

875. Deformation Frequencies of OH Groups in Nitrosyl-ruthenium Complexes.

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The infrared spectra of the hydroxo-complexes of nitrosylruthenium, namely, disodium hydroxotetranitronitrosylruthenate, hydroxotetra-ammine-nitrosylruthenium dichloride, and nitrosylruthenium hydroxide have been compared with those of their deuterated analogues. The strong band at 1000—970 cm^{-1} in the tetranitro- and tetra-ammine complexes arises from the deformation vibration of the hydroxyl group.

ABSORPTION bands in the region 1100—900 cm^{-1} for nitrate- and nitro-complexes of nitrosylruthenium have included assignments¹ to Ru-O and Ru-NO vibrations. Other work² has now shown that in the nitrate-complexes the strong broad band at 1000—940 cm^{-1} arises from the RuO-N stretching vibration (ν_2) of the co-ordinated nitrate-group.³ In order to assign bands occurring at 1000—900 cm^{-1} in the spectra of some complexes of nitrosylruthenium having no nitrate-groups, spectra of the hydroxotetranitro-complex, $\text{Na}_2[\text{RuOH}(\text{NO}_2)_4\text{NO}]$, and its dihydrate and deuterated analogues have been compared with those of the hydroxotetra-ammine complex, $[\text{RuOH}(\text{NH}_3)_4\text{NO}]\text{Cl}_2$, and the hydroxide $\text{RuNO}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$.

Studies^{4,5} on hydroxyl deformation vibrations of inorganic hydroxides have shown that (i) both the stretching (ν) and deformation (δ) frequencies of the hydroxyl group are shifted on deuteration according to Hooke's law for a harmonic oscillator such that $\nu(\text{OH})/\nu(\text{OD})$ and $\delta(\text{OH})/\delta(\text{OD})$ are approximately equal to $\sqrt{2}$, (ii) $\delta(\text{OH})$ tends to zero as the metal-oxygen distance increases (*i.e.*, the hydroxyl group becomes more ionic), and (iii) $\delta(\text{OH})$ increases, and $\nu(\text{OH})$ decreases, as the hydrogen bond becomes stronger.

RESULTS

Tetranitro-complex.—The spectrum of the dihydrate shows two superimposed bands in the region 3650—3450 cm^{-1} , due to O-H stretching vibrations, when a sodium chloride prism is used in its measurement. When a lithium fluoride prism was used, the band at $\sim 3550 \text{ cm}^{-1}$ was resolved into two bands, assigned to the asymmetric and the symmetric stretching vibrations of the H_2O group (Table) and separated from the band at 3499 cm^{-1} arising from the stretching vibration of the hydroxyl group. A very weak band at 3764 cm^{-1} is attributed to a small proportion of free hydroxyl groups. On dehydration, the two bands at 3606 and 3545 cm^{-1} , and the sharp band at 1620 cm^{-1} , assigned to the HOH bending mode, disappear. Accompanying these changes, there is a shift in the bands from 3499 and 995 cm^{-1} in the

¹ Fletcher, *J. Inorg. Nuclear Chem.*, 1958, **8**, 277; Martin, Fletcher, Brown, and Gatehouse, *J.*, 1959, 76.

² Fletcher, Scargill, and Woodhead, unpublished work.

³ Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

⁴ Hartert and Glemser, *Z. Electrochem.*, 1956, **60**, 746.

⁵ Tarte, *Spectrochim. Acta*, 1958, **13**, 107.

spectrum of the dihydrate to 3518 and 923 cm^{-1} respectively in that of the anhydrous complex. The deuterated analogues show frequency shifts in all these bands with ratios $\nu(\text{D})/\nu(\text{H})$ (Table) in accordance with those expected. The bands at 995 cm^{-1} for the dihydrate and at 923 cm^{-1} for the anhydrous complex can therefore be definitely assigned to the deformation vibration of the hydroxyl group.

Stretching and deformation frequencies (OH and OD) (in cm^{-1}).

	H ₂ O(D ₂ O) groups				OH(OD) groups				$\nu(\text{OH})/\nu(\text{OD})$	$\delta(\text{OH})/\delta(\text{OD})$
	$\nu(\text{OH})$	$\delta(\text{OH})$	$\nu(\text{OD})$	$\delta(\text{OD})$	$\nu(\text{OH})$	$\delta(\text{OH})$	$\nu(\text{OD})$	$\delta(\text{OD})$		
$\text{Na}_2[\text{RuOH}(\text{NO})_4\text{NO}], 2\text{H}_2\text{O}$	3606	1620	2688	1185	3499	995	2590	761	1.35	1.31
	3545		2644							
$\text{Na}_2[\text{RuOH}(\text{NO})_4\text{NO}] \dots\dots\dots$	—	—	—	—	3518	923	2595	^a	1.35	~1.3
$[\text{RuOH}(\text{NH}_3)_4\text{NO}]\text{Cl}_2 \dots\dots\dots$	—	—	—	—	3455	971	2548	^b	1.35	~1.3
$\text{Ru}(\text{OH})_3\text{NO}, 2\text{H}_2\text{O} \dots\dots\dots$	—	1633	—	^b	~3200	—	~2390	—	1.34	—

^a Obscured by Nujol. ^b Obscured by contaminant.

Tetra-ammine Complex.—This has one medium and two strong bands in the $3\ \mu$ region. The first, at 3455 cm^{-1} , is assigned to the hydroxyl stretching vibration and the last two, at 3243 and 3092 cm^{-1} , to the N–H asymmetric and symmetric stretching vibrations respectively of the ammine ligands. Two bands occur in the region 1000–800 cm^{-1} and both are shifted on deuteration. However, the relation⁶ between the rocking and the symmetric deformation frequencies of ammine ligands indicates that the band at 849 cm^{-1} is the ammine rocking frequency, so that the band at 971 cm^{-1} may be assigned to the hydroxyl deformation frequency.

Nitrosylruthenium Hydroxide.—The spectrum shows a strong broad band at 3200 and a weak band at 1633 cm^{-1} , both shifted on deuteration and assignable to O–H stretching and H–O–H bending modes (Table). The spectra for preparations from nitric and sulphuric acid solutions show other weak bands in the regions 1500–1250 and 1150–900 cm^{-1} respectively, which are not shifted on deuteration. These bands, which are absent from the spectrum of the preparation from chloride solution, are assigned to nitrate- and sulphato-groups respectively. As there are no bands from 1200 to 670 cm^{-1} which can be assigned to deformation vibrations of the hydroxyl groups, it is concluded that these groups are here more ionic than in the other compounds studied.

DISCUSSION

Comparison of the hydroxyl deformation (δ) and stretching (ν) frequencies in the anhydrous tetranitro-complex with those in the tetra-ammine complex gives -0.76 for the ratio $(\delta_{\text{I}} - \delta_{\text{II}})/(\nu_{\text{I}} - \nu_{\text{II}})$. As this approximates to the value of -0.66 found by Hartert and Glemser⁴ and by Tarte⁵ for hydroxyl groups with hydrogen bonds of intermediate strength, their empirical equation for the radius of the hydroxyl group with reference to the cation, $r(K)_{\text{OH}} = 8.9 \times 10^{-4} (4720 - \delta - 0.7\nu)$, may be used. This gives values of 1.19 and 1.18 Å for the nitro- and ammine complex respectively, and indicates that in them the metal–oxygen distances are similar.

The water molecules in the tetranitro-dihydrate are shown to be weakly hydrogen-bonded by the high stretching frequencies and their ease of removal. On dehydration, a greater shift is observed for the deformation than for the stretching frequency of the hydroxyl group, such that $\Delta\delta/\Delta\nu = -3.8$. Minor changes on dehydration also occur in the nitrosyl frequency (from 1897 to 1905 cm^{-1}) and the frequencies of the nitro-groups (from 1444 to 1441 cm^{-1} and from 1334 to 1340 cm^{-1} with a reduction from 8 to 3 cm^{-1} in the splitting of the band at about 830 cm^{-1}). These shifts are accounted for if (i) the water molecules are hydrogen-bonded to the nitro-groups (forming a cross-linked network in the crystal lattice), (ii) the hydroxyl groups are intermolecularly hydrogen-bonded to

⁶ Svatos, Sweeny, Mizushima, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1957, **79**, 3313.

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the nitrosyl groups ($\text{Ru-O-H} \cdots \text{ONRu}$), and (iii) the metal-oxygen bond length is shorter in the hydrated complex as a consequence of (i).

It has already been noted by Brown⁷ that the nitrosyl frequency is relatively low when hydroxyl groups are present in nitrosylruthenium complexes: this can be attributed to hydrogen-bonding [cf. (ii) above].

EXPERIMENTAL

Determination of Spectra.—Infrared spectra in the region 2–15 μ were obtained at 22° with a Hilger H800 double-beam spectrophotometer equipped with a rock-salt prism. A lithium fluoride prism was used in the 3 μ region to obtain better resolution and frequency measurements. Samples were examined as mulls in Nujol and hexachlorobutadiene, with thin (1–2 mm.) silver chloride windows prepared by rolling plates of ~5 mm. thickness between chromium-plated glazing sheets. When freshly prepared, such windows had good transmission, but deterioration limited their usefulness to about two weeks. Deuterated samples were milled and mounted in a dry-box. Wavelengths were calibrated by means of the 2.999 μ band of ammonia and the characteristic bands of polystyrene.

Preparations.—*Disodium hydroxotetraamminonitrosylruthenate.* The procedure of Fletcher *et al.*⁸ was modified to afford the dihydrate complex free from sodium chloride (formed as a major contaminant by the procedure described) by quickly washing the mixed crystals obtained with alcohol and extracting them with 20 ml. batches of acetone. The acetone was evaporated quickly at room temperature to minimise decomposition, and the residue dissolved in the minimum amount of water from which the complex crystallised at room temperature. After a further recrystallisation from water, the orange-yellow crystals were washed twice with alcohol and dried at room temperature. The anhydrous salt was obtained by drying (1 hr.) the powdered crystals to constant weight at 85–90° {loss, 8.7%. Calc. for $\text{Na}_2[\text{RuOH}(\text{NO})_4\text{NO}]\cdot 2\text{H}_2\text{O}$: 8.7%}. Drying at 110° (cf. ref. 8) caused slight decomposition, shown by a shoulder on the infrared absorption band of the nitrosyl group.

The deuterated analogues were obtained by dissolving the anhydrous salt in 99.7% D_2O and crystallising the product in a desiccator over phosphorus pentoxide; the crystals were removed and dried with filter paper in a dry-box. D_2O of crystallisation was removed by storing the powdered material over phosphorus pentoxide for a few days.

Nitrosylruthenium hydroxide. Separate preparations were made from solutions of nitrosylruthenium complexes in *N*-hydrochloric, nitric, and sulphuric acid. The previous procedure⁸ was modified by continuous centrifugation and readjustment of pH in order to obtain a good yield without recourse to long storage. The precipitates were washed three times each with water (adjustment to pH ~6 to prevent peptisation), alcohol, and acetone, and dried at room temperature [Found: Ru, 47.6; H_2O , 16.1 from chloride solution; Ru, 47.5; H_2O , 16.5 from nitrate solution; Ru, 48.0; H_2O , 17.5 from sulphate solution. $\text{RuNO}(\text{OH})_3\cdot 2\text{H}_2\text{O}$ requires Ru, 46.4; H_2O , 16.5%]. Previous preparations^{7,8} dried at 80° have indicated one molecule of water per ruthenium atom (49–49.8% of Ru). Deuteration was carried out by suspending the solid in D_2O and drying the product over phosphorus pentoxide in a desiccator.

Hydroxotetra-amminonitrosylruthenium chloride. Material supplied by Johnson Matthey & Co. Ltd. was used {Found: Ru, 35.3. Calc. for $[\text{RuOH}(\text{NH}_3)_4\text{NO}]\text{Cl}_2$: Ru, 35.2%}. Deuteration was carried out as for the hydroxide.

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⁷ Brown, *J. Inorg. Nuclear Chem.*, 1960, **13**, 73.

⁸ Fletcher, Jenkins, Lever, Martin, Powell, and Todd, *J. Inorg. Nuclear Chem.*, 1955, **1**, 378.