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RUTHENIUM AND OSMIUM DERIVATIVES
OF POLYPYRIDYLTRIAZINES

by

Amparo Mirasol Escarrilla

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

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of Science and Technology
Ames, Iowa

1961

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INTRODUCTION

There is a close relationship between the elements in the horizontal series of Group VIII of the periodic table. Likewise, there is a similar relationship between the elements in the vertical series of the same group. These elements differ from each other in the filling of the 3d, 4d, and 5d orbitals. The nine elements of this group represent a miniature periodic table.

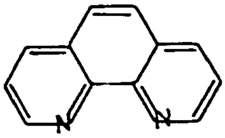
The maximum valency of the elements decrease from the bottom to the top of the vertical series and from the left to the right in a horizontal series. Thus, osmium has the greatest valency and nickel has the least. Table 1 illustrates this property with the fluoride compounds of this group.

Table 1. Fluoride compounds of the group VIII elements

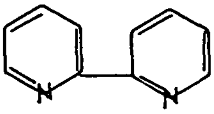
FeF_3	CoF_3	NiF_2
RuF_5	RhF_4	PdF_3
OsF_8	IrF_6	PtF_4

The first vertical series consisting of Fe, Ru, and Os form stable isomorphous complex cyanides. They also form highly colored reversible compounds with 1,10-phenanthroline, bipyridine and terpyridine.

Both the 1,10-phenanthroline,

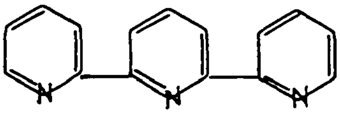


and the 2,2'-bipyridine,

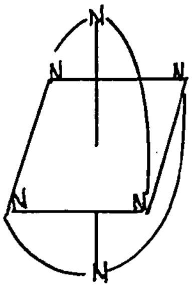


act as a bidentate molecule, the nitrogen atoms in each molecule coordinating with the metal to form a five-membered ring, so-called chelate ring (3).

2,2',2"-Terpyridine,



acts as a tridentate ligand in coupling with metals, all three of the nitrogen atoms being attached to the metal. The two molecules of the base lie at right angles to each other in these metal compounds.



All three members of the iron triad, iron, ruthenium and osmium, have been found to form stable bivalent and trivalent compounds with 1,10-phenanthroline, 2,2'-bipyridine and 2,2',2"-terpyridine. In the case of the 1,10-phenanthroline and bipyridine, the combining ratio is one atom of metal to three of base: $Fe(1,10\text{-phen})_3^{++}$, $Ru(1,10\text{-phen})_3^{++}$, $Os(1,10\text{-phen})_3^{++}$, $Fe(2,2'\text{-bipy})_3^{++}$, $Ru(2,2'\text{-bipy})_3^{++}$, and $Os(2,2'\text{-bipy})_3^{++}$. There are also some evidences of the existence in solution of compounds in which one and two molecules of base are combined with the metal.

In the case of the 2,2',2"-terpyridine, the combining ratio is one to two; these compounds have not been studied as extensively as those of the phenanthroline and bipyridine.

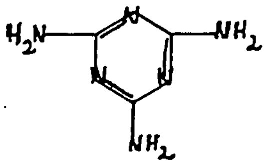
The iron derivatives of 1,10-phenanthroline and 2,2'-bipyridine were first observed by Blau (2). The ferrous compounds are intensely red in color and are oxidized to the ferric compounds which are blue in color. This color change is reversible and the compounds have been used as oxidation-reduction indicators. The reduction potential at which the color changes occur has been measured.

All of the compounds of iron, ruthenium and osmium with 1,10-phenanthroline, 2,2'-bipyridine and 2,2',2"-bipyridine and 2,2',2"-terpyridine are highly colored and have been investigated as oxidation-reduction indicators.

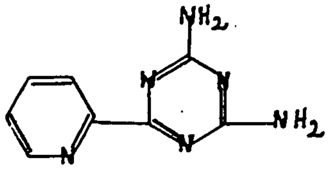
1,10-Phenanthroline and related compounds have been utilized as colorimetric reagents for iron and ruthenium. They have been used to sequester or mask iron in chemical analysis and in certain commercial preparations. They are even of some interest in biochemistry.

The work to be described in this thesis deals with compounds formed by the elements of the iron triad and with pyridyl compounds closely related to the 2,2'-bipyridine and 2,2',2"-terpyridine. The various polypyridyls studied in this work are derivatives of 1,3,5-triazine in which one to three pyridyl groups have been introduced into the triazine ring in such position as to make chelate ring formation with metal atoms possible. These pyridyl-substituted triazines were first prepared by Dr. Francis Case (8) of Temple University. They have the following structures:

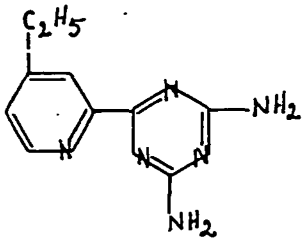
2,4,6-Triamino-1,3,5-triazine-(Melamine)



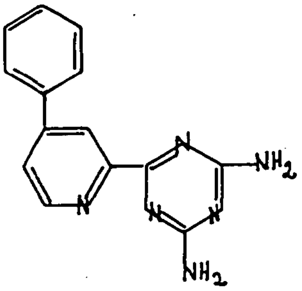
2,4-Diamino-6-(2'-pyridyl)-s-triazine



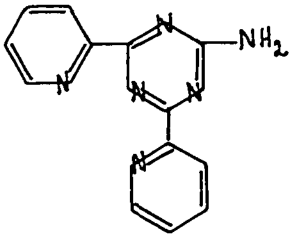
Diamino-4'-ethyl-2'-pyridyl-s-triazine



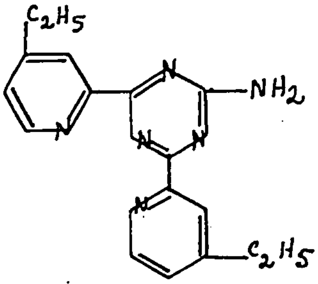
Diamino-4'-phenyl-2'-pyridyl-s-triazine



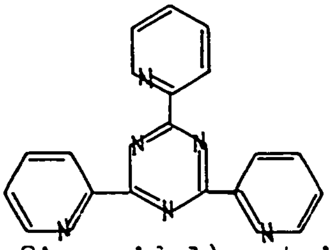
2-Amino-4,6-bis(2'-pyridyl)-s-triazine



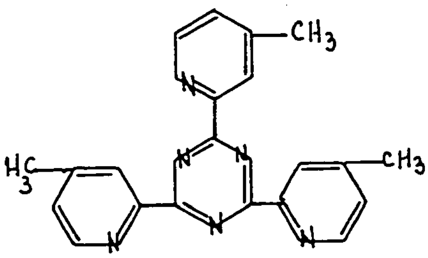
2-Amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine



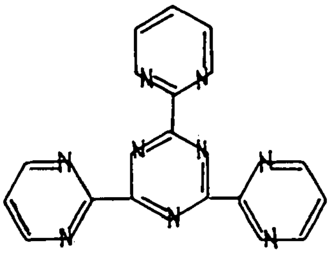
2,4,6-Tris(2'-pyridyl)-s-triazine (TPTZ)



2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine



Tripyrimidyl-s-triazine



The iron derivatives of these compounds except those formed with 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine and tripyrimidyl-s-triazine were studied by Buchanan, Diehl and Smith (5) who recorded their spectra, combining ratios, and molar extinction coefficients. The nature of the iron derivative of 2,4,6-tris(2'-pyridyl)-s-triazine was investigated by Collins, Diehl and Smith (12). They studied also the use of 2,4,6-tris(2'-pyridyl)-s-triazine as a colorimetric reagent for the determination of iron.

This thesis extends the study of these compounds to the other members of the iron triad, namely ruthenium and osmium, and the use of their derivatives as oxidation-reduction indicators.

PART I. IRON COMPOUNDS

Historical Background

The Austrian chemist, Fritz Blau (2), was the first to synthesize 1,10-phenanthroline and 2,2'-bipyridine. He observed that these compounds form highly colored compounds with ferrous iron. At a considerably later period these compounds were utilized as colorimetric reagents for the determination of iron.

The ferrous salts of 1,10-phenanthroline and 2,4'-bipyridine have been observed to be oxidized reversibly to the corresponding ferric compounds. The system,

$$Fe(1,10\text{-phen})_3^{+++} + e^- = Fe(1,10\text{-phen})_3^{++}$$

has a formal reduction potential of 1.06 volts as reported by Hume and Kolthoff (25). Smith and Richter (27,29) have reported the formal potential of the iron tris(2,2'-bipyridine) system as 0.97 volt. This compound has been used also as an oxidation-reduction indicator.

The iron(II) derivative of 2,2',2"-terpyridine has an intense purple color and has been used in the colorimetric determination of iron in sea water and in marine plankton (13). It is oxidized to a green ferric compound but the latter passes readily back to the iron(II) state. The formal reduction potential has been reported to be 0.927 volt (22).

The iron derivatives of various pyridyl-substituted-s-triazines were studied by Buchanan, Diehl and Smith (5). Iron and these dipyridyl and tripyridyl compounds react in the ratio of one to two. The third pyridyl group of the tripyridyl-s-triazine compounds does not become attached to the iron atom. One triazine compound in particular, 2,4,6-tris(2'-pyridyl)-s-triazine, proved to be a particularly good reagent for the spectrophotometric determination of iron and was investigated in detail by Collins, Diehl and Smith (12). The ferrous derivative, $Fe(2,4,6\text{-tris}(2'\text{-pyridyl})\text{-s-triazine})_2^{++}$, is intensely blue in color, the molar extinction coefficient being 22,600 at 593 mμ, the wavelength of maximum absorption. The ferrous derivative is extractable into nitrobenzene. Applications of this reagent were developed for the determination of very small amounts of iron in sea water (10), in limestone, silicates and refractories (12), and in wine (11).

In the present work, the knowledge of the iron derivatives of various pyridyl-substituted triazines is extended by an investigation of their oxidation-reduction characteristics. The behavior of two triazines not earlier available is also reported.

The formal reduction potential of the ferrous derivative with 1,10-phenanthroline was first determined by Walden, Hammett, and Chapman (32) and modified later by Hume and

Kolthoff (25). They used the potentiometric method by employing a potentiometer, and a gold and saturated quinhydrone electrodes in 1 M sulfuric acid. The reduced form of the indicator whose potential is to be studied is titrated with ceric sulfate as oxidizing agent and the potentials are read as small amounts of the titrant are added.

The colorimetric-potentiopoised solution method was devised by Smith and Banick (28). The colorimetric formal reduction potentials of some of the iron(II) compounds of the 1,10-phenanthrolines were determined by preparing potentiopoised solutions from vanadyl chloride. The formal potentials of the vanadyl-vanadate system in 1 F to 8 F sulfuric acid have been studied by Smith and Richter (29). For the half cell reaction,

$$VO_3^- + 4\ H^+ + e^- = VO^{++} + 2\ H_2O$$

the E^o = 1.10 volts. The solutions contained an equimolar portions of vanadium(IV) and vanadium(V) mixed together. The potential of the vanadyl-vanadate couple will depend upon the hydrogen ion concentration, as may be seen from the above equation. That is, an increase in the acidity will affect the potential according to

$$E = E^o + 0.059 \log \frac{(VO_3^-)(H^+)^4}{(VO^{++})}$$

The term potentiopoised is used to refer to a solution which resists a change in potential upon the addition of an oxidizing or reducing agent, and is analogous to acid-base buffer systems. Such a solution is "buffered" with respect to potential rather than to hydrogen ion concentration. In this way, the addition of another oxidation-reduction system, such as an indicator, does not change the potential of the vanadyl-vanadate couple. Thus one can determine the E^{o} of an indicator by adding a few drops of the indicator solution to a series of potentiopoised solutions of varying acid concentrations and observing the point at which the indicator changes color.

Determination of Formal Reduction Potentials of the Iron(II) Compounds by the Colorimetric Method

Materials

2,4,6-Triamino-1,3,5-triazine-(Melamine) Obtained from the American Cyanamid Company. M.P.: 252-254° C. A 1.000×10^{-3} M solution in water containing a few drops of hydrochloric acid was prepared.

2,4-Diamino-6-(2'-pyridyl)-s-triazine Obtained from F.Case. M.P.: 297° C. (5) A 1.0273×10^{-3} M solution in water containing a little hydrochloric acid was prepared.

Diamino-4'-ethyl-2'-pyridyl-s-triazine Obtained from F.Case. M.P.: 246-247° C. A 1.000×10^{-3} M solution in water containing a few drops of hydrochloric acid was prepared.

Diamino-4'-phenyl-2'-pyridyl-s-triazine Obtained from F.Case. M.P.: 264-265° C. A 1.008 x 10^{-3} M solution in water was prepared with a few drops of hydrochloric acid.

2-Amino-4,6-bis(2'-pyridyl)-s-triazine Obtained from F.Case. M.P.: 306-307° C. A 1.024 x 10^{-3} M solution in water containing a few drops of hydrochloric acid was prepared.

2-Amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine Obtained from F.Case. M.P.: 334-335° C. A 1.013 x 10^{-3} M solution in water containing a few drops of hydrochloric acid was prepared.

2,4,6-Tris(2'-pyridyl)-s-triazine This reagent was obtained from The G. Frederick Smith Chemical Co. The melting point was found to be 242-243° C. The melting point was reported by Case (8) to be 244-245° C. and by Collins (9) to be 242-243.5° C. A 1.0005 x 10^{-2} M solution of the compound in water containing a little hydrochloric acid was prepared. Aliquot portions were taken from this solution to prepare more dilute solutions.

2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine Obtained from F.Case. M.P.: 197-198° C. A 1.167 x 10^{-3} M solution in water containing a little hydrochloric acid was prepared.

Tripyrimidyl-s-triazine Obtained from F.Case. M.P.: about 450° C. A 1.000 x 10^{-3} M solution in water was prepared containing a few drops of hydrochloric acid.

1,10-Phenanthroline This reagent was obtained from The G. Frederick Smith Chemical Co.

Hydroxylammonium chloride A ten per cent solution of hydroxylammonium chloride was prepared whenever needed so that a fresh solution was always used.

Preparation of the iron derivatives of polypyridyls

Derivatives of iron(II) with the pyridyl-substituted triazines were prepared by taking 1 ml. of 1.00 x 10^{-3} M solutions of iron and adding 3 ml. of 1.0 x 10^{-3} M pyridyl-substituted triazine. Two ml. of 10 per cent hydroxylammonium chloride were added to reduce the iron. Each of the solutions were treated with 10 ml. of 2 M sodium acetate-2 M acetic acid buffer, the pH adjusted to 6 with 5 M sodium hydroxide, and the mixture diluted to the mark of the 50 ml. volumetric flask.

Recording of spectra and molar extinction coefficient

The per cent transmittancy of the above prepared solutions were measured using the Beckman DU Spectrophotometer with a 1 cm. pyrex cell and water as blank.

The spectra in the visible region of these solutions were recorded using the Cary Spectrophotometer Model 12, with a 1 cm. silica cell and water as blank. The spectrum of ferrous tri(4'-methyl-2'-pyridyl)-s-triazine chloride is shown in Figure 1. The molar extinction coefficient is 25,500 at 605 mμ.

Ferrous tripyrimidyl-s-triazine was colorless at this dilution.

No attempt has been made to record the spectra of the iron compounds in the ultraviolet regions as these have already been studied by Buchanan (4). The spectra of some of these compounds and their molar extinction coefficients have also been studied by Buchanan, Diehl and Smith (5).

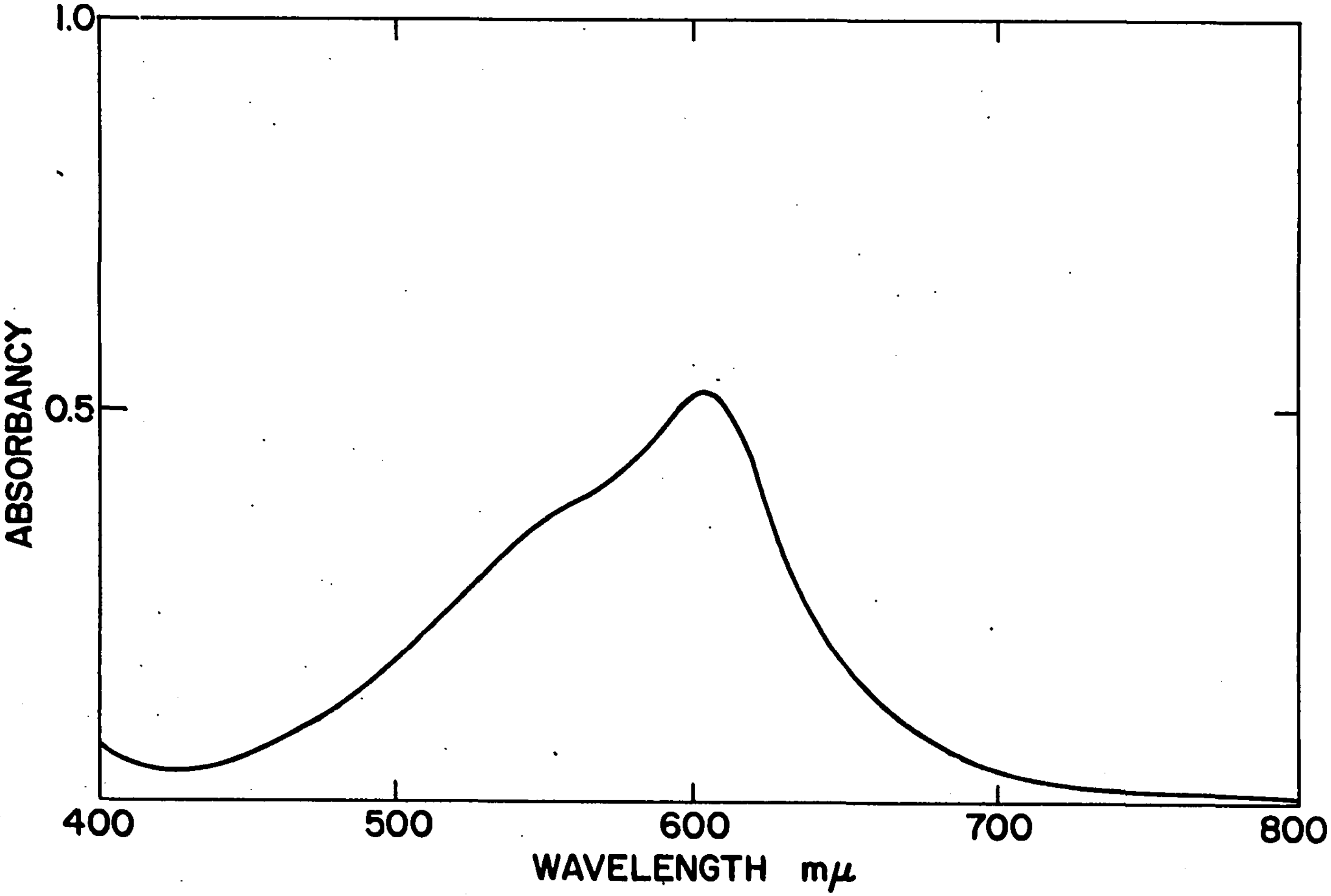
Stability of the iron compounds

In order to determine the stability of the iron(II) compounds of the various pyridyl-substituted triazines, at room temperature and toward light, a series of solutions of these compounds were prepared. Volumes of 1 ml. of 1.00 x 10^{-3} M iron solution in different flasks were treated with 3 ml. of the different bases of concentrations 1.0 x 10^{-3} M, 2 ml. of 10 per cent hydroxylammonium chloride, and 10 ml. of 2 M sodium acetate-2 M acetic acid mixture. The solutions were diluted to 50.0 ml. The per cent transmission of each solution was measured in a 1 cm. pyrex cell with water as blank at the respective wavelengths of maximum absorbance. The measurements were made again after three weeks.

The results showed that the iron derivatives of 2-amino-4,6-bis(4'-ethyl)-2'-pyridyl)-s-triazine, 2-amino-4,6,bis(2'-

Figure 1. The visible spectrum of ferrous 2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine chloride.

Cell length: 1 cm.


1.0
0.5
ABSORBANCY
400
500
600
700
800
WAVELENGTH mμ

pyridyl)-s-triazine and 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine are stable, not decomposing or showing much change due to action of light. The ferrous derivative of 2,4,6-tris(2'-pyridyl)-s-triazine was not stable. The data is shown in Table 2.

Table 2. Stability of iron compounds

No.	Base	Wave length mμ	Readings First per cent T	Readings Second per cent T
1	2-Amino-4,6,-bis(4'-ethyl-2'-pyridyl)-s-triazine	500	66.6	67.1
2	2-Amino-4,6-bis(2'-pyridyl)-s-triazine	500	72.5	71.6
3	2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine	605	37.1	38.0
4	2,4,6-Tris(2'-pyridyl)-s-triazine	595	39.8	66.0

Preparation of potentiopoised solutions

Stock solution: A solution of vanadyl sulfate, $VOSO_4.2H_2O$, was prepared by dissolving 25.0043 grams of material obtained from Fisher Scientific Company, formula weight 190.048, in 360 ml. of 0.5 F sulfuric acid. The blue solution was shaken and allowed to stand overnight. One hundred ml. of this solution was placed in a 250 ml. volumetric flask. Another 100 ml. was treated with 60 grams of ammonium persulfate and warmed in a water bath to oxidize the vanadium to the plus five state. The color changed from blue to yellow. The excess persulfate was destroyed by boiling. The vanadate produced was mixed with the vanadyl solution in the 250 ml. volumetric flask and the blue-green mixture was diluted to volume with 0.5 F sulfuric acid.

Dilute solutions of the desired formal concentration of sulfuric acid were made out of this stock solution, by taking a 5 ml. aliquot, adding the amount of sulfuric acid needed, and diluting the mixture to a volume of 500 ml. with deionized water.

Formal potentials of the potentiopoised solutions

The formal potentials of the prepared potentiopoised solutions were determined by taking the voltage readings of 40 ml. of each of the solutions of the vanadyl-vanadate system in varying formality of sulfuric acid, ranging from 0.01 to 7.0 F sulfuric acid. A Leeds Northrup Type K Potentiometer and galvanometer and a platinum-saturated calomel electrode were used. The readings were taken when the difference in the values between successive readings were within 0.001 of a volt in ten minute interval. The potentials were converted to the hydrogen scale by adding 0.246 volt, the potential of the saturated calomel electrode, to the voltage readings.

The formal potentials of the potentiopoised solutions are given in Table 3. The values found by Smith and Banick (28) are also given for comparison.

A calibration curve was made from the data obtained by plotting the voltage readings in the hydrogen scale, E^0 in volts, against the formality of sulfuric acid. The plot is shown in Figure 2.

Colorimetric method of determination of formal potential of iron(II) derivative

Five ml. portions of each of the potentiopoised solutions were placed in ten ml. test tubes. Five drops of 95 per cent ethyl alcohol were added to each of the solutions and 1 or 2 drops of solutions approximately 0.001 M in the iron compounds were added. The mixtures were shaken and after 1 minute the changes in color were noted. Interpolation between values of formal potentials of the solutions where the greatest change in color occurred were made.

The results of the experiment are shown in Table 4.

Iron Derivatives of Polypyridyltriazine as Oxidation-reduction Indicators

An attempt was made to use the iron derivatives of the polypyridyltriazine as oxidation-reduction indicators. Titrations of standard solutions of ferrous ethylenediammonium

Table 3. Formal potentials of potentiopoised solutions

Formality H_2SO_4	E^o(Smith) volts vanadyl chloride	E^o(found) volts vanadyl sulfate	Formality H_2SO_4	E^o(Smith) volts vanadyl chloride	E^o(found) volts vanadyl sulfate
0.01	-	0.84_2	3.5	1.120	1.12_7
0.1	0.910	0.91_1	3.75	-	1.13_6
0.25	-	0.94_8	4.0	1.143	1.14_5
0.5	0.975	0.98_3	4.25	-	1.16_1
0.75	0.993	0.99_8	4.5	1.182	1.16_9
1.0	1.008	1.02_0	4.75	-	1.18_1
1.25	-	1.02_8	5.0	1.193	1.18_9
1.5	1.030	1.04_3	5.25	-	1.19_5
1.75	-	1.05_7	5.5	1.211	1.20_0
2.0	1.056	1.06_6	5.75	-	1.20_6
2.25	-	1.08_2	6.0	1.226	1.21_0
2.5	1.089	1.08_7	6.5	-	1.22_8
2.75	-	1.10_0	7.0	-	1.24_0
3.0	1.103	1.10_4			
3.25	-	1.11_9			

sulfate and sodium arsenite in 1 M perchloric acid were made. For the purpose of comparison, similar titrations were run using ferrous 1,10-phenanthroline sulfate as indicator. The procedures and results are given in the following pages.

Figure 2. Calibration curve for the potentiopoised solutions.

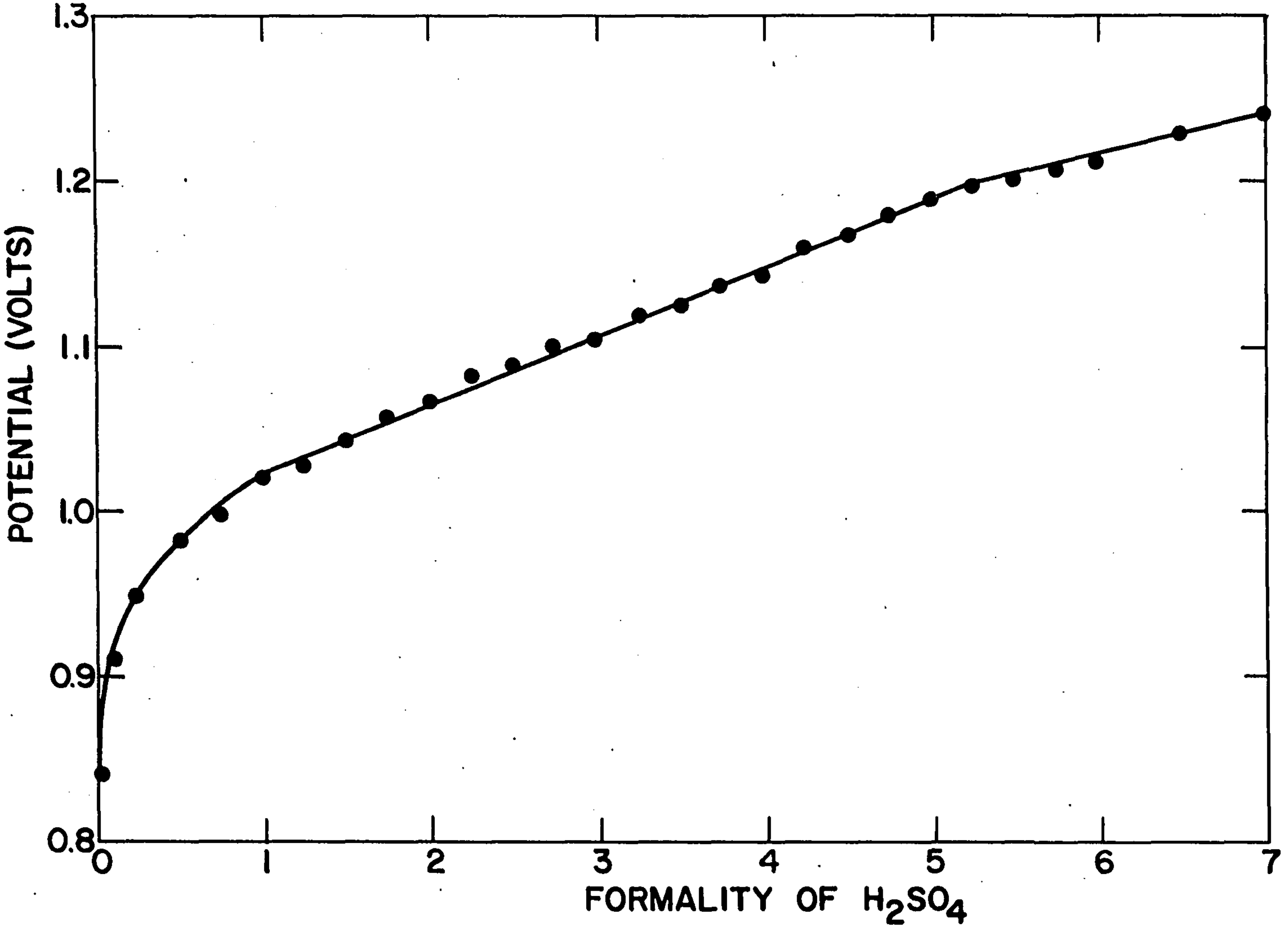

POTENTIAL (VOLTS)
1.3
1.2
1.1
1.0
0.9
0.8
0
1
2
3
4
5
6
7
FORMALITY OF H_2SO_4

Table 4. Formal reduction potentials of the iron(II) compounds of 1,10-phenanthroline and related compounds

Chemical name of compound	E^o(previous) potentiometric method	Formality H_2SO_4	E^o(found) colorimetric method	Color change reduced-oxidized
1,10-Phenanthroline chloride		2.0	1.06_8	orange-yellow
1,10-Phenanthroline sulfate	1.06 (27)	2.0	1.06_6	orange-yellow
2,4,6-Tris(2'-pyridyl)-s-triazine chloride		2.5	1.08_5	blue-yellow
2,4,6-Tris(2'-pyridyl)-s-triazine iodide		2.5	1.08_9	blue-yellow
2-Amino-4,6-bis(4-ethyl-2'-pyridyl)-s-triazine chloride		2.25	1.07_0	purple-colorless
2-Amino-4,6-bis(2'-pyridyl)-s-triazine chloride		3.0	1.09_7	purple-yellow
2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine chloride		3.0	1.10_3	blue-colorless

Sulfatoceric acid A solution of sulfatoceric acid was prepared by dissolving 99.7022 grams of ceric sulfate in 168 ml. of concentrated sulfuric acid. This solution was diluted with 100 ml. of water, stirred, and allowed to stand. Another 100 ml. of water was added, the solution stirred and allowed to stand, and this was repeated until a volume of 1 liter was obtained. The mixture was allowed to stand for 5 days, after which it was filtered.

Dilute solutions were prepared from this stock solution to make the ceric sulfate 1 M in sulfuric acid. The sulfatoceric acid solutions were standardized against ferrous ethylenediammonium sulfate using ferrous 1,10-phenanthroline sulfate as indicator.

Sodium arsenite The sodium arsenite solution was prepared from arsenious oxide, National Bureau of Standard sample No. 83 a, by dissolving 9.8900 grams in 80 ml. of 1 N sodium hydroxide. The solution was neutralized with sulfuric acid until slightly acid to litmus. The solution was diluted to a volume of 2 liters.

This solution was standardized by titrating 25 ml. aliquot with standard 0.0574 M sulfatoceric acid in 1 M sulfuric acid, in the presence of 2 drops of 0.01 M osmium tetroxide and using ferrous 1,10-phenanthroline sulfate as indicator. The concentration of the sodium arsenite solution was found to be 0.1002 M.

Titration of ferrous ethylenediammonium sulfate

About 0.50 gram of standard ferrous ethylenediammonium sulfate was dissolved in 25 ml. of deionized water and 25 ml. of 2 M perchloric acid. Three drops of 0.002 M ferrous bis-(2,4,6-tri(2'-pyridyl)-s-triazine) iodide was used as one of the indicators. The solution was titrated with 0.0574 M sulfatoceric acid in 1 M sulfuric acid. The color change was from dark blue, which disappeared early, through grayish-green to a dark yellow color. The end point was taken as the abrupt appearance of a dark yellow color. The titration was compared with one using 3 drops of 0.002 M ferrous 1,10-phenanthroline sulfate as indicator.

Another titration was studied using a solution indicator of ferrous bis(2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine chloride which was prepared as follows: Twenty ml. of 1.84 x 10^{-3} M iron solution was reduced with 5 ml. of 10 per cent hydroxylammonium chloride. Twenty-five ml. of 1.0012 x 10^{-2} M 2,4,6-tris(2'-pyridyl)-s-triazine was added to the mixture which had a very intense blue color. Four drops of this solution indicator were used in the titration, the end point changing from deep blue, through grayish-green to yellow. The appearance of a dark yellow color was taken as the end point. The results are shown in Table 5.

Table 5. Titration of ferrous ethylenediammonium sulfate using ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide as indicator

Indicator	Weight used(g)	Ml. 0.0574 M $Ce(SO_4)_2$ used	Weight found(g)	Per cent relative error	Average per cent relative error
$Fe(TPTZ)_2I_2$	0.5010	22.90	0.5015	+0.10	
	0.5004	22.85	0.5004	0.00	
	0.5010	22.85	0.5004	-0.12	-0.01
$Fe(Me\text{-}pyr)_2Cl_2$	0.5005	22.90	0.5015	+0.20	
	0.5010	22.90	0.5015	+0.10	
	0.5006	22.85	0.5004	-0.04	+0.06
$Fe(1,10\text{-}phen)_3SO_4$	0.5001	22.80	0.4993	-0.16	
	0.5015	22.87	0.5009	-0.12	
	0.5000	22.85	0.5004	+0.08	-0.03

Titration of sodium arsenite

Twenty-five ml. of standard solution of sodium arsenite which was 0.1002 M, was treated with 2 drops of 0.01 M osmium tetroxide as catalyst, twenty-five ml. of 2 M perchloric acid and 3 drops of 0.002 M ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide. The titration was compared with one using ferrous 1,10-phenanthroline sulfate as indicator. The results of the titrations with 0.0574 M sulfatoceric acid in 1 M sulfuric acid are given in Table 6.

Table 6. Titration of sodium arsenite using ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide

Indicator	Ml. 0.0574 M $Ce(SO_4)_2$ used	Molarity $Ce(SO_4)_2$ found	Per cent relative error	Average per cent relative error
$Fe(TPTZ)_2I_2$	43.70	0.1003	+0.10	
	43.73	0.1004	+0.20	
	43.73	0.1004	+0.20	+0.16
$Fe(1,10\text{-phen})_3SO_4$	43.75	0.1005	+0.30	
	43.75	0.1005	+0.30	
	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.20

Discussion

Of the compounds of iron with pyridyl-substituted triazines not investigated before, the ferrous 2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine gave the highest molar extinction coefficient of 25,500 at 605 mμ. The visible spectrum of this compound is shown in Figure 1. The ferrous derivatives of 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine, 2-amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine, 2-amino-4,6-bis(2'-pyridyl)-s-triazine are stable to light and ordinary room conditions in three weeks time.

In the titration experiment with the iron(II) indicators, it was observed that the dark blue solutions of ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide, and ferrous 2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine chloride decolorized before the expected end point as compared with the titrations using ferrous 1,10-phenanthroline sulfate as indicator, leaving only a pale blue tinge which gradually changed through gray to yellow. The appearance of the dark yellow tinge, however, was distinct enough to be observed.

The results of the titration indicated that the iron(II) compounds of the polypyridyltriazines gave satisfactory end points, the average relative error being -0.01 per cent, using ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide for the titration of ferrous iron, while ferrous 2,4,6-tris

(4'-methyl-2'-pyridyl)-s-triazine gave an error of +0.06 per cent. The relative error of titration of sodium arsenite with ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide was +0.16 per cent.

PART II. RUTHENIUM COMPOUNDS

Historical Background

In 1947, Dwyer, Humpoletz and Nyholm (23) prepared ruthenium tris-1,10-phenanthroline by refluxing an aqueous solution of potassium pentachlorohydroxyruthenate with 1,10-phenanthroline resulting in a greenish-brown solution to which they added hypophosphorous acid neutralized with caustic soda. This solution was heated and filtered and potassium iodide was added. The solid formed was crystallized from water. The perchlorate salt was prepared by adding perchloric acid to the hot filtrate after refluxing the mixture. The crystals were purified from water. They found the reduction potential to be 1.29 volts in 1 N nitric acid.

In 1949, Dwyer and Gyarfas (21) found the redox potential of ruthenium tris-1,10-phenanthroline to be 1.17 ± .003 volts. At equal acid concentrations, they found the potential of the 1,10-phenanthroline compounds higher than the 2,2'-bipyridyl analogues.

Burstall (6) in 1936, prepared tris-2,2'-bipyridylruthenous chloride hexahydrate, $Ru(2,2'\text{-bipy})_3Cl_2.6H_2O$, by heating ruthenium trichloride and 2,2'-bipyridyl at a temperature of 260° C. for three hours. The mass was cooled and extracted with benzene. The residue was dissolved in water, filtered from any insoluble material and crystallized by evaporation. It was recrystallized from hot water and dried over sulfuric acid. He observed that tetrapyridine is formed as a by-product.

In 1942, Steigman, Birnbaum and Edmonds (30) used the ruthenium bipyridyl as an oxidation-reduction indicator. Dwyer, Humpoletz and Nyholm (23) found a standard reduction potential of 1.33 volts for the system,

$$\underset{\text{blue}}{Ru(2,2'\text{-bipy})_3^{+++}} + e^- = \underset{\text{red}}{Ru(2,2'\text{-bipy})_3^{++}}$$

They found that the complete oxidation to the unstable blue Ru(III) required the use of a nitrate or sulfatoceric acids.

In 1949, Dwyer (15) prepared the ruthenium derivative of 2,2'-bipyridine by refluxing an aqueous alcoholic mixture of potassium pentachlorohydroxy ruthenate, the organic base and sodium hypophosphite. The orange needles were recrystallized from hot water and dried over sulfuric acid. They found the formal potential to be 1.257 volts.

In Part II of this work, the ruthenium derivatives of various pyridyl-substituted triazines are described. The nature and composition of the ruthenium 2,4,6-tris(2'-pyridyl)-s-triazine are reported and its properties compared with the analogous compound of iron, already studied by Buchanan, Diehl and Smith (5) and Collins, Diehl, and Smith (12).

Preparation of Ruthenium Derivative of Tripyridyl-s-triazine

Materials

The different pyridyl-substituted triazines used in the preparation of the ruthenium compounds have been described in the Introduction and in Part I, iron compounds.

Ruthenium chloride

A stock solution of ruthenium chloride was prepared by dissolving 4.0096 grams of ruthenium chloride, obtained from the American Platinum Metals Company, in 200 ml. of 10 per cent hydrochloric acid.

The ruthenium chloride solution was standardized (1) as follows: Four ml. aliquot of the stock solution were pipetted into previously ignited and weighed porcelain boats. The solutions were carefully evaporated under an infra red lamp to almost dryness. They were placed in a silica tube, about 2 feet long, and hydrogen gas was passed through to displace the air from the tube for about 20 minutes. The tube was gradually heated, electrically, to red heat for about 30 minutes, to reduce the ruthenium chloride to metallic ruthenium. The heating was stopped and the boat was cooled in a hydrogen atmosphere to room temperature. The metal was weighed to constant weight.

The stock solution was found to contain 7.037 mg. of ruthenium per ml. of solution, or 6.920 x 10^{-2} M in ruthenium. Dilute solutions were prepared from this stock solution.

Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride

A solution of 1.0004 grams of ruthenium chloride in water was treated with 10 grams of hydroxylammonium chloride. To this solution, 3.503 grams of 2,4,6-tris(2'-pyridyl)-s-triazine was added and a few drops of 6 N hydrochloric acid. The pH of the solution was adjusted to 5 with 5 M sodium hydroxide. The solution was boiled for 4 hours in a water bath. The excess tripyridyl triazine was filtered off. The filtrate containing the ruthenium tripyridyl-s-triazine chloride was evaporated down to saturation point after which the crystals formed were filtered off. The crystals were again dissolved in a little water and evaporated to almost dryness in a water bath. This was cooled over ice, any liquid present was decanted. The crystals were washed with water and the excess chloride was extracted with ether. The ruthenium tripyridyl-s-triazine chloride crystals were dried over calcium chloride in a vacuum desiccator. Melting point: 212-214° C.

The ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride was analyzed for ruthenium by direct ignition as described below and for chloride as described below. Found:

Ru 12.53, Cl 9.25. Calculated for Ru(tripyridyl triazine)$_2$ Cl$_2$: Ru 12.77, Cl 8.90.

The ruthenium was determined by placing about 50 mg. of the compound in a previously ignited and weighed porcelain boat. The boat was then placed in a silica tube in the furnace and hydrogen gas was passed through it for 20 minutes. The tube was heated for 30 minutes to about 800° C. and then cooled in the hydrogen stream and weighed as ruthenium metal.

For the chloride determination, about 50 mg. of the compound was dissolved with water and passed through a column of IR-120 in the hydrogen form. The colorless eluate of hydrochloric acid obtained was titrated with standard 0.0100 N silver nitrate, using 5 ml. of 1 per cent dextrin and the sodium salt of dichlorofluorescein as indicator (14).

Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate

An IR-400 perchlorate column was prepared by passing about 500 ml. of 2 M solution of sodium perchlorate dropwise through a column of IR-400 in the chloride form. The column was washed thoroughly with deionized water to remove any excess sodium and chloride ions. The presence of chloride was tested with silver nitrate upon acidifying the eluate with nitric acid. The sodium ions were tested by the use of the flame test.

Some ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride crystals prepared as above were dissolved in a little water and stirred overnight with the resin prepared as described above. The ruthenium solution with the resin were placed in the column and the perchlorate solution was allowed to flow dropwise through the column. The column was then rinsed with deionized water. The solution of ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate which passed through the column and the rinsings were evaporated to dryness in a water bath. The crystals, presumably Ru(tripyridyltriazine)$_2$(ClO$_4$)$_2$, were washed with ether and dried in the vacuum desiccator over calcium chloride. The crystals started decomposing at about 120° C., turned brown and were carbonized at 260° C., finally turned white at 300° C. Melting point may be above this temperature.

Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide

To a solution of 1.0000 gram of ruthenium chloride in a little water was added 10 grams of hydroxylammonium chloride. To this solution, 3.5006 grams of 2,4,6-tris(2'-pyridyl)-s-triazine were added and a few drops of 6 N hydrochloric acid. The mixture was diluted to about 300 ml. with deionized water. The pH of the solution was adjusted to 5 with 5 M sodium hydroxide. The mixture was heated over a boiling water bath for 4 hours. Any excess tripyridyltriazine was filtered off. The ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride solution was again heated to boiling and

6 grams of potassium iodide dissolved in water was added to it. The solution was evaporated down to saturation point. These crystals were purified by extracting the excess potassium iodide with ether using soxhlet extractor for about 30 hours. The crystals of ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide were dried over calcium chloride in a vacuum desiccator. The dark brown, prismatic crystals were red by reflected light. The compound started to decompose at 120° C., turning black at a higher temperature.

As in the analysis of ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride, the ruthenium bis(2,4,6-tri-(2'-pyridyl)-s-triazine) iodide was analyzed for ruthenium by direct ignition over an atmosphere of hydrogen and the iodide was analyzed by the adsorption indicator method. Found: Ru 10.40, I 25.90; calculated for Ru(tripyridyl-triazine)$_2$I$_2$: Ru 10.38, Cl 25.83.

The determination of iodide was carried out by dissolving about 30 mg. of the sample in water and passing the solution through a column of IR-120 resin in the hydrogen form. The colorless hydroiodic acid obtained was titrated with 0.0100 N silver nitrate using eosin indicator.

Nature of the Ruthenium 2,4,6-Tris(2'-Pyridyl)-s-Triazine Chloride

In order to compare the properties of the ruthenium tripyridyl-s-triazine compounds in solution with those of the solid materials in the preceeding section, a study was made to see if the compounds were the same. Another purpose of this work was to see if the system can be used for the spectrophotometric determination of ruthenium.

Variations with pH

A series of solutions containing the same reagents in the same concentrations but differing only in pH, were prepared by mixing the following:

5 ml. of a solution which was 1.0197×10^{-3} M in ruthenium

5 ml. of 1.0012×10^{-2} M 2,4,6-tris(2'-pyridyl)-s-triazine

4 ml. of 10 per cent hydroxylammonium chloride

10 ml. of 20 per cent sodium chloride

The pH of these solutions were adjusted with 5 M sodium hydorxide and 5 M hydrochloric acid to cover the range 1 to 10. The mixtures were heated in a boiling water bath for two hours. When cold, the solutions were diluted to the 50 ml. mark with deionized water and the per cent transmittancy was read using the Beckman DU Spectrophotometer, a 1 cm. pyrex cell and a blank. All the per cent transmittancy were read at the maximum absorbance of the respective solutions.

A tabulated data and results are given in Table 7. The plot of the change in absorbancy with pH is shown in Figure 3.

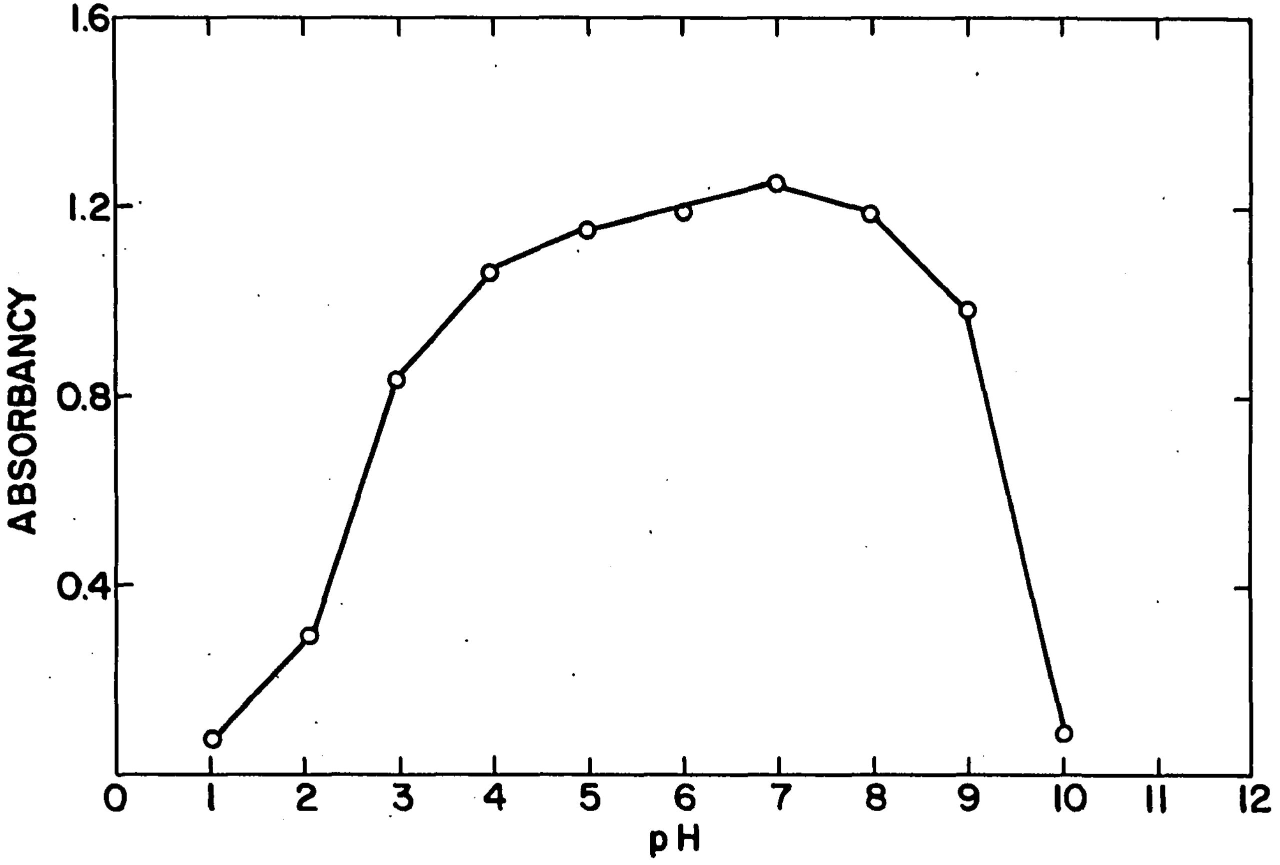
The other mixtures decomposed as the pH was taken above pH 10. The best working range is between pH 4.5 to 8.5 where the compound is relatively stable.

The absorbance maximum shifts to the lower wave length as the pH increases and becomes almost constant at 506 mμ from pH 5 to 10.

Table 7. Variations with pH of ruthenium tripyridyl triazine

No.	pH	Color	Per cent T	Absorbancy	Wave length mμ	Molar extinction coefficient
1	1.02	light violet	86.8	0.0615	540	603
2	2.09	dark violet	52.1	0.2832	538	2,777
3	2.99	purple	14.6	0.3356	530	8,195
4	3.99	purple	9.0	1.0458	510	10,256
5	5.00	purple	7.0	1.1549	506-510	11,326
6	6.00	purple	6.5	1.1871	506	11,641
7	7.00	purple	5.7	1.2441	506-510	12,201
8	8.05	purple	6.4	1.1938	506	11,707
9	9.05	red orange	10.4	0.9830	506	9,640
10	9.99	red orange	8.2	0.0862	506	845

Figure 3. Variation with pH of ruthenium tripyridyl triazine chloride.


1.6
1.2
0.8
0.4
ABSORBANCY
0
1
2
3
4
5
6
7
8
9
10
11
12
pH

Conformity to Beer's Law

A calibration curve was made by preparing a series of solutions containing varying amounts of ruthenium chloride, containing 1.0197 x 10^{-3} M in ruthenium. To the solutions, 2 ml. of 10 per cent hydroxylammonium chloride, 25 ml. of 1.0000 x 10^{-3} M 2,4,6-tris(2'-pyridyl)-s-triazine, and 10 ml. of 20 per cent sodium chloride were added. The pH of the solutions was adjusted to about 6 with 5 M sodium hydroxide and diluted to the neck of a 50 ml. volumetric flask. The mixtures were heated in a constant boiling water bath for two hours, cooled and diluted with water to the mark.

The per cent transmittancy was read at 506 mμ, using water as blank and a 1 cm. pyrex cell. The molar extinction coefficient obtained from this graph was 11,600. This calibration curve shows that small amounts of ruthenium can be determined using tripyridyl triazine as a colorimetric reagent. Beer's law is followed as shown by the straight line plot. The data is given in Table 8., and the plot of the absorbancy versus the concentration of ruthenium is given in Figure 4.

Spectrophotometric titration

To determine the ratio of ruthenium to 2,4,6-tris-(2'-pyridyl)-s-triazine in the compound, a spectrophotometric titration was made using 4 ml. of 1.0005 x 10^{-3} M 2,4,6-tris-(2'-pyridyl)-s-triazine, 2 ml. of 10 per cent hydroxylammonium

Table 8. Calibration curve for ruthenium tripyridyl triazine chloride

No.	Ml. Ru	=○= Ru in 50 ml. x 10^{+5} M	Per cent T	Absorbancy
1	0	0	99.3	0.0031
2	1	2.04	58.8	0.2306
3	2	4.08	33.9	0.4698
4	3	6.12	20.5	0.6882
5	4	8.16	11.5	0.9393
6	5	10.20	6.8	1.1675

chloride, 5 ml. of 20 per cent sodium chloride, and varying amounts of ruthenium chloride solutions which was 1.73 x 10^{-4} M in ruthenium. The pH of the solutions were adjusted to 6 with 5 M sodium hydroxide. The mixtures were heated in a constant boiling water bath for 2 hours, cooled to room temperature and diluted to the 50 ml. mark with deionized water. The per cent transmission were read using a 1 cm. pyrex cell, at 506 $m\mu$ and water as blank.

The plot of absorbancy vs. the ml. of ruthenium solution is shown in Figure 5. The curve is rounded in their neighborhood of the end-point and extrapolation of the linear portions give an end-point at the ratio Ru to triazine of 1 to 2.02. A ratio of 1 to 2 gives the best explanation of the data but it is apparent that the formation constant is not great and that a significant excess of triazine is needed to convert the ruthenium to the colored compound. The data is given in Table 9.

Figure 4. Calibration curve for ruthenium bis(2,4,6-tri-(2'-pyridyl)-s-triazine chloride.

Wavelength: 506 mμ Cell length: 1 cm.

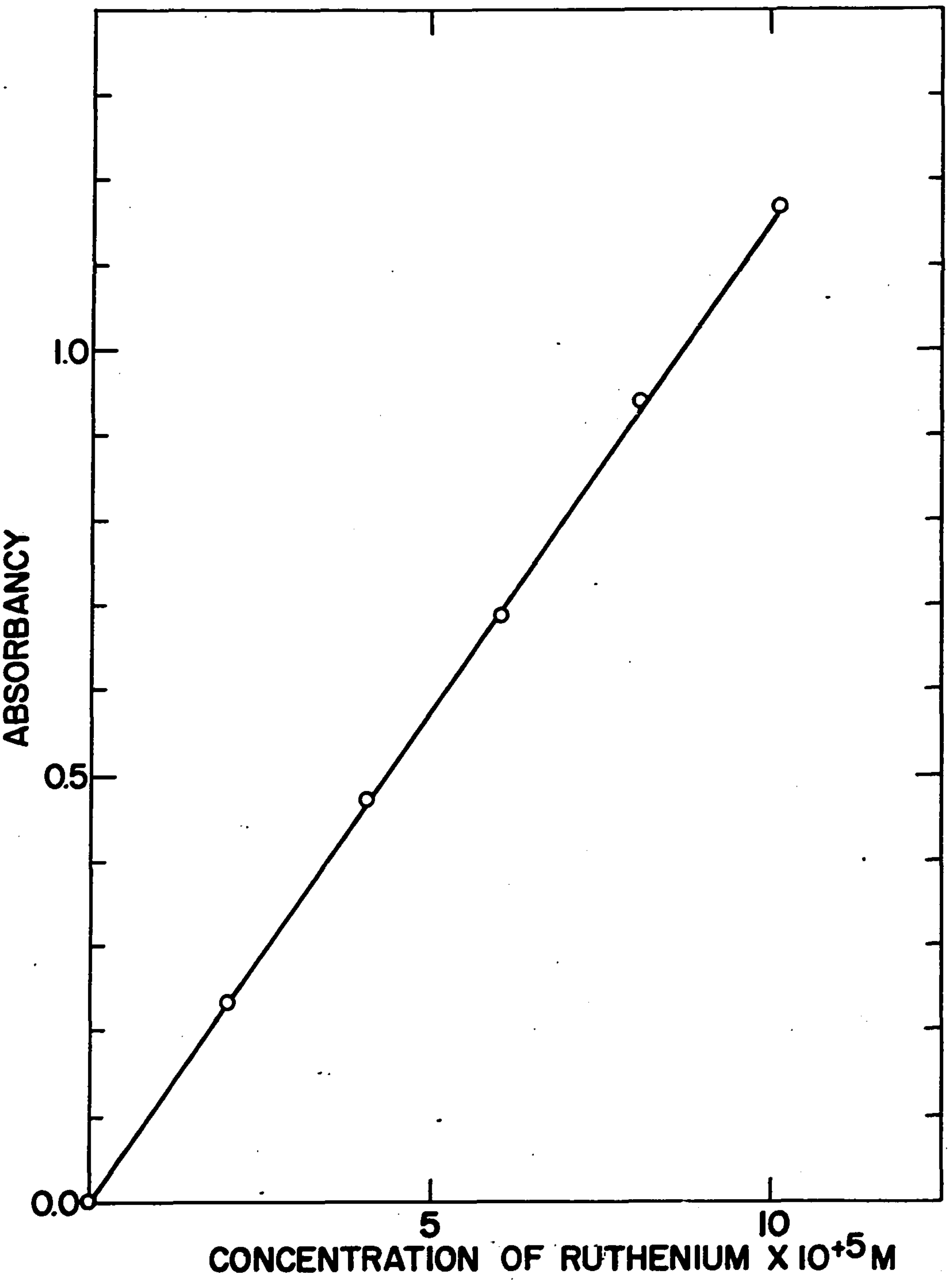

ABSORBANCY
1.0
0.5
0.0
5
10
CONCENTRATION OF RUTHENIUM X 10+5 M

Table 9. Spectrophotometric titration of tripyridyl-s-triazine with ruthenium

No.	Ml. of Ru $1.73 \times 10^{+4}$M	≈ Ru x 10^{+5} M in 50 ml.	Per cent T	Absorbancy
1	0	0	100.0	0
2	2	0.692	87.1	0.0600
3	4	1.384	75.9	0.1198
4	6	2.076	67.0	0.1739
5	8	2.768	60.1	0.2211
6	10	3.460	56.7	0.2464
7	12	4.152	55.2	0.2581
8	14	4.844	52.4	0.2807
9	16	5.536	50.0	0.3010
10	18	6.228	48.8	0.3116
11	20	6.920	48.0	0.3188
12	22	7.610	48.1	0.3279
13	24	8.304	47.0	0.3279
14	26	8.996	45.6	0.3410
15	28	9.688	46.0	0.3372
16	30	10.380	45.1	0.3458
17	32	11.072	44.0	0.3565

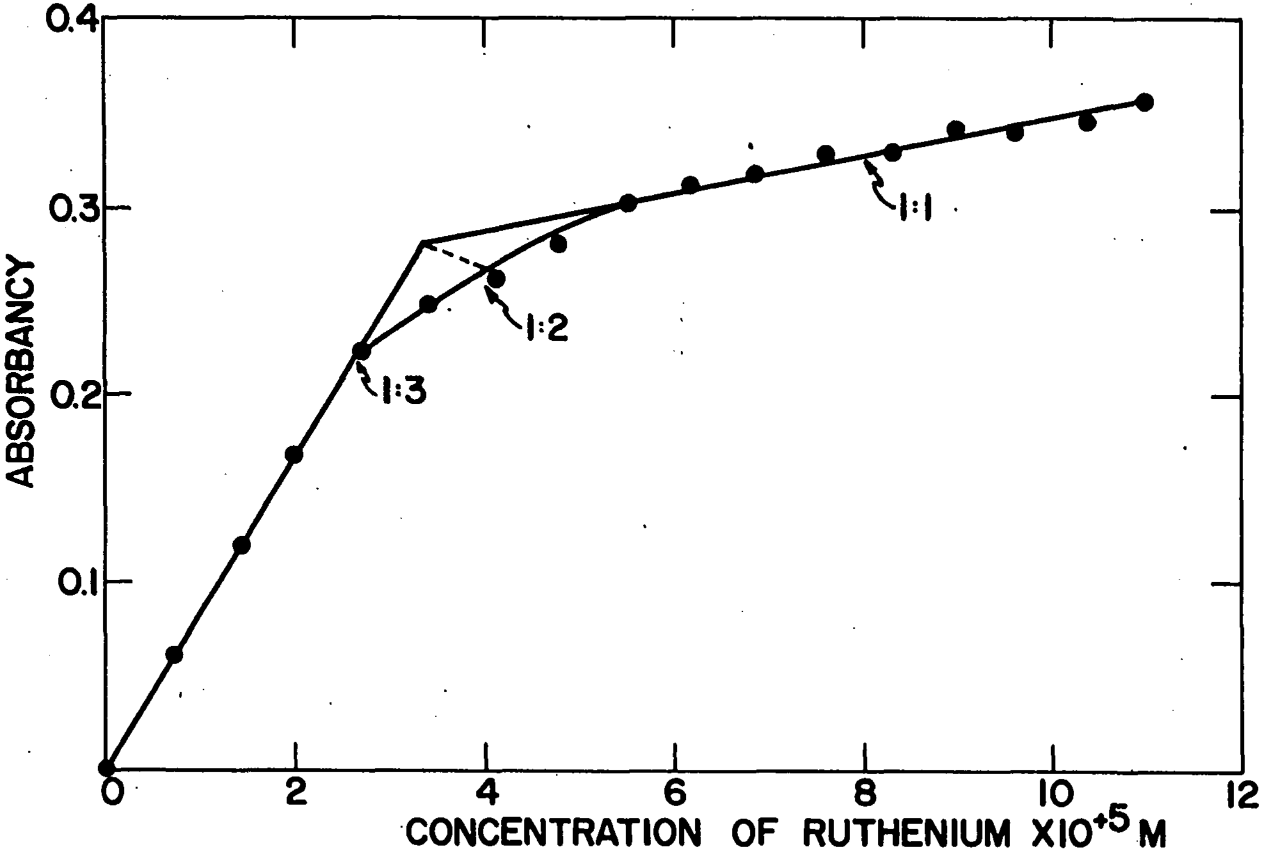
Determination of composition by the method of continuous variations

To examine further the combining ratio of ruthenium to tripyridyl triazine in the compound, another method, Job's method of continuous variations (31), was employed.

Into each of sixteen 50 ml. volumetric flasks was placed from 0-15 ml. of a solution which was 1.0197×10^{-3} M in ruthenium increasing in increments of 1 ml. 1.0005×10^{-3} M solution of 2,4,6-tris(2'-pyridyl)-s-triazine was added to each solution so that the total volume of the two solutions in each flask was 15 ml. The ruthenium chloride was

Figure 5. Spectrophotometric titration of tripyridyl triazine with ruthenium.

Wavelength: 506 mμ   Cell length: 1 cm.


0.4
0.3
0.2
0.1
ABSORBANCY
0
2
4
6
8
10
12
CONCENTRATION OF RUTHENIUM X10^{+5} M
1:3
1:2
1:1

reduced by the addition of 2 ml. of 10 per cent hydroxylammonium chloride. Ten ml. of 20 per cent sodium chloride solution was added to adjust the solutions to essentially equal ionic strength. The pH of the solutions were adjusted to 6 with 5 M sodium hydroxide. The mixtures were diluted up to near the neck of the flask and heated in a constant boiling water bath for 2 hours to develop the color fully. When cooled, the volume was taken up to the mark with deionized water.

The absorbancy was measured at 506 mμ using a 1 cm. pyrex cell and water as blank. The absorbancy was plotted against the mole fraction of ruthenium after correcting for the differences in concentration of the ruthenium and the 2,4,6-tris(2'-pyridyl)-s-triazine solutions, and the fact that one of the solutions, ruthenium chloride, was originally colored. The data is given in Table 10 and the graph is shown in Figure 6. The peak is sharp and leaves no question that the combining ratio is definitely one ruthenium atom to two molecules of 2,4,6-tris(2'-pyridyl)-s-triazine.

Absorption spectra

Visible spectrum of ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride A solution of ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride was prepared by mixing 3 ml. of 1.0197 x 10^{-3} M ruthenium chloride solution, 10 ml.

Table 10. Continuous variations study of ruthenium(II) with tripyridyl triazine

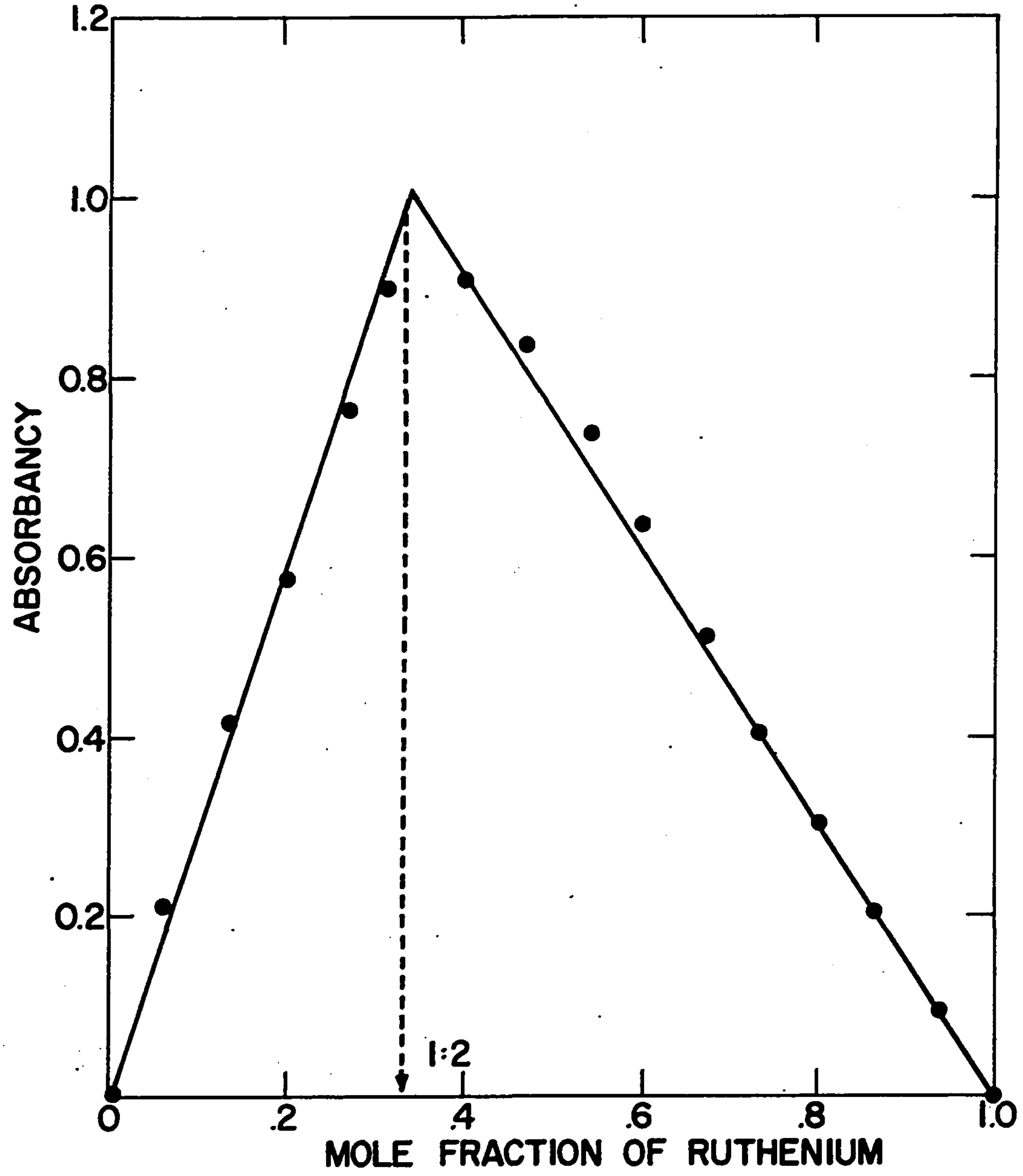
No.	Ml. Ru	Ml. TPTZ	Mole fraction Ru	Per cent T	Absorbance (corrected)
1	0	15	0	96.0	0
2	1	14	.0662	59.0	.2121
3	2	13	.1356	37.3	.4133
4	3	12	.2030	25.5	.5795
5	4	11	.2704	16.8	.7617
6	5	10	.3376	13.0	.3751
7	6	9	.4045	12.0	.9098
8	7	8	.4710	14.3	.8347
9	8	7	.5380	18.0	.7347
10	9	6	.6040	22.6	.6359
11	10	5	.6770	30.0	.5139
12	11	4	.7360	38.2	.4099
13	12	3	.8030	48.4	.3082
14	13	2	.8690	62.0	.2016
15	14	1	.9350	79.3	.0987
16	15	0	1.0000	98.0	0

of 1.0005 x 10^{-3} M 2,4,6-tris(2'-pyridyl)-s-triazine, 2 ml. of 10 per cent hydroxylammonium chloride and 10 ml. of 20 per cent sodium chloride, in a 50 ml. volumetric flask. The pH of the solution was adjusted to 6 with 5 M sodium hydroxide. Water was added up to the neck of the flask, and the mixture was heated in a constant boiling water bath for two hours to develop the color fully. On cooling, the mixture was diluted to the mark with water.

The spectrum of this solution was obtained using the Cary Spectrophotometer Model 12, a 1 cm. silica cell and water as blank.

Figure 6. Continuous variations study of ruthenium (II) with tripyridyl triazine.

Wave length: 506 mμ Cell length: 1 cm.


1.2
1.0
0.8
0.6
0.4
0.2
ABSORBANCY
1:2
0
.2
.4
.6
.8
1.0
MOLE FRACTION OF RUTHENIUM

The spectrum showed a maximum absorbance at 506 mμ, which is shown in Figure 14, letter D.

Ultraviolet spectrum of ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride A solution containing 5 ml. of 1.698 x 10^{-4} M in ruthenium, 5 ml. of 5 per cent hydroxylammonium chloride, 10 ml. of 1.0 x 10^{-2} M 2,4,6-tris(2'-pyridyl)-s-triazine was prepared by boiling in a water bath for 2 hours. The pH of the mixture was 6. When cooled, the mixture was diluted to 100 ml. One ml. aliquot of this solution was diluted again to a volume of 100 ml. with deionized water. The solution then contained 8.49 x 10^{-8} M ruthenium.

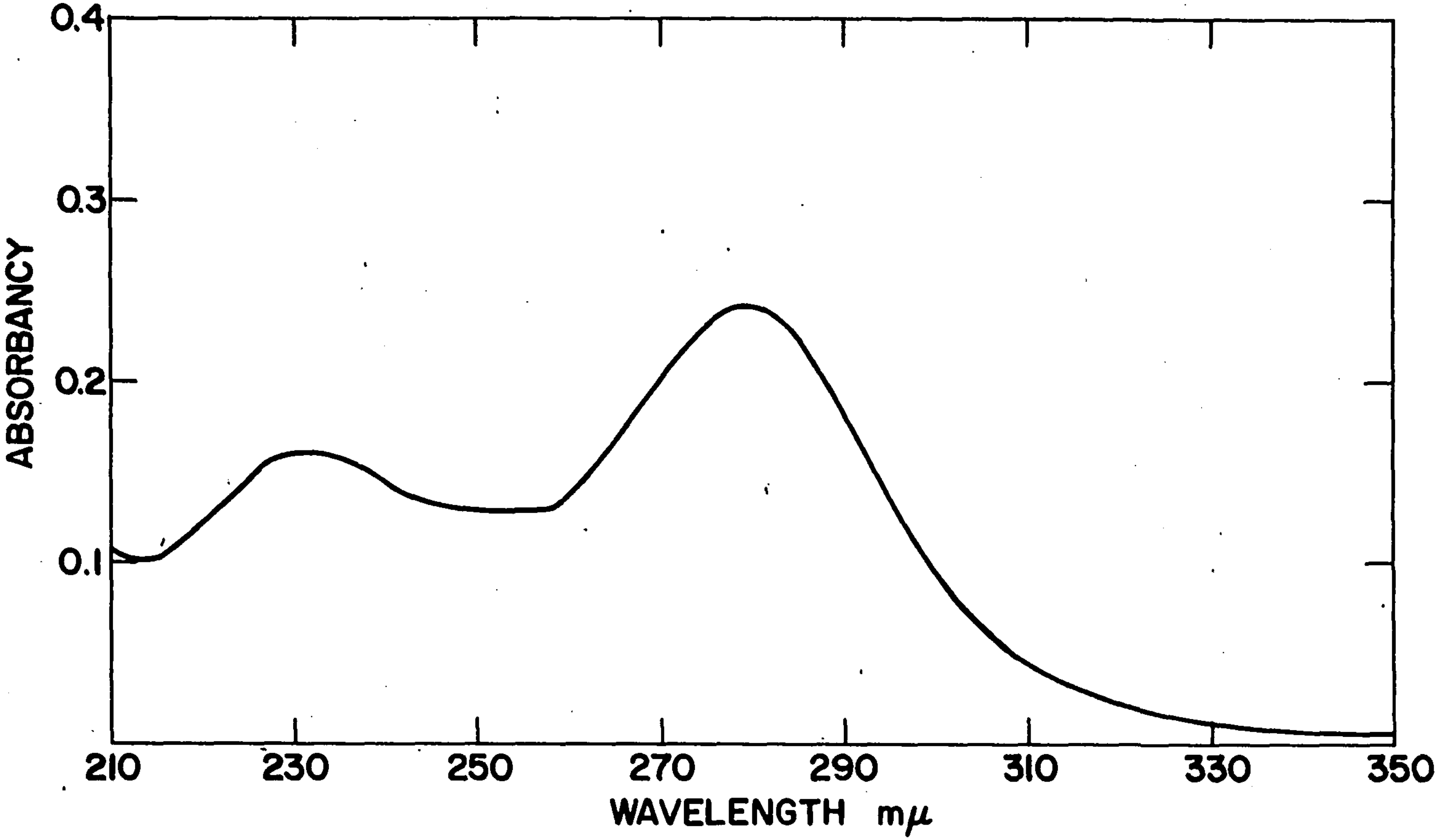
The spectrum of this solution was run in the ultraviolet region using the Cary Spectrophotometer Model 14, a 1 cm. silica cell and water as blank.

The spectra showed two peaks, one at 230 mμ and another higher peak at 280 mμ. The spectrum is shown in Figure 7.

Extraction into nitrobenzene

A solution of 15 ml. of ruthenium chloride, which contained 1.73 x 10^{-4} M in ruthenium was placed in a 100 ml. volumetric flask. Four ml. of 10 per cent hydroxylammonium chloride was added as reducing agent and 1 ml. of 1.0012 x 10^{-2} M of 2,4,6-tris-(2'-pyridyl)-s-triazine was added as complexing agent. Twenty ml. of 20 per cent sodium chloride

Figure 7. The ultraviolet spectrum of ruthenium tripyridyl triazine chloride. Cell length: 1 cm.


0.4
0.3
0.2
0.1
ABSORBANCY
210
230
250
270
290
310
330
350
WAVELENGTH mμ

was added and the mixture was diluted with water up to the neck of the flask. The pH of the mixture was adjusted to 6 with 5 M sodium hydroxide. This was boiled for 2 hours over a water bath, cooled and diluted to the mark with deionized water.

Ten ml. portions of this solution were extracted three times with 7 ml. of nitrobenzene, each time, and placed in a 25 ml. volumetric flask. Different amounts of sodium perchlorate solid were added during the extraction. The per cent transmission was read against pure distilled nitrobenzene as blank at 512 mμ. The per cent transmission of the original solution was also read at 506 mμ against water as blank.

The data obtained are given in Table 11. A plot of molar extinction coefficient vs. the number of grams of sodium perchlorate used is given in Figure 8.

Iron if present in the sample to be analyzed can be removed from the solution by precipitation in alkaline medium and subsequent filtration, followed by the reduction of the ruthenium and addition of the triazine as complexing agent. If iron is present in small quantities, it can be removed by using bathophenanthroline and isoamyl alcohol. Extraction will eliminate interferences from ions not soluble in nitrobenzene.

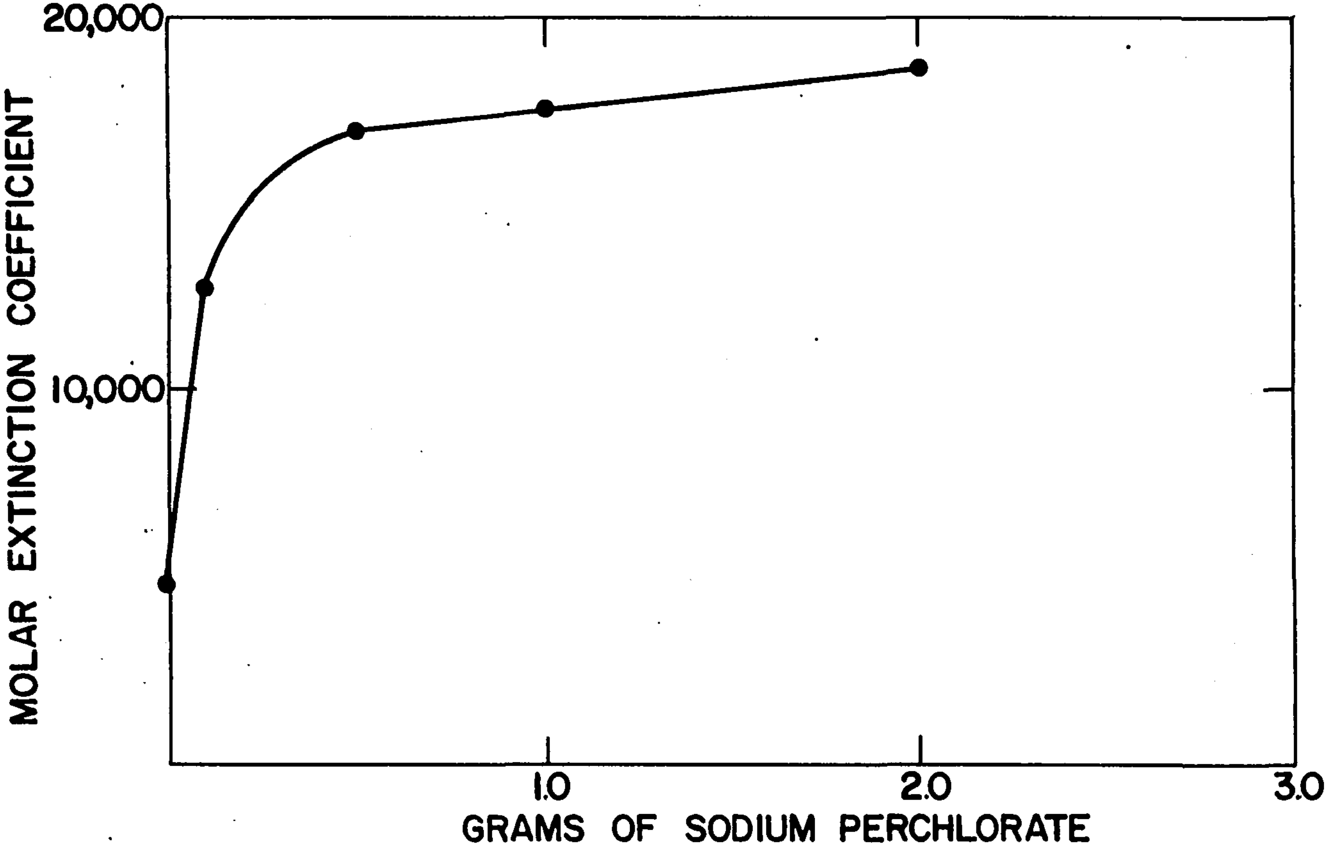
Table 11. Extraction of ruthenium tripyridyl triazine into nitrobenzene

Solutions	Grams $NaClO_4$ added	mμ	Per cent T	Absorbancy	Molar extinction coefficient (apparent)
1. original water soln.	0	506	55.0	0.2596	10,000
2. nitrobenzene	0	512	89.0	0.0506	4,870
3. "	0.1	512	73.8	0.1319	12,700
4. "	0.5	512	66.6	0.1765	17,000
5. "	1.0	512	65.7	0.1824	17,570
6. "	2.0	512	64.0	0.1938	18,670

The plot shows that the sodium perchlorate effects an increase in the amount of ruthenium bis(2,4,6-tri(2'-pyridyl) s-triazine) chloride extracted into the nitrobenzene. The amount of the ruthenium compound almost doubles upon addition of 2 grams of the sodium perchlorate. Three extractions were made of each solution, the residual aqueous solution was essentially colorless, and the effectiveness of the extraction is recorded as an "apparent" molar extinction coefficient. It is possible that the sodium perchlorate pushes the ruthenium compound out of the aqueous layer, a sort of "salting out" effect, and the ruthenium compound enters the nitrobenzene layer with the sodium perchlorate to form ion pairs and thus increase the molar extinction coefficient. With 2 grams of sodium perchlorate almost all of the ruthenium

Figure 8. The effect of sodium perchlorate salt on the molar extinction coefficient of ruthenium tripyridyl triazine when extracted into nitrobenzene.

Wave length: 512 mμ Cell length: 1 cm.


20,000
10,000
MOLAR EXTINCTION COEFFICIENT
1.0
2.0
3.0
GRAMS OF SODIUM PERCHLORATE

compound is extracted into the organic medium, as seen from the plateau in the curve.

Reactions of Other Derivatives of Pyridyl-substituted Triazines with Ruthenium

Preparation of solutions

Solutions of the ruthenium derivatives of the various pyridyl-substituted triazines available were prepared by mixing varying amounts of a standard solution of ruthenium chloride and more than three times as much of each of the different pyridyl-substituted triazines in a 50 ml. volumetric flask. To each of the mixtures, 2 ml. of 10 per cent hydroxylammonium chloride was added to reduce the ruthenium to Ru(II) and 10 ml. of 20 per cent sodium chloride to maintain a constant ionic strength of the solutions. The pH of each of the solutions were adjusted to about 6 with 5 M sodium hydroxide. The mixtures were diluted with deionized water up to near the neck of the flask. These solutions were heated in a constant boiling water bath for two hours to fully develop the color. When cooled to room temperature, they were diluted to the mark with deionized water.

The amount of ruthenium and pyridyl-substituted triazine used for the different solutions are given below.

Solution A: 5 ml. of 1.0034 x 10^{-4} M in ruthenium
2 ml. of 1.00 x 10^{-3} M in reagent triazine
B: 10 ml. of 1.0034 x 10^{-4} M in ruthenium
5 ml. of 1.00 x 10^{-3} M in reagent triazine
C: 2 ml. of 1.0197 x 10^{-3} M in ruthenium
10 ml. of 1.00 x 10^{-3} M in reagent triazine
D: 3 ml. of 1.0197 x 10^{-3} M in ruthenium
10 ml. of 1.00 x 10^{-3} M in reagent triazine
E: 2.5 ml. of 1.0197 x 10^{-3} M in ruthenium
8.0 ml. of 1.00 x 10^{-3} M in reagent triazine

Absorption spectra and molar extinction coefficient

The spectra of the above prepared solutions of the different ruthenium derivatives of polypyridyls were recorded in the visible region with the use of the Cary Spectrophotometer Model 12, a 1 cm. silica cell and water as blank. The spectra of these solutions are shown in Figures 9 to 16. The spectrum of the ruthenium derivative with 1,10-phenanthroline has been studied by Banks and O'Laughlin (1).

The per cent transmittancy of each of the solutions was read with the Beckman DU Spectrophotometer, a 1 cm. pyrex cell and water as blank. From these data, the molar extinction coefficients were computed. The results are given in Table 12.

Figure 9. The visible spectra of ruthenous bis(2,4-diamino-6-(2'-pyridyl)-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00×10^{-5} M ruthenium

B = 2.00×10^{-5} M ruthenium

C = 4.08×10^{-5} M ruthenium

D = 6.12×10^{-5} M ruthenium

E = 10.197×10^{-5} M ruthenium

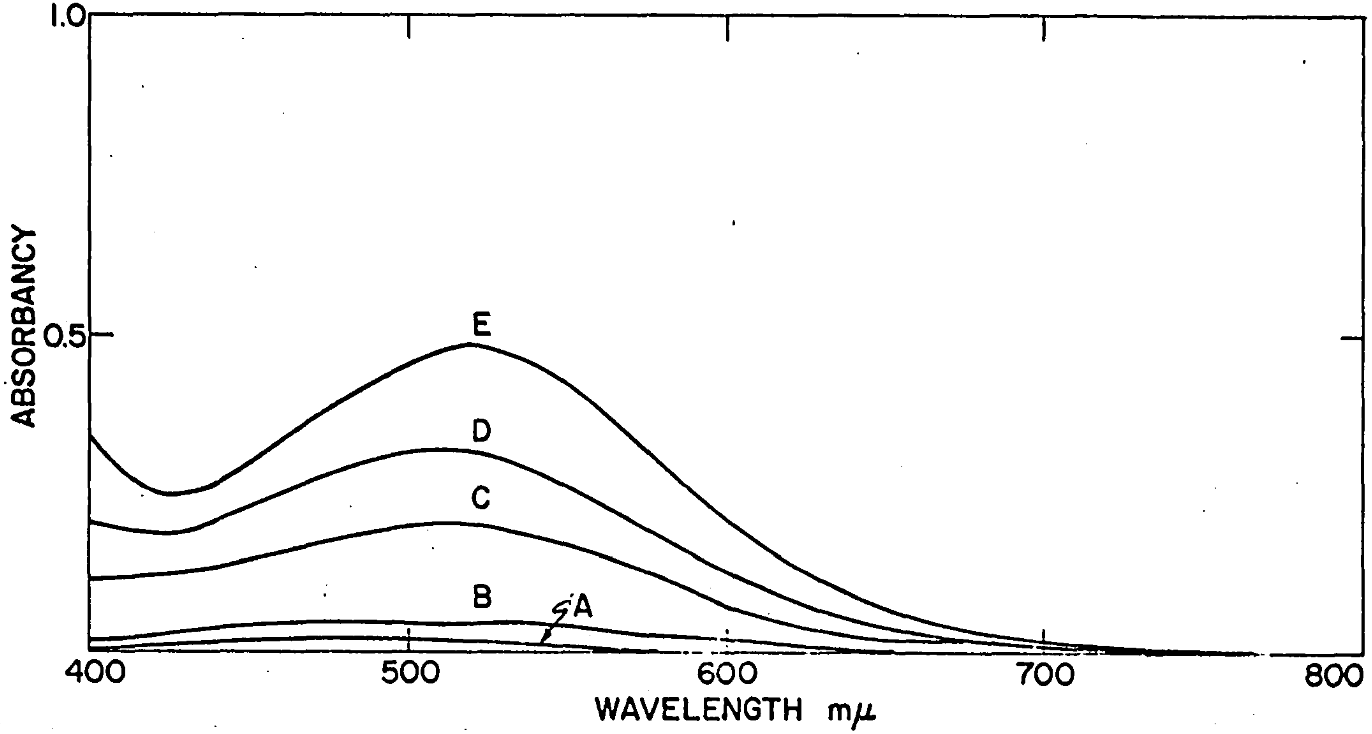

1.0
0.5
ABSORBANCY
E
D
C
B
A
400
500
600
700
800
WAVELENGTH mμ

Figure 10. The visible spectra of ruthenous bis(diamino-4'-ethyl-2'-pyridyl-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00×10^{-5} M ruthenium

B = 2.00×10^{-5} M ruthenium

C = 4.08×10^{-5} M ruthenium

D = 6.12×10^{-5} M ruthenium

E = 10.197×10^{-5} M ruthenium

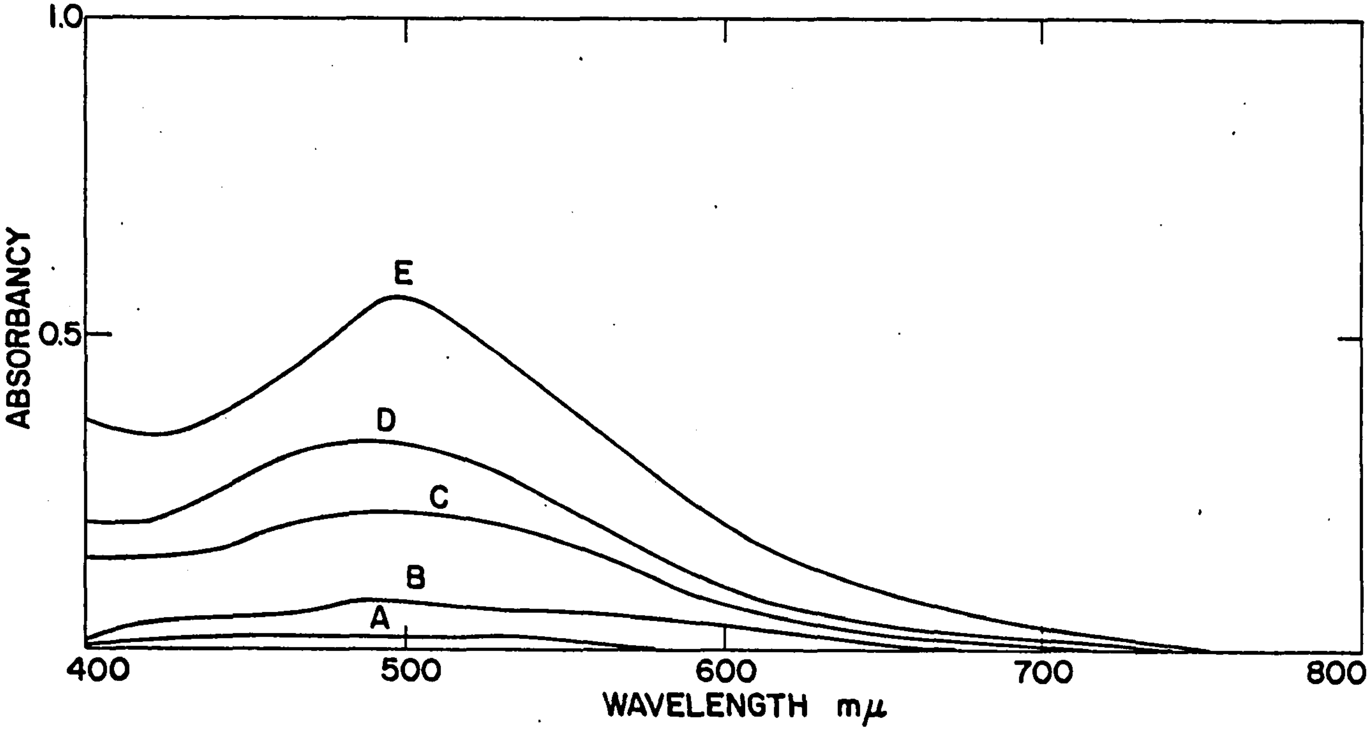

1.0
0.5
ABSORBANCY
E
D
C
B
A
400
500
600
700
800
WAVELENGTH mμ

Figure 11. The visible spectra of ruthenous bis(diamino-4'-phenyl-2'-pyridyl-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00 x 10^{-5} M ruthenium

B = 2.00 x 10^{-5} M ruthenium

C = 4.08 x 10^{-5} M ruthenium

D = 6.12 x 10^{-5} M ruthenium

E = 10.197 x 10^{-5} M ruthenium

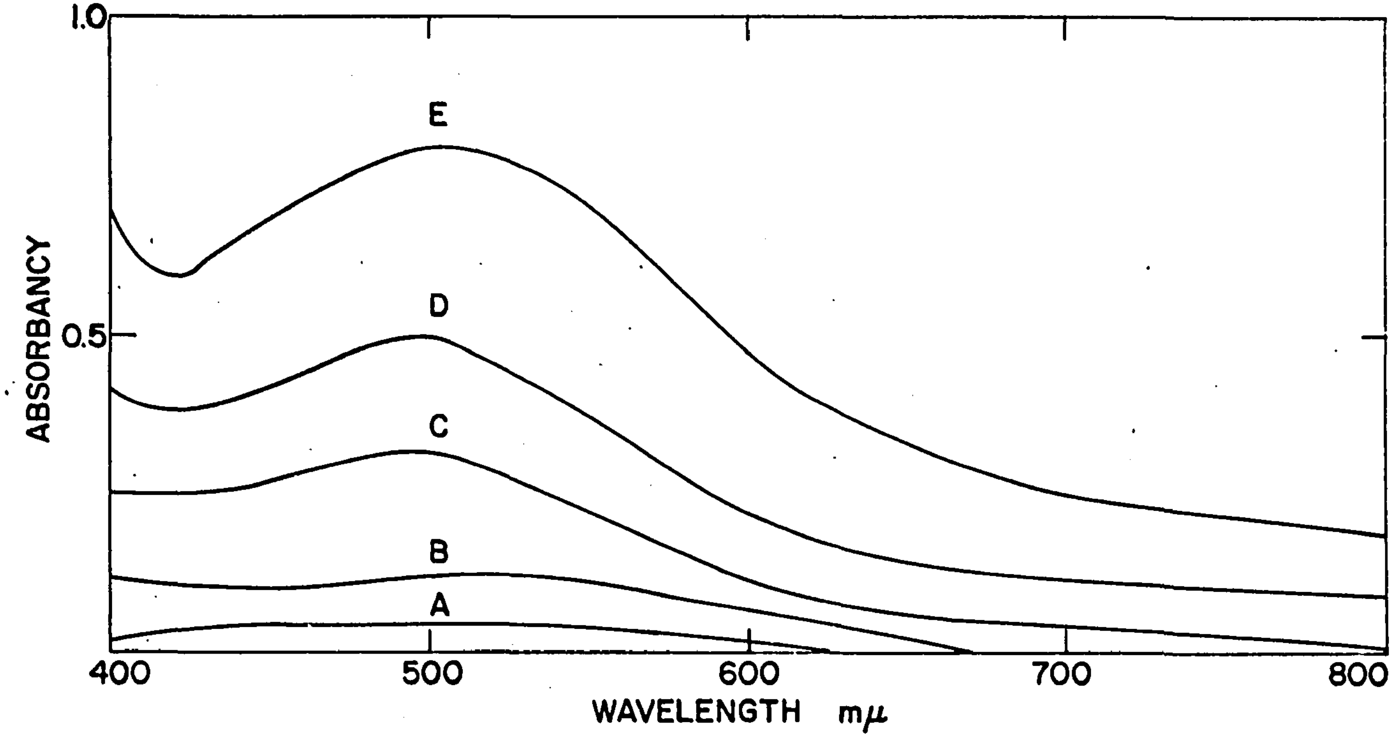

1.0
0.5
ABSORBANCY
E
D
C
B
A
400
500
600
700
800
WAVELENGTH mμ

Figure 12. The visible spectra of ruthenous bis(2-amino-4,6-bi (2'-pyridyl)-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00×10^{-5} M ruthenium

B = 2.00×10^{-5} M ruthenium

C = 4.08×10^{-5} M ruthenium

D = 6.12×10^{-5} M ruthenium

E = 10.197×10^{-5} M ruthenium

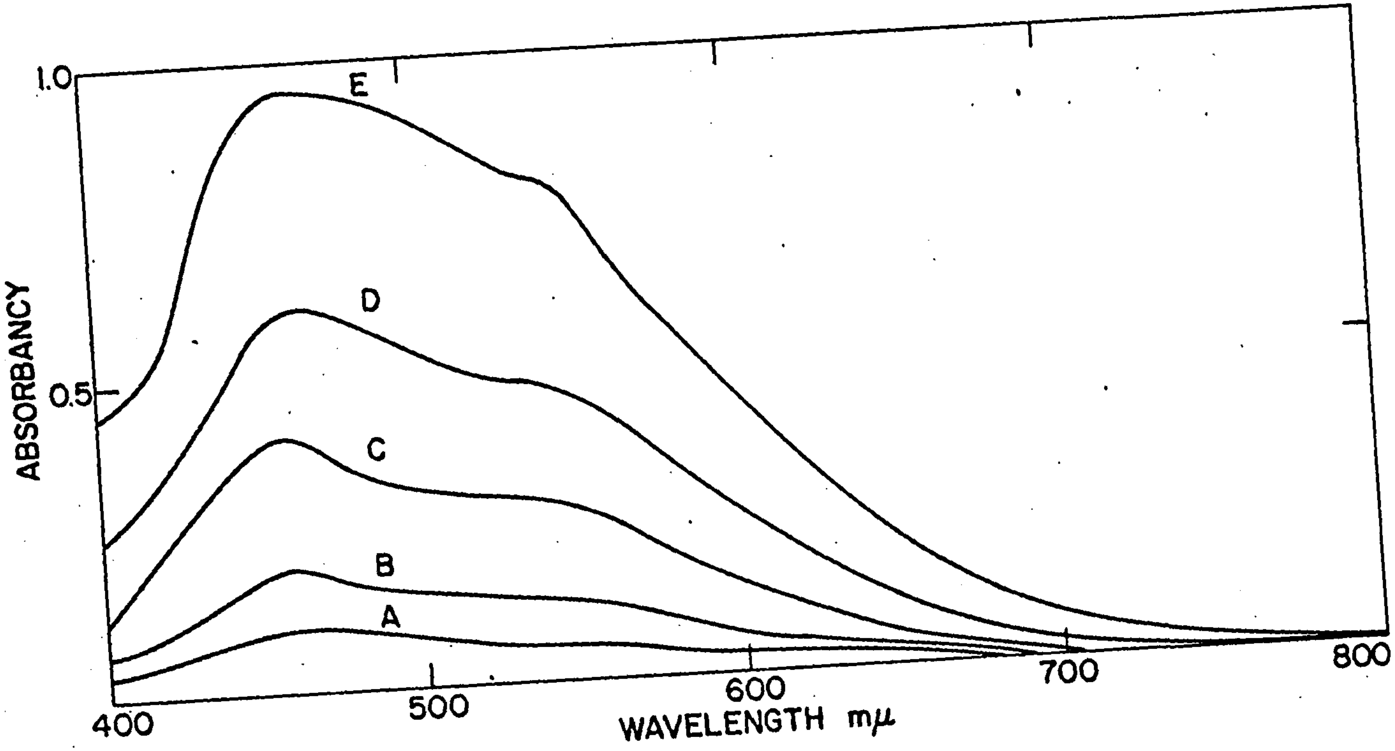

ABSORBANCY
1.0
0.5
WAVELENGTH mμ
400
500
600
700
800
E
D
C
B
A

Figure 13. The visible spectra of ruthenous bis(2-amino-4,6-bi(4'-ethyl-2'-pyridyl)-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00 x 10^{-5} M ruthenium

B = 2.00 x 10^{-5} M ruthenium

C = 4.08 x 10^{-5} M ruthenium

D = 6.12 x 10^{-5} M ruthenium

E = 10.197 x 10^{-5} M ruthenium

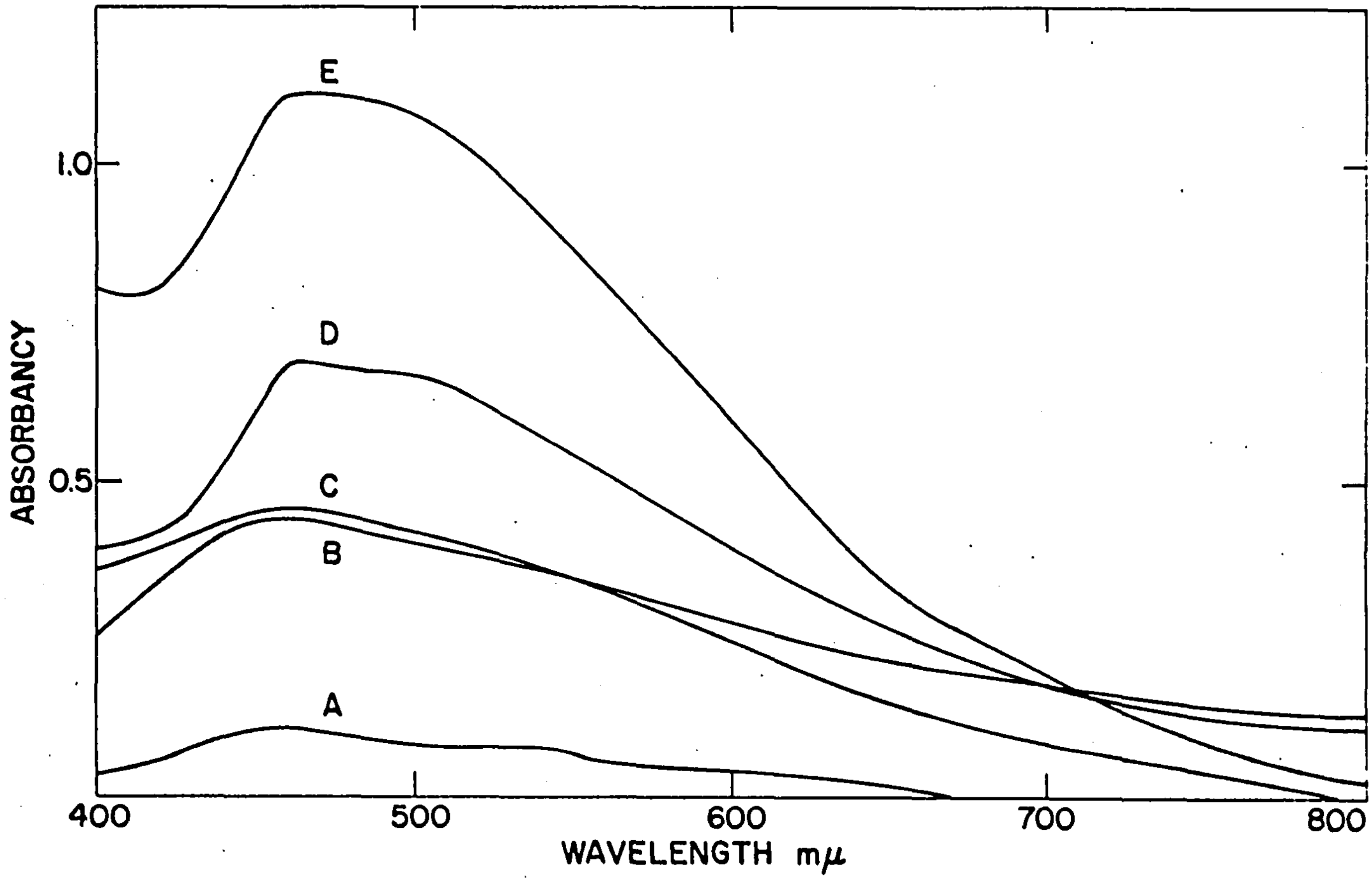

E
D
C
B
A
1.0
0.5
ABSORBANCY
400
500
600
700
800
WAVELENGTH mμ

Figure 14. The visible spectra of ruthenous bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00 x 10^{-5} M ruthenium

B = 2.00 x 10^{-5} M ruthenium

C = 4.08 x 10^{-5} M ruthenium

D = 6.12 x 10^{-5} M ruthenium

E = 10.197 x 10^{-5} M ruthenium

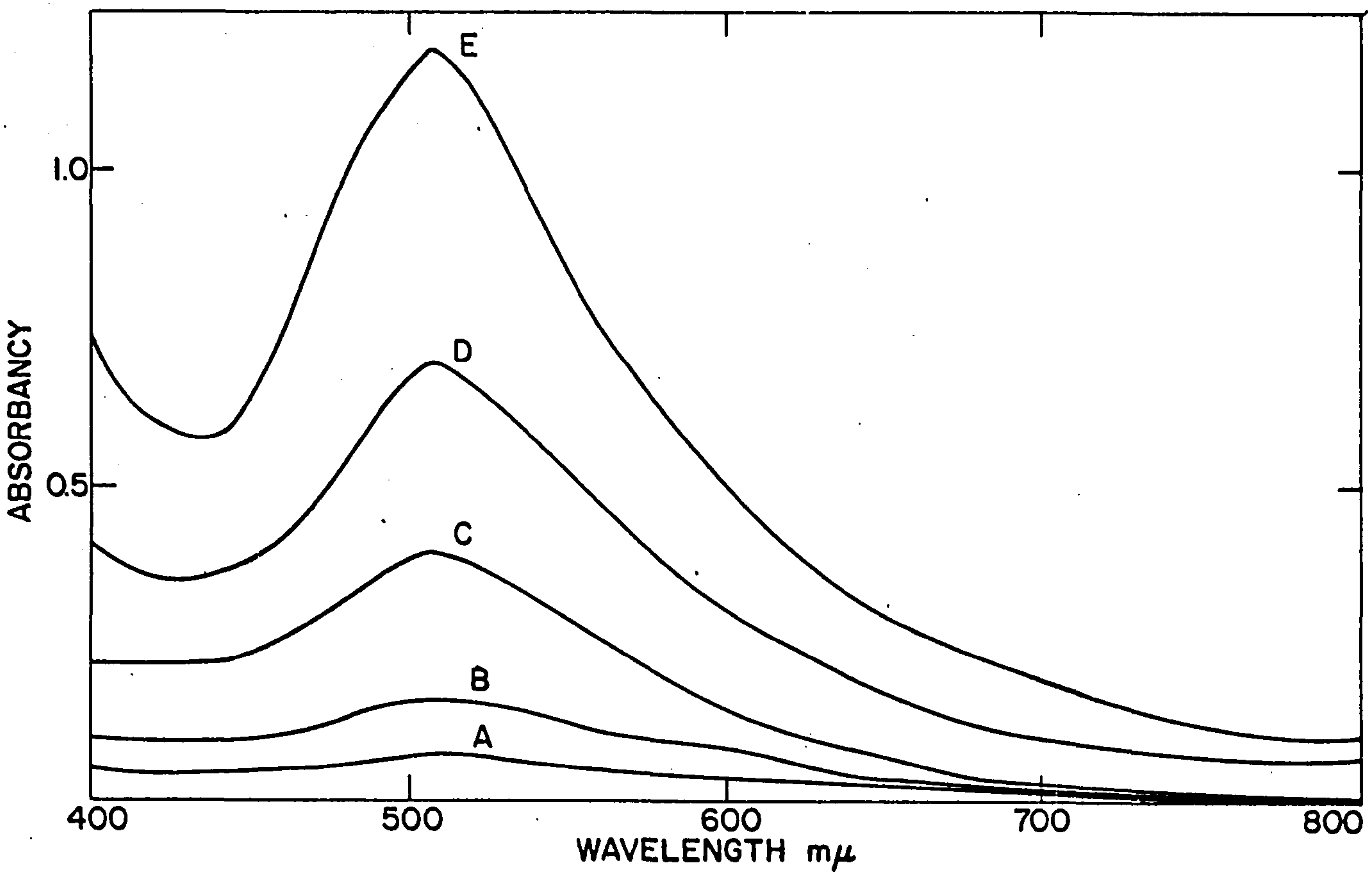

E
D
C
B
A
1.0
0.5
ABSORBANCY
400
500
600
700
800
WAVELENGTH mμ

Figure 15. The visible spectra of ruthenous bis(2,4,6-tri-(4'-methyl-2'-pyridyl)-s-triazine) chloride.

Cell length: 1 cm.

A = 1.00 x 10^{-5} M ruthenium

B = 2.00 x 10^{-5} M ruthenium

C = 4.08 x 10^{-5} M ruthenium

D = 6.12 x 10^{-5} M ruthenium

E = 10.197 x 10^{-5} M ruthenium

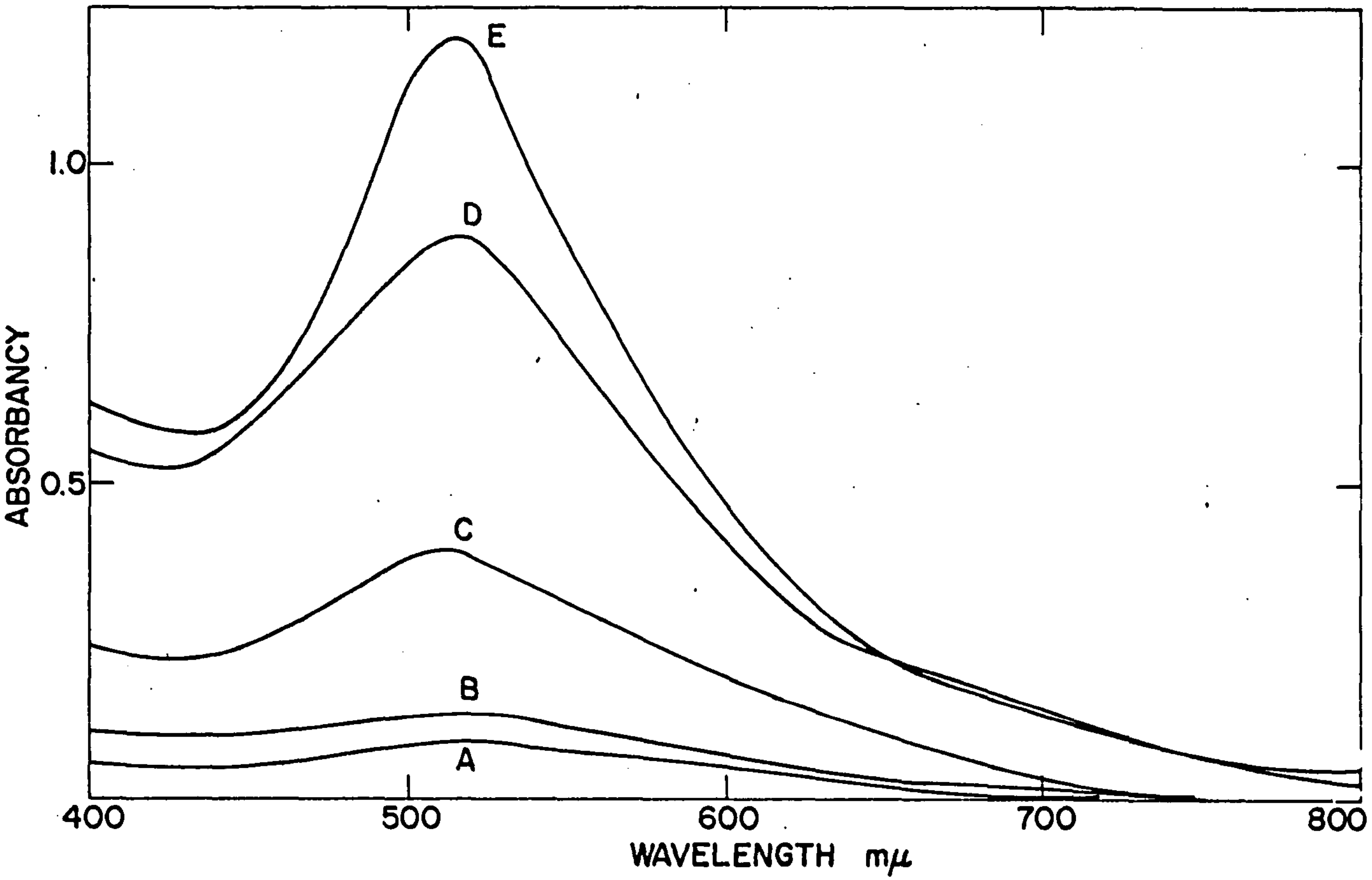

E
D
C
B
A
1.0
0.5
ABSORBANCY
400
500
600
700
800
WAVELENGTH mμ

Figure 16. The visible spectra of ruthenous bis(tripyrimidyl-s-triazine) chloride.

Cell length: 1 cm.

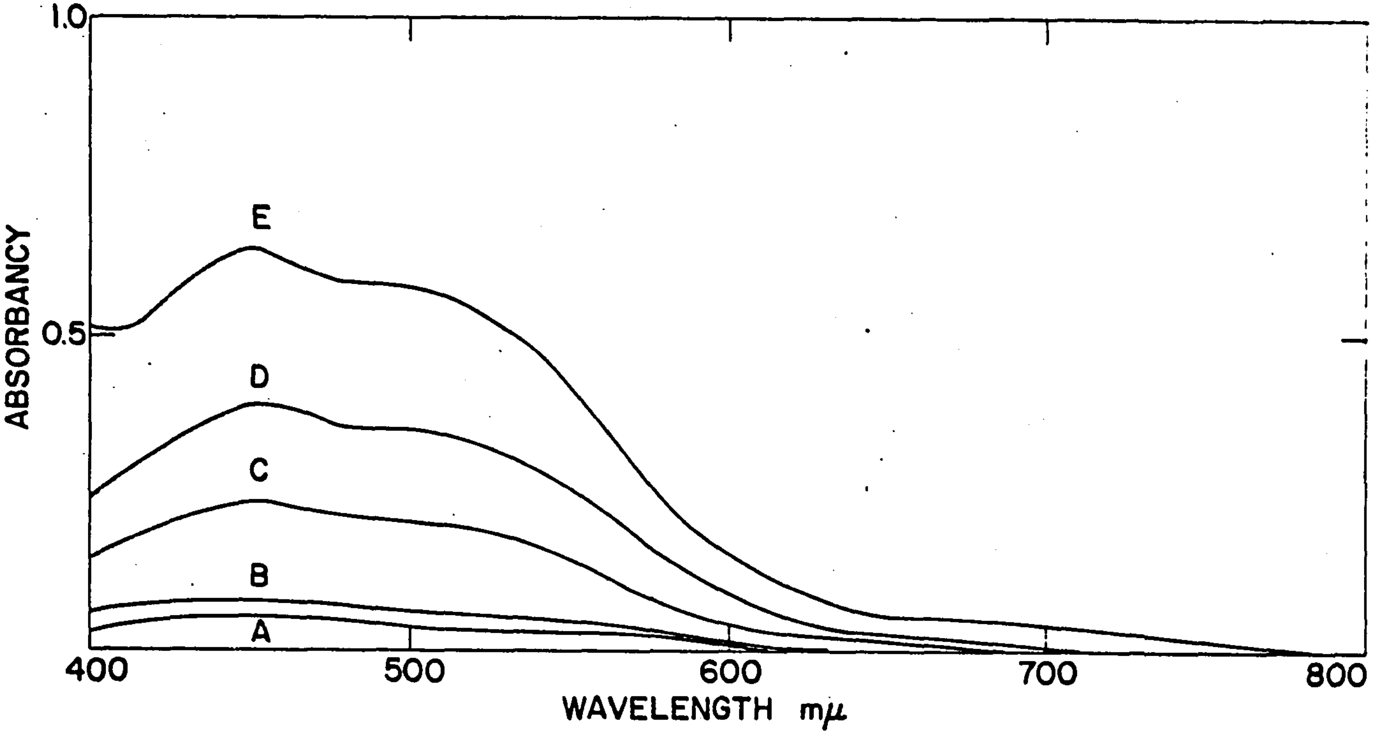
A = 1.00 x 10^{-5} M ruthenium

B = 2.00 x 10^{-5} M ruthenium

C = 4.08 x 10^{-5} M ruthenium

D = 6.12 x 10^{-5} M ruthenium

E = 10.197 x 10^{-5} M ruthenium


1.0
0.5
ABSORBANCY
E
D
C
B
A
400
500
600
700
800
WAVELENGTH mμ

Ruthenium does not yield a colored compound with melamine which has three amino groups attached symmetrically to the triazine ring. Neither does it react with iron to form a colored compound (5). Ruthenium does react with those triazines containing one or more 2'-pyridyl groups. The intensity of the color increases with the number of pyridyl groups, Table 12. Substitution in the pyridyl ring increases further the molar extinction coefficient, thus ruthenium bis(2-amino-4,6-bi(4'-ethyl-2'-pyridyl)-s-triazine) chloride has a higher value than that of the compound without the ethyl substituent, ruthenium bis-(2-amino-4,6-bi(2'-pyridyl)-s-triazine) chloride, 11,300 compared to 10,000.

2-Amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine, 2-amino-4,6-bis(2'-pyridyl)-s-triazine, 2,4,6-tris(2'-pyridyl)-s-triazine and 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine are very highly colored compounds and have the highest molar extinction coefficients of the compounds studied. These compounds will be good for the colorimetric determination of ruthenium.

Stability of the ruthenium compounds

The stability of the ruthenium compounds were studied by preparing two series of solutions. The first series contained 2 ml. of 1.0197 x 10^{-3} M ruthenium and the second series contained 3 ml. of the same solution of ruthenium.

Table 12. Reaction of pyridyl-substituted triazines with ruthenium(II)

Chemical name	Color	Wavelength maximum absorption $m\mu$	Molar extinction coefficient
2,4,6-Triamino-1,3,5-triazine (Melamine)	colorless	--	--
2,4-Diamino-6-(2'-pyridyl)-s-triazine	purple	510	5,000
Diamino-4'-ethyl-2'-pyridyl-s-triazine	purple	490	5,400
Diamino-4'-phenyl-2'-pyridyl-s-triazine	purple	500	8,000
2-Amino-4,6-bis(2'-pyridyl)-s-triazine	purple	460	10,000
2-Amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine	purple	460	11,300
2,4,6-Tris(2'-pyridyl)-s-triazine	purple	506	11,600
2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine	purple	520	11,800
Tripyrimidyl-s-triazine	orange	450	6,300
1,10-phenanthroline	orange	450	13,400

All the solutions were treated with 10 ml. of each of the different bases whose concentrations were about 1.00 x 10^{-3} M, 2 ml. of 10 per cent hydroxylammonium chloride and 10 ml. of 10 per cent sodium chloride. The pH of the solutions were adjusted to 6 with 5 M sodium hydroxide. The mixtures were heated in a constant boiling water bath for two hours, cooled and diluted to a volume of 50 ml.

The per cent transmittancy of these solutions were read with a 1 cm. pyrex cell and water as blank at their respective maximum absorbance. After three weeks, the per cent transmittancy were read again for comparison. The results are tabulated in Table 13.

The results showed that most of the ruthenium compounds were relatively stable at room temperature in three weeks time. Ruthenium diamino-4'-ethyl-2'-pyridyl-s-triazine chloride produced the greatest change in per cent transmittancy. The increase in per cent transmittancy may be due to some decomposition of the compound.

Formal Reduction Potential of Ruthenium Compounds

Potentiometric method

Ruthenium 2,4,6-tris(2'-pyridyl)-s-triazine chloride

A solution of ruthenium 2,4,6-tris-(2'-pyridyl)-s-triazine chloride was prepared by dissolving 0.0208 gram of the compound in 25 ml. of deionized water. Twenty-five ml. of 2 M

Table 13. Stability of ruthenium compounds

Chemical name	Wavelength maximum absorption $m\mu$	Per cent transmittancy			
		First series		Second series	
		Reading		Reading	
		first	second	first	second
2,4-Diamino-6-(2'-pyridyl)-s-triazine	510	63.0	62.1	50.1	49.8
Diamino-4'-ethyl-2'-pyridyl-s-triazine	490	60.6	60.6	47.5	47.4
Diamino-4'-phenyl-2'-pyridyl-s-triazine	490	48.0	62.1	32.2	54.5
2-Amino-4,6-bis(2'-pyridyl)-s-triazine	460	39.3	36.7	26.8	24.0
2-Amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine	460	35.4	36.3	30.8	26.2
2,4,6-Tris(2'-pyridyl)-s-triazine	506	40.0	43.8	30.1	33.0
2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine	520	40.6	44.0	31.1	32.7
Tripyrimidyl-s-triazine	450	58.2	61.2	47.5	53.1
1,10-Phenanthroline	450	28.3	27.7	16.2	18.0

sulfuric acid was added and 5 ml. of 0.05 M ferrous sulfate. Nitrogen gas was bubbled through the solution to keep it from air oxidation as well as to stir the solution. The solution was titrated with 0.0277 M sulfatoceric acid in 1 M sulfuric acid. The voltage was read as small volumes of the titrant were added from a Machlet buret, using a Leeds and Northrup Type K Potentiometer, a platinum and a saturated calomel electrode. The titration curve is shown in Figure 17.

The indicator end point was found to be 1.18_6 volts versus the hydrogen electrode. The color change was from purple to orange.

Ruthenium 2,4,6-tris(2'-pyridyl)-s-triazine perchlorate 0.1003 gram of ruthenium 2,4,6-tris-(2'-pyridyl)-s-triazine perchlorate was dissolved in 10 ml. of water and 15 ml. of 2 M sulfuric acid. Five ml. of 0.05 M ferrous sulfate was added and the voltage readings were taken as small portions of 0.0277 M sulfatoceric acid in 1 M sulfuric acid were added. The formal potential versus the hydrogen electrode was found to be 1.18_1 volt. The plot of the voltage readings against the volume of sulfatoceric acid used is shown in Figure 18.

Colorimetric method

Using the series of potentiopoised solutions prepared and described in Part I, Iron Compounds, and whose formal

Figure 17. Titration of ferrous iron and ruthenium tripyridyl-s-triazine chloride with sulfatoceric acid in 1 M sulfuric acid.

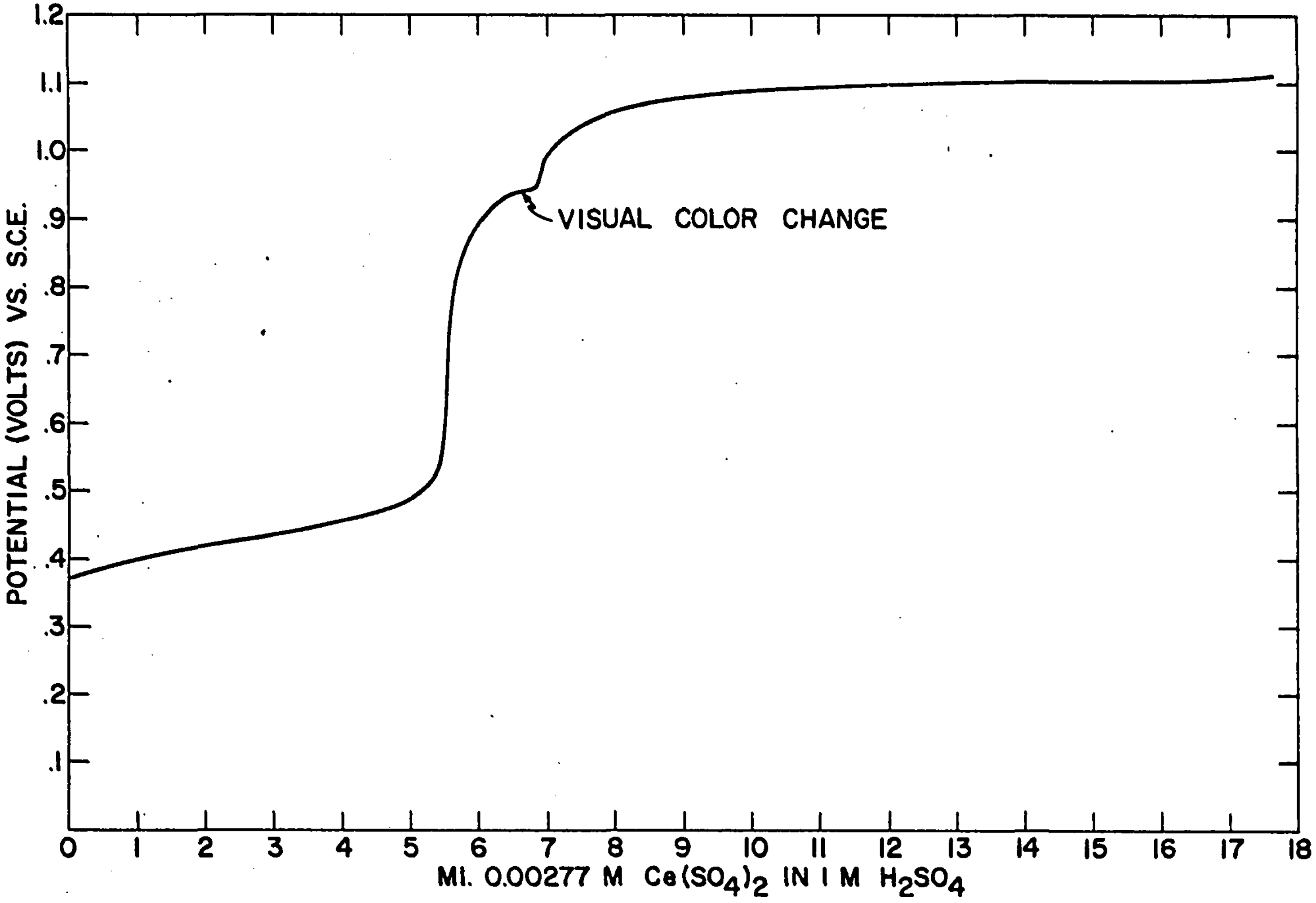
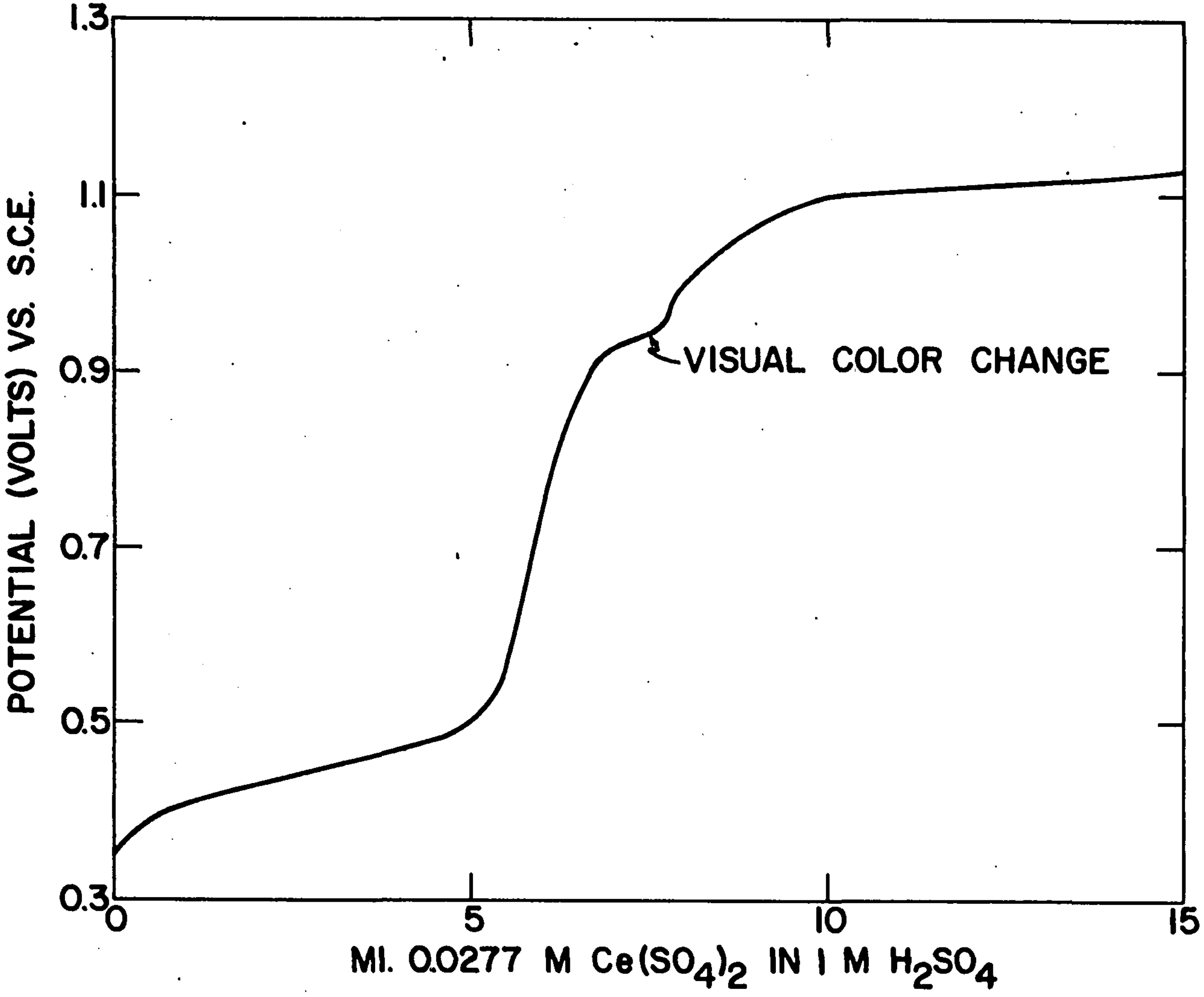

POTENTIAL (VOLTS) VS. S.C.E.
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
VISUAL COLOR CHANGE
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Ml. 0.00277 M Ce(SO4)2 IN 1 M H2SO4

Figure 18. Titration of ferrous iron and ruthenium tripyridyl triazine perchlorate with sulfatoceric acid in 1 M sulfuric acid.


1.3
1.1
0.9
0.7
0.5
0.3
POTENTIAL (VOLTS) VS. S.C.E.
0
5
10
15
MI. 0.0277 M Ce(SO$_4$)$_2$ IN I M H$_2$SO$_4$
VISUAL COLOR CHANGE

potentials have been determined, the formal reduction potential of the different ruthenium derivatives of the polypyridyl-s-triazines were determined in the same manner.

The values obtained are tabulated in Table 14.

Ruthenium Bis(2,4,6-Tri(2'-Pyridyl)-s-Triazine) Perchlorate as an Oxidation-Reduction Indicator

A study was made to determine the applicability of the ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate as oxidation-reduction indicator. A series of titrations of standard solutions of ferrous ethylene-diammonium sulfate and sodium arsenite were carried out. The end points were compared with titrations of solutions using 1,10-phenanthroline sulfate as indicator. The procedures and results are given in the pages that follow.

Titration of ferrous ethylenediammonium sulfate

About 0.50 gram of standard ferrous ethylenediammonium sulfate was dissolved in 25 ml. of water and 25 ml. of 2 M perchloric acid. Three drops of 0.002 M indicator was added and the solution was titrated with 0.0574 M sulfatoceric acid in 1 M sulfuric acid. The results are summarized in Table 15.

Table 14. Formal reduction potentials of ruthenium compounds

Chemical name	Anion	E^o(previous) potentiometric method	Formality H_2SO_4	E^o(found) colorimetric method	Color change reduced-oxidized
2,4-Diamino-6-(2'-pyridyl)-s-triazine	chloride		4.0	1.15_0	orange-yellow
Diamino-4'-ethyl-2'-pyridyl-s-triazine	chloride		4.75	1.18_0	purple-yellow
Diamino-4'-phenyl-2'-pyridyl-s-triazine	chloride		4.75	1.18_1	purple-orange
2-Amino-4,6-bis(2'-pyridyl)-s-triazine	chloride		5.0	1.18_7	purple-orange
2-Amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine	chloride		5.0	1.18_7	purple-orange
2,4,6-Tris(2'-pyridyl)-s-triazine	chloride	1.18_6	5.0	1.18_8	purple-orange
2,4,6-Tris(2'-pyridyl)-s-triazine	perchlorate	1.18_1	5.0	1.18_8	purple-orange
2,4,6-Tris(2'-pyridyl)-s-triazine	iodide		5.0	1.18_8	purple-orange
2,4,6-Tris(4'-methyl-2'-pyridyl)-s-triazine	chloride		5.0	1.18_5	purple-orange
Tripyrimidyl-s-triazine	chloride		4.5	1.15_8	orange-yellow
1,10-Phenanthroline	chloride	1.17±.003 (23)	4.25	1.16_1	orange-yellow
1,10-Phenanthroline	perchlorate	1.29 (21)			

Table 15. Titration of ethylenediammonium sulfate using ruthenium 2,4,6-tris(2'-pyridyl)-s-triazine indicator

Indicator	Weight used(g)	Ml. 0.0574 M $Ce(SO_4)_2$used	Weight found(g)	Per cent relative error	Average per cent relative error
$Ru(TPTZ)_2(ClO_4)_2$	0.5015	22.90	0.5015	0.00	
	0.5020	22.90	0.5015	-0.08	-0.04
$Ru(TPTZ)_2I_2$	0.5017	22.90	0.5015	-0.04	
	0.5004	22.87	0.5009	+0.10	+0.03
$Ru(1,10\text{-phen})_3Cl_2$	0.4999	22.80	0.4993	-0.12	
	0.5005	22.85	0.5004	-0.02	-0.07
$Fe(1,10\text{-phen})_3SO_4$	0.5001	22.80	0.4993	-0.16	
	0.5015	22.87	0.5009	-0.12	
	0.5000	22.85	0.5004	+0.08	-0.03

Titration of sodium arsenite

Twenty-five ml. of standard 0.1002 M sodium arsenite was treated with 25 ml. of 2 M perchloric acid and 2 drops of 0.01 M osmium tetroxide as catalyst. Three drops of the prepared ruthenium indicator was added and the mixture was titrated against 0.0574 M sulfatoceric acid in 1 M sulfuric acid. The titration was compared with one using ferroin as indicator. The results are given in Table 16.

The ruthenium 1,10-phenanthroline indicator was prepared by taking 20 ml. of ruthenium chloride which was 2.26 x 10^{-5} M in ruthenium and reduced it with 2 grams solid hydroxylammonium chloride. Thirty ml. of 1.0106 x 10^{-2} M 1,10-phenanthroline was added and the mixture was boiled over a water bath for two hours to develop the color fully.

Discussion

Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride has been prepared by boiling a solution of ruthenium chloride, 2,4,6-tris(2'-pyridyl)-s-triazine and hydroxylammonium chloride, the pH of the mixture being adjusted to 5 with sodium hydroxide. The material was obtained in the form of purple crystals. The compound has the composition, $Ru(TPTZ)_2Cl_2$ as borne out by chemical analysis. It is soluble in water, and can be extracted into nitrobenzene if sodium perchlorate

Table 16. Titration of sodium arsenite using ruthenium 2,4,6-tri(2'-pyridyl)-s-triazine as indicator

Indicator	Ml. 0.0574 M $Ce(SO_4)_2$ used	Molarity $Ce(SO_4)_2$ found	Per cent relative error	Average per cent relative error
$Ru(TPTZ)_2(ClO_4)_2$	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.10
$Ru(TPTZ)_2I_2$	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.10
$Ru(1,10\text{-phen})_3Cl_2$	43.75	0.1005	+0.30	
	43.75	0.1005	+0.30	
	43.70	0.1003	+0.10	+0.23
$Fe(1,10\text{-phen})_3SO_4$	43.75	0.1005	+0.30	
	43.75	0.1005	+0.30	
	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.20

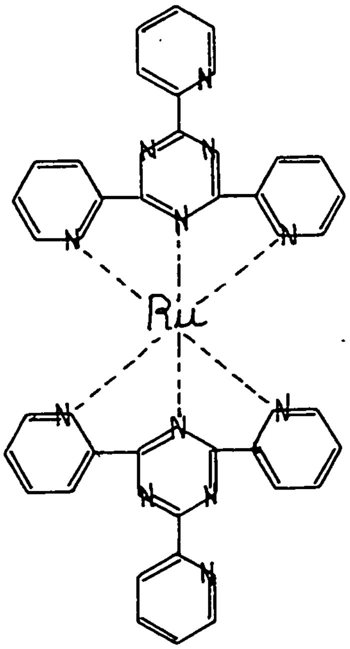
is added to the solution. The composition of the ruthenium tripyridyl compound in solution is the same as that isolated as the solid. That is, a spectrophotometric titration showed that the ratio of the ruthenium to the tripyridyl triazine is 1:2. A study of the system by the method of continuous variations gave the same result.

The absorption spectrum of ruthenium bis(2,4,6-tri-(2'-pyridyl)-s-triazine) chloride shows a maximum in the visible region at 506 mμ and two maxima in the ultraviolet region, a lower one at 230 mμ and a higher one at 280 mμ. The spectrum resembles the ultraviolet spectrum of the corresponding iron derivative.

The compound is stable over the pH range 4.5 and 8.5. Solutions of the compound at pH 6 follows Beer's Law. The molar extinction coefficient in aqueous medium is 11,600, at this pH, the value increasing as the pH is increased, to 12,200 at pH 7. However, the excess 2,4,6-tris(2'-pyridyl)-s-triazine precipitates out at any pH above 6 and had to be removed. In nitrobenzene, the absorption spectrum resembles that in water solution but the molar extinction coefficient has been found to increase as the amount of sodium perchlorate added was increased, from 10,000 to 18,600. This may be due to the fact that as more sodium perchlorate is added, the "salting out effect" becomes greater, so that more of the ruthenium compound leaves the solution in ion pairs with the perchlorate and go to the nitrobenzene layer.

2,4,6-Tris(2'-pyridyl)-s-triazine can be used as colorimetric reagent for the determination of ruthenium by extracting the compound in the presence of sodium perchlorate into the nitrobenzene. Other triazines which form likewise, highly colored compounds with ruthenium(II) and have high molar extinction coefficients are: 2-amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine, 2-amino-4,6-bis(2'-pyridyl)-s-triazine and 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine. These compounds will be good colorimetric reagents for the determination of ruthenium.

It is apparent that the ruthenium-TPTZ compound is similar in nature to the iron compound and has the structure



in which each of the tripyridyl-s-triazine molecules occupy three coordination positions about the ruthenium atom. Presumably the triazine molecule is planar and the planes of the two molecules lie at right angles.

The spectra of the different pyridyl-s-triazine derivatives of ruthenium have been obtained in the visible region and their molar extinction coefficients have been determined. Ruthenium bis(2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine had the highest value of 11,800. Melamine which has three symmetrical amino groups in the triazine nucleus does not produce any colored compound with ruthenium. It was observed that the molar extinction coefficient of these derivatives of ruthenium increased as the amino groups in the triazine nucleus are replaced by the pyridyl groups and with the subsequent addition of a side chain in the pyridyl ring.

The ruthenium compounds have been found to be relatively stable, after exposure to ordinary room temperature for three weeks causing no decomposition. Only ruthenium diamino-4'-phenyl-2'-pyridyl-s-triazine decomposed to a great extent on standing.

Four of the substituted polypyridyl-s-triazine studied fluoresce under ultraviolet radiation. They are: 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine, diamino-4'-ethyl-2'-pyridyl-s-triazine, diamino-4'-phenyl-2'-pyridyl-s-triazine and 2,4-diamino-6-(2'-pyridyl)-s-triazine.

The formal reduction potential of the ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride has been determined potentiometrically and found to be 1.18_6 volt. The oxidation potential as determined colorimetrically was found to be 1.18_8 volt. The formal oxidation potentials of the ruthenium derivatives determined by the use of the potentiopoised solutions were very slightly higher than the values obtained potentiometrically, because of the differences in intensities of the colors of the reduced and oxidized forms. The formal potentials of the ruthenium compounds were higher than the formal potentials of their iron analogs.

The ruthenium tripyridyl triazine compounds have been examined as possible oxidation-reduction indicators. Titrations were run with standard ferrous ethylenediammonium sulfate and sodium arsenite using standard sulfatoceric acid in 1 M sulfuric acid. The titrations were compared with ferrous 1,10-phenanthroline sulfate as indicator. The results were found satisfactory especially with ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate as the end point was very distinct, that is, the abrupt disappearance of the violet tinge from the purple color and the appearance of the orange shade. The average per cent relative error was -0.04 per cent with ferrous ethylenediammonium sulfate and +0.10 per cent with sodium arsenite. Ferrous 1,10-phenanthroline sulfate gave -0.03 and +0.20 per cent relative error respectively.

PART III. OSMIUM COMPOUNDS

Historical Background

The 1,10-phenanthroline derivative of bivalent osmium, $Os(1,10\text{-phen})_3I_2$, was prepared by Dwyer, Gibson and Gyarfas (19) in 1950 by the reaction between 1,10-phenanthroline and ammonium bromoosmate in glycerol solution at 250-270° C. and the subsequent addition of potassium iodide. The dark, greenish-brown solution of $Os(1,10\text{-phen})_3^{++}$ can be reversibly oxidized to the red $Os(1,10\text{-phen})_3^{+++}$. The compound has been used as oxidation-reduction indicator with a reduction potential of 0.822 volt in 1 N hydrochloric acid (17).

Dwyer and Gibson (18) used the perchlorate salt in a series of titrations of iron with the dichromate. The end-point was found to be distinct, the color change of the osmium 1,10-phenanthroline perchlorate in the presence of chromium sulfate was yellow-green to blue-green. The titrations were done in 1 N sulfuric and in the presence of phosphoric acid. The reagent is said to be stable in its aqueous saturated solution.

In 1950, Burstall, Dwyer and Gyarfas (17) prepared dichloro-bis-2,2'-bipyridineosmium(II) chloride trihydrate, $Os(2,2'\text{-bipy})_2Cl_2.3H_2O$, by heating potassium osmichloride and 2,2'-bipyridine at 260° C. for 1 hour. The dark brown solid obtained was extracted with benzene to remove any excess 2,2'-bipyridine.

The crystals were washed with water and air dried. The filtrate after the crystallization was made alkaline with sodium hydroxide, boiled, cooled, and filtered from the hydrated osmium oxide. It was acidified with hydrochloric acid and evaporated to dryness. The green chloride was extracted with alcohol and the residue crystallized from a little water.

Dark green $Os(2,2'\text{-bipy})_3Cl_2$ was obtained by Dwyer (16) by pyrolysis of potassium hexachloroosmate, osmium metal and 2,2'-bipyridine at 250° C., or ammonium hexachloroosmate and 2,2'-bipyridine without the osmium metal. It was isolated as the perchlorate and Dwyer, Gibson and Gyarfas (20) found the reduction potential in 0.1 N acid to be 0.86 volt, while the standard reduction potential in 1 N hydrochloric acid was 0.819 volt. This ion acts as a reversible oxidation-reduction indicator. Burstall, Dwyer and Gyarfas (7) found the system in concentrated nitric or sulfuric acid changed color with ceric sulfate with a potential of approximately 1 volt.

$$\underset{\text{red}}{(Os(2,2'\text{-bipy})_3)^{+++}} + e^- = \underset{\text{green}}{(Os(2,2'\text{-bipy})_3)^{++}}$$

In 1937 Morgan and Burstall (26) prepared osmium bis(2,2',2"-terpyridyl) chloride tetrahydrate by fusing potassium osmichloride ($K_2(OsCl_6)$), metallic osmium and 2,2',2"-tripyridyl at 250-260° C. for 3 hours. The product was extracted with benzene and the aqueous extract after filtration was evaporated to produce the green needles of the chloride salt. The corresponding iodide salt was prepared by adding potassium iodide to a solution of the chloride.

In 1954, Dwyer and Gyarfas (22) prepared the osmium bis-(2,2',2"-terpyridyl) perchlorate by treating a warm solution of the complex iodide with dilute perchloric acid and recrystallizing it from hot water. The powder was suspended in ice water and oxidized by shaking in a current of chlorine. The unreacted material was filtered off and the filtrate was treated with 20 per cent sodium perchlorate. The green needles formed were washed with 2 per cent perchloric acid and purified with ether. The crystals were dried in vacuo. The potential of the system,

$$Os(2,2',2''\text{-trpy})_2^{+++} + e^- = Os(2,2',2''\text{-trpy})_2^{++}$$

was found to be -0.856 volt in 0.1 F acid. Its standard reduction potential was 0.9866 + 0.0005 volt.

Since both iron and ruthenium compounds of the 2,4,6-tri(2'-pyridyl)-s-triazine have been found to form the bistridentate type of salt with the general type, $(M2tripy)X_2$, where M is the metal, it was of interest to learn if the next member of the iron triad would follow the same octahedral arrangement.

Furthermore, the terpyridyl compounds of osmium which have been prepared were found to be unstable in the oxidized form and although highly colored and possessed of a good color change, (green in the reduced form and red in the oxidized form), yet not recommended as an oxidation-reduction indicator.

In Part III of this work are reported investigations on the composition, structure, properties and uses of the compound formed between osmium and 2,4,6-tri(2'-pyridyl)-s-triazine.

Preparation of Osmium Derivative of Tripyridyl-s-Triazine

Materials

The reagents and solutions used in the study of the osmium compounds have been described previously in Parts I and II of this work.

The preparation of the osmium chloride solution and the standardization of the original reagent, osmium chloride, is described in this section.

In order to determine the composition of the osmium derivative with 2,4,6-tris(2'-pyridyl)-s-triazine, osmium bis-(2,4,6-tri(2'-pyridyl)-s-triazine) chloride and osmium bis-(2,4,6-tri(2'-pyridyl)-s-triazine) iodide have been prepared and analyzed. The procedures and results are shown on the following pages.

Osmium chloride

A solution of osmium chloride was prepared by dissolving 1.0010 grams of osmium chloride obtained from the American Platinum Works, in 100 ml. of deionized water. The stock solution was 2.312×10^{-2} M in osmium.

The osmium chloride was standardized by taking 50 milligrams of the original osmium chloride and placed it in a previously ignited and weighed porcelain boat. The material was covered with ammonium chloride solid, and heated in a stream of hydrogen gas in a tube. The temperature of the furnace was gradually raised and taken to red heat. The hydrogen gas was finally displaced with carbon dioxide, and the boat was taken to room temperature for weighing.

Duplicate analysis of the osmium chloride gave an average of 43.95 per cent osmium; The American Platinum Works, now a Division of Engelhard Industries, Inc., reported a value of 43.94 per cent osmium metal content.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride

One gram of osmium chloride was fused in a beaker with three grams of 2,4,6-tris(2'-pyridyl)-s-triazine at 260° C. in an oven for one hour. The mixture was stirred and cooled to room temperature. The fused mixture was extracted with benzene five times to remove any unreacted tripyridyltriazine. The residue was dissolved and boiled with deionized water. Ten ml. of 6 N hydrochloric acid were added to it and then the compound was reduced by the addition of 10 grams of hydroxylammonium chloride. The pH was adjusted to about 5 with 5 M sodium hydroxide and the mixture was again boiled and stirred vigorously. The filtrate was evaporated to near saturation in a water bath. The crystals were then filtered and washed with a small amount of ice water, several times with ether and dried over calcium chloride in a vacuum. The osmium tripyridyl triazine chloride obtained was purple in color, showing a greenish reflection under the microscope. It was somewhat soluble in benzene. The melting point was 120-121° C. The compound was analyzed for osmium(distillation-thiourea, details in next paragraph), tripyridyl-s-triazine (two methods, see below), and chloride(silver nitrate titration). The results are given in Table 17. The compound is undoubtedly $Os(tripyridyltriazine)_2Cl_2$.

Determination of osmium. Distillation-colorimetric method

A calibration curve was prepared by distilling varying aliquot portions of osmium chloride containing 2.312×10^{-3} M osmium. The osmium chloride was treated with 25 ml. of 1:1 nitric acid and 5 ml. of 1:1 sulfuric acid. Dry air was allowed to pass through the solution for a few minutes after

Table 17. Osmium bis-(2,4,6-tripyridyl-s-triazine) chloride

Substance sought	Method used	Per cent found	Average per cent	Per cent mol. wt.	Ratio
Osmium	colorimetric	15.8 16.0	15.9	.0835	
TPTZ	UV	57.2 57.9	57.5	.184	1: 210 Os: TPTZ
Chloride	adsorption	5.81 6.02	5.92	.167	1: 2.00 Os: Chloride

Empirical formula:

$$Os_1(TPTZ)_{2.10}Cl_{2.00}$$

which the solution mixture was heated. The heating was gradually increased with a variac and the temperature raised and taken to boiling of the mixture with a timer. The osmium tetroxide was absorbed into 25 ml. of 5 per cent thiourea (33) in 1:1 hydrochloric acid-ethyl alcohol. After 50 minutes, all the osmium had been distilled, the current was cut off and the set-up (1) cooled to room temperature. The delivery tube and receivers were all flushed with 1:1 hydrochloric acid-ethyl alcohol mixture which was also used to dilute the distillate and washings to 50 ml.

The transmittancy was measured immediately at 480 mμ using a Beckman DU Spectrophotometer, a 1 cm. pyrex cell, and the 1:1 hydrochloric acid-ethyl alcohol mixture as blank.

Ten milligram sample of the osmium compound was distilled in the same manner as above and the amount of osmium was determined colorimetrically.

Determination of 2,4,6-tris(2'pyridyl)-s-triazine. Ultraviolet method

2,4,6-Tris(2'-pyridyl)-s-triazine was found to have two peaks in the ultraviolet region (4). Measurement at one of these absorbance peaks would be a means of determining the amount of the triazine present in the remaining solution in the distilling flask after the osmium content has been removed. Since the iodide is also removed because it is more likely oxidized to iodate and not distilled, and since the chloride will not affect the absorption spectra in the ultraviolet region, this idea was placed on an experimental basis.

The absorption spectra of several solutions containing known amounts of 2,4,6-tris(2'-pyridyl)-s-triazine were recorded in the ultraviolet region. It was observed that the absorbance maximum shifts to the lower wavelength as the pH is increased.

A calibration curve was prepared by running the spectra of solutions containing varying amounts of standard 2,4,6-tris(2'-pyridyl)-s-triazine and 10 ml. of 10 per cent sodium acetate. The pH of each solution was adjusted to 5 with 5 M sodium hydroxide and 6 M hydrochloric acid. All reagents used were iron free. The Cary Spectrophotometer Model 12, a 1 cm. silica cell and a blank of water were used. The curve was linear from 1.0 to 20.0 x 10^{-6} M 2,4,6-tris-(2'-pyridyl)-s-triazine.

From 2-50 milligrams of the sample were placed into the distilling flask and the distillation was run with a slow bubbling of air, and at a controlled temperature. The osmium was distilled off into the thiourea mixture using all iron-free reagents wherever possible. The iron was removed from the reagents by treatment with bathophenanthroline and extraction into isoamyl alcohol. The nitric acid used was distilled. The distillation was run in the same manner as in the determination of osmium.

After the distillation, the remainder of the solution in the distilling flask was diluted with deionized water in a 100 ml. volumetric flask and taken up to the mark after cooling to room temperature. Aliquots of this solution were taken and to them was added 10 ml. of 10 per cent sodium acetate. The pH was adjusted to 5 with 5 M sodium hydroxide. The volume was again taken up to the 100 ml. mark with deionized water. The absorbance of the reagents similarly prepared but without 2,4,6-tris(2'-pyridyl)-s-triazine was measured as a blank. Its absorbance at 290 mμ, which was the wavelength where the absorbance maximum of the different solutions fall in the preparation of the calibration curve, was subtracted from that of the other solutions.

Determination of 2,4,6-tris(2'-pyridyl)-s-triazine as ferrous derivative

2,4,6-Tris(2'-pyridyl)-s-triazine has been found by Collins, Diehl and Smith (12) to be a good colorimetric reagent for iron. The combining ratio of iron(II) with tripyridyl-s-triazine has been found to be 1:2 by spectrophotometric titration, continuous variations study and by analysis. The molar extinction coefficient is 22,600 at 593 mμ in aqueous solution. Advantage of these facts was made in the determination of tripyridyl-s-triazine in the osmium compounds by the addition of excess iron.

A calibration curve was prepared by taking aliquot portions of standard solutions of tripyridyl triazine with a concentration of 1.0005×10^{-4} M and mixed with 25 ml. of standard iron solution whose concentration was 1.84×10^{-3} M. The iron was reduced with 2 ml. of 10 per cent hydroxylammonium chloride. The mixture was treated with 10 ml. of iron free 10 per cent sodium acetate and the pH adjusted with iron free 5 M sodium hydroxide, to pH 5. The solutions were diluted to the 100 ml. mark in volumetric flasks. The per cent transmission were read in the Beckman DU Spectrophotometer at 593 mμ using a 1 cm. pyrex cell and a blank.

The calibration curve was linear within the range of 10 to 50 x 10^{+6} M tripyridyl triazine with excess iron.

Separate aliquot portions of the diluted solutions left in the distillation flask after the removal of osmium were treated in the same manner as in the preparation of the calibration curve. The per cent transmission was read at 593 mμ with a blank.

Taking a concentration of 40 x 10^{+6} M tripyridyl triazine in the straight portion of the plot described above, this corresponds to an absorbance of 0.278. From this data the molar extinction coefficient of 6,950 was obtained and used in the determination of the concentrations of the different unknowns.

Determination of chloride

About 50 milligrams of the osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride were dissolved in deionized water and passed through an ion exchange column in the hydrogen form. The eluate was titrated against the standard 0.0100 N silver nitrate using 10 drops of 0.1 per cent of the sodium salt of dichlorofluorescein indicator. Five ml. of 1 per cent dextrin was added to prevent coagulation of the silver chloride. The titration was carried to the slightly pink end point.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate

A column of Amberlite IR-400 in the chloride form was converted to the perchlorate form by passing about 500 ml. of 2 M sodium perchlorate dropwise through the bed. After the eluate was free of chloride the column was rinsed with deionized water to remove the excess sodium perchlorate.

A water solution of osmium tripyridyl triazine chloride was stirred with Amberlite IR-400 in the perchlorate form with a magnetic stirrer for 16 hours. The resin was filtered off and washed with deionized water. The combined washings and filtrate were evaporated to dryness in a water bath. The crystals so obtained were washed with ether and dried at 110° C. for 2 hours. The compound decomposes at about 200° C., turns brown and is carbonized at about 254° C.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide

About 1 gram of osmium trichloride was fused with about 3 grams of 2,4,6-tris(2'-pyridyl)-s-triazine in a 125 ml. iodine flask at 260° C. in an oven for about 1 hour. The compound formed was cooled to about 100° C. and was dissolved in about 100 ml. of warm water. This was acidified with 5 ml. of 6 N hydrochloric acid and reduced with 4 grams of hydroxylammonium chloride. The mixture was taken to boiling. It was made alkaline with 5 M sodium hydroxide and on cooling, the excess 2,4,6-tris(2'-pyridyl)-s-triazine was filtered off. The solution was boiled again and 4 grams of potassium iodide was added. The mixture was cooled over an ice bath and the osmium tripyridyl triazine iodide crystals were filtered off. The crystals were purified by extracting the excess potassium iodide with ether for 30 hours and dried over calcium chloride in a vacuum desiccator. Melting point: 232-233° C.

The compound was analyzed for osmium by the distillation-thiourea method, for tripyridyl-s-triazine by the ultraviolet and iron methods, and for iodide by passage through IR-120 in the hydrogen form and titration with silver nitrate with eosin as indicator. The results are summarized in Table 18. The compound is $Os(TPTZ)_2I_2$.

Nonaqueous Titrations of Osmium 2,4,6-Tris(2'-Pyridyl)-s-Triazine

In order to gain insight into the structure of osmium 2,4,6-tris(2'-pyridyl)-s-triazine some titrations in nonaqueous medium were performed. Pyridyl groups not attached to the osmium metal were determined by direct titration of the compound in nonaqueous solution with standard perchloric acid in acetic acid.

About 30-50 milligrams sample were dissolved in various solvents with acetic acid anhydride and allowed to stand

Table 18. Osmium bis-(2,4,6-tripyridyl)-s-triazine) iodide

Substance sought	Method used	Per cent found	Average per cent	Per cent mol. wt.	Ratio
Osmium	colorimetric	14.91			
		15.07	14.99	.0788	
TPTZ	ultraviolet	49.60			
		49.00			
		49.00			
		49.00			
		49.00			
		50.24			
		49.01	49.26	.1579	1: 2.00 Os: TPTZ
TPTZ	excess iron	50.20			
		49.01			
		49.03	49.41	.1583	1: 2.01 Os: TPTZ
Iodide	adsorption	21.01			
		21.08	21.05	.1659	1: 2.11 Os: Iodide

Empirical formula:

$$Os_1(TPTZ)_{2.01}I_{2.11}$$

overnight to allow the anhydride to react with the water present. The solutions were titrated with 0.01 N perchloric acid in acetic acid and acetic acid anhydride. The voltage readings were plotted versus the ml. of perchloric acid used, using the Beckman Model G pH meter, a glass and a fiber type calomel electrode.

The osmium tripyridyltriazine under study was not very soluble in the different solvents used: glacial acetic acid, nitromethane and acetonitrile. The perchlorate and the iodide salts had to be heated with the solvents to put them to solution. The water which came from the 70 per cent perchloric acid had to be removed since its presence did not give any good end-point break. The best solvent was glacial acetic acid in acetic acid anhydride which gave a good end-point break at the second equivalence point for chloride, perchlorate and iodide salts investigated. The curves for the titration are shown in Figures 19 and 20.

0.1 N perchloric acid was prepared by mixing 8.5 ml. of 70 per cent perchloric acid with 200 ml. of glacial acetic acid and added 20 ml. of acetic anhydride (24). This was allowed to stand overnight after dilution to 1 liter. One hundred ml. of the above 0.1 N perchloric acid was diluted with glacial acetic acid to make 1 liter of 0.01 N perchloric acid.

The perchloric acid was standardized as follows: 0.2007 grams of potassium acid phthalate was dissolved in hot acetic acid. After cooling to room temperature, the solution was diluted to exactly 100 ml. with glacial acetic acid. Exactly 10 ml. of this solution were diluted with

Figure 19. Titration curve for osmium tripyridyl triazine chloride in glacial acetic acid.

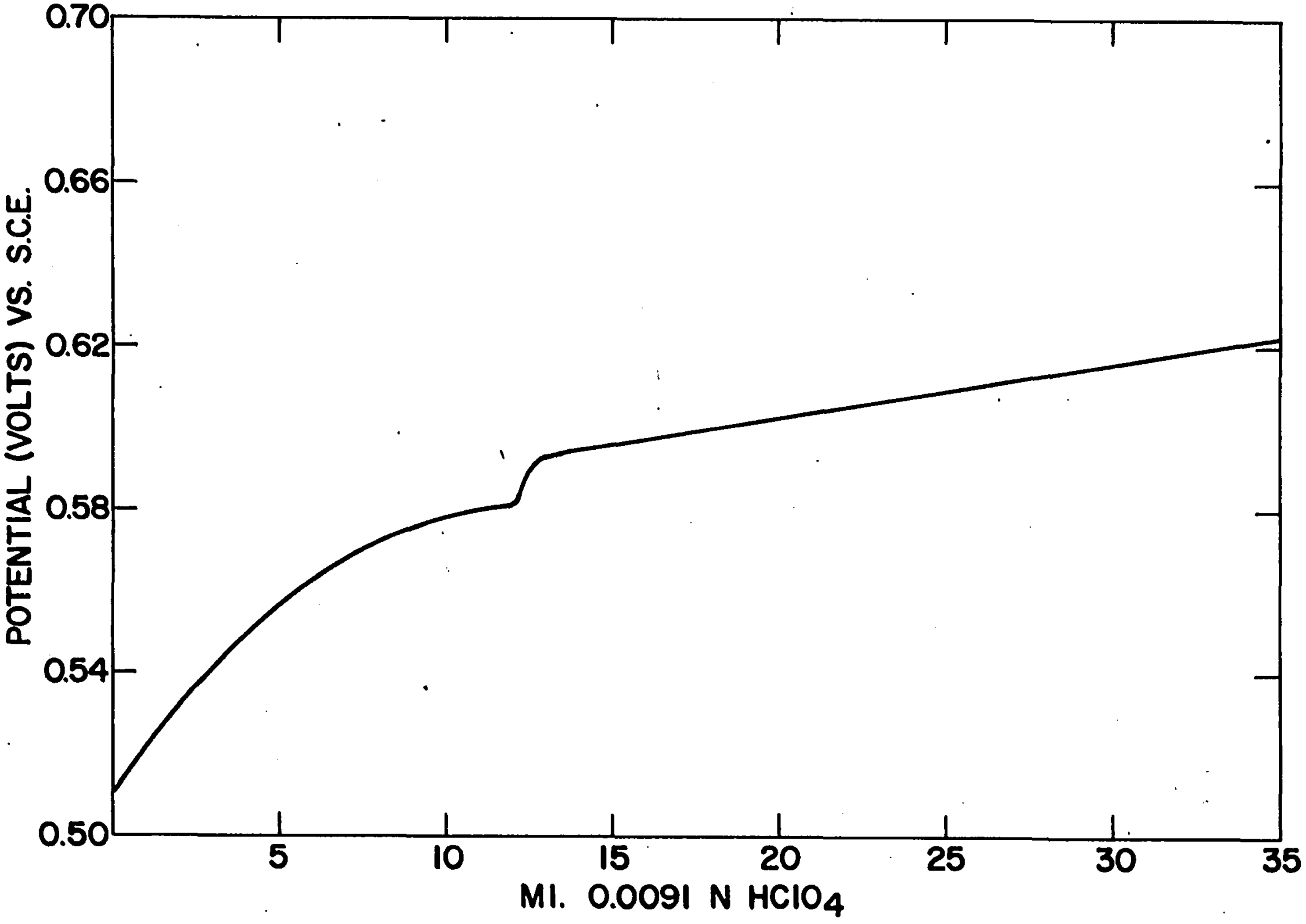
Weight taken: 0.0502 g.

Solvent: 50 ml. glacial acetic acid

2 ml. acetic anhydride

1 equivalent: 6.23 ml.

2 equivalent: 12.46 ml.



POTENTIAL (VOLTS) VS. S.C.E.
0.70
0.66
0.62
0.58
0.54
0.50
5
10
15
20
25
30
35
Ml. 0.0091 N $HClO_4$

Figure 20. Titration curve for osmium tripyridyl triazine perchlorate in glacial acetic acid.

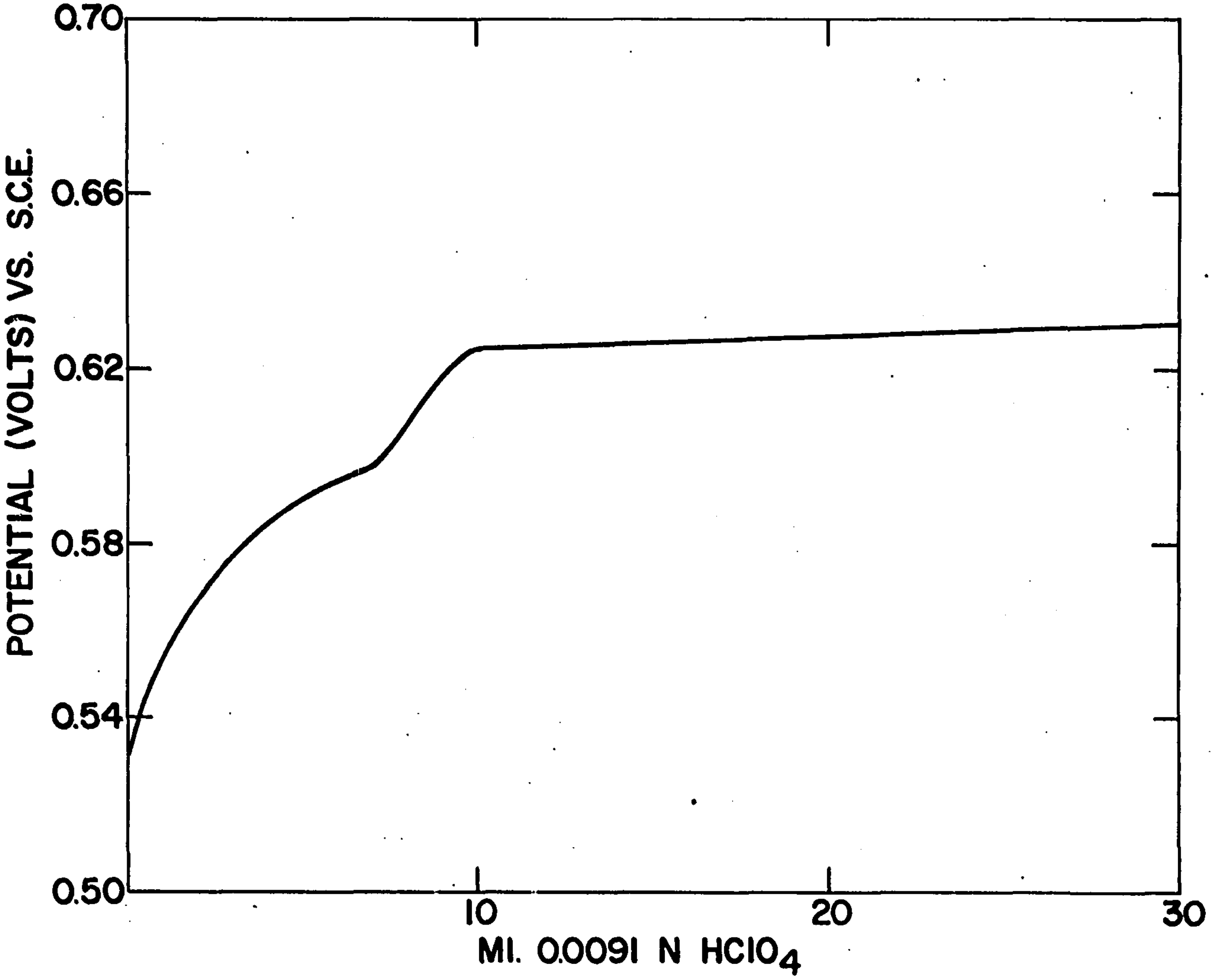
Weight taken: 0.0381 g.

Solvent: 25 ml. glacial acetic acid
2 ml. acetic anhydride

1 equivalent: 4.13 ml.

2 equivalents: 8.26 ml.

3 equivalents: 12.39 ml.


0.70
0.66
0.62
0.58
0.54
0.50
10
20
30
POTENTIAL (VOLTS) VS. S.C.E.
Ml. 0.0091 N $HClO_4$

benzene to 100 ml. The solution was 0.001 N in potassium acid phthalate.

Ten ml. of the 0.001 N potassium acid phthalate was titrated with the above perchloric acid using methyl violet indicator to the first permanent blue color. An indicator blank was run with 1 ml. of benzene and 1 drop of the indicator. The first standard solution prepared was 0.0091 N, while the second was 0.0108 N.

Absorption Spectra

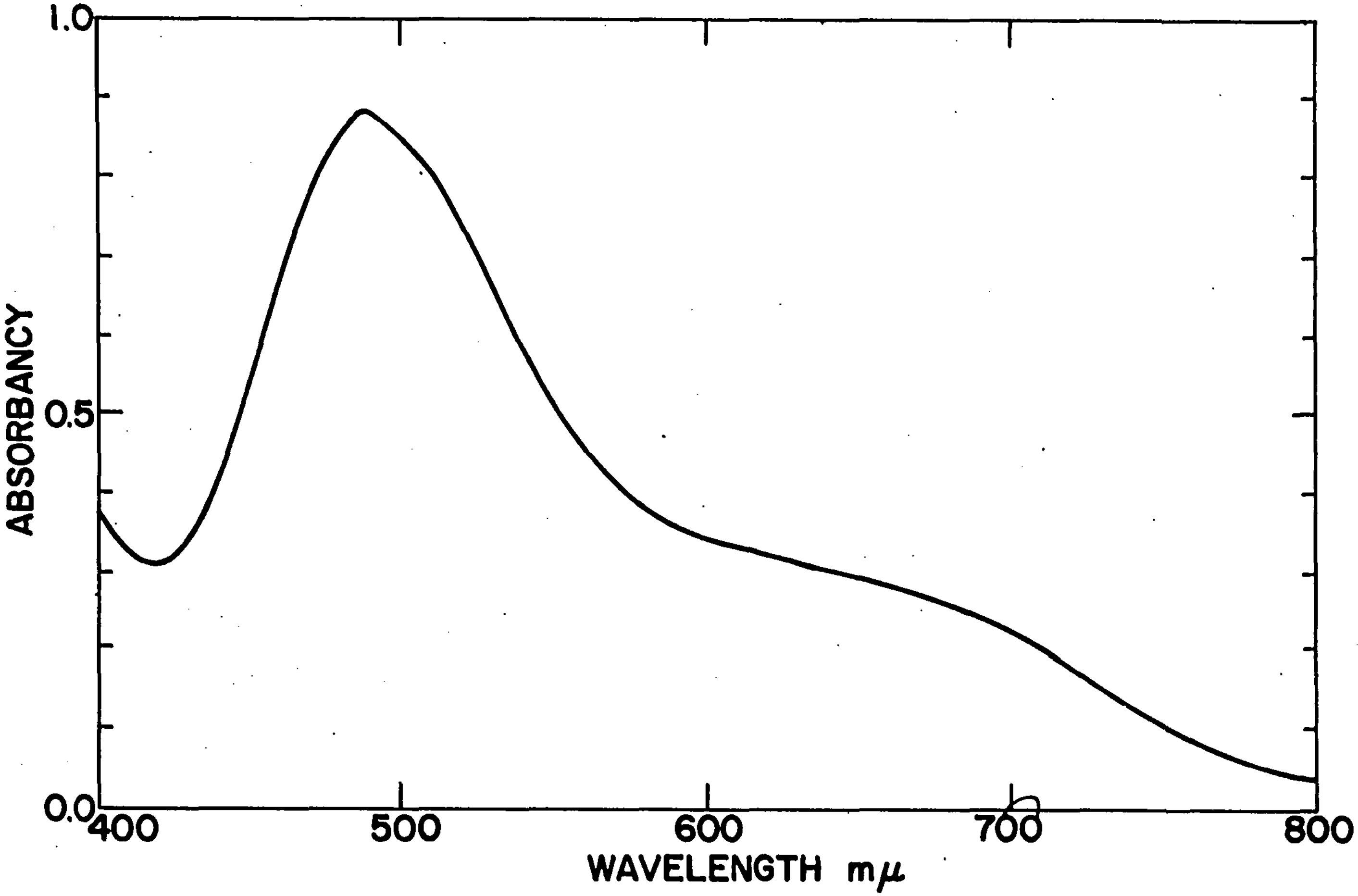
Visible region

The prepared osmium derivatives were dissolved in 10 ml. of ethyl alcohol and diluted with deionized water to a volume of 25 ml.

The absorption spectra of these derivatives were recorded in the visible region using a Cary Spectrophotometer Model 12, 1 cm. silica cell, and a blank containing alcohol and water. The spectrum of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride is shown in Figure 21. The molar extinction coefficients of the derivatives are as follows: osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine)chloride, 1,540; osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine)perchlorate, 1,340; osmium 1,10-phenanthroline chloride, 970.

Figure 21. The visible spectrum of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride, $Os(TPTZ)_2Cl_2$.

Cell length: 1 cm.


1.0
0.5
0.0
ABSORBANCY
400
500
600
700
800
WAVELENGTH mμ

Ultraviolet region

The same solutions used in the recording of spectra of the osmium compounds in the visible region were diluted with deionized water so that the concentrations were about 10^{-5} M. The spectra of these solutions were recorded in the ultraviolet region using a 1 cm. silica cell and water and alcohol mixture as blank. The spectrum of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride is shown in Figure 22.

It was observed that the maximum absorbance in the spectra of the different osmium tripyridyl-s-triazine compounds in the visible region was 485 mμ. In the ultraviolet, two peaks were observed. One maximum occurs at about 283 mμ and the second and lower peak occurs at about 245 mμ.

Formal Reduction Potential of Osmium Compounds

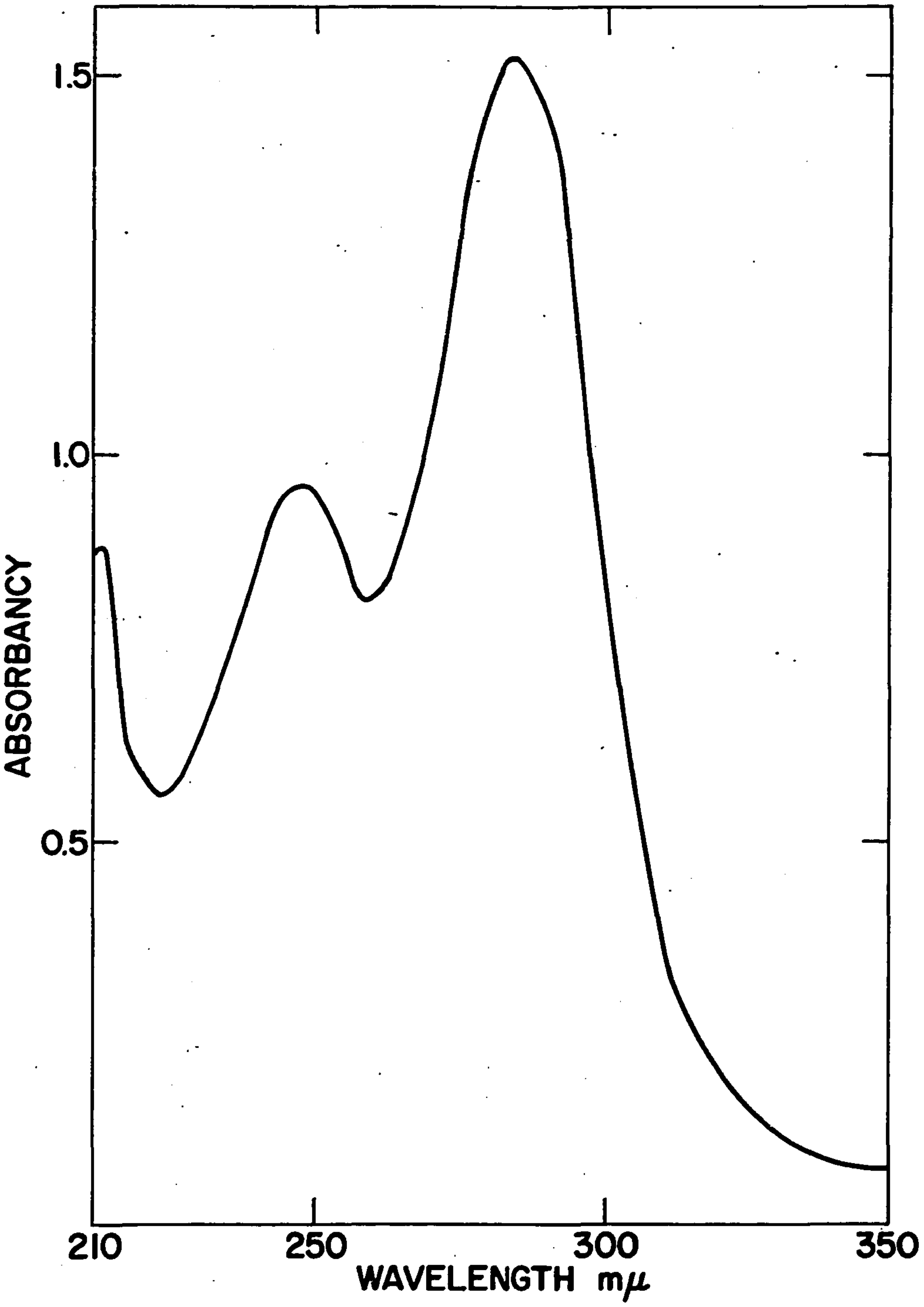
Potentiometric method

The formal reduction potentials of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride and osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate in 1 M sulfuric acid were determined using the Leeds and Northrup Type K Potentiometer and galvanometer. A platinum electrode and a saturated calomel electrode attached to an agar bridge were used.

The procedure and results are given in the next pages.

Figure 22. The ultraviolet spectrum of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride, $Os(TPTZ)_2Cl_2$.

Cell length: 1 cm.


1.5
1.0
0.5
ABSORBANCY
210
250
300
350
WAVELENGTH mμ

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride

0.0408 gram of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride was dissolved in 8 ml. of deionized water and 10 ml. of 2 M sulfuric acid. To the mixture, 2 ml. of 0.05 M ferrous sulfate solution was added. Nitrogen gas was passed slowly through the closed vessel to displace any oxygen present, as well as to provide stirring of the mixture. The mixture was titrated with 0.0277 M sulfatoceric acid in 1 M sulfuric acid. The formal reduction potential vs. hydrogen was found to be 1.02_2 volts.

The plot of the voltage reading versus the milliliter of titrant is shown in Figure 23.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate

0.0417 gram of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate was dissolved in 8 ml. of warm deionized water and to it was added 10 ml. of 2 M sulfuric acid and 2 ml. of 0.05 M ferrous sulfate solution. The mixture was titrated with 0.0277 M sulfatoceric acid in 1 M sulfuric acid to an abrupt change of color, from purple to orange. The formal reduction potential was found to be 1.08_2 volt versus the hydrogen electrode.

The plot of the voltage reading against the milliliter of sulfatoceric acid used is given in Figure 24.

Figure 23. Potentiometric titration of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride in the presence of ferrous sulfate with 0.0277 M sulfatoceric acid in 1 M sulfuric acid.

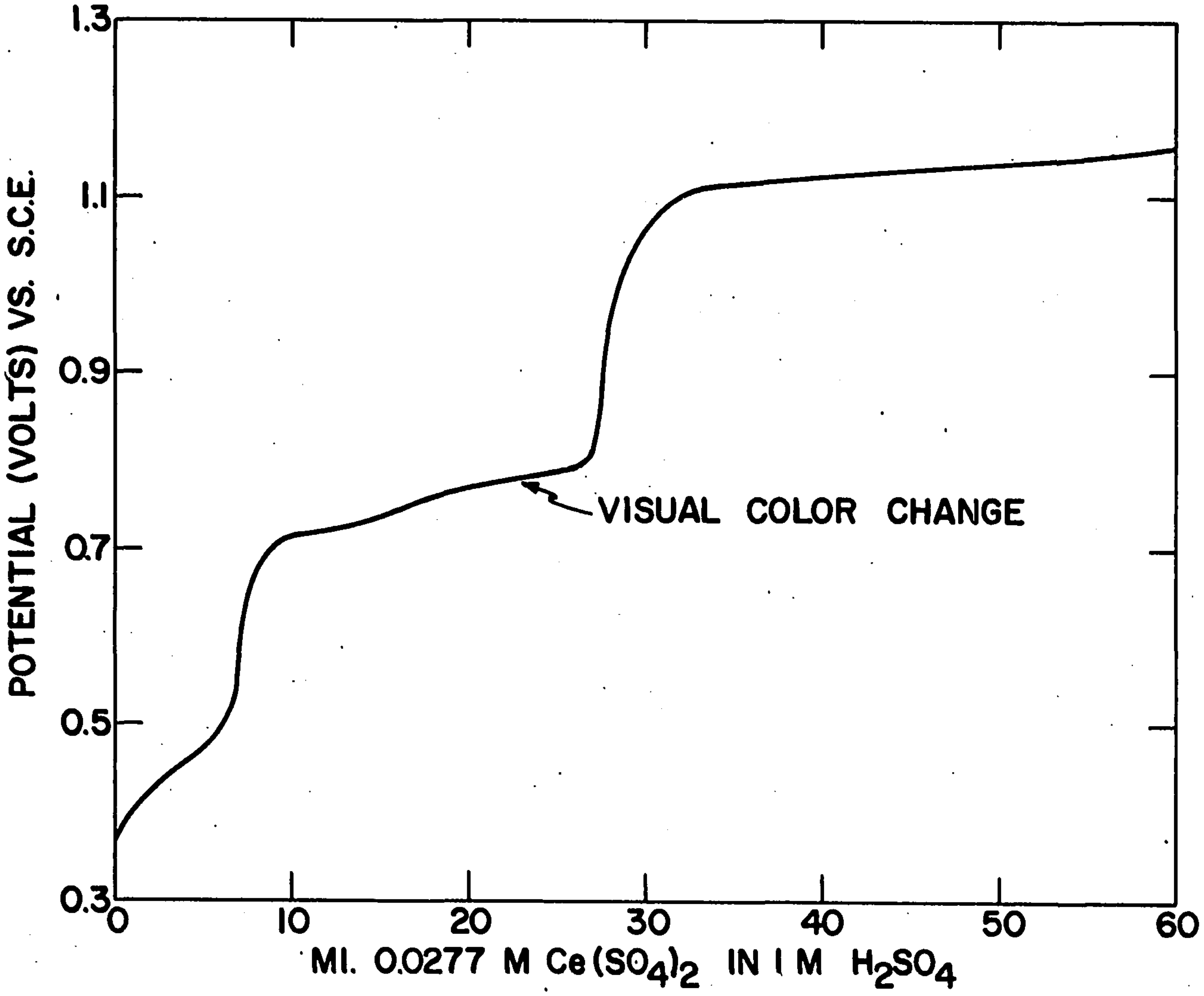
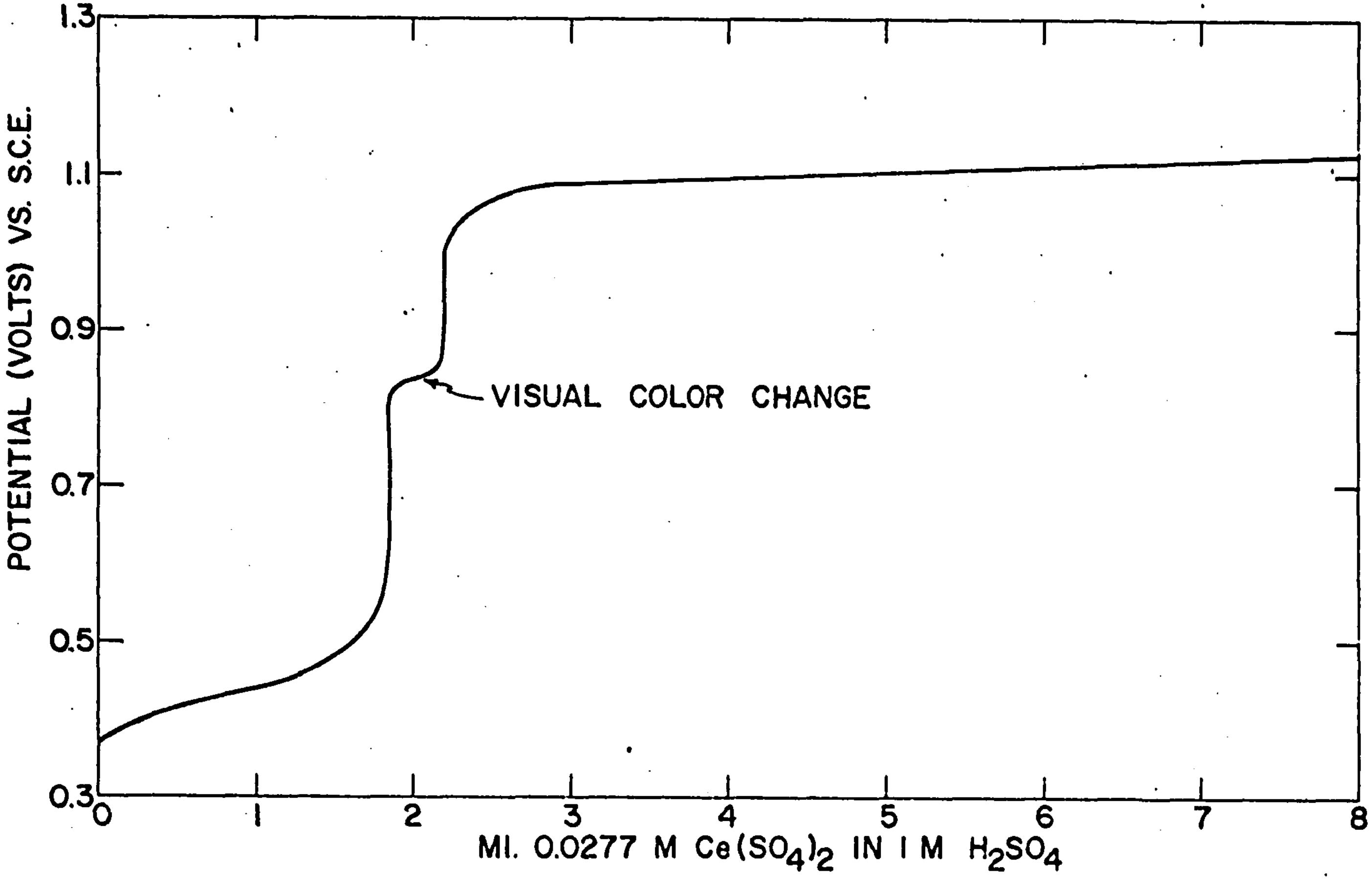

POTENTIAL (VOLTS) VS. S.C.E.
1.3
1.1
0.9
0.7
0.5
0.3
0
10
20
30
40
50
60
Ml. 0.0277 M Ce(SO4)2 IN 1 M H2SO4
VISUAL COLOR CHANGE

Figure 24. Potentiometric titration of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate in the presence of ferrous sulfate with 0.0277 M sulfatoceric acid in 1 M sulfuric acid.


POTENTIAL (VOLTS) VS. S.C.E.
1.3
1.1
0.9
0.7
0.5
0.3
0
1
2
3
4
5
6
7
8
VISUAL COLOR CHANGE
Ml. 0.0277 M $Ce(SO_4)_2$ IN 1 M H_2SO_4

Colorimetric method

As in the determination of the formal potentials of the iron and ruthenium derivatives as described in Part I by the use of the potentiopoised solutions, the formal potentials of the osmium compounds were likewise determined colorimetrically. The formal potentials of the osmium compounds found both by the potentiometric and colorimetric methods are given in Table 19.

Osmium 1,10-phenanthroline chloride was prepared and its colorimetric formal potential was determined for comparison with the known formal potential. The procedure for its preparation is given below.

Osmium 1,10-phenanthroline chloride One gram of osmium trichloride and five grams of 1,10-phenanthroline were fused at 260° C. in an oven for one hour. The compound was purified in the same manner described above for osmium tripyridyl triazine compounds.

The fusion residue was dark brown and did not contain any colored material soluble in benzene. Under the microscope the product was brown in color with a greenish reflection. A dilute aqueous solution of the compound showed a slight flourescence. Melting point: 118-120° C.

Table 19. Formal reduction potentials of the osmium compounds

Compound	E^o(previous) potentiometric method	Formality H_2SO_4	E^o(found) colorimetric method	Color change reduced-oxidized
$Os(1,10\text{-phen})_3Cl_2$		0.1	0.91_0	brown-greenish
$Os(1,10\text{-phen})_3I_2$	0.822 (1 N HCl, Dwyer)			
$Os(TPTZ)_2Cl_2$	1.02_2	2.37	1.08_4	violet-orange
$Os(TPTZ)_2(ClO_4)_2$	1.08_2	2.5	1.09_2	violet-orange
$Os(TPTZ)_2I_2$		2.37	1.08_4	violet-orange
$Os(2,2'\text{-bipy})_3Cl_2$	0.819 (1 N HCl, Dwyer)			

Osmium Bis(2,4,6-Tri(2'-Pyridyl)-s-Triazine) Perchlorate as an Oxidation-Reduction Indicator

In 1950, Dwyer, Gibson and Gyarfas (18) used osmium 1,10-phenanthroline perchlorate as an internal redox indicator for the determination of ferrous iron with potassium dichromate. The titration was done in normal sulfuric acid in the presence of phosphoric acid. They compared the titration using also diphenylamine indicator. The results showed a mean of 0.1 per cent error for osmium 1,10-

phenanthroline perchlorate, and a mean of +0.7 per cent using diphenylamine indicator.

A study was made in order to determine the applicability of the osmium tripyridyl triazine compounds as oxidation-reduction indicators. Titrations of standard ethylenediammonium sulfate and standard sodium arsenite in 1 M perchlorate acid, with sulfatoceric acid in 1 M sulfuric acid were investigated. The end point indicator change was compared against ferrous 1,10-phenanthroline sulfate as indicator. The procedures and results are given in the pages that follow.

Titration of ferrous ethylenediammonium sulfate

About 0.5 gram of pure standard ferrous ethylenediammonium sulfate was dissolved in 25 ml. of deionized water. Twenty-five ml. of 2 M perchloric acid and 3 drops of 0.002 M indicator were added. The solutions were titrated against standard 0.0574 M sulfatoceric acid in 1 M sulfuric acid. The results are summarized in Table 20.

Titration of sodium arsenite

Twenty-five ml. of standard solution of sodium arsenite which was 0.1002 M, was pipetted into a beaker and 2 drops of 0.01 M osmium tetroxide was added as catalyst. Twenty-five ml. of 2 M perchloric acid and three drops of 0.002 M osmium

Table 20. Titration of ferrous ethylenediammonium sulfate with sulfatoceric acid

Indicator	Weight taken(g)	Ml. 0.0574 M $Ce(SO_4)_2$ used	Weight found(g)	Per cent relative error	Average per cent relative error
$Os(TPTZ)_2(ClO_4)_2$	0.5016	22.90	0.5024	-0.02	
	0.5038	22.95	0.5036	-0.04	-0.03
$Os(1,10\text{-phen})_3Cl_2$	0.5009	22.85	0.5004	-0.10	
	0.5019	22.90	0.5015	-0.08	-0.09
$Fe(1,10\text{-phen})_3SO_4$	0.5001	22.80	0.4993	-0.16	
	0.5015	22.87	0.5009	-0.12	
	0.5000	22.85	0.5004	+0.08	-0.03

indicator was added. The solution was titrated with 0.0574 M sulfatoceric acid in 1 M sulfuric acid. A summary of the results are given in Table 21.

Table 21. Titration of sodium arsenite with sulfatoceric acid

Indicator	Ml. 0.0574 M $Ce(SO_4)_2$ used	Molarity $Ce(SO_4)_2$	Per cent relative error	Average per cent relative error
$Os(TPTZ)_2Cl_2$	43.75	0.1005	+0.30	
	43.70	0.1003	+0.10	+0.20
$Os(TPTZ)_2(ClO_4)_2$	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.10
$Os(TPTZ)_2I_2$	43.75	0.1005	+0.30	
	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.16
$Os(1,10\text{-phen})_3Cl_2$	43.80	0.1006	+0.40	
	43.75	0.1005	+0.30	+0.35
$Fe(1,10\text{-phen})_3SO_4$	43.75	0.1005	+0.30	
	43.75	0.1005	+0.30	
	43.70	0.1003	+0.10	
	43.70	0.1003	+0.10	+0.20

Discussion

Osmium 1,10-phenanthroline chloride was prepared by fusion of osmium chloride and 1,10-phenanthroline at 260° C. in a muffle furnace for one hour. The formal reduction potential was found to be 0.91_0 volt in 0.1 F sulfuric acid.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride was prepared by fusion of osmium chloride and 2,4,6-tris-(2'-pyridyl)-s-triazine at 260° C. for one hour. The purified salt was analyzed for osmium, 2,4,6-tris(2'-pyridyl)-s-triazine and chloride. The compound had the composition: osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride, $Os(TPTZ)_2Cl_2$.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate was prepared by converting osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride to the perchlorate using a strong base anion exchange resin.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide was prepared by fusion of osmium chloride and 2,4,6-tris(2'-pyridyl)-s-triazine at 260° C. for one hour. Potassium iodide was added to the reduced solution of the chloride to convert it to the iodide. Excess iodide was removed by extraction with ether.

A further study of the structure of the compound was made by titration in nonaqueous medium of the different compounds with perchloric acid. Results showed that only two pyridyl groups are free, the nitrogens being titrated by the perchloric acid. The titrations also showed that one of the free nitrogen atoms may be weaker than the first as it forms one break at one equivalence in acetonitrile, two breaks at the first and second equivalence point in nitromethane and one break at the second equivalence point in glacial acetic acid medium. The formula for the compounds are thus: $Os(TPTZ)_2Cl_2$, $Os(TPTZ)_2(ClO_4)_2$, and $Os(TPTZ)_2I_2$.

The osmium tripyridyl-s-triazine derivative was examined for its formal reduction potential, both potentiometrically and colorimetrically. The system for the reversible reaction is

$$\underset{\text{orange}}{Os(TPTZ)_2^{+++}} + e^- = \underset{\text{purple}}{Os(TPTZ)_2^{++}}$$

The formal reduction potential of osmium bis(2,4,6-tri-(2'-pyridyl)-s-triazine) chloride as determined potentiometrically is 1.02_2 volts in 1 M sulfuric acid while its formal potential determined colorimetrically is 1.08_4 volts in 2.37 F sulfuric acid. The formal reduction potential of osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate in 1 M sulfuric acid was 1.08_2 volts using the potentiometric method, and 1.09_2 volts in 2.5 F sulfuric acid, as determined by the colorimetric, potentiopoised solution method.

The potential is greatly dependent on the concentration of acid in the solution, E^o increasing with increasing acid concentration. Some differences in the values obtained for the standard potential arise also from the differences in the intensities of the colors of the reduced and oxidized forms, that is, the ratio of the concentrations is not unity at the apparent color change as in obtaining the standard reduction potential from a potentiometric titration.

Osmium tripyridyl-s-triazine ion is a good oxidation-reduction indicator. It has a very sharp color change, from purple to orange. The end-point is an abrupt disappearance of the violet tinge. Both the reduced and oxidized forms are stable and the reaction is reversible. Results of the titrations of ferrous ethylenediammonium sulfate and sodium arsenite solutions in 1 M perchloric acid, with standard sulfatoceric acid in 1 M sulfuric acid showed very reliable results using osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate as indicator. The average per cent relative error in the determination of ferrous ethylenediammonium sulfate was -0.03 per cent using osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate indicator, while ferroin indicator also gave -0.03 per cent error. In the determination of the molarity of sodium arsenite, osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate indicator gave an average relative error of +0.10 per cent, while ferrous 1,10-phenanthroline sulfate indicator gave an average of +0.20 per cent error.

SUMMARY

The reactions of nine pyridyl-substituted s-triazines with iron, ruthenium, and osmium have been investigated. A number of new compounds have been isolated in solid form. A number of systems were investigated only in solution, principally through measurements of absorption spectra and reduction potential. The tri-pyridyl-substituted triazines all combine with iron, ruthenium and osmium in the ratio of two molecules of the organic base to one atom of metal. All these compounds are highly colored, the iron compounds being blue, the ruthenium and osmium compounds, purple. The iron compounds can be prepared easily at room temperature in aqueous solution, the ruthenium compounds can be made by boiling a mixture of the components in aqueous solution, but the osmium compounds can be prepared by fusion of osmium chloride with the base.

The results of this study showed that the ruthenium and osmium tripyridyl triazine perchlorate salts are reliable oxidation-reduction indicators. The formal reduction potentials of these indicators were measured both potentiometrically and colorimetrically, the agreement between the methods being good.

Among the new iron compounds, the deep blue ferrous derivative of 2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine

has been found to be particularly noteworthy because it has a high molar extinction coefficient, 25,500 at the wavelength of maximum absorption, 605 mμ ; it could be a good colorimetric agent for the determination of iron inasmuch as the intense color is developed very quickly at room temperature and is stable.

The iron derivatives of 2-amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine, 2-amino-4,6-bis(2'-pyridyl)-s-triazine and 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine are stable to light, that is, they do not fade on exposure to light or on standing at ordinary room temperature.

The reduction potentials of four iron(II) derivatives of polypyridyl-s-triazines and 1,10-phenanthroline were determined colorimetrically utilizing the colorimetric, potentiopoised solution method of Smith. The value found for the derivative of 1,10-phenanthroline was 1.06_6 (previously reported 1.06) (25); for 2,4,6-tris(2'-pyridyl)-s-triazine in 2.5 F sulfuric acid, 1.08_5 volts; for 2-amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine in 2.25 F sulfuric, 1.07_0 volts; for 2-amino-4,6-bis(2'-pyridyl)-s-triazine in 3 F sulfuric acid, 1.09_7 volts; and for 2,4,6-tris(4'-methyl-2'-pyridyl)-s-triazine, in 3 F sulfuric acid 1.10_3 volts.

The iron(II) compounds of the polypyridyltriazines were found to be satisfactory as oxidation-reduction indicators in the titration of iron with cerate solutions, the color change being from blue to grayish-green to pale yellow to the end point which was deep yellow. The best color change was with ferrous bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide. The average relative error in the titrations of ferrous ethylenediammonium sulfate and sodium arsenite was +0.08 per cent.

The ruthenium derivatives of the pyridyl-s-triazines were prepared by boiling a mixture of ruthenous chloride and the triazine for an extended period.

Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride was isolated and its composition established by analysis for ruthenium and chloride. Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate was prepared by passing the chloride through a strong base anion exchange resin in the perchlorate form. The iodide was prepared from the chloride by simple double decomposition; it also was analyzed to establish its composition. The combining ratios of ruthenium and 2,4,6-tri(2'-pyridyl)-s-triazine, one to two, was also established by spectrophotometric titration and by the method of continuous variations.

The absorption spectrum of ruthenium bis(2,4,6-tri-(2'-pyridyl)-s-triazine) chloride was investigated in some detail. The system, ruthenium chloride-2,4,6-tris(2'-pyridyl)-s-triazine, conforms to Beer's law, at pH 6, the molar extinction coefficient being 11,600 at 506 mμ, the wavelength of maximum absorption. It is formed completely over the pH range 4.5 to 8.5. This ruthenium compound can be extracted into nitrobenzene, in which solution it has a molar extinction coefficient of 18,600. 2,4,6-Tripyridyl-s-triazine thus should provide a good method for the determination of ruthenium for the molar extinction coefficient is high and the possible interferences few.

All of the pyridyl-substituted triazines, nine in number, yield colored compounds with ruthenium with one exception, 2,4,6-triamino-1,3,5-triazine(Melamine). The absorption spectra of these highly colored compounds were obtained; all show one peak in the visible region and two peaks in the ultraviolet region. These compounds are stable toward light at room temperature.

As the amino group attached to the triazine ring is replaced by a pyridyl group and further, as substitution is made in the pyridyl ring, the molar extinction coefficient increases. This fact is illustrated by the series of compounds: 2,4,6-triamino-1,3,5-triazine(Melamine); 2,4,6-diamino-6-(2'-pyridyl)-s-triazine and diamino-4'-ethyl-2'-pyridyl-s-triazine. The first compound does not react with the metal ions, the molar extinction coefficients for the other two are 5,000 and 5,400 respectively. The di(2'-pyridyl) triazines: 2-amino-4,6-bis(2'-pyridyl)-s-triazine and 2-amino-4,6-bis(4'-ethyl-2'-pyridyl)-s-triazine, molar extinction coefficients of 10,000 and 11,300 respectively. The tri(2'-pyridyl) substituted triazines: 2,4,6-tris(2'-pyridyl)-s-triazine and 2,4,6-tri(4'-methyl-2'-pyridyl)-s-triazine, molar extinction coefficients 11,600 and 11,800 respectively.

The formal reduction potentials of the ruthenium compounds of the various pyridyl-substituted triazines were determined colorimetrically using the potentiopoised solution method and the potentiometric method.

Ruthenium bis(2,4,6-tri(2'-pyridyl)-s-triazine) changes from purple to orange on oxidation, the formal reduction potential being 1.18_8 volts. It is very satisfactory for the titration of ferrous iron or of sodium arsenite with sulfatoceric acid.

Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) chloride was prepared by fusing osmium chloride and the triazine at 260° C. for one hour. The composition was established by analysis for osmium(distillation-thiourea colorimetric method), 2,4,6-tris(2'-pyridyl)-s-triazine(spectrophotometric measurement in the ultraviolet), and chloride. The analysis gave the empirical formula of $Os_1(TPTZ)_{2.10}Cl_{2.00}$. Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) perchlorate was prepared by passing the chloride through IR-400 in the perchlorate form. Osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) iodide was prepared from the chloride by double decomposition with potassium iodide and extraction with ether; its composition was established by analysis, the results yielding the empirical formula, $Os_1(TPTZ)_{2.01}I_{2.11}$. The composition indicates that only two of the pyridyl groups of each tripyridyl-s-triazine molecule are attached to the osmium atom and this was shown experimentally by titrating the unattached pyridyl groups with perchloric acid in nonaqueous solution. Nitromethane, acetonitrile and glacial acetic acid were used as solvents and two equivalents of perchloric acid per mole of compound were required.

The osmium bis(2,4,6-tri(2'-pyridyl)-s-triazine) ion is a satisfactory oxidation-reduction indicator, the color change, from purple (with a distinct violet tinge) to orange on oxidation, being very sharp. The formal reduction potential measured varied slightly with the nature of the anion present and the method used for the measurements, the potential being about 1.09 volts. Excellent results with this indicator were obtained in the titration of iron and of arsenite with quadrivalent cerium.

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