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The Ruthenium Complexes Formed by the Reactions of Nitrosylruthenium(III) with Tin(II) in Hydrochloric Acid Solution

Masao MUKAIDA

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho, Chiyoda-ku, Tokyo

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The complexes formed by the reactions of nitrosylruthenium(III) in hydrochloric acid solutions with tin(II) chloride were investigated. The following reaction products, $(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$, [1]; $(Me_4N)_4[RuCl_6(SnCl_3)_2(NO)_2]\cdot H_2O$, [2]; $(Me_4N)_4[RuCl(SnCl_3)_5]$, [3] and $K_3[Ru_2Cl_8(H_2O)_2N]$, [4] were isolated as crystals and were characterized. On the basis of chemical and thermal analyses, and on the basis of observations of the magnetic properties, the conductivities, and the infrared spectra, it was concluded that complexes [1], [2], and [3] contain terminal or bridging nitrosyl groups and/or a coordinating $SnCl_3^-$ group, and that complex [4] contains a bridging nitrido group. The presence of the binuclear complex, "$K_3[Ru_2Cl_9(NO)_2]$," which has both the terminal and singly-bridged nitrosyl groups was also suggested. The relations among those complexes were discussed.

The polynuclear metal complexes bridged by carbonyl or nitrosyl groups have recently been studied. Few binuclear ruthenium complexes bridged by nitrosyl groups have been studied. Attention has also recently been focussed on the metal-metal bonds in metal complexes. Complexes of platinum metals with metal-tin bonds have been studied considerably.[1–5] However, nitrosylruthenium complexes with the coordinating $SnCl_3^-$ groups have not yet been reported on. In this study, the binuclear ruthenium complexes bridged by nitrosyl groups and the complexes with ruthenium-tin bonds were prepared by the reactions of nitrosylruthenium(III) with tin(II) in hydrochloric acid solutions. They are $(Me_4N)_2[RuCl_3(SnCl_3)_2(NO)]$ and $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$. The complexes will be discussed on the basis of their properties. Two other complexes were also isolated from the reactions of nitrosylruthenium(III) with tin(II). One was $(Me_4N)_4[RuCl(SnCl_3)_5]$, which was identical with the complex prepared from ruthenium (III and IV) and tin(II) in a hydrochloric acid solution.[6] The other was $K_3[Ru_2Cl_8(H_2O)_2N]$, which had been mentioned by Brizard[7] and Charonnat[8] and which has recently been established by Cleare and Griffith[9] and by Ciechanowicz and Skapski.[10]

Nitrosylruthenium(III) is a fairly stable group when exposed to mild chemical reactions. It has been suggested that the reduction of nitrosylruthenium(III) compounds is clearly a field which should be more fully investigated.[11] It was thought that the complexes prepared in this study would give valuable information on the reaction of nitrosylruthenium(III) with tin(II) in hydrochloric acid solutions.

Experimental

Materials. Nitrosylruthenium(III) in a hydrochloric acid solution was prepared by the conventional method.[12] This solution was adjusted to contain 8 mg Ru/m*l* in 3M hydrochloric acid and was used as the starting solution for the syntheses of the complexes in this study. The ^{15}N-labeled nitrosylruthenium(III) in a hydrochloric acid solution was prepared by the method

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reported by Miki,[13,14] it was used for the syntheses of the ^{15}N-substituted complexes. All the other reagents used were of an analytical grade.

Measurements. The infrared spectra were measured with Leitz 221(4000—400 cm^{-1}), JASCO DS-301 (4000—700 cm^{-1}), Hitachi EPI-L(700—200 cm^{-1}), and Hitachi FIS-1(500—40 cm^{-1}) IR spectrometers. The KBr disk, Nujol mull, HCB mull and polyethylene film techniques were used. The magnetic properties were measured by the Gouy method. An electromagnet was used at the maximum field strength of *ca.* 9 kG. The conductivities of the complexes were measured in nitromethane or distilled water at 30°C with a Yokogawa Universal Bridge, BV-Z-13A. The visible spectra were measured with a Hitachi-Perkin-Elmer 139 spectrometer. The differential thermal analyses were carried out with a Shimadzu DT-2B apparatus. The measurements were made at a heating rate of 10°C/min in an atmosphere. The powder X-ray diffraction data for finely-powdered samples were obtained with a Rigaku-Denki X-ray diffractometer 2001.

The ruthenium in the complexes was determined by the ruthenate method[15] after the samples had been ignited at a rather low temperature. The tin was determined as tin dioxide after tin(IV) cupferrate had been precipitated and had been ignited.[16] The chlorine was determined gravimetrically as silver chloride. The potassium and the tetramethyl ammonium ion were determined by the use of tetraphenyl borate. Elementary analyses were made by the Institute of Physical and Chemical Research, Japan.

Preparations of Complexes. **$(Me_4N)_2[RuCl_3(SnCl_3)_2(NO)]$, Complex [1].** The starting solution (1.58 mmol Ru(III)NO in 20 m*l*) was evaporated to dryness on a water bath. The residue was dissolved in 30 m*l* of 4M hydrochloric acid, and then $SnCl_2 \cdot 2H_2O$ (1.5 g, 6.7 mmol) was added gradually. The solution was subsequently vigorously stirred about 20 min at room temperature (20—25°C). After the solution had been filtered, a $(Me_4N)Cl$ solution (500 mg/5 m*l* H_2O) was added to obtain orange needle crystals. The crystals were filtered, washed several times with ethanol and with ether, and dried *in vacuo*, giving 400 mg of the complex. The complex is slightly soluble in both nitromethane and DMF. Found: Ru, 11.87; Sn, 28.13; Cl, 37.91; (Me_4N), 17.92%. Calcd for $(Me_4N)_2[RuCl_3(SnCl_3)_2(NO)]$: Ru, 12.08; Sn, 28.40; Cl, 38.27; (Me_4N), 17.71%.

$(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2] \cdot H_2O$, Complex [2]. The starting solution (1.58 mmol Ru(III)NO in 20 m*l*) was evaporated to dryness on a water bath. The residue was dissolved in 16 m*l* of 3M hydrochloric acid, and $SnCl_2 \cdot 2H_2O$ (1.7 g, 7.6 mmol) was added. The solution was then stirred vigorously about 30 min at room temperature (20—25°C) and subsequently left to stand for 24—30 hr. After the solution had then been filtered, a $(Me_4N)Cl$ solution (0.5 g/10 m*l* H_2O) was added. After this solution had stood for a long period, black or dark brown crystals were separated out. The crystals were filtered, washed several times with water, ethanol, and dried *in vacuo*, giving 200 mg of the complex. The complex is insoluble in most organic solvents.

Found: Ru, 16.27; N, 6.58; Sn, 19.14; Cl, 34.41; (Me_4N), 24.26%. Calcd for $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2] \cdot H_2O$: Ru, 16.31; N, 6.78; Sn, 19.16; Cl, 34.34; (Me_4N), 23.89%.

$(Me_4N)_4[RuCl(SnCl_3)_5]$, Complex [3]. *Method 1.* To the starting solution (1.58 mmol Ru(III)NO in 20 m*l*), 6M hydrochloric acid (60 m*l*) and $SnCl_2 \cdot 2H_2O$ (1.5 g, 6.7 mmol) were added. The mixed solution was then concentrated to about 20—30 m*l* by boiling it. Again, to the resulting solution, 3M hydrochloric acid (60 m*l*) and $SnCl_2 \cdot 2H_2O$ (0.5 g, 2.2 mmol) were added, and the solution was boiled for 10 min. After this solution had then been filtered, a $(Me_4N)Cl$ solution (1 g/10 m*l* H_2O) was added until crystals appeared. These orange-yellow crystals were separated out. The crystals were washed several times with an ethanol-hydrochloric acid mixture and with ether, and dried *in vacuo*, giving 300 mg of the complex. The complex is slightly soluble in both nitromethane and DMF.

Method 2. An alternative procedure for the preparation of this complex is as follows. The starting solution (1.58 mmol Ru(III)NO in 20 m*l*) was evaporated to dryness on a water bath. The residue was dissolved in 20 m*l* of 6M hydrochloric acid, and $SnCl_2 \cdot 2H_2O$ (1.7 g, 7.6 mmol) was added to the solution. The mixed solution was left to stand overnight at room temperature (20—25°C). After the solution had then been filtered, a $(Me_4N)Cl$ solution (1 g/10 ml H_2O) was added. An orange-yellow complex was thus obtained.

Found: Ru, 6.76; Sn, 38.80; Cl, 36.01; (Me_4N), 18.77%. Calcd for $(Me_4N)_4[RuCl(SnCl_3)_5]$: Ru, 6.48; Sn, 38.08; Cl, 36.45; (Me_4N), 18.99%.

$K_3[Ru_2Cl_8(H_2O)_2N]$, Complex [4]. This complex was prepared by the reduction of nitrosylruthenium(III) with tin(II) or with formaldehyde.

Procedure with Tin(II) Chloride. To the starting solution (1.58 mmol Ru(III)NO in 20 m*l*), potassium chloride (1 g) and $SnCl_2 \cdot 2H_2O$ (2.2 g, 9.8 mmol) were added. The mixture solution was completely evaporated to dryness on a water bath. The product was dissolved with a 3M hydrochloric acid solution (15—20 m*l*) and was then concentrated until crystals appeared. After the solution had then stood overnight, the reddish-brown crystals thus obtained were filtered and washed several times with water-ethanol and ether, and dried *in vacuo*, giving 100—150 mg of a crude product. A mixture of the crude product (250 mg), potassium chloride (0.5 g), and $SnCl_2 \cdot 2H_2O$ (2 g) was dissolved in 6M hydrochloric acid (30 m*l*) by heating, after which the solution was heated vigorously in a flask equipped with a reflux condenser for 2—4 hr. When the resulting solution was concentrated by evaporation, crystals were separated out. The reddish-brown crystals thus obtained were filtered, washed several times with a water-ethanol (1 : 1) mixture and with ether, and dried *in vacuo*, giving 30 mg of the complex. Recrystallization was made from 3M hydrochloric acid containing small amounts of potassium chloride. The complex is slightly soluble in water, but it is not soluble in any organic solvent.

Found: Ru, 30.25; N, 2.27; H, 0.81; Cl, 43.78; K, 17.50% (Ru, 30.18; N, 1.90; H, 0.73; Cl, 42.34;

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TABLE 1. THE COMPLEXES PREPARED FROM THE REACTIONS OF Ru(III)NO WITH Sn(II) IN HYDROCHLORIC ACID SOLUTIONS

	Formula	Color in solid state	Absorption maxima (mμ) (ε in parentheses)	
1,	$(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$	orange	440 (9.0×10^2) 326 (1.8×10^4)	*1
2,	$(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$	black-dark brown	—	
3,	$(Me_4N)_4[RuCl(SnCl_3)_5]$	orange-yellow	444 (1.3×10^3) 293 (2.2×10^4)	*1
4,	$K_3[Ru_2Cl_8(H_2O)_2N]$	reddish brown	440 (1.1×10^2) sh 360 (5.0×10^2) sh	*2
5,	"$K_3[Ru_2Cl_9(NO)_2]$"	brown	—	

*1: in 3M hydrochloric acid solution, *2: in aqueous solution.

K, 17.38% for the crude product). Calcd for $K_3[Ru_2Cl_8(H_2O)_2N]$: Ru, 30.92; N, 2.14; H, 0.61; Cl, 43.47; K, 17.95%. The evaporation of a D_2O solution of the complex gave a deuterium-substituted complex as crystals.

Procedure with Formaldehyde. To the starting solution (1.58 mmol Ru(III)NO in 20 m*l*), enough potassium hydroxide was added to make the pH of the solution higher than 13. After the mixed solution had then been boiled vigorously for about 30 min, the solution gradually turned from brown to pale-violet, and finally to dark red. While a formalin solution (10 m*l*) was poured, drop by drop, into the solution, a gelatinous, brown precipitate was thrown down from the solution. The precipitate thus obtained was centrifuged and then washed several times with water. The precipitate was subsequently dissolved in a hydrochloric acid solution containing 0.3 g of potassium chloride, and the solution was concentrated by evaporation. After the solution had stood overnight, the reddish-brown crystals thus obtained were filtered, washed several times with a water-ethanol (1 : 1) mixture and with ether, and dried *in vacuo*, yielding 50 mg of a crude product.

Found: Ru, 30.31; N, 2.22; H, 0.71; Cl, 41.60; K, 17.58% for the crude product.

Results and Discussion

From the reactions between nitrosylruthenium(III) and tin(II) chloride under the various reaction conditions, two complexes were newly prepared and two complexes which had recently been reported were isolated. The analytical data were in good agreement with the calculated compositions. The complexes are summarized in Table 1, along with the absorption maxima in their visible and UV spectra. All the complexes are fairly stable in an atmosphere. However, exposure to sunlight changes complexes [1] and [3] from the original orange to dark gray. The conditions of preparing complexes [1] and [2] were rigid, and the methods of these preparations were specially examined.

The type of electrolyte in complex [1] was examined by the use of the conductivities in solutions according to the method reported by Feltham and Hayter.[17] The results shown in Table 2 indicate that complex [1] is an electrolyte of the 2 : 1 type and that no appreciable dissociations of the $SnCl_3^-$ group occur in nitromethane solutions.

TABLE 2. TYPE OF ELECTROLYTE AS DETERMINED BY CONDUCTIVITY MEASUREMENTS

Complex	Solvent	Λ_0 (ohm^{-1})	$\frac{\Lambda_0-\Lambda_e}{\sqrt{C}}$	Type of electrolyte
$(Me_4N)_2$-$[RuCl_3(SnCl_3)_2NO]$	CH_3NO_2	156	660	2:1
$K_3[Ru_2Cl_8(H_2O)_2N]$	H_2O	214	321	3:1

temperature; 30°C, concentration range; 10^{-2}—10^{-3}M. In order to determine the type of electrolyte, the data on $(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$ were compared with those on $[(C_6H_5)_4As]Cl$ and $[Co(phen)_3](ClO_4)_3$, and the data on $K_3(Ru_2Cl_8(H_2O)_2N]$ with those on $[Co(NH_3)_6]Cl_3$.

On the differential thermal analysis of complex [2], a distinct endothermic peak at 100—130°C was found, accompanied by a relatively small endothermic peak at about 140°C (Fig. 1). A violent decomposition started at 200°C. Infrared spectroscopy suggested that the two endothermic peaks may be based on the dehydration of crystalline water and the structural change in the complex. The gravimetric determination of the crystalline water was impossible.

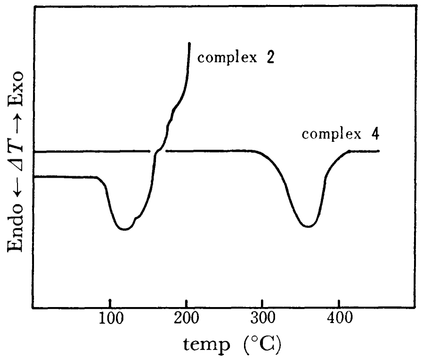

Fig. 1. DTA curves of $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$, complex [2] and $K_3[Ru_2Cl_8(H_2O)_2N]$, complex [4].

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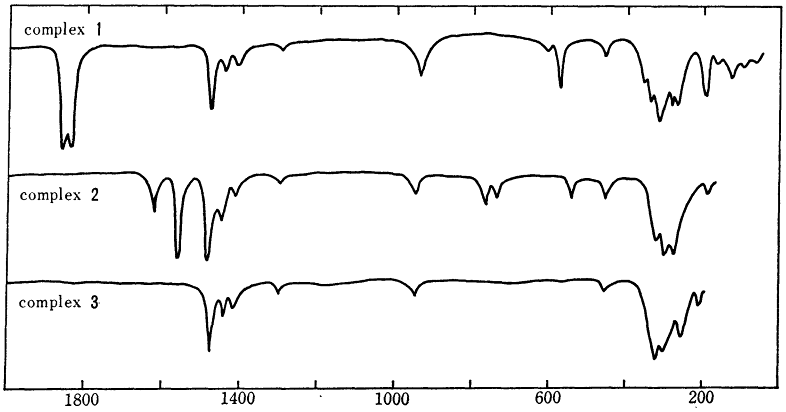

Fig. 2. Infrared spectra of $(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$, complex [1], $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$, complex [2] and $(Me_4N)_4[RuCl(SnCl_3)_5]$, complex [3].

Complex [3] was identical with a complex which has previously been prepared by the reaction of ruthenium (III and IV) with the tin(II) in a hydrochloric acid solution.[6]

Complex [4] was prepared by two methods similar to those described by Brizard;[7] the two methods yielded identical complexes. The complex is thought to be the same as that reported by Cleare and Griffith.[9] Complex [4] was shown to be an electrolyte of the 3 : 1 type by the conductivity measurements (Table 2), this supports the formula of complex [4]. A differential thermal analysis was made of complex [4] in order to determine the nature of water in the complex. The DTA curve obtained is shown in Fig. 1. The endothermic peak at about 300—380°C is thought to be caused by the dehydration of the coordinating waters from the complex, because the weight loss (5.66%) at 380°C corresponds to the two molecules of water in the complex and the dehydration temperature observed is considerably higher than the general dehydration temperature for water of crystallization.

The structures of the complexes will be discussed on the basis of the infrared spectra and the diamagnetisms.

Infrared Spectra. As Figs. 2 and 3 and Tables 3 and 4 show, complexes [1], [2], [3] and [4] display quite different spectra, indicating that their structures are also different.

In general, terminal nitrosyl groups in metal complexes are characterized by absorption bands due to the NO stretching vibration. The NO stretching absorptions of complex [1], $(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$, were easily identified, because the NaCl region is free from ligand absorptions except for the absorptions due to the nitrosyl group. Thus, the strong bands at 1865 cm^{-1} and 1842 cm^{-1} can be assigned to the NO stretching frequencies, which are close to those for $K_2[RuCl_5NO]$.[18–20] The remaining two bands in the region about 600—550 cm^{-1} of complex [1] must be attributed to the Ru–NO bending and the Ru–NO stretching frequencies. If a linear Ru–N–O arrangement is assumed, there are three possible isomers of complex [1], one *trans* (C_{2v}) and two *cis* (C_s), with respect to the $SnCl_3^-$ ligands. However, the stereochemistry of complex [1] was not determined by the symmetry treatment and the observation of the infrared absorption bands. Since the NO and the $SnCl_3^-$ ion have strong *trans* effects, so that the *trans* positions of the NO and $SnCl_3^-$ groups may be expected to

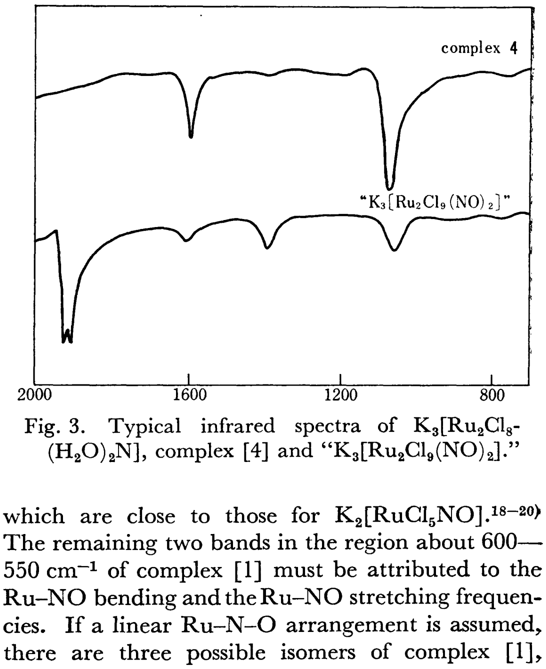

Fig. 3. Typical infrared spectra of $K_3[Ru_2Cl_8(H_2O)_2N]$, complex [4] and "$K_3[Ru_2Cl_9(NO)_2]$."

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Table 3. Infrared spectra of $(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$, [1], $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$, [2], and $(Me_4N)_4[RuCl(SnCl_3)_5]$, (3)

Complex [1]	Complex [2]	^{15}N-Complex [2]	Complex [3]	Tentative assignments
	3390 m 3370 sh	3390 m 3370 sh		ν OH
1865 vs 1842 vs				ν NO (terminal)
	1625 m	1625 m		δ H_2O
	1566 vs	1538 vs		ν NO (bridging)
	769 s 747 m 543 m	756 m 734 s 527 m		ν Ru-N (bridging) δ RuNO (bridging) in-plane and out-of-plane
606 w				ν Ru-N (terminal)
581 s				δ RuNO (terminal)
360 sh 341 sh 328 vs 293 vs 277 vs	322 sh 303 vs 271 vs	321 sh 320 vs 271 vs	326 vs 310 sh 253 s	ν metal-Cl
200 s	190 w		212 m	ν Ru-Sn
163 w 131 s 87 m				lattice vibration

Absorption bands due to $(Me_4N)^+$ ion are not cited.
Figures are given in cm^{-1}.
Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; sp, split; br, broad.

Table 4. Infrared spectra of $K_3[Ru_2Cl_8(H_2O)_2N]$, [4]

Ordinary	^{15}N-Substituted	Deuterated	$K_3[Ru_2Br_8(H_2O)_2N]$	Tentative assignments
3360 s 3210 sh	3360 s 3210 sh	(3360 w)	3350 s	ν OH
		2450 s 2300 sh		ν OD
1611 s	1610 s		1601 s	δ H_2O (scissoring)
	(1403 vw, br)	(1420 vw, br)	(1401 m)	ν NO (bridging) ?
		1190 m		δ D_2O (scissoring)
1082 vs	(1080 w)	1079 vs	1053 vs	ν_{as} Ru-N-Ru
	1047 vs			ν_{as} Ru-^{15}N-Ru
~600 w, br	~600 w, br		~560 w, br	δ H_2O (wagging)
543 w	528 w	551 w	527 w	δ Ru-N-Ru
		~450 w, br		δ D_2O (wagging)

be labile,[21,22] a stable structure of complex [1] can be presumed to be *cis* with respect to any two of the $SnCl_3^-$ and NO groups. However, it has been stated, with regard to the isomerism of the $[PtCl_2(SnCl_3)_2]^{2-}$ ion, that the *cis* isomer is more stable thermodynamically, while the *trans* isomer is favoured kinetically.[3]

The features of the spectra of complex [2], $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$, were markedly different from those of complex [1]. No absorption band was observed in the region of 1700—1900 cm^{-1}, where the bands due to the stretching vibrations of the terminal nitrosyl group in nitrosylruthenium complexes had previously been reported. However, a strong absorption band appeared at 1566 cm^{-1}. Since absorption bands due to the stretching vibrations of the bridging nitrosyl group in metal complexes have been found in the region of 1550—1300 cm^{-1},[23-25] the band at 1566

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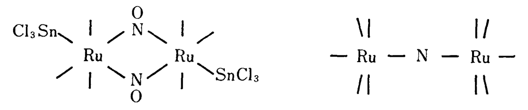
cm^{-1} can be assigned to the stretching vibration of the bridging nitrosyl group in complex [2]. The infrared investigation of the bridging nitrosyl groups has not yet dealt with the absorption bands in the lower frequency region. However, three absorption bands were observed, at 769, 747, and 543 cm^{-1}, in complex [2], instead of the two bands due to the skeletal vibrations of the Ru–NO(terminal) group. If the binuclear skeleton shown in Fig. 4, which has a center of symmetry, is assumed for complex [2], there should be three bands, due to Ru–N stretching, RuNO in-plane bending, and RuNO out-of-plane bending vibrations. The three absorption bands observed in the lower region can thus be explained. These three bands and the bands at 1566 cm^{-1} were shifted by the ^{15}N-substitution. The skeletal structure of complex [2] as shown in Fig. 4 is suggested on the basis of its infrared absorptions. The dimeric nature thus presumed could not be confirmed by molecular weight and electroconductivity measurements, because of its low solubility with regard to organic solvents. However, when complex [2] was heated at about 150°C, the infrared absorption due to the stretching vibration of the bridging nitrosyl group disappeared and that of the terminal nitrosyl group appeared. This observation suggests a bridge cleavage on the heating of complex [2] and supports its dimer structure.



complex [2] complex [4]

Fig. 4. Proposed skeletal structures for $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$, complex [2] and $K_3[Ru_2Cl_8(H_2O)_2N]$, complex [4].

The infrared spectra of complex [3], $(Me_4N)_4[RuCl(SnCl_3)_5]$, differ greatly from those of complexes [1] and [2]. No absorption bands due to the NO group were found in complex [3]. This confirms that complex [3] does not contain a nitrosyl group.

One of the most interesting investigations was the examination of the Ru–Sn bond in complexes [1], [2] and [3]. The absorption bands due to Ru–Cl stretching and Sn–Cl stretching vibrations have previously been reported.19, 26–28) A direct comparison of the far infrared spectra of complexes [1], [2] and [3] shows that the bands in the region of 360—250 cm^{-1} must be ascribed to metal-halogen vibrations. In order to make tentative assignments of the remaining bands, it was assumed that the bands observed in the region lower than about 160 cm^{-1} are to be attributed to lattice vibrations in these complexes. Consequently, the strong bands at about 200 cm^{-1} were assigned to the Ru–Sn stretching vibration: 200 cm^{-1} for complex [1], 190 cm^{-1} for complex [2],[*1] and 212 cm^{-1} for complex [3]. These assignments are in agreement with those of the absorptions due to metal-tin vibrations in the other metal-tin complexes.29,30) Thus, it was demonstrated that ruthenium-tin bonds are present in complexes [1], [2], and [3].

Very recently, Cleare and Griffith have reported the preparation of a bridging nitrido complex, $K_3[Ru_2Cl_8(H_2O)_2N]$ (complex [4]), by the Brizard method.7)

An X-ray diffraction study of this binuclear complex has indicated that the ruthenium atoms, which lie in mirror planes, have a distorted octahedral coordination with water molecules *trans* to the nitrogen.10) The main features of the infrared spectra of complex [4] in this study were similar to those reported by Cleare and Griffith. Complex [4] displays five absorption bands, at 3360, 1611, 1082, ~600, and 543 cm^{-1}, over the range of 4000—400 cm^{-1}. The band at 1082 cm^{-1} was often accompanied by a shoulder peak at 1045 cm^{-1}. A very weak broad band at about 1410 cm^{-1} was often found. In order to distinguish the bands due to coordinating water from those connected with the nitrogen atom, isotopic substitutions on hydrogen and nitrogen atoms were carried out. The bands at 3360, 1611, and 600 cm^{-1} shifted to at 2450, 1190, and ~450 cm^{-1} respectively in the deuterated complex. Thus, these three bands were assigned to the OH stretching and H_2O bending (scissoring and wagging) vibrations.28) On ^{15}N-substitution the two remaining bands, at 1082 and 543 cm^{-1}, shifted to the lower-frequency side. It has been reported that a metal complex such as $[Os_2N(NH_3)_8Br_2]Br_3$, which has a bridging nitrido group, is characterized by a strong absorption band in the 1100 cm^{-1} region.31) On the basis of the structure of complex [4] (Fig. 4), which has been determined by X-ray study,10) the bands at 1082 and 543 cm^{-1} can be assigned to the asymmetric stretching and bending frequencies respectively of the linear Ru–N–Ru skeleton. On the ^{15}N-isotopic substitution, these bands shifted to 1047 and 528

[*1] The author wishes to thank Mr. T. Takakuwa of the Japan Spectroscopic Co., Ltd., for this infrared spectral data.

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cm^{-1} respectively. These band shifts observed were in good agreement with the calculated ones, 34 and 17 cm^{-1}, which were estimated for the linear three-body model of Ru–N–Ru with the Ru–N distance of 1.718 A.[10] This agreement for the 1082 cm^{-1} band was shown also by Cleare and Griffith.[9]

When the crude product obtained in preparing complex [4] was not heated with Sn(II) in 6M hydrochloric acid, it usually exhibited a broad band at 1409 cm^{-1} with a medium intensity. The repeated recrystallization of the crude product gradually reduced the intensity of the absorption band at 1409 cm^{-1}, but it could not remove the band completely. This absorption band shifted slightly from 1409 to 1403 cm^{-1} on ^{15}N-substitution. The crude product showed identical features in its ^{15}N-substitution for the 1082 and 543 cm^{-1} bands, in its electronic spectra, and in its X-ray powder pattern with that of the purified complex, except that the band at 1409 cm^{-1} was present in the crude product.

It may be suggested that a complex with a singly-bridging nitrosyl group such as $K_3[Ru_2Cl_8(H_2O)_2NO]$ is present in the crude product of complex [4] and that the absorption band at 1409 cm^{-1} is due to the stretching vibration of the singly-bridging nitrosyl group. The disappearance of the absorption band of the crude product of complex [4] on the digestion in 6M hydrochloric acid may be caused by the rupture of the N–O bond in the bridging nitrosyl group and the formation of a bridging nitrido structure. On the other hand, it is also probable that the impurity in the crude product of complex [4] is a material which gives an infrared band only at 1409 cm^{-1}. The present study can not distinguish these possibilities. The impurity in the crude product of complex [4] will be discussed again later in connection with our other findings.

Complex [4] was dehydrated at 400°C under a nitrogen atmosphere, as has been described above. The infrared spectra of the complex heated exhibited two sharp bands at 1592 and 1063 cm^{-1} instead of the three bands at 3360, 1611, and 1082 cm^{-1} usually found in complex [4]. The corresponding two bands were observed at 1594 and 1031 cm^{-1} in the ^{15}N-substituted complex. The recrystallization of the complex dehydrated with a hydrochloric acid solution containing potassium chloride yielded the original complex [4]. These observation suggest a fairly stable skeletal structure of complex [4]. The appearance of the band at 1592 cm^{-1} in the dehydrated complex remained an unsolved problem. A proper assignement of the band at 1592 cm^{-1} was not made, though this infrared region is expected to be that for the stretching vibration of the bridging nitrosyl group. The other band, at 1063 cm^{-1}, is thought to correspond to the band at 1082 cm^{-1} in complex [4]; it may be suggested that the RuNRu skeleton is present in the dehydrated complex.

The preparation of the binuclear complex which has both terminal and singly-bridging nitrosyl groups was attempted. Preparation: to the starting material (0.79 mmol Ru(III)NO in 10 ml), 3M hydrochloric acid (20ml), potassium chloride (0.5 g), and $SnCl_2 \cdot 2H_2O$ (0.5 g, 2.2 mmol) were added. The mixed solution, in a porcelain dish, was then heated on a water bath for about 30 min. After the solution had subsequently stood for about a week, reddish-brown crystals were obtained. The composition of these crystals compared fairly well with the formula of $K_3[Ru_2Cl_9(NO)_2]$.

Found: Ru, 29.28; N, 3.61; Cl, 44.34; K, 17.38; Sn, 0.15%. Calcd for $K_3[Ru_2Cl_9(NO)_2]$: Ru, 28.91; N, 4.01; Cl, 45.76; K, 16.79%.

The nitrogen content determined was always less than the calculated value. There remains some uncertainty as to the purity of this product. The solubility of this product was much less than that of $K_2[RuCl_5NO]$, but greater than that of complex [4]. However, the recrystallization from hydrochloric acid solutions was not succesful, and it was

Table 5. Infrared spectra of "$K_3[Ru_2Cl_9(NO)_2]$"

^{14}N-Complex	^{15}N-Complex	Tentative assignments
3640 vw	3620 vw	ν NO (terminal) overtone ?
3360 m 3200 w, sh	3360 m 3200 w, sh	ν OH (impurity)
1913 vs 1903 vs	(1903 m) 1872 vs 1862 vs	ν NO (terminal)
1610 m-w	1610 m-w	δ H_2O (scissoring, impurity)
1405 m-w	1399 m-w	ν NO (bridging)
1082 m	(1082 vw) 1047 s-m	ν_{as} Ru-N-Ru
587 w		δ Ru-NO (terminal)
543 w	528 w	δ Ru-N-Ru

Table 6. Powder X-ray diffraction data (CuK_α)

$K_2[RuCl_5NO]$		"$K_3[Ru_2Cl_9(NO)_2]$"		$K_3[Ru_2Cl_8(H_2O)_2N]$	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
5.7230	0.86	5.7674	1.00	6.9972	1.00
5.5796	1.00	5.6041	0.21	6.4816	0.83
5.2448	0.14	4.9926	0.28	5.4835	0.14
5.1695	0.19	4.7918	0.11	4.2629	0.11
4.7663	0.49	3.5309	0.35	3.9656	0.43
3.9498	0.10	3.1399	0.17	3.8635	0.29
3.5131	0.34	3.0153	0.28	3.5036	0.14
3.3175	0.30	2.8823	0.26	3.4634	0.31
3.0113	0.17	2.8029	0.11	3.4048	0.23
2.9847	0.21	2.7120	0.10	3.2639	0.17
2.8661	0.20	2.5902	0.10	2.8914	0.14
2.7962	0.51	2.4993	0.37	2.8116	0.20
2.7128	0.49	2.3962	0.06	2.7040	0.15
2.5872	0.43	2.2906	0.08	2.6804	0.10
2.3889	0.26	2.2333	0.09	2.5404	0.80
2.0970	0.16	2.0429	0.12	2.1691	0.11
2.0562	0.15	1.9239	0.09	1.9835	0.14
1.8682	0.14	1.7666	0.15	1.7603	0.10

Relative intensities were estimated by comparing the hight of the peak. Less intensity lines are omitted.

observed that the recrystallization brought the decomposition to $[RuCl_5NO]^{2-}$ and/or the crude product of complex [4].

The infrared spectra of this product exhibited its major absorption bands at 3360, 1913, 1903, 1610, 1405, and 1082 cm^{-1} over the 4000—400 cm^{-1} range (Table 5) and are thought to involve absorption bands corresponding to those of complex [4]. The relative intensities of these absorption bands sometimes varied with the samples, and the intensity of the band at 1405 cm^{-1} decreased with an increase in the intensities of the bands at 3360, 1610, and 1082 cm^{-1}. However, the band at 1405 cm^{-1} was a sharp and symmetric band. This band may correspond to the band of the crude product of complex [4] at 1409 cm^{-1}.

The bands at 1913, 1903, and 1082 cm^{-1} are thought to be due to the terminal NO group and the asymmetric stretching vibration of the Ru–N–Ru group respectively. The four bands at 1913, 1903, 1405, and 1082 cm^{-1} shifted on ^{15}N-substitution, as is shown in Table 5. The bands at 3360 and 1610 cm^{-1} may be caused by the coordinating waters of complex [4], an impurity in this product. These observations, along with the chemical properties, indicate that the "$K_3[Ru_2Cl_9(NO)_2]$" complex, with a singly-bridging and a terminal nitrosyl group, may exist and that the sharp absorption bands observed at 1405 cm^{-1} may be due to the stretching vibration of the singly-bridging nitrosyl group in the complex, although the sample used in this infrared study was not pure enough. The X-ray powder patterns of the "$K_3[Ru_2Cl_9(NO)_2]$", $K_2[RuCl_5NO]$ complex and of complex [4] were compared (Table 6); it was thus shown that "$K_3[Ru_2Cl_9(NO)_2]$" is not a mixture of $K_2[RuCl_5NO]$ and complex [4].

When the final filtrate in the preparation of "$K_3[Ru_2Cl_9(NO)_2]$" was allowed to stand for a long time, red crystals were rarely obtained. The infrared spectra of this material exhibited only a strong band at 1408 cm^{-1} in the NaCl region and one at 1400 cm^{-1} for the ^{15}N-substituted material. Though this material is expected to have an interesting structure, the details on this particular crystals have not yet been clarified. However, these findings seem to support the idea that the crude product of complex [4] contains an impurity which gives an infrared band only at 1409 cm^{-1}.

Diamagnetisms. All the complexes prepared were diamagnetic. It is clear that $(Me_4N)_2[RuCl_3(SnCl_3)_2NO]$ (complex [1]) and $(Me_4N)_4[RuCl(SnCl_3)_5]$ (complex [3]) are diamagnetic. The oxidation state of the RuNO group in complex [1] is III, while that of ruthenium in complex [3] is II.

The diamagnetisms of $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$ (complex [2]) will be explained on the basis of the skeletal structure, shown in Fig. 4. Complex [2] involves the skeletal group of $Ru_2(NO)_2$, the oxidaton state of which is IV. The formal oxidation states of the ruthenium atoms and nitrosyl groups may be designated as follows: (i) both ruthenium atoms with II, and both bridging nitrosyl groups with zero, or (ii) both ruthenium atoms with III, and both the bridging nitrosyl groups with -1. The diamagnetism of this complex may be satisfactorily understood on the basis of the resonating four-member ring system, which accommodates two electrons of two nitrosyl groups in the case of (i), or those of two ruthenium atoms in the case of (ii), to make the spins of the two electrons paired. The diamagnetism of the binuclear manganese complex has similarly been explained by a four member-ring bridged with two nitrosyl groups.[23] Direct Ru(III)-Ru(III) interaction may also be possible in the case of (ii). Thus, the skeletal structure proposed can explain both the infrared spectra and the diamagnetism of complex [2].

The diamagnetism of $K_3[Ru_2Cl_8(H_2O)_2N]$ has been explained by assuming that the spin-pairing of $4d_{xz}$ and $4d_{yz}$ ruthenium orbitals takes place *via* the $2p_\pi$ nitrogen orbital.[9]

Reactions of Nitrosylruthenium(III) with Tin(II). The reactions of nitrosylruthenium(III) with tin(II) in hydrochloric acid solutions were quite complicated. The isolation of the reaction products is thought to give qualitative information on the reactions, although the isolation depends on the formation of complex ions, the solubilities of the salts of the complex ions formed, and the equilibria which involve the complex ions. The observed relations of these complexes are summarized in Fig. 5. The reactions of nitrosylruthenium(III) in this study may be divided into two broad classes: the coordinations of $SnCl_3^-$ on the ruthenium atom and the changes in the nitrosylruthenium(III) group. The differences in the conditions of preparing complexes [1], [2], and [3] indicate that the donation of $SnCl_3^-$ groups to the ruthenium atom of the nitrosylruthenium(III) group occurs first of all, and that the RuNO group then undergoes dimerization to form a binuclear skeleton bridged doubly by two nitrosyl groups; finally, the elimination of nitrosyl group occurs.

The reaction of $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$ with tin(II) chloride in the presence of potassium chloride in a hydrochloric acid solution yields a large amount of $[RuCl(SnCl_3)_5]^{4-}$ and a very small amount of $K_3[Ru_2Cl_8(H_2O)_2N]$ (complex [4]).

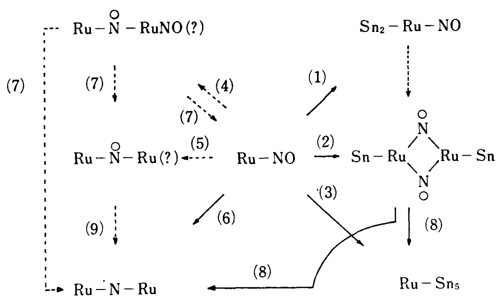

Fig. 5. Reactions of Ru(III)NO with Sn(II). (Only skeletons are cited.) (1)—(6): preparation routes, (7): decomposition of "$K_3[Ru_2Cl_9(NO)_2]$" in hydrochloric acid, (8): reaction of $(Me_4N)_4[Ru_2Cl_6(SnCl_3)_2(NO)_2]\cdot H_2O$ with Sn(II) and (9): reaction of the crude product of $K_3[Ru_2Cl_8(H_2O)_2N]$ with Sn(II).

A consideration of the conditions for preparing "$K_3[Ru_2Cl_9(NO)_2]$", and $K_3[Ru_2Cl_8(H_2O)_2N]$ suggests that the formation of the skeletal structures becomes easier in the order of: Ru(N)Ru$<$Ru(NO)Ru$<$Ru(NO)Ru(NO) (easiest), if $K_3[Ru_2Cl_8(H_2O)_2(NO)]$ is assumed to be present in the crude product of complex [4].

When nitrosylruthenium(III) and tin(II) (in the mole ratio of 1 : 0.8) were concentrated with potassium chloride under gentle warming, dipotassium pentachloronitrosylruthenate(III) was obtained. On the other hand, nitrosylruthenium(III) can be changed to ruthenium(II) by the method described in the preparation of complex [3].

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