16. *The Nitratonitrosylruthenium Complex*, $RuN_3O_{7.5}$.

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The ruthenium compound obtained by the reaction of nitric oxide with ruthenium tetroxide in carbon tetrachloride and referred to as $Ru_2N_6O_{15}$ by Martin and by Fletcher *et al.* has been further studied. Infrared examination has included the use of the ^{15}N form of the complex. The reactions involved in its preparation and its behaviour in both organic and aqueous media indicate that it may be a nitrato-complex containing two bisnitrosylruthenium groups linked by an oxo-bridge. Infrared absorptions of a number of other compounds containing the Ru–O bond are reported.

The ruthenium compound, originally formulated as $Ru_2N_6O_{15}$, was prepared by Martin[1] whilst endeavouring to obtain anhydrous, acid-free nitrosylruthenium nitrates. It was first suggested[2] that it is a binuclear oxygen-bridged nitrosylruthenium compound containing nitro-groups; the infrared spectrum (see below), however, shows the presence of nitrato- but of no nitro-groups. Then it was suggested[3] that each half of the molecule contains two bidentate nitrato-groups; however, reactions of its aqueous solutions more nearly correspond with the presence of one nitrato-group per atom of ruthenium. While there are good reasons for believing that each ruthenium atom in the complex is associated with at least one nitrosyl and one nitrato-group, the properties of the complex give no positive evidence about the arrangement of the third nitrogen atom: they indicate a structure of an unusual nature containing more than one ruthenium atom.

Experimental

Preparation and Stoicheiometry.—The compound $RuN_3O_{7.5}$ was prepared as previously described,[1, 2] by the action of dry nitric oxide on a dry solution of ruthenium tetroxide in carbon tetrachloride. Recent preparations confirmed the view that moisture, even in traces, leads to wide variations in composition, the ruthenium content varying from 32% to 39%, whereas rigorously dried reagents yield material constant in composition within narrow limits, and not differing significantly from our earlier preparations[1, 2] [Found (three preparations): Ru, 38·6, 38·8, 38·5; N, 15·6, 15·9, 15·6. Calc. for $Ru_2O_{15}N_6$: Ru, 38·4; N, 15·9%].

It has been shown[1, 2] that the preparative reaction employs a ratio of four mols. of nitric oxide to one of ruthenium tetroxide. In this experiment a known volume of dry nitric oxide was allowed to react with an excess of ruthenium tetroxide dissolved in carbon tetrachloride in a closed flask. When reaction was complete, the concomitant reduction in pressure enabled carbon tetrachloride to be admitted through a side tube. A volume corresponding to about seven-eighths of the original volume of nitric oxide entered. The residual gas was completely soluble in carbon tetrachloride since, after shaking of the flask, further ingress of carbon tetrachloride filled it.

Another experiment proved the gas to be very soluble in water. That it was nitrous oxide was confirmed by a mass spectrography, which disclosed also some nitrogen and traces of argon. Since the $^{40}A : N_2$ ratio in the sample ($^{40}A = 1{\cdot}22\%$ calc. on N_2) was almost identical with that in normal air (1·21%), the nitrogen in the sample was an atmospheric contamination. The only significant gaseous product is thus nitrous oxide. Any oxygen would of course have reacted to form nitrogen peroxide, which, incidentally, is not readily detected by mass spectrography.

This leads to the stoicheiometry: $8NO + 2RuO_4 = Ru_2N_6O_{15} + N_2O$.

Properties and Behaviour of the Complex.—The complex is pale orange-brown, diamagnetic ($\chi_g = -0{\cdot}08 \times 10^6$ at 21°), and very hygroscopic.

(*a*) Nitron acetate precipitates, from a cold, freshly prepared aqueous solution of the complex, a buff-coloured material containing most of the ruthenium. In a boiling mixture the

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[1] Martin, Ph.D. Thesis, London, 1955.

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

[3] Fletcher, Internat. Symp. on the Chemistry of the Coordination Compounds, Suppl. to *Ricerca sci.*, 1958.

buff precipitate decomposes, the ruthenium forms a pink solution (probably as a nitrosylruthenium acetate), and a precipitate of nitron nitrate is left. In 6 out of 10 experiments the number of nitrate groups found was one (and never less than one) per atom of ruthenium; in 4 out of 10 the number varied between 1·0 and 1·5.

(*b*) Ferrous solutions are quantitatively oxidised by nitrate in the presence of molybdate ions.[4] Since $RuNO^{III}$ does not normally oxidise ferrous ion, it should be possible to ascertain the number of nitrate groups in $RuN_3O_{7\cdot5}$ by its reaction with a ferrous solution. Aqueous solutions again showed a minimum of one nitrate group per ruthenium atom, (1·3—1·5 in 7 out of 10 cases).

(*c*) Water leads to the evolution of oxygen; the volume liberated varied from about 0·4 to 0·6 g.-atom of oxygen per g.-atom of ruthenium. Fresh aqueous solutions also decolorise permanganate. They are acidic and become more so on ageing or boiling. Plots of conductometric titrations with sodium hydroxide show well-defined but variable points of inflection (reminiscent of the neutralisation of a strong acid) which suggest an equivalent weight of about 400.

Although neither nitro- nor nitrito-groups are indicated by infrared examination (see below), nitrite is present in the supernatant liquid when alkaline solutions are boiled to precipitate nitrosylruthenium trihydroxide, $RuNO(OH)_3$ (cold alkalis do not give a precipitate). Thus, in an experiment in which the compound was dissolved in water, the reaction balance for oxygen, nitro-, and nitrate groups proved to be: O, 0·50; NO_2^-, 0·21; NO_3^-, 1·55. If the nitro-groups and the nitrate groups in excess of one arise through the oxidation of a nitrosyl group by oxygen in the molecule which is not associated with the nitrogen atoms, *e.g.*, by a reaction of the type, $[RuO_2(NO)_2NO_3]_2O + H_2O \longrightarrow 2RuNO^{3+} + xHNO_3 + yHNO_2 + zO_2$, the following relation should hold: (atoms of liberated oxygen) + (number of nitro-groups) + 2(number of nitrate groups minus one) = 2 for each ruthenium atom. The experimental figures cited give, per ruthenium atom, $0{\cdot}5 + 0{\cdot}21 + (2 \times 0{\cdot}55) = 1{\cdot}81$.

Passing hydrogen sulphide through hot aqueous solutions of the compound precipitates chocolate-brown nitrosylruthenium tri(hydrogen sulphide) [Found: Ru, 42·2; N, 6·0; S, 44·2. Calc. for $RuNO(SH)_3$ (cf. ref. 2): Ru, 43·9; N, 6·1; S, 42·7%]. The filtrate does not contain all the unprecipitated nitrogen; almost one nitrogen atom per ruthenium atom is lost from the hot system. Similar precipitation can be obtained from hot ethanolic solutions, and again nitrogen is lost.

(*d*) Most solvents containing oxygen (ethers, ketones, alcohols, esters) dissolve the solid compound readily. Its solubility in dioxan and acetophenone is low and it is insoluble in carbon tetrachloride, paraffins, benzene, etc. Boiling ethanol is oxidised rapidly to acetaldehyde; boiling acetone is slowly oxidised. Apparent molecular weights, determined ebullioscopically in the latter solvent, were over 500 ($Ru_2N_6O_{15}$ requires 526) and decreased slowly with continued boiling. In camphor (Rast's micro-method) the values were about 600 although some thermal decomposition occurred with the liberation of brown fumes. Cryoscopic observations in dioxan and acetophenone gave very variable values which decreased rapidly from about 327 to the anomalously low figure of 37: obviously there is extensive reaction with these and other solvents.

(*e*) Concentrated acids react with the solid. Cold sulphuric acid causes slight effervescence; with hot acid the colour changes to pinkish-brown, presumably by the formation of nitrosylruthenium sulphate, and thereby prevents the extraction of ruthenium into organic solvents. Cold hydrochloric acid slowly liberates brown fumes; the hot acid converts the compound rapidly into a raspberry-red solution of nitrosylruthenium chloride. Hot nitric acid yields a solution of nitrato-complexes of nitrosylruthenium; the reaction affords a convenient method of preparing these.[2]

Optical Examination.—(a) *Infrared spectra.* The infrared spectrum was examined in the region 2000—700 cm.$^{-1}$ and has been reproduced in ref. 3. The frequencies observed for this compound and for the compound containing ^{15}N (prepared by using NO enriched in ^{15}N) are listed in Table 1. The nitrosyl group gives rise to a very strong sharp peak at 1976 cm.$^{-1}$ (with ^{15}N the peak is observed at 1923 cm.$^{-1}$, the calculated shift being to 1921 cm.$^{-1}$); there is no splitting of this band. Bands at 1543 and 1276 cm.$^{-1}$ in the ^{14}N sample are assigned to ν_4 and ν_1 respectively [5] of the co-ordinated nitrato-group ($-O{\cdot}NO_2$); the intensity of ν_1 is greater

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[4] Kolthoff, Sandell, and Moskowitz, *J. Amer. Chem. Soc.*, 1933, **55**, 1454.

[5] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

than that of ν_4, but these intensities are usually comparable. They are shifted by 38 and 46 cm.$^{-1}$ respectively on ^{15}N substitution. Other bands arising from the co-ordinated nitrato-group occur at 847 (ν_6) and 788 cm.$^{-1}$ (ν_3 or ν_5).

Two broad bands at about 1160 and 970 cm.$^{-1}$ show insignificant shifts on ^{15}N substitution: the band centred at 970 cm.$^{-1}$ is not attributed to the ν_2 vibration of the nitrato-group (this vibration does not appear in other RuNO nitrato-complexes). Both bands may arise from vibrations of Ru–O bonds. The spectra of a number of other complexes, including those without nitrato-, nitro-, or nitrito-groups, containing ruthenium–oxygen bonds show similar broad bands between 900 and 1200 cm.$^{-1}$ (Table 2), and thereby support the hypothesis that this bond gives rise to frequencies in this region (cf. frequencies for other metal–oxygen bonds shown in Table 2).

TABLE 1. *Infrared absorption bands (cm.$^{-1}$) for* $RuN_3O_{7\cdot5}$.

	100% ^{14}N	Approx. 73% ^{15}N	Approx. 81% ^{15}N		100% ^{14}N	Approx. 73% ^{15}N	Approx. 81% ^{15}N
^{14}NO	1976 vs, sp	1988 m, sh	1988 sh		~1160 m, b	~1152 m, vb	~1156 s, b
^{15}NO ...		1931 vs, sp	1923 vs, sp				1029 w
ν_2 H_2O? ...	1631 vw	1623 w	1639 w, sh		~970 s, vb	~956 m, b	~954 s, b
			1610 w, sh	ν_6 $O\cdot{}^{14}NO_2$	847 w	849 w, b	841 w
ν_4 $O\cdot{}^{14}NO_2$	1543 s	1513 s, sh	1502 sp, sh	ν_6 $O\cdot{}^{15}NO_2$ ...		817 w, b	822 w
ν_4 $O\cdot{}^{15}NO_2$		1475 vs	1468 vs	ν_3 or ν_5	788 w	786 m, b	786 w
ν_1 $O\cdot{}^{14}NO_2$	1276 s	1305	1304 m, sh	ν_5 or ν_3 $O\cdot NO_2$	765 w	766 m, b	759 m, b
ν_1 $O\cdot{}^{15}NO_2$		1259 s	1256 vs				

s = strong, vs = very strong, m = medium, w = weak, b = broad, vb = very broad, sp = sharp, sh = shoulder, vw = very weak.

The spectra were determined on a Grubb-Parsons double-beam infrared spectrometer equipped with an S3A monochromator and rock-salt optics. The samples were prepared as mulls in Nujol (2—15 μ) or hexachlorobutadiene (5—8 μ) in the regions of Nujol absorption. The rock-salt plates were coated with a fine film of polystyrene to prevent reaction with the compound.

TABLE 2.

Compound	Frequency (cm.$^{-1}$)		Compound	Frequency (cm.$^{-1}$)	Ref.
$[RuNO(NO_3)_3(H_2O)_2],2H_2O$	994 s, b		UO_2^{2+}	800—900 sym.	*a*
$Na_2[RuNO(NO_2)_4OH],2H_2O$	997 s	1170 vw		850—1000 asym.	
$[RuNO(NO_2)_2OH(H_2O)_2]$ ...	965 m	1151 m	OsO_4	935	
$RuNO(OH)_3$	939 w, vb	1098 m, b	$K[OsO_3N]$ ...	858, 890	*b*
RuO_2	1021 w	1094 w	$VOCl_3$	1035	*c*
$K_4[Ru_2Cl_{10}O]$	973 w	1153 w, 1164 w			

[a] Jones, *Spectrochim. Acta*, 1958, **10**, 395. [b] Lewis and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12. [c] Miller and Cousins, *J. Chem. Phys.*, 1957, **26**, 329.

A weak band at approximately 1630 cm.$^{-1}$ arises either as an overtone or combination band or from the bending vibration (ν_2) of the water molecule; if the latter, the amount of water present is very small.

(b) *Microscopic examination* (by E. WAIT). Use of polarised light revealed that the substance possessed no visible crystallinity and was not optically birefringent; hence it is either cubic in symmetry or, more probably, is amorphous. Studies by *X*-ray methods are therefore likely to be unrewarding.

DISCUSSION

The non-integral ratio of oxygen to ruthenium and the apparent molecular weight suggest that the compound is at least binuclear. An oxo-bridge between ruthenium atoms has been established for the ion $[Ru_2Cl_{10}O]^{4-}$ and there is evidence from other work in these laboratories that the linear oxygen-bridged group Ru–O–Ru is of wide occurrence: its existence in this complex would account for the observed diamagnetism (absence of unpaired electrons) even if the ruthenium is present as Ru(IV).

The consistent failure to find two nitrate groups per ruthenium atom excludes the composition $RuNO(NO_3)_2\cdot O\cdot RuNO(NO_3)_2$. A variant (suggested by Addison [6]) of this bidentate nitrate formulation is the bridging of two ruthenium atoms by such a group. Numerous structures with such bridging can be postulated for this complex, particularly

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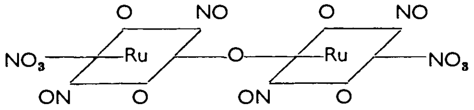
[6] Addison, Discussion in ref. 3.

if it is a polymer of relatively high molecular weight. Its existence as a polymer is consistent with its amorphous nature, which, however, is also characteristic of many non-polymeric compounds when prepared by precipitation.

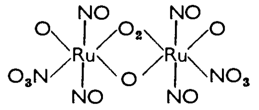
In the absence of evidence for such bridging, we suggest that the complex has two nitrosyl groups attached to each ruthenium atom, *i.e.*, is $RuO_2(NO)_2NO_3{\cdot}O{\cdot}RuO_2(NO)_2NO_3$. Although there are very many nitrosylruthenium compounds [*i.e.*, containing the RuNO(III) radical], polynitrosylruthenium compounds are limited to the pentanitrosyl, $Ru(NO)_5$, and the complex, $RuO_4(NO)_2$ (prepared by an addition reaction between nitric oxide and ruthenium tetroxide [7]); the latter has a limited range of stability, is readily hydrolysed, and decomposes with loss of nitric oxide. Ruthenium's congener, iron, is also attached to two nitrosyl groups in certain nitrosyl halides, *e.g.*, $Fe(NO)_2I$, and Roussin's red salts, *e.g.*, $Fe(NO)_2SK$.

The observed properties of the complex in aqueous solution are consistent with our formulation: replacement of oxygen atoms by aquo-groups and the lability of the second nitrosyl group could lead to the liberation of oxygen, together with oxidation of the second NO group to mixtures of nitro- and nitrato-groups in proportions dependent on the conditions. The absence of splitting of the NO band observed in the infrared spectrum demands that two nitrosyl groups, if attached to one ruthenium atom, should be *trans* to one another (splittings up to 100 cm.$^{-1}$ have been observed for all compounds containing two or more *cis*-NO groups). Such a *trans*-dinitrosyl structure would be unstable, as is this complex even to the extent of smelling of oxides of nitrogen. The occurrence of the nitrosyl peak at a higher wave number than is usual for mononitrosyl ruthenium complexes (we have found values from 1840 to 1950 cm.$^{-1}$ in other RuNO complexes) is consistent with the strengthening of the N–O bond that would be expected if there are two *trans*-nitrosyl groups. By analogy with UO_2^{2+}, one would expect the (RuO_2) groups in our formulation to be linear: the structure proposed is therefore:



If each NO group carries a charge of +1 as in mononitrosylruthenium complexes, the ruthenium valency is IV.

To account for the release of oxygen, a structure with a single peroxo-bridge was also considered but rejected in terms of the overall properties. It has however been suggested by a Referee that a possible structure is:



One of the remarkable features of the reaction between nitric oxide and ruthenium tetroxide in carbon tetrachloride is the evolution of nitrous oxide. The significance of this may be to imply that the reaction is of a condensation type between unstable nitrosyl intermediates, *e.g.*:

$$-Ru \ldots \boxed{ON + NO} \ldots Ru- \longrightarrow (Ru{-}O{-}Ru) + N_2O$$

The reaction is quite different from that between liquid nitric oxide and ruthenium tetroxide at low temperatures.[7]

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[7] Hair and Robinson, personal communication.