

382. *Ruthenium Red.*

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Experiments have shown* that the ruthenium red cation is $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+}$ in which there are two oxo-bridges and the average oxidation number of ruthenium is $+10/3$. The cation is oxidised reversibly by a one-electron change to the more paramagnetic brown cation $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{7+}$. The relation to other polynuclear complexes is discussed.

JOLY¹ formulated ruthenium red as $\text{Ru}_2\text{Cl}_4(\text{OH})_2 \cdot 7\text{NH}_3 \cdot 3\text{H}_2\text{O}$, and Morgan and Burstall,² who prepared from it supposed mononuclear complexes of ruthenium, as $[\text{Ru}^{\text{III}}(\text{OH})\text{Cl}(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$. The latter structure was rejected by Gleu and Breuel³ because $[\text{Ru}^{\text{III}}(\text{OH})\text{Cl}(\text{NH}_3)_4]^+$ is paramagnetic whereas ruthenium red is diamagnetic. It has been suggested that the highly coloured cation is polynuclear, but further evidence on its structure has not been advanced.

Our interest in ruthenium red arose from a view that the diamagnetism and intense colour of many complexes of ruthenium are due to their being polynuclear. In particular, the occurrence in solution of an aquochloro-⁴ and an aquonitrato-complex^{5,6} as transient violet species with unusually high molar extinction coefficients ($\epsilon_{\text{Ru}} \sim 20,000$ at λ_{max} ~ 550 m μ) suggested a chromatic group similar to that in ruthenium red for which we find that ϵ_{Ru} is 21,000 at λ_{max} 532 m μ . It has now been shown that this cation, here called ruthenium red, has no complexed halogen groups, and behaves as a trinuclear complex in which, associated with three ruthenium atoms, there are 14 nitrogen atoms which can be liberated as ammonia. This suggests that the red cation has two oxo-bridges, as in (I), to satisfy hexa-co-ordination of the ruthenium atoms. This cation is oxidised, reversibly,



in acid solution to a brown cation (II). The average oxidation state of ruthenium atoms in the respective cations are $10/3$ and $11/3$. The approach to diamagnetism shown by the red cation points to a linear configuration of the Ru-O-Ru-O-Ru group.

* The main conclusions from this work were given in April 1959 to the International Conference on Co-ordination Chemistry, London (*Chem. Soc. Spec. Publ.* No. 13, p. 136, and U.K.A.E.A. Document AERE-R2877, 1959).

¹ Joly, *Compt. rend.*, 1892, **115**, 1299.

² Morgan and Burstall, *J.*, 1936, 41.

³ Gleu and Breuel, *Z. anorg. Chem.*, 1938, **237**, 350.

⁴ Wehner and Hindman, *J. Phys. Chem.*, 1952, **56**, 10.

⁵ Fletcher, Jenkins, Lever, Martin, Powell, and Todd, *J. Inorg. Nuclear Chem.*, 1955, **1**, 378.

⁶ Woodhead, unpublished results; Fletcher, *J. Inorg. Nuclear Chem.*, 1958, **8**, 277.

EXPERIMENTAL AND RESULTS

Preparations.—*Ruthenium red chloride.* Joly,¹ and Morgan and Burstall,² prepared their red compound from reactive anhydrous ruthenium trichloride made at 360–400° from the metal, chlorine, and a little carbon monoxide. An industrial method is to age aqueous commercial ruthenium chloride, largely polynuclear aquochloro-complexes⁶ of Ru^{IV}, in an excess of ammonia for several days. Our experiments indicate that it is formed slowly when [Ru^{III}(NH₃)₆]Cl₃ in aqueous ammonia is exposed to air, it being immaterial how the hexammine solution is made. Greater concentration of hexammine increases the yield and, as Joly found, allows the red to be crystallised when the aged and warm solution is cooled; it also makes the ethyl alcohol precipitation used by Morgan and Burstall unnecessary, thereby giving a better separation from the more soluble by-products of ageing.

Commercial ruthenium trichloride (5 g.; Ru 38%), tested by infrared spectroscopy for freedom from nitrosylruthenium (an impurity found in several batches), in 0.25N-hydrochloric acid (25 ml.) was reduced to Ru^{III} by 2 hours' refluxing with ethyl alcohol (5 ml.). The liquid was evaporated to 5 ml. (~4M-Ru) and ammonia (*d* 0.880; 20 ml.) was added. Ruthenium red was formed when the solution, at *ca.* 90°, was exposed to air for 2–3 hr. with frequent additions of ammonia. To the 10 ml. of liquor with its crystalline deposit, 10 ml. of water were added; the mixture was heated to 80° and centrifuged whilst hot. The supernatant liquid, cooled to 0°, gave on centrifugation 1.1 g. of solid (ϵ_{Ru} 9100 at 532 m μ in H₂O). Further evaporation of the mother-liquor with more ammonia, produced two additional crops of 1.06 g. and 1.03 g. with ϵ_{Ru} 11,800 and 1380 respectively at 532 m μ . Solutions of the three fractions showed a peak at 725 m μ , particularly marked in the first, relating to an unidentified complex. Each fraction was recrystallised by digesting it with 0.5N-ammonia (10 ml.) at 60°, centrifuging the mixture whilst hot, and cooling the supernatant liquid to 0°. The three crops were washed with ice-cold water, ethyl alcohol, and diethyl ether; after drying in air at room temperature, they weighed 0.25, 0.28, and 0.08 g. respectively (yield 11.5%). They were similar spectrophotometrically, with λ_{max} 532 m μ (ϵ_{Ru} 20,500 \pm 2% in water), and in ruthenium content (range, 0.7%). In another preparation (λ_{max} 532 m μ ; ϵ_{Ru} 21,400 in H₂O) of the *salt*, a 20% yield was attained and the three crops were combined before recrystallisation {Found: Ru, by Woodhead's method,⁷ 35.7, 35.1; N, by distillation with Devarda's alloy, 22.1, 22.4; Cl, by Volhard's method after decomposition by boiling with 2N-KOH, 24.4, 24.2; H₂O, by Karl Fischer's method, 8.1. [Ru₃O₂(NH₃)₁₄]Cl₆·4H₂O requires Ru, 35.3; N, 22.8; Cl, 24.8; H₂O, 8.4%}. The solubility of the salt in 0.1N-ammonia at 0° was 36 g./l. When heated to constant weight at 85°, it lost 4.2%, corresponding to the formation of the dihydrate. Another preparation, heated at 110°, lost 6.8, 8.3, 8.9% after 1, 2, and 3 hr., respectively, but there was no loss of nitrogen: the spectrum of the residue showed that about 10% of the red cation had been oxidised to the brown cation, and as the complex aged in air its weight increase (3.7%) corresponded to the formation of the dihydrate.

Ruthenium brown nitrate. Commercial ruthenium red (1.5 g. as chloride), in aqueous ammonia (pH 10; 100 ml.), was freed from impurities, *e.g.*, nitrosylruthenium complexes, and from chloride by two preliminary precipitations of this relatively insoluble (0.34 g./l. in water at 25°) nitrate from hot, dilute nitric acid. The precipitates were dissolved, with auto-reduction to the red cation, in ammonia at pH 10. The purified *salt* was then reprecipitated from hot 0.2N-nitric acid, washed with 0.01N-nitric acid, ethyl alcohol, and ether, and dried at room temperature (yield 0.4 g., 31%). The spectrum (Fig. 1), λ_{max} 460 m μ (ϵ_{Ru} 14,100) in 0.01N-nitric acid, did not change after yet a further reprecipitation {Found: Ru, 28.0; total N, by Devarda's alloy, 26.7; Cl, <0.1. [Ru₃O₂(NH₃)₁₄](NO₃)₇·5H₂O requires Ru, 27.6; N, 26.8%}.

When the salt was boiled in 2M-sodium hydroxide in the absence of Devarda's alloy, the nitrogen liberated as ammonia after 3 hr. was only 15.4% (calc. N as NH₃, 17.8%). Failure to release all the nitrogen as ammonia is attributed to the formation of very stable amido-complexes of Ru^{VI} (see below).

Ruthenium brown sulphate. To ruthenium red (0.77 g.) in 0.25N-sulphuric acid (50 ml.) was added 0.05N-ceric sulphate until the red colour was discharged (19 ml.). The precipitate formed was centrifuged off, washed with 0.01N-sulphuric acid until free from red colour, then with alcohol and ether, and dried at room temperature (yield 79%). The *salt* was light brown {Found: Ru, 29.4; N, 18.6; SO₄, 31.0; H₂O, by Karl Fischer's method, 12.8; Cl, 0.8.

⁷ Woodhead, U.K.A.E.A. Document, A.E.R.E.—R-3279, 1960.

[Ru₃O₂(NH₃)₁₄]₂(SO₄)₇·15H₂O requires Ru, 29.1; N, 18.8; SO₄, 31.9; H₂O, 12.9%}. The loss, 8.8%, on heating to constant weight at 85° corresponds to the formation of the tetrahydrate. Thermogravimetric analysis showed no further loss in weight up to 170° but after heating to 200° the infrared spectrum indicated slight decomposition. The salt was too insoluble (0.02 g./l. in 0.01N-sulphuric acid at 25°) for a reliable absorption spectrum to be obtained. It dissolved rapidly in aqueous ammonia or alkali in which it gave a solution of ruthenium red with λ_{max} 532 m μ (ϵ_{Ru} 21,000).

Properties of Solids.—*Infrared spectra.* The red (as chloride) and the brown (as nitrate and sulphate) were examined (see Table) as mulls in Nujol and hexachlorobutadiene in the 2—15 μ region with a Hilger H800 double-beam spectrometer, the specimens being first dried to constant weight at 85°. The mulls were mounted as thin films between rock-salt windows. For deuteration (~90%), the red chloride was dissolved in D₂O and dried under a vacuum at room temperature. The red complex differs from the brown complex in two respects. First, the band at 3477 cm.⁻¹, assigned to the stretching vibration of H₂O in the red chloride is shifted to 3361 cm.⁻¹ in the brown nitrate and to 3380 cm.⁻¹ in the brown sulphate. Secondly, the ammine symmetric deformation and rocking bands in the red complex have shoulders on the low-frequency side which are shown to be separate bands by deuteration: the ratio, 1 : 2.5, of the absorption densities of the symmetric deformation bands in the deuterated form suggests that four of the fourteen ammine ligands in the complex are different from the other ten. Bands

Infrared absorption frequencies (cm.⁻¹).

Red chloride	Brown nitrate	Brown sulphate	Assignment	Group
3477 (2594) m	3361 sh	3380 sh	} O-H (O-D) stretch	H ₂ O (D ₂ O)
3422 (2542) sh				
3237 (2415) s	3200 s	3197 s	} N-H (N-D) stretch	NH ₃ (ND ₃)
3131 (2279) s	3096 s	3164s		
1614 (1183) s,b (1155) sh	1615	1630 s,b	} Degenerate deformation	NH ₃ (ND ₃) and H ₂ O (D ₂ O)
1295 sh (1056) m	*			
1276 (976) s	*	1336 s	} Symmetric deformation	NH ₃ (ND ₃)
842 sh		856 m,b		
817 m,b	*		} Rocking	NH ₃

Data for deuterated samples are in parentheses.

* Obscured by nitrate-ion absorptions.

due to nitrate and sulphate ions, with none due to nitrate- or sulphato-groups, were present respectively in the spectra of the two brown salts. There were no bands at 1510—1550 cm.⁻¹ or 1000—1030 cm.⁻¹ which could be attributed to —NH₂ frequencies.

Magnetic susceptibility (by W. E. GARDNER and J. PENFOLD). Gleu and Breuel³ reported that ruthenium red is diamagnetic. The susceptibilities of our brown nitrate and red chloride were measured by the Faraday method with a Sucksmith ring balance and a tantalum standard at five different field strengths. Values of χ_g for the brown nitrate were 5.60×10^{-6} and 1.44×10^{-6} at 77° and 293° K respectively. On the assumptions that the factor θ in the Curie-Weiss law is zero and that the diamagnetic correction is negligible, μ_{eff} is $2.83 - \sqrt{77 \times 5.60 \times 10^{-6} \times 1097/3} = 1.13$ B.M. per ruthenium atom. For the red chloride, χ_g was 0.75×10^{-6} at 293° K and the corresponding value of μ_{eff} , on the same assumptions, is 0.77 B.M. per ruthenium atom. No significance in terms of unpaired electrons can be attributed to the absolute values of μ_{eff} ; however, the difference $3(1.13 - 0.77) = 1.1$ B.M., between μ_{eff} for the three ruthenium atoms in the red and the brown complexes is consistent with a change in the sum of the oxidation states of the three ruthenium atoms from an even (+10) to an odd (+11) number.

Properties of Solutions.—*Chlorine present as chloride ion.* (a) Electromigration. Aqueous ruthenium red chloride (3×10^{-3} M-Ru) was placed in the centre compartment of an electromigration cell from which anode and cathode compartments were separated by sintered-glass discs. After 3 hr. at ~8 v/cm., 93% of the chlorine was in the anode compartment, all the red ion was in the cathode compartment, and the original liquid was colourless. (b) Solvent Extraction. An aqueous solution of ruthenium red chloride, after equilibration for 5 min. with an equal volume of 0.1M-di-(2-ethylhexyl) hydrogen phosphate in kerosene, lost its colour entirely (>99%) to the organic phase and retained all its chlorine (94%). The spectrum, λ_{max} 460 m μ ($\epsilon_{\text{Ru}} \sim 12,000$), of the organic phase showed that there had been rapid atmospheric oxidation to the brown complex. These values were unaltered when the ruthenium was brought

back into an aqueous phase by equilibration with 0.1N-hydrochloric acid. They changed, however, to those for the red cation when the acid solution was brought to pH 9 with ammonia.

Charge on the red cation. This may be deduced from its extraction from aqueous solution by alkyl esters of phosphoric acid (the extraction of cations being related to a variable raised to the power of their charge); from its retention on cation-exchange resins; and from its dyeing natural fibres. A charge of about +6 (5.90 and 5.73) for the red cation of a specimen prepared in this work was found by Grinberg *et al.*⁸ by ion-exchange. The equivalent conductivities of aqueous ruthenium red chloride at 21° c are 81, 105, 131, and 136 mhos at dilutions of one equivalent in 81, 401, 2017, and 4050 l.; Λ_{∞} for the cation is therefore 136 - 70 (chloride contribution) = 66. Application of Ostwald's rule gives for $(\Lambda_{1024} - \Lambda_{32})/10.8$ a value of $(124 - 61)/10.8 = 5.8$ for the charge on the red cation.

Stoichiometry for Red Complex \rightleftharpoons Brown Complex.—The occurrence of three (or multiples of three) ruthenium atoms in the complex is established by the stoichiometry of this equilibrium. To fresh solutions of ruthenium red chloride (5–10 mg.) in 1–2N-sulphuric acid (10–20 ml.) was added 0.005M-ceric sulphate. A sharp change from +0.35 to +0.8 v (Gleu and Hubold⁹ found 0.55 v) between the platinum electrode and standard saturated calomel electrode occurred after 0.33, 0.33, and 0.32 equivalent of oxidant per ruthenium atom. Spectrophotometric measurements showed the red had been converted into the brown complex. Similar stoichiometry (0.35 equiv.) was observed with ferric ion, although the potential change was less sharp. Oxidation by air was avoided by adding the solid to an excess of the ferric solution and back-titrating.

The brown products from some of these oxidations were back-titrated potentiometrically, in an atmosphere of nitrogen, to the red complex with 0.01N-titanous sulphate. After the addition of 0.30–0.35 equivalent of reductant per ruthenium atom the potential dropped to that for ruthenium red. Successive oxidations with Fe^{3+} and reductions with Ti^{3+} of the same solution were possible.

Average Oxidation Number of Ruthenium.—Most of the methods used to determine the oxidation number of ruthenium in its complexes are inapplicable to ruthenium red. In hydrochloric acid, it is not reduced by the stannous ion or zinc which convert Ru^{III} into Ru^{II} in some complexes. In hot sulphuric acid, ceric ions, although they oxidise all the ruthenium to the tetroxide, also oxidise some of the nitrogen-containing groups by reactions discussed below. In cold alkali, neither permanganate nor perruthenate oxidises all the ruthenium in the red complex to a definite state but gives mixtures of colourless Ru^{III} complexes, insoluble hydrated oxides, and Ru^{VI} complexes. With permanganate, 2.1 equivalents, and with perruthenate, 1.4 equivalents, were required to cause the disappearance of the 532 μ peak in the spectrophotometric titrations.

When, however, ruthenium complexes are added to hot alkaline solutions of oxidising agents the ruthenium is oxidised specifically to Ru^{VI} , and Gall and Lehmann¹⁰ applied this reaction at 100° to determine the oxidation number in ammine-free chloro-complexes with manganate ($\text{MnO}_4^{2-} \rightarrow \text{MnO}_2 + 2e$). But with ruthenium red at 100° we found this procedure to fail through a catalytic decomposition of manganate by the colourless complexes formed, although this catalysis was insignificant by the ruthenate ion, RuO_4^{2-} , produced in the oxidation of $\text{K}_2[\text{RuCl}_6 \cdot \text{H}_2\text{O}]$. However, using a solution of $\text{K}_2[\text{RuCl}_6]$ added to manganate in the presence of ammonia, we have shown that catalysis is negligible at about 30°, and that the colourless ruthenium complexes so produced by oxidation (Found, 2.05 and 2.08 equiv. of manganate per Ru atom) are in the +6 state.

In the determination, to 15 ml. of 0.0028M-manganate in 2N-sodium hydroxide at 40°, 8 ml. of a solution (3.2×10^{-3} M-Ru) of the red chloride in 2N-ammonia were added. The mixture was centrifuged, then cooled to room temperature, and the optical density of the supernatant liquid determined from 385 to 650 μ . The procedure was repeated with successive small additions of the ruthenium red solution:

Ruthenium red solution added (ml.)	8.0	9.0	9.5	9.8
Optical density at 605 μ (for manganate)	0.67	0.27	0.12	0.04

The end-point (9.7 ml.) for the complete consumption of manganate was determined graphically.

⁸ Grinberg, Trofimov, and Stepanova, *Radiokhimiya*, 1960, 2, 78.

⁹ Gleu and Hubold, *Z. anorg. Chem.*, 1935, 223, 305.

¹⁰ Gall and Lehmann, *Ber.*, 1927, 60, 2491.

The precipitated manganese dioxide, which was not removed during the titration, held no ruthenium, nor was the element present in solution as RuO_4^{2-} or RuO_4^- , all of it having been converted into colourless Ru^{VI} complexes. The equivalents per ruthenium atom, 2.75 and 2.7 for the red chloride and 2.6 for the red nitrate, give $6-2.7 = 3.3$ for the oxidation state of ruthenium. In a titration of the nitrate when an excess of ammonia was not present, 22% of the ruthenium appeared as RuO_4^{2-} and none as RuO_4^- .

The alkaline manganate was prepared by adding a slight excess of sodium formate to potassium permanganate in 2N-sodium hydroxide, stirring for 15 min., storage for 24 hr., and removal of the precipitated manganese dioxide by centrifugation. After acidification, the manganate solutions were standardised with ferrous sulphate.

Behaviour with Ceric Ion in Sulphuric Acid.—At room temperature ceric ion discharged the colour of ruthenium red when the average oxidation state reached +4.3 and some of the ruthenium was slowly deposited as oxide.

At 100°, instead of only the ruthenium being oxidised to tetroxide, as happens with other complexes,¹¹ much ceric ion was consumed in a side-reaction. Ruthenium red chloride was dissolved in 1—2M-sulphuric acid containing an excess of ceric sulphate and some silver sulphate to prevent interference from chloride ions. The mixture was boiled and the ruthenium tetroxide formed was carried by a stream of nitrogen into N-oxalic acid.¹² The amounts recovered were 70—95% of the total, as measured by the optical density at 375 m μ . The silver chloride was filtered off from the remaining liquid and the excess of oxidant titrated with ferrous sulphate. The ammonium ion was determined by boiling some of the solution with sodium hydroxide, and the nitrate by re-boiling the residual solution with Devarda's alloy. The equivalents of oxidant consumed per mole of cation varied (51, 63, 58, 36, 35, and 59) but always greatly exceeded the 14 required for oxidation from a +10/3 to a +8 state. Nitric acid was also present in the solution.

This behaviour is attributed to the formation of colourless amido- Ru^{VI} complexes, typified by $[\text{RuO}_2(\text{OH})_2(\text{NH}_2)_2]^{2-}$ (III) in which all the nitrogen atoms are subsequently oxidised to nitric acid:



Ruthenium red has enough NH_3 groups for all the ruthenium to pass through the anion (III); this with Reaction 1 would require 62 equivalents and the fraction of nitrogen converted into nitric acid would be $6/14 = 0.43$. One of the oxidations gave 63 equivalents, 0.5 of the nitrogen as nitric acid and 0.47 as ammonia, which is in quantitative agreement with the sequence. But the reaction is sensitive to variation in procedure, for in another the respective figures were 35, 0.18, and 0.83, indicating that ~40% of the ruthenium passed through the sequence and the balance was oxidised through RuO_4^{2-} to ruthenium tetroxide.

These colourless Ru^{VI} intermediates ($\epsilon_{\text{Ru}^{\text{VI}}} < 100$ at < 400 m μ) are those formed when ammonia is added to solutions of RuO_4^{2-} . Krauss¹³ studied this reaction and obtained by evaporation an uncharacterised black product. We found that when the excess of ammonia was expelled at room temperature the atomic ratio N/Ru in the solution fell to *ca.* 2, and slowly to 1.9—1.6 when warmed. The ruthenium complexes in the solution are very stable. At 100° in 2.5N-sodium hydroxide, RuO_4^{2-} was not formed and very little hydrated ruthenium dioxide was precipitated after several hours; all the nitrogen was liberated only after prolonged boiling with Devarda's alloy. Solutions of the complexes in sulphuric acid were stable at 100° and consumed 10—12 equivalents of ceric ions per ruthenium atom with the formation of ruthenium tetroxide. This approximates to that expected by the stoichiometry of Reaction 1 and the charge change $\text{Ru}^{\text{VI}} \longrightarrow \text{Ru}^{\text{VIII}}$.

Absorption Spectra and Deprotonation.—The Figure shows the spectrum, measured with a Unicam S.P. 500 spectrophotometer, at 20—22° of the red chloride in water and the brown nitrate in 0.01N-nitric acid. λ_{max} for the red cation increased by 3—5 m μ as the pH was raised from 7 to 10. As the wavelength of the point of intersection for mixtures of the red and brown cations also increased with pH, by *ca.* 10 m μ from pH 3 to 7, it is likely that λ_{max} for the brown cation is also a function of the acidity.

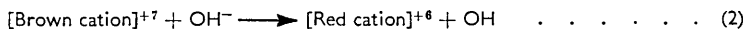
The brown nitrate is weakly acidic, and the pH, 4.6, of a solution of 11.4×10^{-6} mole in

¹¹ Martin, *J.*, 1952, 2682.

¹² Mesarić and Branica, *Croat. Chem. Acta*, 1958, 30, 81.

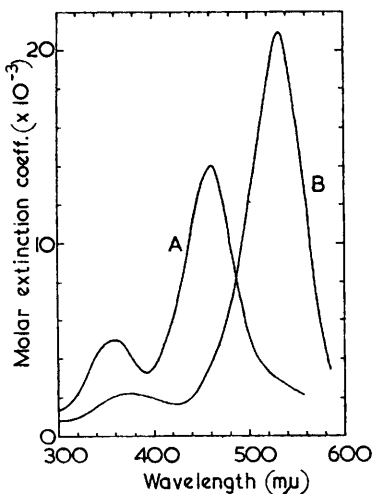
¹³ Krauss, *Z. anorg. Chem.*, 1924, 132, 301.

50 ml. of water implies that about 10% of the complex is ionised. Its spectrophotometric titration with sodium hydroxide (13.5×10^{-6} mole for the complete conversion at pH 7.5 of the brown into the red complex), together with absence of change in the specific conductance ($\kappa = 195 \times 10^{-6}$ mho), is in accordance with the reaction:



After addition of a further 11.5×10^{-6} mole of sodium hydroxide, the pH was 9.3 (cf. 10.4 calculated for no reaction) and κ had only increased to 197×10^{-6} mho. With another 25×10^{-6} mole of alkali, the pH was 10.3 and κ had increased to 262. This suggests that the red cation can also be deprotonated and that the small increases in λ_{max} with pH that occur for both cations are due to the formation in solution, by hydrogen bonding of water to ammine groups,¹⁴ of cations of lower charge, *e.g.*, for the brown, $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{7+} \longrightarrow [\text{Ru}_3\text{O}_2\text{NH}_2(\text{NH}_3)_{13}]^{6+}$, and for the red, $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+} \longrightarrow [\text{Ru}_3\text{O}_2\text{NH}_2(\text{NH}_3)_{13}]^{5+}$.

Absorption spectra of:
A, Brown complex in 0.01N-nitric acid.
B, Red complex in water.



Oxidation by Air.—Spectrophotometry showed that acidic solutions of the red cation were oxidised to the brown cation not only by Ce^{4+} , Fe^{3+} , HNO_3 , etc., but also by air (20% in 24 hr. in 0.1N-hydrochloric acid). Rapid oxidation has been observed² in 2N-hydrochloric acid. The rate of oxidation in air is favoured by conditions which tend to remove solvated water from the cation, such as heating of the solid or solvent extraction from aqueous solution.

Destruction of Structure.—Decolorisation of the red cation occurs both in acid and in alkaline solutions. At 80° in 2N-sodium hydroxide there was complete destruction of the cation in about 1 min., but even after long storage only 20—43% of the ruthenium was precipitated as hydrated dioxide, the remainder entering such complexes of Ru^{VI} as (III). Boiling for a few minutes with N-hydrochloric acid converted the red complex entirely into a pale yellow solution; the rapidity of the decomposition is attributed to the formation of strong chloro-complexes—the spectrum suggested those of Ru^{III} . In contrast, boiling with M-nitric acid produced the brown complex and little decomposition.

DISCUSSION

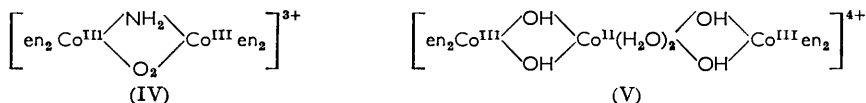
The evidence advanced in the last section has led to the formulation of ruthenium red as (I). Although there are no recorded complexes with structures analogous to this trinuclear oxo-bridged one, others show certain features in common with it. Thus the red complex¹⁵ (IV) is diamagnetic and undergoes a reversible, one-electron oxidation, for which the potential varies considerably with pH, to a paramagnetic, green complex; the nitrate of the oxidised complex is also insoluble. The bluish-red complex (V) prepared by

¹⁴ Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

¹⁵ Thompson and Wilmarth, *J. Phys. Chem.*, 1952, **56**, 5.

Werner¹⁶ also shows resemblances: thus it appears as one of several products of a slow atmospheric oxidation of mononuclear complexes of the metal in a relatively low oxidation state and is decomposed by hydrochloric acid to mononuclear complexes.

A feature of ruthenium red is its lack of paramagnetism. Other complexes possessing



this property are the binuclear $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ which has the linear Ru-O-Ru, and the binuclear rhodo-chromium complex¹⁷ $[\text{Cr}_2\text{O}(\text{NH}_3)_{10}]^{4+}$ which has the linear Cr-O-Cr. When the latter is modified by protonation of the oxygen atom, the erythro-complex formed is paramagnetic. Besides $[\text{Ru}_2\text{OCl}_{10}]^{4-}$, there are other complexes with ruthenium in oxidation states $> +3$ which are almost diamagnetic⁶ and must be polynuclear complexes as yet uncharacterised.

Non-integral values for the oxidation state of ruthenium are not confined to the red and the brown complexes here described; they are found in a chloro-complex¹⁸ (+3.5) and in aquo-complexes¹⁹ (+4.2—4.6). The existence of several polynuclear complexes of ruthenium with low magnetic moments is therefore likely, and they will often be highly coloured as are the solutions of the aquochloro- and aquonitrato-complexes which gave rise to this work. For the former, Wehner and Hindman⁴ proposed $[\text{Ru}^{\text{IV}}(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_2]^{0}$: Joly²⁰ made from anhydrous ruthenium trichloride a solid likely to be the same violet complex; it formed ruthenium red with aqueous ammonia and was designated, first, RuOHCl_2 and later¹ $\text{Ru}_2(\text{OH})_2\text{Cl}_2$. In our view it is more probably $[\text{Ru}_3\text{O}_2\text{Cl}_6(\text{H}_2\text{O})_6]^{0}$ with the linear Ru-O-Ru-O-Ru grouping that occurs in ruthenium red.

We have not been able to determine fully the rôle of water in salts of the red and the brown complexes. Two molecules of water remain with each trinuclear unit up to about 85°; these may be loosely attached to the two bridging oxygen atoms, in the manner, shown by X-ray study, of water in $\text{K}_4[\text{Ru}_2\text{OCl}_{10}]\cdot\text{H}_2\text{O}$.

It is now clear that the ruthenium red chloride, and the various solids prepared by Morgan and Burstall² by treatment of its aqueous solution severally with HCl, HNO_3 , HBr, HI, KBr, KI, $\text{K}_2\text{RuNOCl}_5$, and K_2PtCl_6 , were contaminated with other amines of ruthenium because alcohol was used for precipitation. Salts such as their chloro-iodide would be mixtures of the chloride and iodide of ruthenium red. In the light of our work, their other preparations* fall into two classes: (i) Purple salts, obtained from solutions of the red chloride by the addition of potassium salts, which are the iodide (VII), nitrosyl-ruthenium pentachloride (IX), and platinochloride of the ruthenium red cation in which another anion replaces chloride. (ii) Other salts, which are the chloride (II), bromide (V), and iodide (VIII) of the ruthenium brown cation mixed with salts of the other anions present in the solutions. For instance, the nitrate (III) contained chlorine and must have been a mixture of the brown nitrate and chloride.

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* The Roman numerals are those given by Morgan and Burstall.²

¹⁶ Werner, *Ber.*, 1907, **40**, 4426.

¹⁷ Wilmarth, Graff, and Gustin, *J. Amer. Chem. Soc.*, 1956, **78**, 2683.

¹⁸ Pshenitsyn and Ginzburg, *Zhur. neorg. Khim.*, 1957, **2**, 112.

¹⁹ Cady, Ph.D. Thesis, University of California at Berkeley, U.S.A., 1957.

²⁰ Joly, *Compt. rend.*, 1892, **114**, 291.