

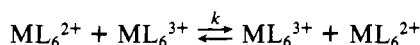
## Infrared and Raman Spectra of the Hexaaquaruthenium Ions: Normal-Coordinate Analysis for $\text{Ru}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ru}(\text{H}_2\text{O})_6^{3+}$

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Infrared and Raman spectra of the Tutton salt  $\text{Rb}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , of the alum  $\text{CsRu}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , and of their  $\text{H}_2^{18}\text{O}$ -substituted analogues have been measured at room temperature. Lattice constants are  $a = 12.447$  (4) Å for cubic  $\text{CsRu}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $a = 9.132$  (4) Å,  $b = 12.527$  (5) Å,  $c = 6.251$  (2) Å, and  $\beta = 106.30$  (5)° for monoclinic  $\text{Rb}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The vibrational spectra are analyzed in terms of the point-mass model using the generalized valence force field for octahedral symmetry, no splitting of the vibrational bands being observed owing to lower site symmetries. The force constants for the totally symmetric metal-water stretching vibration are 1.91 (1) mdyne Å<sup>-1</sup> for  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  and 2.98 (2) mdyne Å<sup>-1</sup> for  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ . Within the classical limit the rate constant calculated for the self-exchange reaction of the  $\text{Ru}(\text{H}_2\text{O})_6^{3+/2+}$  couple is  $\log k = 1.8$ .

The force constants for the symmetric metal-ligand stretching vibrations together with the corresponding distances represent the crucial information for estimating rates  $k$  of self-exchange reactions<sup>1</sup>, e.g.



In a recent paper<sup>2</sup> we reported the crystal and molecular structures of the *p*-toluenesulfonate salts of  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ . The structural results were used to estimate the self-exchange rate of the  $\text{Ru}(\text{H}_2\text{O})_6^{3+/2+}$  couple, with the assumption of a value of 2.5 mdyne Å<sup>-1</sup> for the relevant average force constants. We noticed that surprisingly few studies of vibrational properties of aqua ions<sup>3</sup> have been reported, in sharp contrast to the well-documented ammine complexes.<sup>4,5</sup> We therefore carried out a Raman and infrared spectroscopic study of the solid hexaaquaruthenium salts to determine the force constants of the Ru-H<sub>2</sub>O bond in both oxidation states, II and III. The previously unknown Tutton salt and alum of ruthenium were prepared for this investigation because the few vibrational modes of the sulfate anion are not expected to seriously interfere with the vibrations of the hexaaqua ions.

### Experimental Section

**A. Samples.** Crystals of  $\text{K}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (I) and the Tutton salt  $\text{Rb}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (II) were grown by slow cooling of an aqueous solution containing  $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$  (tos = *p*-toluenesulfonate),<sup>2</sup>  $\text{Rb}_2\text{SO}_4$  (or  $\text{K}_2\text{SO}_4$ ), and  $\text{H}_2\text{SO}_4$  in exactly stoichiometric proportions. The analogous procedure was applied to grow crystals of the alum  $\text{CsRu}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (III). Elemental analyses confirmed the given stoichiometries. The crystals of both compounds are perfectly stable under ambient conditions.  $\text{H}_2^{18}\text{O}$  (91%, MSD Isotopes) was used to prepare isotopically substituted samples by recrystallization. Owing to its considerably higher rate of substitution the labeled Ru(II) sample was prepared first. The corresponding Ru(III) compound was obtained by subsequent oxidation with  $\text{O}_2$ . The degree of isotopic substitution, 90% and 66%  $^{18}\text{O}$  for II (two separate preparations) and 90%  $^{18}\text{O}$  for III, was determined by mass spectroscopy.

**B. Unit Cell Dimensions.** The lattice constants for II and III were determined by least-squares refinement of KCl-calibrated ( $a_0 = 6.29294$  (8) Å<sup>6</sup> powder patterns (Cu  $K_{\alpha}$ , Guinier-De Wolff camera) with 22 (II) and 16 (III) reflections (Table I).

Table I. Crystal Data for  $\text{M}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (M = K, Rb) and  $\text{CsRu}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ <sup>a</sup>

	$\text{K}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{Rb}_2\text{Ru}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{CsRu}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
<i>a</i> , Å	8.950 (2)	9.132 (4)	12.447 (4)
<i>b</i> , Å	12.268 (3)	12.527 (5)	
<i>c</i> , Å	6.135 (1)	6.251 (2)	
$\beta$ , deg	105.27 (3)	106.30 (5)	
<i>Z</i>	2	2	4
$d_{\text{exptl}}$ , g cm <sup>-3</sup>	2.45 (1)	2.78 (1)	2.21 (1)
$d_{\text{caled}}$ , g cm <sup>-3</sup>	2.45	2.77	2.21
space group	$P2_1/a$	$P2_1/a$	$Pa\bar{3}$

<sup>a</sup> Throughout this paper numbers in parentheses represent estimated standard deviations.

**C. Spectroscopy.** Infrared spectra (4000-200 cm<sup>-1</sup>) of polyethylene pellets and Nujol mulls of II and III were recorded on a Perkin-Elmer IR 580. Powder samples in a glass capillary (III) or as pressed pellets (II) mounted on the sample rotator (Spex Illuminator 1459 equipped with Lasermate 1460) were used for measuring Raman spectra (~100-1200 cm<sup>-1</sup>). Spectra were excited with the 647.1-nm line of a Coherent Kr laser. The scattered radiation was dispersed in a Spex 1402 double-monochromator and recorded with a RCA 31034 photomultiplier using a photon-counting attachment. All the spectra were measured at room temperature at least three times for identical and freshly prepared samples.

### Results

**Sulfate Vibrations.** The four fundamental vibrational modes of the  $\text{SO}_4^{2-}$  anion are observed at the expected frequencies (Table II).<sup>5</sup> Tetrahedral symmetry is almost completely retained in the alum structure,<sup>7</sup> and hence no splitting of the degenerate modes  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  is observed for III. Moreover,  $\nu_1$  and  $\nu_2$  show essentially no infrared intensity, as required for tetrahedral symmetry. The site symmetry of  $\text{SO}_4^{2-}$  in the structure of the Tutton salts is 1.<sup>8</sup> Therefore, all fundamentals are infrared active and the degenerate modes are split (Table II). Small shifts (1-6 cm<sup>-1</sup>) are observed for the bending modes in the  $^{18}\text{O}$ -labeled samples. We attribute these shifts either to isotope effects producing slight variations in the strength of O-H...O hydrogen bridges or to consequences of a coupling of sulfate vibrations to  $\text{Ru}(\text{H}_2\text{O})_6^{n+}$  modes. A complete single-crystal vibrational analysis would be required to resolve this problem, which is not expected to significantly affect our analysis. These shifts do not arise from partial oxygen exchange of  $\text{SO}_4^{2-}$ , since the stretching mode  $\nu_1$  is completely unaffected.

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Table II. Infrared (IR) and Raman (R) Frequencies (in cm<sup>-1</sup>) for Rb<sub>2</sub>Ru(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (II) and CsRu(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (III)

	Ru(H <sub>2</sub> O) <sub>6</sub> <sup>n+</sup>							
	II		II- <sup>18</sup> O <sup>a</sup>		III		III- <sup>18</sup> O <sup>b</sup>	
$\nu_1(A_{1g})$ R	424 (1)		409 (1)		532 (1)		504 (1)	
$\nu_2(E_g)$ R	399 (1)		384 (1)		477 (2)		455 (2)	
$\nu_3(T_{1u})$ IR	426 (2)		409 (2)		529 (2)		510 (2)	
$\nu_4(T_{1u})$ IR	268 (4)		260 (4)		333 (3)		320 (3)	
$\nu_5(T_{2g})$ R	210 (1)		203 (1)		278 (1)		264 (1)	
	SO <sub>4</sub> <sup>2-</sup>							
	II		II- <sup>18</sup> O <sup>a</sup>		III		III- <sup>18</sup> O <sup>b</sup>	
	R	IR	R	IR	R	IR	R	IR
$\nu_1(A_1)$	977 (1)	980	978 (1)	980	977 (1)		976 (1)	
$\nu_2(E)$	439 (1)	460	437 (1)	460	434 (1)		428 (1)	
	447 (1)		447 (1)					
$\nu_3(T_2)$	1070	1100	1074	1100	1082 (1)	1075	1080 (1)	1075
	1096		1098					
	1113		1114					
$\nu_4(T_2)$	601 (1)	610	602 (1)	610	609 (1)	605	606 (1)	600
	621 (1)	630	623 (1)	630				

<sup>a</sup> 90% <sup>18</sup>O for samples used in infrared spectra (IR), 66% <sup>18</sup>O for samples used in Raman spectra (R). <sup>b</sup> All the spectra were run with samples of 90% <sup>18</sup>O.

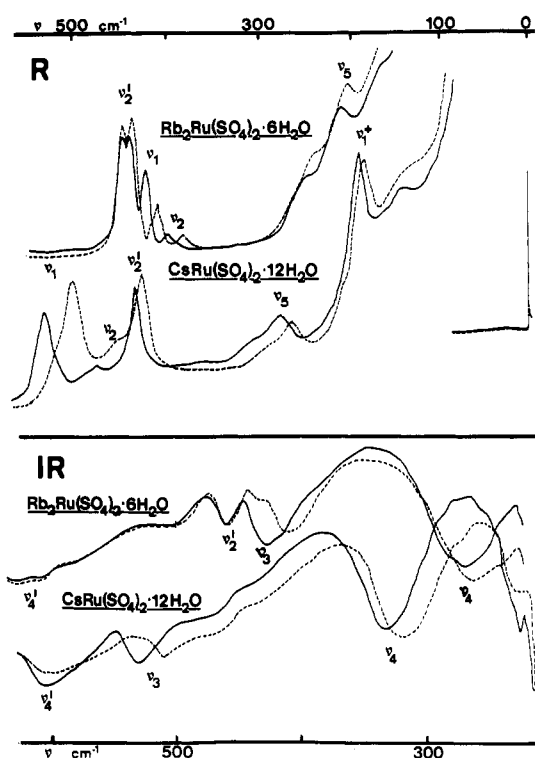


Figure 1. Raman (R) and infrared spectra (IR) of Rb<sub>2</sub>Ru(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and CsRu(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O. Broken lines represent spectra of <sup>18</sup>O-substituted compounds:  $\nu_2'$ ,  $\nu_4'$ , sulfate bands;  $\nu_1'$ , Cs(H<sub>2</sub>O)<sub>6</sub><sup>+</sup> band.

**Ru(H<sub>2</sub>O)<sub>6</sub><sup>n+</sup> Vibrations.** We restrict our study of the vibrational spectra to the internal modes of the Ru(H<sub>2</sub>O)<sub>6</sub><sup>n+</sup> coordination octahedra. The external modes of coordinated water molecules (rocking, wagging, twisting) are not dealt with in our analysis. These vibrations occur between 600 and 1000 cm<sup>-1</sup> in the infrared spectra of the alums and have been discussed by Beattie.<sup>9</sup> Moreover, we do not include the internal modes of the water molecule in our analysis.

The infrared and Raman spectra of II and III in the relevant frequency range are displayed in Figure 1. The infrared spectrum of III presents the same overall features as the infrared spectra reported for a series of other alums.<sup>9</sup> We notice

Table III. Force Constants (mdyn Å<sup>-1</sup>) for the Internal Vibrations of Ru(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Ru(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> (Generalized Valence Force Field<sup>a</sup>)

	Ru(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	Ru(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>
$F_{11}(A_{1g})$	1.91 (1)	2.98 (2)
$F_{22}(E_g)$	1.68 (2)	2.42 (2)
$F_{33}(T_{1u})$	1.59 (2)	2.36 (2)
$F_{34}(T_{1u})$	0.14 (9)	0.13 (4)
$F_{44}(T_{1u})$	0.27 (2)	0.38 (2)
$F_{55}(T_{2g})$	0.12 (1)	0.20 (1)
$f_x$	1.67	2.48
$f_{rr}$	0.04	0.09
$f_{rr'}$	0.08	0.12

<sup>a</sup> We use Nakamoto's nomenclature,<sup>5</sup> e.g.  $F_{11} = f_x + 4f_{rr} + f_{rr'}$ . Calculations were performed with the following values for the reduced masses: Ru, 0.009 894; H<sub>2</sub>O, 0.055 506; H<sub>2</sub><sup>18</sup>O (66%), 0.051 717; H<sub>2</sub><sup>18</sup>O (90%), 0.050 464.

the same general intensity pattern for Ru(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Ru(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>:  $I(\nu_1) \gg I(\nu_5) > I(\nu_2)$  for the Raman spectra and  $I(\nu_4) \gg I(\nu_3)$  for the infrared spectra. The actual site symmetry of Ru(H<sub>2</sub>O)<sub>6</sub><sup>n+</sup> is S<sub>6</sub> in the alum<sup>7</sup> and  $\bar{1}$  in the Tutton salt.<sup>8</sup> No splitting of the vibrational bands, however, can be observed at room temperature in the spectra of II and III, which could be attributed to a lower point symmetry. The analysis of the spectra is therefore discussed in terms of octahedral symmetry,  $O_h$ . The internal vibrational modes of the hexaaqua ions are thus represented by three stretching modes ( $A_{1g}$ ,  $E_g$ ,  $T_{1u}$ ) and three deformation modes ( $T_{1u}$ ,  $T_{2g}$ ,  $T_{2u}$ ).<sup>5</sup> The g modes are Raman active,  $T_{1u}$  is infrared active, and  $T_{2u}$  is inactive as a fundamental. The assignment of the five fundamentals is fully supported by the spectra of the <sup>18</sup>O-labeled samples. A survey of the experimental frequencies (Table II) shows a remarkably narrow clustering around 0.80 for the five frequency ratios  $\nu_i(\text{II}):\nu_i(\text{III})$ ,  $i = A_{1g}, E_g, T_{1u}, T_{1u}, T_{2g}$ .

The normal-coordinate analysis for the vibrations of the ruthenium aqua ions was carried out with the assumption of the water ligands as point masses. We adopted the generalized valence force field (GVFF) and followed the procedure outlined by Nakamoto,<sup>5</sup> which has been applied successfully in the analogous treatment of the hexammine complexes.<sup>4</sup> The set of force constants obtained by the straightforward application of this formalism is presented in Table III. The five fundamentals calculated with these force constants agree with the observed frequencies within less than 2 cm<sup>-1</sup>. The

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overall pattern of the vibrational frequencies and the force constants for  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$  correlates well with corresponding data for the better documented hexaammines. A comparison of our results with the incomplete analysis of the ruthenium hexaammines<sup>4,10</sup> shows the general relationship  $\nu_1(\text{Ru}(\text{NH}_3)_6^{2+}) \approx \nu_2(\text{Ru}(\text{H}_2\text{O})_6^{2+})$  and  $\nu_1(\text{Ru}(\text{NH}_3)_6^{3+}) < \nu_1(\text{Ru}(\text{H}_2\text{O})_6^{3+})$ . This observation is consistent with the corresponding metal-ligand distances and with a  $\pi$  interaction possible for water but not for ammonia.<sup>11</sup>

### Discussion

To our knowledge, the present study reports the first normal-coordinate analysis for the two hexaaqua ions of a redox couple. This, together with the structural data,<sup>2</sup> makes possible a reliable calculation of the reorganization energy of the inner coordination sphere for the  $\text{Ru}(\text{H}_2\text{O})_6^{2+} - \text{Ru}(\text{H}_2\text{O})_6^{3+}$  self-exchange reaction. Since our efforts to measure the internal  $\text{Ru}(\text{H}_2\text{O})_6^{\text{rt}}$  frequencies in solution (up to 1.5 M in  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  or  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ ) were unsuccessful, we use the solid-state properties as the best available vibrational data for the hexaaqua ions to estimate the redox kinetics of the dissolved species. In terms of the harmonic approximation the inner-sphere reorganization energy within the classical limit<sup>1</sup> is given by

$$\Delta G_{\text{in}}^* = \frac{3f_{\text{II}}f_{\text{III}}(\Delta r)^2}{f_{\text{II}} + f_{\text{III}}}$$

In this expression  $f_{\text{II}}$  and  $f_{\text{III}}$  represent the force constants of  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ , respectively.  $\Delta r$  is the differ-

ence of the metal-ligand distances between the oxidized and reduced complex. Following Marcus,<sup>12</sup> we use the force constants  $F_{11}$  ( $A_{1g}$ ) of the breathing vibration for  $f_{\text{II}}$  and  $f_{\text{III}}$ . With  $\Delta r = 0.09$  (2)  $\text{\AA}$ ,  $f_{\text{II}} = 1.91$  (1)  $\text{mdyn \AA}^{-1}$ , and  $f_{\text{III}} = 2.98$  (2)  $\text{mdyn \AA}^{-1}$ , we obtain 4.1 (1.8)  $\text{kcal mol}^{-1}$  for  $\Delta G_{\text{in}}^*$ . Within the given standard deviation the same value for  $\Delta r$  was determined by an EXAFS study of aqueous solutions of  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ .<sup>13</sup> Assuming a value of 10.9  $\text{kcal mol}^{-1}$  for the sum of the other contributions to the activation energy for electron transfer,<sup>1</sup>  $\Delta G^*$ , we calculate  $\log k = 1.82$  (1.8) for the rate of the  $\text{Ru}(\text{H}_2\text{O})_6^{2+/3+}$  self-exchange. It has to be emphasized that the uncertainty in  $\Delta G_{\text{in}}^*$  and  $\log k$  is predominantly due to the error in  $\Delta r$ .<sup>2</sup> Our result in terms of the classical limit of the Marcus theory agrees well with  $\log k = 1.78$  (45) as estimated by Sutin<sup>11</sup> using the Marcus cross relation for a series of redox reactions. From a current study of the  $\text{Ru}(\text{H}_2\text{O})_6^{2+/3+}$  self-exchange a preliminary value of  $\log k = 1.4$  (2) is obtained.<sup>14</sup> The rate calculated according to the Marcus theory is fully compatible with this directly determined experimental result.

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**Registry No.** II, 88703-97-3; III, 88729-59-3;  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$ , 30251-71-9;  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ , 30251-72-0.

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## Low-Temperature Synthesis and Properties of $\text{Co}_9\text{S}_8$ , $\text{Ni}_3\text{S}_2$ , and $\text{Fe}_7\text{S}_8$

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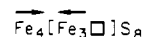
$\text{Co}_9\text{S}_8$ ,  $\text{Ni}_3\text{S}_2$ , and  $\text{Fe}_7\text{S}_8$  were prepared as single-phase polycrystalline materials by heating the appropriate metal sulfates in a controlled mixture of  $\text{H}_2$  and  $\text{H}_2\text{S}$  at low temperature. The products were characterized by X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility measurements. The X-ray diffraction pattern and field-dependent magnetic susceptibility of  $\text{Fe}_7\text{S}_8$  were affected by the thermal history of the sample. The observed differences can be related to the vacancy ordering associated with ferrimagnetic  $\text{Fe}_7\text{S}_8$ .

### Introduction

Delafosse et al.<sup>1-4</sup> have shown that sulfides of nickel and cobalt can be prepared by heating their anhydrous sulfates in a stream of  $\text{H}_2/\text{H}_2\text{S}$  at low temperatures. However, the experimental conditions for obtaining  $\text{Ni}_3\text{S}_2$  and  $\text{Co}_9\text{S}_8$  were not specified. In addition, it has been shown<sup>5,6</sup> that both  $\text{Co}_9\text{S}_8$  and  $\text{Ni}_3\text{S}_2$  permit little variation from ideal stoichiometry. For both compounds, there was no observable variation in the lattice parameter as determined from X-ray analyses. Magnetic measurements of  $\text{Co}_9\text{S}_8$  confirmed its narrow homogeneity range.

Synthetic samples of the low-temperature phase of  $\text{Fe}_7\text{S}_8$  have been prepared by Lotgering,<sup>7</sup> and magnetic measurements confirmed the work of other investigators<sup>8-10</sup> that the spon-

taneous magnetism of  $\text{Fe}_7\text{S}_8$  represents a ferrimagnetic structure that is based upon an ordering of iron vacancies. This can be represented by the formula



If this model is correct, then randomization of the vacancies

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