Fifty cc. of nitric acid of 1.2 sp. gr. are heated to boiling in a flask of 700 cc. capacity. The source of heat is removed and five grams of the oil to be analyzed added. The flask is then heated on the water-bath, with frequent shaking, for fifteen to twenty minutes, and about 400 cc. of cold water added. After the liquid has become entirely cold, fifty cc. of petroleum ether are added and the flask agitated. The oil which remains unacted upon dissolves in the ether, while the resin remains in suspension. The liquid is poured into a tapped separator, leaving the lumps of solid resin as far as possible behind in the flask. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a tared flask. Another portion of petroleum ether is added to the resin remaining in the flask and allowed to act upon it for about ten minutes, when it is added to that in the tared flask. After distilling off the ether the oil is weighed. Mineral oils lose about ten per cent. in this way, and hence the weight of oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

Allen found mineral oils to lose ten to twelve per cent. on treatment with nitric acid. *Pharm. Jour.*, [3], **11**, 266.

A mixture of seventy-six per cent. of mineral oil with twenty-four per cent. of rosin oil gave, by this method, 76.8 per cent. of mineral oil.

RUTHENIUM AND ITS NITROSOCHLORIDES.[1]

By James Lewis Howe.

A FEW years ago A. Joly[2] published the results of an investigation on the supposed tetrachloride of ruthenium of Claus, in which he showed that the double salts of this compound, the "red salt" of Claus, are in reality double salts of a nitrosochloride, $RuCl_3NO$. When his work came to my notice I was engaged in studying the compounds of ruthenium, especially seeking to discover a simple and certain way of forming the supposed tetrachloride. Being engaged at present on other compounds of ruthenium, I present in this paper results reached,

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[1] Read before the Cincinnati Section, March 15. 1894.

[2] *Compt. rend.*, 107, 998; 108, 854.

chiefly respecting the nitrosochlorides. For the unexpected formula of these compounds I am indebted to Joly, as at the time of his publication I had not analyzed any of the compounds; the rest of the work was entirely independent of his researches, and in the cases where the same work has been carried out by each of us, his results are in every respect confirmed.

The crude ruthenium was purified by fusion with caustic potash and saltpeter, and distillation of the dissolved melt in a stream of chlorine, as RuO_4. Good results were also obtained by treating the solution of the melt with potassium permanganate and sulphuric (or nitric) acid in the retort, and distilling. In either case the RuO_4 was received in dilute alcoholic potash. When the precipitate, or that obtained by treating a solution of the melt with nitric acid, is boiled for several days with aqua regia, in a flask provided with a return condenser, the ruthenium is completely converted into the nitrosochloride. (In his first paper Joly describes the formation of the nitrosochloride by treatment of $RuCl_3$ with a nitrite, and in his second paper by treatment with a large excess of nitric acid.) The solution in aqua regia is evaporated to dryness on a water-bath, the residue dissolved in water and treated with the chloride on an alkali; the corresponding double chloride then crystallizes out, either directly or on evaporation of the solution. The following salts have been studied, the analyses of the potassium and ammonium salts being given merely in confirmation of Joly's results.

1. *Potassium Ruthenium Nitrosochloride, or Potassium Nitrosochlorruthenate.* $2KCl, RuCl_3NO$, or K_2RuCl_5NO.—Formed by direct precipitation of very concentrated solutions of $RuCl_3NO$ with KCl solution, or by evaporation of the mixed solutions. The analyses, as well as those of the other salts, were made by heating the salt in a stream of hydrogen and collecting the hydrochloric acid evolved in a solution of silver nitrate. The nitrogen of the NO group is reduced and deposited in the cooler portion of the combustion tube as ammonium chloride. Claus' analytical error, which led him to the formula $2KCl, RuCl_4$, was in not directly estimating the evolved chlorine, the loss Cl_3NO differing very slightly in weight from Cl_4.

Analysis.

	Calculated.	Found. I.	Found. II.
Cl_3NO (loss)	34.98	34.77	34.38
Cl_3	27.27	26.98	27.07
NO (difference)	7.71	7.79	7.30
Ru	26.77	26.65	25.99
2KCl	38.24	38.41	....
Cl_2 (in 2KCl)	18.18	....	18.62

Solubility.

At 25° .... 100 parts water dissolve 12 parts salt.
At 60° .... " " " " 80 " "

2. *Ammonium Ruthenium Nitrosochloride.* $2NH_4Cl, RuCl_3NO$. —Formed as above from $RuCl_3NO$ and NH_4Cl.

Analysis.

	Calculated.	Found.
Cl_5	50.96	50.34
Ru	30.02	29.61

Solubility.

At 25° .... 100 parts water dissolve 5 parts salt.
At 60° .... " " " " 22 " "

3. *Rubidium Ruthenium Nitrosochloride.* $2RbCl, RuCl_3NO$ and $2RbCl, RuCl_3NO, 2H_2O$.—When very concentrated solutions of $RuCl_3NO$ and RbCl are mixed there is precipitated a small amount of rather pale-purple anhydrous salt. If solutions less concentrated are mixed and evaporated over sulphuric acid, the hydrated salt crystallizes out in large crystals, accompanied by some of the anhydrous salt. On evaporating a solution of the hydrated salt to dryness on the water-bath, or even on heating its solution, it is almost completely converted into the anhydrous salt.

a. Anhydrous Salt.—Fine pale-purple powder, which may be recrystallized from hot water in small, almost black crystals, closely resembling the potassium and ammonium salts, and which, like these, give a pale-purple powder in the mortar.

Analysis.

	Calculated.	Found. I.	Found. II.
Cl_3NO (loss)	28.27	....	28.13
Cl_3	22.04	....	21.89
NO (difference)	6.23	....	6.24
Ru	21.64	....	21.35
2RbCl ($Rb = 85.2$)	50.09	....	50.52
Ratio Ru : 2RbCl	1 : 2.314	1 : 2.294	....
Ratio Ru : Cl_3	1 : 1.018	1 : 1.017	....

(I was a mixture of anhydrous and hydrated salt.)

SOLUBILITY.

At 25° .... 100 parts water dissolve 0.57 parts salt.
At 60° .... " " " " 2.13 " "

b. Hydrated Salt.—Large dark-purple crystals, losing their water of crystallization very readily over sulphuric acid, and difficult to completely free from the adhering anhydrous salt.

ANALYSIS.

	Calculated.	Found. I.	Found. II.
Cl_3NO, $2H_2O$ (loss)	33.26	31.70	32.43
Cl_3	21.51	20.83	19.42
NO (difference)	5.79	NO and $2H_2O$ } 10.87	NO 5.98
Ru	20.13	20.50	19.75
2RbCl	46.60	47.	....
$2H_2O$	6.96	....	7.03

(I had lost some water by standing over sulphuric acid before the first weighing was made.)

SOLUBILITY.

At 25° ...... 100 parts water dissolve 114.3 parts salt.

4. *Cesium Ruthenium Nitrosochloride.* 2CsCl, $RuCl_3NO$ and 2CsCl, $RuCl_3NO$, $2H_2O$.—As with the rubidium salts, when very concentrated solutions of $RuCl_3NO$ and CsCl are mixed, cesium ruthenium nitrosochloride is partly precipitated as the anhydrous salt, while on evaporating the less concentrated cold mixed solutions over sulphuric acid, large crystals of the hydrated salt are formed. Some of the anhydrous salt is usually formed at the same time, even in the cold. On evaporating a solution of the very soluble hydrated salt on the water-bath to dryness, it is completely changed into the very slightly soluble anhydrous salt. I have not found it possible to form the hydrated salt from the anhydrous, nor to obtain the anhydrous salt in crystals large enough to be seen by the naked eye.

a. Anhydrous Salt.—Fine pale-purple powder, not differing in appearance from the rubidium salt, but less soluble.

ANALYSIS.

	Calculated.	Found. I.	Found. II.	Found. III.
Cl_3NO (loss)	23.61	23.85	....	23.56
Cl_3	18.41	17.93	18.19	18.41
NO (difference)	5.20	5.92	....	5.15
Ru	18.08	17.62	....	17.85
2CsCl ($Cs = 132.7$)	58.31	58.40	....	57.90

SOLUBILITY.

At 25° ...... 100 parts water dissolve 0.20 parts salt.
At 60° ...... " " " " 0.56 " "

b. Hydrated Salt.—Large dark-purple crystals, often ten millimeters long or broad. Loses water of crystallization readily over sulphuric acid.

ANALYSIS.

	Calculated.	Found.
$Cl_3NO, 2H_2O$ (loss)	28.10	28.11
Cl_3	17.32	16.92
NO (difference)	4.90	5.59
Ru	17.01	16.63
2CsCl	54.88	55.13
$2H_2O$	5.87	5.60

SOLUBILITY.

At 25° ..... 100 parts water dissolve 105.8 parts salt.

The properties of the nitrosochlorides agree almost, if not completely, with those ascribed to ruthenium tetrachloride by Claus[1] and M. C. Lea.[2] The most remarkable property, to which Joly has also called attention, is their stability.

Two and four-tenths grams of the potassium salt was heated with gradually increasing temperature in an air-bath. Up to above 250° the loss was less than 0.5 per cent. Direct heat was then applied to the crucible till the salt was partially decomposed, Cl and NO being evolved. The whole was then treated with water, and from the soluble portion the original undecomposed salt was crystallized. No trace of ruthenium trichloride was present, showing that the NO is not given off until the chlorine also passes off.

The solutions of the nitrosochlorides are unacted on by urea in acid or alkaline solutions, nor are they reduced by $FeSO_4$, Cu_2Cl_2, or $SnCl_2$. Hydrogen dioxide has no effect in acid solutions; in alkaline solutions oxygen is evolved, the solution becoming decolorized, but the change appears to be the same as that when the original solution is treated with excess of alkali.

Potassium permanganate has no reaction in acid solutions, but in alkaline solutions (with fixed alkalies) on boiling the green color of the manganate appears, soon followed by the

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[1] *Bul. de l'Acad. Imp. de St. Pet.*, **1**, 107; **4**, 457.

[2] *Am. J. Sci.*, **38**, 81, 248.

brown precipitate of the hydroxide, and the ruthenium salt is reduced to its trivalent condition. The solution after the reaction, gives the test for nitric acid, which is not the case with the original solution. It is then probable that the NO group is oxidized off by the permanganate.

Sodium hypobromite also reacts with the nitrosochloride in the cold, with evolution of gas; on acidifying with hydrochloric acid, RuO_4 is evolved with the bromine, a reaction analogous to the characteristic reaction of the trichloride with potassium chlorate and hydrochloric acid.

Potassium ferrocyanide gives no reaction in the cold with the nitrosochloride, but when *neutral* on boiling the solution becomes intensely deep brown, almost opaque unless very dilute. In acid solutions this reaction does not take place. Alkaline solutions become amber on boiling, but on careful neutralization with hydrochloric acid the brown coloration appears. An excess of acid changes the brown to a much less dense olive green, very different from the bright green produced by the trichloride with the ferrocyanide.

Sulphur dioxide has little effect in the cold, but when led into the warm alkaline solution of the nitrosochloride the solution gradually loses its rose color and becomes amber, and a precipitate is formed, very slightly soluble in water.

Potassium cyanide decolorizes the solution of the nitrosochloride on warming and a double salt seems gradually to be formed.

Oxalic acid has no apparent effect.

These last three reagents all have decided reactions with the trichloride and are now being further studied.

In the solutions of the heavy metals I have obtained no precipitates with the nitrosochloride, except with mercurous salts and those of silver. In both these cases a buff precipitate is thrown down, but on heating with nitric acid it is decomposed, the ruthenium passing into solution, the silver or mercurous chloride being left. Lead salts do not precipitate the nitrosochloride.

Copper sulphate gives no reaction, but on warming with excess of caustic alkali the copper hydroxide passes into solution, giving the azure-blue characteristic of Fehling's solution. From this, cuprous oxide is precipitated on warming with grape sugar.

When NO is led into a solution of ruthenium trichloride a change takes place, and the solution no longer gives the reactions for the trichloride; nor does it appear to contain the nitrosochloride. Differential characteristics for the nitrosochloride solutions as compared with the trichloride are the following:

Solutions rose becoming salmon pink on dilution.

No precipitate with excess of alkali.

No purple color on boiling with potassium thiocyanate.

No reaction with ammonia and sodium thiosulphate.

Deep brown on boiling with potassium ferrocyanide in neutral solution.

This last reaction is most characteristic.

Several attempts have been made by me to prepare a higher ruthenium chloride than the trichloride, but unsuccessfully.

RuO_4 dissolved in hydrochloric acid, yields on standing only $RuCl_3$; the same is true of RuO_4 dissolved in chlorine water.

RuS_2 was oxidized with HCl and $KClO_3$; much of the ruthenium was volatilized as RuO_4, while the residue consisted solely of $RuCl_3$.

In order to prove conclusively that the "red salt" of Claus was the nitrosochloride it was formed according to the method used by Claus; *viz.*, oxidation of RuS_2 with nitric acid.

ANALYSIS.

	Calculated.	Found.
Cl_3	26.77	26.95

It seems at first sight entirely unexpected that we should find the group NO directly connected with a metal, but it is by no means unique. The affinity of ferrous salts for NO is familiar, and there are several comparatively stable compounds in which the group NO appears to be attached to iron, as the nitrosopentasulphide and nitrosoheptasulphide, and the nitrosothiocarbonate. In the nitroprussides the NO group replaces in part the CN of the ferrocyanides. Iron and ruthenium occupy analogous positions in the periodic system, and as osmium is the third member of the series we should expect to find a similar and strong affinity of osmium for NO; indeed, Joly[1] has proposed to show that the osmiamic acid of Fritzsche and Struve has an

[1] *loc. cit.*

analogous constitution to the nitrosocompounds of ruthenium.

POLYTECHNIC SOCIETY, LOUISVILLE, KY.,
March, 1894.

ON THE CRYSTALLIZATION OF $2CsCl, RuCl_3NO, 2H_2O$ AND $2RbCl, RuCl_3NO, 2H_2O$.

BY N. D. CLARK.

These salts are isomorphous and crystallize in the monoclinic system. They show a similar habit and the crystals of both salts that were submitted for examination measured as much as ten millimeters in length.

The forms which were identified are

a, 100, i — ī	*m*, 110, I	*e*, 101, — 1 — ī
c, 001, O	*d*, 021, 2 — ì	*o*, î01, 1 — ī

The habit is prismatic like Figs. 1 and 2, while Fig. 3 represents a basal projection of Fig. 2. Of the forms in the prismatic zone *m* is always prominent while *a* is small and frequently fails. The prevailing forms that terminate the prisms are *d* and *o*, while *c* and *e* are usually either small or altogether wanting.

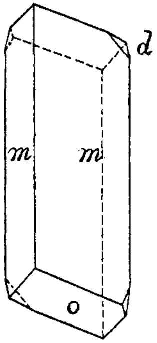

FIG. 1.

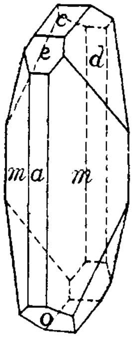

FIG. 2.

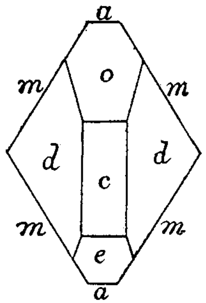

FIG. 3.

The axial ratios that are given beyond were calculated from the measurements that are marked by asterisks in the accompanying tables; the values cannot be regarded as very exact, as the crystal faces were slightly rounded and not adapted for accurate measurement. On the cesium salt the error in the fundamental measurements is regarded as not exceeding ± 8′, while with the rubidium salt the error may exceed twice that amount.

	$\breve{a} : \bar{b} : \dot{c}$	
$2CsCl,RuCl_3NO,2H_2O$	1.698 : 1 : 1.177	$\beta = 76°, 11'$
$2RbCl,RuCl_3NO,2H_2O$	1.692 : 1 : 1.242	$\beta = 76°, 50\frac{1}{2}'$

		Measured.	Calculated.	Measured.	Calculated.
		$2CsCl,RuCl_3NO.2H_2O$.		$2RbCl,RuCl_3NO.2H_2O$.	
$a \wedge c$	$100 \wedge 001$	76°, 11′*	....	76°, 50′, 30″*	....
$c \wedge e$	$001 \wedge 101$	30°, 0′*	....	31°, 18′	31°, 28′, 28″
$d \wedge d$	$021 \wedge 0\bar{2}1$	132°, 45′*	....	135°, 4′*	....
$m \wedge m$	$110 \wedge \bar{1}10$	62°, 13′	62°, 27′, 59″	117°, 30′*	....
$a \wedge m$	$100 \wedge 110$	58°, 45′	58°, 46′, 6″	58°, 50′	58°, 45′
$m \wedge d$	$110 \wedge 021$	33°, 18′, 30″	33°, 35′	....	33°, 37′, 33″
$c \wedge o$	$001 \wedge \bar{1}01$	38°, 34′, 30″	38°, 53′, 23″	39°, 32′	40°, 37′, 9″
$a \wedge e$	$100 \wedge 101$	46°, 12′	46°, 11′	46°, 6′	45°, 22′, 2″
$d \wedge c$	$021 \wedge 001$	66°, 22′, 30″	66°, 30′	....	67°, 32′
$a \wedge o$	$\bar{1}01 \wedge 100$	65°, 13′, 30″	64°, 55′, 37″	63°, 33′	62°, 32′, 21″

Both salts show a perfect cleavage parallel to *a* and a poorer one parallel to *c*. The plane of the optical axes is the clinopinacoid; the double refraction is strong, and the optical orientation such that cleavage plates parallel to *a* show in convergent polarized light an optical axis almost in the center of the field.

This investigation was made in the mineralogical-petrographical laboratory of the Sheffield Scientific School, under the direction of Prof. S. L. Penfield, to whom the author's thanks are due.

AN IMPROVED MERCURY THERMOMETER FOR HIGH TEMPERATURES.[1]

BY W. NIEHLS.

THE ordinary mercury thermometers give accurate values up to 250° C. When the thermometer tube above the mercury is filled with nitrogen under pressure, readings are possible up to 450° C.

Early in 1893 I submitted to the Physikalisch-Technische Reichsanstalt, at Charlottenburg, Berlin, which, as is well known, tests the correctness of normal thermometers, etc., models of high temperature thermometers which were capable of giving accurate readings up to 550° C. Since then minor details of construction have been satisfactorily completed, and in the following, I will briefly describe the perfected instrument.

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[1] Read before the Cincinnati Section, April 16, 1894.