (*c*), Black | ...... | 3, White | Violet soln., (*d*) | ...... | ...... |

TABLE I (*Concluded*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| Phosphorus, red, on boiling | 2, Dark gray | 2, Bronze-gray | 3, Black | 3, Black | 3, Gray-black | 2, Black |
| Potassium chloride, satd. soln. on warming | (*b*) | (*b*) | 1 (*c*) (*h*), Red | (2) (*c*), Black | (*b*) | 3, 2 (*a*), Yellow |
| Potassium iodide, aq. soln. on warming | 2 (*c*), Black | (1) Brown-red | 2, Red-brown | Green soln., (*d*) 1 (*h*), Black | ...... | Blood-red soln. |
| Potassium nitrite, satd. soln. on warming | ...... | 3, 2 (a), White | ...... | ...... | ...... | 2, Yellow (*m*), ($K_2PtCl_6$) |
| Potassium nitrite and ammon. sulfide | Blood-red soln. | (1), Brown-red | 2, Red-brown | Yellow soln. | Green soln., 1, (*h*), green | (3, 2), Buff |
| Potassium thiocyanate, concd. aq. soln. | Red, then violet soln. | ...... | 1 (*h*), Black | Rose soln. (*c*), blue soln. (*a*) | ...... | ...... |
| Sodium carbonate, on warming | ...... | (2), Yellow | (2), Red-(*c*) brown | Violet soln. and 2, black | ........ | ...... |
| Sodium hydroxide, concd. aq. soln. | Green soln., and 3, 2 (*c*) (*a*), black | Green soln., and 2 (*c*, *a*), yellow to brown | 3, 2 (*c*, *a*), Brown | Brownish-red | Green soln., violet soln., 2 (*a*), brown-black | Orange soln., and 1 (*b*), yellow to black |
| Sodium hydroxide and $ClO_2$ gas | ...... | Yellow, red, blue soln. | ...... | ...... | ...... | ...... |
| Sodium nitroprusside, concd. aq. soln. | ...... | ...... | 3, Red-gray | ...... | ...... | ...... |
| Sodium thiosulfate, concd. aq. soln. | 2 (*c*), Brown | 3, 2 (*h*), Brown | 3, Black | 2, Red, 2 (*d*), brown-black | (3, 2) (*c*), Brick red | 2 (*c*, *i*), Red-brown |
| Stannous chloride, on warming | Blue soln. Yellow soln., (*c*) | Blood-red soln., (*c*) | Blue, green soln., (1) (*c*), Black | Yellow soln. (*c*) | Lemon yellow soln., (*c*) | Orange, then red; (*c*), black, 2 |
| Sulfurous acid, satd. aq. soln. of $SO_2$ | ...... | ...... | Green soln. | Yellow, green, then blue soln. | ...... | Red, then pale yellow soln. |
| Zinc, metal. | Blue soln., (3,2), black | 3, Black | 3, Black | (3, 2), Black | (3, 2), Black | 3, Black |

## TABLE II

### REACTIONS WITH ORGANIC REAGENTS

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| Acids, aliphatic, subst. (*a*) Iodo-acetic acid, 2% soln. in alcohol | ...... | (1) (*c*, *h*), Brown | Brown-2 (*c*) Black | Green soln. (*c*) | ...... | (1) (*c*, *h*), Red-brown |
| Amino acids, aromatic (*a*) Anthranilic acid, satd. aq. soln. | ...... | ...... | ...... | Violet soln. (*h*) | ...... | Blood (*h*), red soln. |
| Acids, arom., subst. (*a*) 5-Nitrosalicylic satd. aq. soln. | ...... | ...... | 2 (*h*), Black | ...... | ...... | ...... |
| (*b*) 4-Nitrochlorobenzene-2-sulfonic; dil. alc. soln. | ...... | ...... | Green-brown soln. (1), black | ...... | Green soln. | ...... |
| Alkaloids (*a*) Aconitine, concd. aq. soln. | ...... | ........ | ...... | Rose soln. | ...... | ...... |
| (*b*) Atropine, concd. soln. in 10% alc. | ...... | 1, Buff-rose | ...... | ...... | ...... | ...... |
| (*c*) Brucine, satd. soln. in 30% alc. | 1 (*h*), Yellow | 2, Buff | 3, 2 (*a*), Orange | 3, 2 (*a*), Yellow | 3, 2 (*a*), Red | 3, Yellow (*a*) |
| (*d*) Caffeine, satd. (hot) aq. soln. | ...... | ...... | (3, 2) (*a*), Yellow | ...... | ...... | ...... |
| (*e*) Cinchonine, HCl, satd. aq. soln. | ...... | 2, Flesh | (1) Green-black | ...... | ...... | 2, Orange |
| (*f*) Morphine sulfate, concd. aq. soln. | ...... | 2, Orange | ...... | ...... | ...... | 1 (*h*), Yellow |
| (*g*) Quinine HCl, satd. aq. soln. | ...... | 2, Orange | (3), Cream (*a*) | (2), Gray | ...... | (3) (a), Orange |
| (*h*) Strychnine $H_2SO_4$, satd. (3%) aq. soln. | 2, Yellow | 2, Orange | 3, Buff | 3, White | 3, Brown-yellow | 3, Yellow |
| (*i*) Theobromine, satd. (0.7%), aq. soln. | ...... | ...... | 2, Yellow | ...... | ...... | ...... |

TABLE II (*Continued*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| Amines, aliphatic (*a*) Diethylamine HCl, concd. aq. soln. | ...... | ...... | (1), Red | (1), Black | ...... | ...... |
| (*b*) Dimethylamine, 10% aq. soln. | (1), Green | 2, White | (1), Brown | Green, then violet soln. (*d*) | ...... | (1), Yellow |
| (*c*) Ethylenediamine, 10% aq. soln. | Green-brown soln. 1 (*h*), black | (3, 2), Yellow | 3, 2 (*a*), Pink | ...... | ...... | (1) (*a*), Yellow |
| Amines, arom. non-subst., (*a*), Aniline sulfate, satd. aq. soln. | (1), Blue-green | 2, Flesh | 1, Yellow | Violet soln.; red soln. (*d*) | Blue soln., 2, blue-green | 2, Yellow; (*c*), black |
| (*b*) Benzidine, satd. sol. in alc., HAc | 1, Yellow | 2 (*k*), Green-yellow | (3, 2) (*c*), Orange | Violet soln. and 1, yellow | 2 (*c*), Gray | 2 (*c*, *k*), Black |
| (*c*) Diphenylamine, satd. alc. soln. | ...... | 1 (*c*), Black | 1 (*c*), Black | Green, violet brown soln. | Green, then violet soln. | Green soln. and 1, (*c*), black |
| (*d*) β-Naphthylamine-HCl, satd. aq. soln. | (2), Brown-black | 2, Orange | 3, Yellow | Blue soln. and (1), black | 3, 2 (*c*), White | 2, Yellow |
| Amines, arom. subst. (except nitroso) (*a*) *o*-Aminophenol (satd. aq. soln.) | ...... | ...... | 2 (*c*), Black | 1 (*h*), Black | ...... | ...... |
| (*b*) Na 5-Nitrodiphenylamine-2-sulfonate, concd. aq. soln. | ...... | ...... | 1 (*h*) and red-brown soln. | ...... | ...... | (1) (*h*), and red-brown soln. |
| (*c*) *o*-Tolidine, concd. soln. in dil. alc. | Orange soln. (*c*) | 2, Orange | ...... | Green soln. then rose (*c*) | ...... | 2, Yellow |
| Amines, heterocyclic (*a*) Hexamethylene-tetramine, 8% aq. soln. | ...... | ...... | 3, 2 (*a*), Yellow | Orange soln. (*c*) | (3, 2) (*a*), Red | 3, 2 (*a*), Yellow |

Table II (*Continued*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| Amines, nitroso, aliphatic (*a*) Nitrosodiethylamine, aq. soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| Amines, nitroso, arom. (*a*) "Cupferron," dil. aq. soln. ($C_6H_5N.NO.ONH_4$) | ...... | 2 (*c*), Chocolate | 2, Buff | 2 (*d*), Red-brown | ...... | 2 (*c*), Black |
| (*b*) Diphenylnitrosoamine, concd. alc. soln. | 1 (*c*), Red-brown | ...... | 1, Brown | ...... | ...... | 2, Yellow |
| (*c*) Methylphenylnitroso-amine, concd. alc. soln. | ...... | ...... | ...... | Green soln. (*c*, *d*) | ...... | (1) (*c*), Green |
| (*d*) *p*-Nitrosodimethylaniline, concd. aq. soln. | ...... | ...... | (3 ,2) (*c*), Black | 2 (*c*), Black | 2, Black | (3, 2) (*c*), Brown-black |
| (*e*) *p*-Nitroso-aniline, concd. alc. soln. | ...... | ...... | 2, Red | (1) (*c*), Red-brown | ...... | 2, Rose-brown |
| (*f*) α-Nitroso-β-naphthylamine, soln. in alc. and HAc | ...... | ...... | ...... | ...... | ...... | ...... |
| Carbamides, aliphatic (*a*) Alloxan, concd. aq. soln. | ...... | (1) (*c*), White | ...... | Green soln. (*c*, *d*) | Green soln., (*c*) | ...... |
| (*b*) Semicarbazide HCl, concd. aq. soln. | ...... | 1, Orange | ...... | ...... | ...... | ...... |
| (*c*) Urea, concd. aq. soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| Hydrazine, aromatic (*a*) Phenylhydrazine HCl | ...... | (2) Orange (*h*) | 3 (*c*), Black | ...... | ...... | 2, (*c*), Red |
| (*b*) Phenylhydrazine *p*-sulfonate, in dil. NaOH soln. | ...... | ...... | 2, Brown, then black | ...... | ...... | 2 Brown, then black |
| Hydroxy compounds, arom., non-subst. (*a*) Phenol, aq. soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| (*b*) Hydroquinol, satd. aq. soln. | ...... | ...... | (1) (*c*), Black | Green soln.<br>Blue soln. (*c*, *d*) | ...... | Red-brown soln. (*c*) |

TABLE II (*Continued*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| (*c*) Pyrocatechol, concd. aq. soln. | ...... | ...... | (1), Black | Blue-violet soln. | ...... | Red-brown soln. (*c*) |
| (*d*) Resorcinol, concd. aq. soln. | Violet soln. (*c*, *e*) | ...... | ...... | Green soln. and 1, black (*c*, *e*) | ...... | Red-brown soln. (*c*) |
| (*e*) Phloroglucinol, satd. aq. soln. | Rose, then violet (*l*) | ...... | ...... | ...... | ...... | Red-brown soln. (*h*) |
| (*f*) Pyrogallol, concd. aq. soln. | Rose-violet soln. (*c*) | ...... | Red soln. and 1 (*e*), black | Blue soln. | ...... | Red-brown soln. (*c*) |
| Hydroxy-azo compounds, arom., subst., (*a*) Na-*p*-Hydroxy-azobenzene-*p*-sulfonate | ...... | ...... | ...... | ...... | ...... | ...... |
| Ketones, arom. non-subst. (*a*) Benzophenone, concd. alc. soln. | ...... | ...... | (1), Black (*h*) | Violet soln. (*d*) | ...... | ...... |
| Nitrohydroxy compounds, arom. (*a*) 1-Nitro-2-naphthol, concd. alc. soln.• | 1 (*c*), Black | ...... | (3, 2), Maroon | (1) (*c*), Brown-black | ...... | (3, 2) (*c*), Dark brown |
| (*b*) *p*-Nitrophenol, concd. aq. soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| Nitroso compounds, arom., non-subst. (*a*) Nitrosobenzene, concd. soln. in 75% alc. | ...... | (2) (*c*), Black | ...... | ...... | ...... | ...... |
| Nitroso compounds, arom. subst. (*a*) *o*-Nitroso-benzaldehyde (in HAc and alc.) | ...... | ...... | ...... | ...... | ...... | ...... |
| (*b*) *o*-Nitrosochlorobenzene, concd. alc. soln. | ...... | ...... | 2 (*c*), Black | 1 (*c*), Black | ...... | ...... |
| (*c*) *p*-Nitroso-*o*-cresol (concd. soln. in dil. alc.) | 2, (*c*, *h*), Black | 3, 2 (*h*), Red | 2 Yellow | (1) (*c*, *h*), (*d*), Black | (1) (*c*, *h*), Black | 2 (*c*), Red |

TABLE II (*Continued*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| (*d*) Nitroso-R-salt.[a] 1% aq. soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| α-Nitroso β-hydroxy compounds, aromatic (*a*) *o*-Nitrosophenol, in alc. and HAc soln. | ...... | 2 (*c*, *h*), Brown-black | ...... | ...... | ...... | (2) (*c*), Black |
| (*b*) Dinitrosoresorcinol concd. alc. soln. | Rose soln. and 1 Black (*e*), | 3 (*e*), Red-brown | 3 (*e*), Red-brown | ...... | ...... | 3 (*e*, *c*), Brown |
| (*c*) α-Nitroso-β-naphthol, concd. soln. in 50% HAc | 1, (*h*) Brown | (1) (*c*), Red-brown | 3, Red | 1 (*c*, *h*, *d*), Black | 1 (*c*, *h*), Yellow | 2 (*c*, *h*), Red-brown |
| (*d*) α-Nitroso-β-anthrol, in soln. in alc. and HAc | (2), (*e*), Green-black | ...... | ...... | ...... | ...... | ...... |
| (*e*) Nitrosophenanthrol, in alc. and HAc soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| (*f*) α-Nitroso-β,β-anthraquinol, in alc. soln. | ...... | ...... | ...... | ...... | ...... | ...... |
| Nitrosohydroxy compds., aromatic (not α-, β)(*a*) *p*-Nitrosophenol (aq. soln.) | Deep violet soln. (*c*) | 2 (*c*), Orange | 3, Orange | ...... | ...... | (1) (*c*), Red-brown |
| Oximes, aliphatic, (*a*) Acetoxime, concd. aq. soln. | ...... | ...... | ...... | ........ | ...... | ...... |
| (*b*) Dimethylglyoxime, 1% alc. soln. | ...... | ...... | 3, Yellow | ...... | ...... | 2 (*c*, *a*), Bronze, then blue |
| (*c*) Oxalenediamidoxime, concd. aq. soln. | ...... | ...... | 3, Yellow-white | ...... | ...... | (3, 2), Dark brown |
| Oximes, aromatic (*a*) α-Benzildioxime, satd. soln. in alc. | ...... | ...... | 3, Orange (*c*) | ...... | ...... | Green, 3 (*c*, *a*) |
| (*b*) β-Naphthoquinonedioxime-2, 1-sulfonate | ...... | ...... | ...... | ...... | ...... | ...... |

[a] Containing: 1-Nitroso-2-hydroxy-3,6-sodium sulfonate radicals.

TABLE II (*Continued*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| (*c*) Quinone dioxime, dil. soln. in dil. alc. | ...... | ...... | (2) (*c*), Black | ...... | ...... | (3, 2) (*c*) Gray-yellow |
| Oximes, heterocyclic (*a*) Camphoroxime, dil. soln. in dil. alc. | ...... | ...... | ...... | ...... | ...... | ...... |
| (*b*) Carvoxime, concd. soln. in dil. alc. | ...... | ...... | ...... | ...... | ...... | ...... |
| (*c*) α-Furil dioxime, 5% alc. soln. | Red-brown soln. violet soln. (*e*) | (2) (*e*), Yellow | (3,2), Yellow | ...... | ...... | 3 (*c*, *a*), Red-brown |
| Pyridine and deriv. (*a*) Pyridine, concd. aq. soln. | ...... | ...... | 1 (*c*), Yellow-white | ...... | ...... | 3, 2, Yellow (*a*) |
| (*b*) α-Picoline, concd. aq. soln. | ...... | 2 (*c*), Yellow | (3, 2) (*a*), Yellow | ...... | ...... | 2, Yellow (*i*) |
| Quinoline and deriv. (*a*) Quinoline, concd. in dil. alc. | ...... | 2, Orange | ...... | ...... | ...... | 2, Yellow |
| (*b*) 8-Hydroxyquinoline, satd. alc. soln. | ...... | 2, Yellow | 2 (*a*), Yellow | Green soln. (*c*) | (1), (*c*)(*h*), Red | (3, 2) (*k*), Yellow |
| (*c*) 6-Nitroquinoline, concd. aq. soln. | ...... | ...... | (3, 2), Maroon | ...... | ...... | ...... |
| Quinones | | | | | | |
| (*a*) Na β-naphthoquinone-4-sulfonate (aq. soln.) | Green soln.; violet-brown, 2, (*e*) | ...... | ...... | ...... | ...... | 2, Yellow, (*e*) |
| (*b*) Na anthraquinone-β-sulfonate (concd. aq. soln.) | ...... | ...... | ...... | ...... | ...... | ...... |
| Thio compounds aliphatic (*a*) Allyl-thiourea (concd. aq. soln.) | Green, then blue soln. | 2, Flesh | 2, Yellow | Rose, then violet soln. (*c*) | ...... | 2, Yellow |
| (*b*) Ethylmercaptan, 2% aq. soln. | 2 (*c*), Yellow | 2 (*c*), Yellow | 3, Orange | 2 (*d*), Black | ...... | 3, Yellow |
| (*c*) Potassium ethyl xanthate (concd. aq. soln.) | Brown-green, 3,2 (*c*, *h*, *e*) | (3, 2)(*e*), Orange | (3, 2) (*e*), Yellow | 2 Green-black, (*e*) | 1 (*c*, *h*, *e*), Yellow | 3 (*c*, *e*), Orange, then brown |

TABLE II (*Concluded*)

| Reagent | Ru | Rh | Pd | Os | Ir | Pt |
|---|---|---|---|---|---|---|
| (*d*) Thio-urea, in aq. 9% soln. | Green, then blue soln. | 1, Orange | ...... | Deep rose soln., (*d*) | ...... | (3, 2) (*c*), Orange |
| Thio compounds, arom. (*a*) Diphenylthiocarbazide, (concd. soln., in 5% alc.) | Green-brown, (3,2) (*c*) | (3, 2) (*c*), Red-brown | 3, Red | 3 (*d*), Green | 3, Yellow-white | 3, Orange |
| (*b*) Diphenyl-thio-urea, concd. alc. soln. | 2, Orange, then brown (*c*) | 2, Cream (*i*) | 2, Cream (*i*) | 2, White (*i*) | 2, Gray-brown (*i*) | Yellow, then black (*c*), (*i*) |
| (*c*) Phenyl-thio-urea, satd. soln. in alc. | ...... | 3, Orange (*c*) | 3, Brown (*c*) | 2, Red-brown | ...... | 3, Orange, (*c*) |
| (*d*) Phenyl-thiohydantoic acid (satd. soln. in very dil. alc.) | ...... | (3, 2) (*c*), Orange | (3, 2) (*c*), Orange | (3, 2) (*c*), Black | ...... | 2 (*c*), Orange |
| (*e*) Thiocarbanilide, satd. alc. soln. | Green soln. (*c*) | ...... | ...... | Rose soln. (*c*) | ...... | ...... |
| Trisazines, aliphatic (*a*) Tetraformaltrisazine, dil. HCl soln. | Red-brown soln. (*c*) | 3 (*a*), Orange, (*i*) | 2, Yellow (*c*) | ...... | ...... | 2 (*a*, *i*), Yellow |

(*a*) In the presence of alcohol.
(*b*) Some precipitation occurs only on evaporation of reagent solution with a concentrated solution of the metal.
(*c*) On boiling.
(*d*) On boiling with potassium osmate.
(*e*) In ammonium hydroxide solution.
(*f*) In excess of reagent, and on standing several hours.
(*g*) Precipitate is soluble in excess of reagent.
(*h*) On standing overnight.
(*i*) Precipitate easily soluble in excess of reagent.
(*j*) In a solution alkaline with sodium hydroxide.
(*k*) In acetic acid solution.
(*l*) After making the solution alkaline with potassium nitrite and then boiling.
(*m*) Precipitate is soluble on boiling.

case of complete precipitation of the metal, the color of its solution is removed. However, it is not necessarily true that, because of the removal of color from the solution by the reagent, the metal has been completely precipitated. In some cases the reaction proceeds slowly and reaches its maximum effect only after the material has stood overnight. Several instances were noted, as will be seen in the footnotes referred to from Tables I and II in which the reaction was quantitative only in the presence of alcohol or by the addition of a compound containing a common ion with the reagent used. As a rule these two factors aid in reducing the solubility of most inorganic compounds of the platinum metals.

In the preceding table, the figure "3" indicates that the metal is precipitated quantitatively from a pure solution of its chloride. This was indicated by the colorless supernatant liquid and proved by filtering and testing portions of the filtrate separately with hydrogen sulfide gas at 80° and with zinc dust. When no precipitate was formed with hydrogen sulfide and no spongy metal that was insoluble in dilute hydrochloric acid was precipitated with zinc dust, the precipitation was complete. The figure "2" indicates that the metal is precipitated qualitatively, that is, although the test detects small quantities of the individual metals, the precipitation is not complete enough to be termed quantitative in the sense implied above. The figure "1" indicates slight precipitation. The figures "3, 2" indicate that the precipitation is quantitative only under the conditions mentioned in the corresponding footnotes. If the figure is enclosed in parentheses, the degree of precipitation indicated is reached only on standing for several hours. The sign .... indicates no reaction.

## Conclusions

From a study of the reactions produced by the action of about 120 compounds, both inorganic and organic, on dilute chloride solutions of the platinum metals, the following conclusions were drawn.

1. In general, the most reactive classes of inorganic compounds, acting with the formation of metallic precipitates are the sulfides, thiosulfates, hydroxides (caustic), halides, certain reducing agents as hydrazine, hydroxylamine and phosphorus and certain metals, as zinc or magnesium, more highly electropositive than platinum. Most of the precipitates are formed in weak hydrochloric acid solutions, but in the case of the reagent hydrazine, an alkaline medium is best.

2. In general, the most reactive types of organic compounds are the alkaloids, oximes, aromatic amines, non-substituted nitrosohydroxy compounds, nitroso aromatic amines, pure hydroxy compounds and aminohydroxy compounds.

3. There is a marked difference in the apparent ease with which these metals act toward both classes of reagents with the formation of insoluble

compounds and definitely colored solutions. The metals arranged according to the number of precipitates or color reactions produced with the total number of reagents tried would fall in the order: *palladium, platinum, rhodium, osmium, ruthenium and iridium,* respectively. This order has no obvious relationship to the order of their atomic weight or atomic number —this being, in terms of their increase, ruthenium, rhodium, palladium, osmium, iridium and platinum. It does, however, tend to show a definite relationship between the number of planetary electrons in the next to the last orbit (the orbit furnishing their "secondary valence") in each metal, to the precipitation of that metal with the formation of complex salts.

In the five-orbit series, ruthenium, rhodium and palladium, there are, respectively, 14, 15 and 16 electrons in the fourth orbit. In the six-orbit series, osmium, iridium and platinum, there are, respectively, 14, 15 and 16 electrons in the fifth orbit. Hence it is safe to assume that, with the exception of iridium, *the nearer the platinum metal approaches its saturation value, in terms of electrons, in the next to its last electronic orbit, the more reactive is that metal toward the formation of coördinated salts.* This assumption has been predicted in special cases, such as the glyoximes, $\alpha$-nitroso-$\beta$-hydroxy compounds and 8-hydroxyquinolines; it is now generalized by this review.

4. Several new color reactions were found which are useful in qualitatively detecting these metals in a pure solution of themselves, these being (A) for ruthenium, a deep violet solution obtained by boiling with phloroglucinol (after the ruthenium solution has been made alkaline with potassium nitrite); a blue solution on warming with allyl-thio-urea, a deep violet solution on warming with *p*-nitrosophenol; (B) for osmium, on warming with aniline sulfate solution; potassium osmate yields a deep rose solution, potassium chloro-osmate yields a violet one; a deep blue solution obtained with $\beta$-naphthylamine hydrochloride, pyrocatechol or pyrogallol; (C) for iridium, a deep blue solution on warming with aniline sulfate; (D) for platinum, a blood-red solution that changes to dark brownish-red on boiling with pyrocatechol or pyrogallol and, when the platinum solution is rendered ammoniacal, the same coloration is produced with resorcinol.

5. Many insoluble compounds were obtained with various new reagents. The adaptability of certain of these to remove the metal from a mixture of the others of the group, thus obtaining a gravimetric separation of the group, is now under investigation.

The author wishes to acknowledge the kind coöperation of Dr. James Lewis Howe, of Washington and Lee University, who suggested the problem, and of Mr. W. B. Sellars of the University of North Carolina, who prepared several of the organic compounds used in the above tests.

## Summary

1. The reaction of many reagents, selected from the principal classes

of both inorganic and organic compounds, upon dilute chloride solutions of the six platinum metals has been studied.

2. These tests were carried out under various conditions of concentration, temperature and degree of acidity, and the results have been tabulated.

3. The degree of completeness of the precipitation was determined in many cases and so noted in the tables given.

4. Several new color reactions have been found which are useful in qualitatively detecting several of the metals when free from large amounts of the others of the group.

5. Theoretical considerations relative to the formation of coördinated salts are discussed.

CHAPEL HILL, NORTH CAROLINA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

# A QUALITATIVE SEPARATION OF THE PLATINUM METALS

BY S. C. OGBURN, JR.[1]

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The analytical separation of the platinum metals presents difficulties that are seldom encountered with the other metals. Their resistance to chemical solution, the volatility, from solution, of the tetroxides of osmium and ruthenium, the interferences they present in a mixture, their catalytic effect in causing the oxidation or reduction of analytical reagents, and the general similarity of their actions towards chemical compounds are but a few of the obstacles that might be mentioned. The actual success of methods of analysis now in general use, composed of both assay determinations and tedious distillation and fractional precipitation procedures, is contingent upon many factors—more than those apparent from a glance—in the steps of the process.

It was with a view of obtaining a short, successive gravimetric separation of the metals, that would be as nearly quantitative as possible, that this investigation was begun.

During a study of their reactions[2] with a large number of organic and inorganic compounds, certain precipitates were obtained that effected the removal of the metals from individual chloride solutions. These were carefully reviewed and tables made showing the nature of the precipitation, that is, whether qualitative or quantitative, and whether the tests were valid in a mixture of the metals of the group. Using the reagents from

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[1] This paper is constructed from a thesis presented to the faculty of the Graduate School of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Ogburn, THIS JOURNAL, 48, 2493 (1926).