Nonetheless, the outer-sphere reorganizational barrier should be identical for both reactions (eq 33) as should Z (eq 32). In the absence of long-range electron transfer in the excited state self-exchange or of significant structural differences either in Ru-N bonds or in the bpy ligands between Ru(bpy)$_3{}^{3+}$ and the excited state, the two self-exchange rates should be identical.

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Vibrational Spectra, Resonance Raman Spectra, and Electronic Spectra of the μ-Oxo-decachlorodiruthenium(IV) Ion

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Abstract: The infrared and Raman spectra of the complexes $K_4[Ru_2OCl_{10}]$, $Rb_4[Ru_2OCl_{10}]$, and $Cs_4[Ru_2OCl_{10}]$ have been recorded and the observed bands assigned. The $Ru_2OCl_{10}{}^{4-}$ ion displays the resonance Raman effect, most spectacularly for the potassium salt, when irradiated with an exciting line whose frequency falls within the contour of the lowest allowed band of the ion at ca. 20 000 cm^{-1}. These spectra are characterized by a large increase in the intensity of the Raman band arising from the ν_1(Ru-O-Ru), a_{1g}, stretching fundamental, together with the appearance of an overtone progression reaching $7\nu_1$ at room temperature and $12\nu_1$ at 100 K for the potassium salt. Six other progressions are also observed in the resonance Raman spectrum of this ion at room temperature (eight others at 100 K), in each of which it is ν_1 which acts as the progression forming mode. The observation of such progressions has permitted the determination of ω_1, x_{11}, and several cross terms x_{1n}. The ω_1 values decrease with increasing size of the cation (decreasing lattice energy), viz. 256.5 (K^+), 254.7 (Rb^+), and 249.9 (Cs^+) cm^{-1}. Excitation profiles for four of the Raman bands have been plotted. That for ν_1 reaches a maximum at ca. 20 000 cm^{-1}, from which observation it is concluded that the resonant electronic transition is the axially polarized, electric dipole allowed ${}^1A_{2u} \leftarrow {}^1A_{1g}$ component of the $(e_u{}^b)^4\,(e_g)^3\,(b_{2g})^2\,(b_{1u})^2\,(e_u{}^*)^1 \leftarrow (e_u{}^b)^4\,(e_g{}^4)\,(b_{2g})^2\,(b_{1u})^2$ transition of the Ru-O-Ru π-bond system; the observation that the depolarization ratio of ν_1 is $\approx 1/3$ at resonance confirms this conclusion. The results suggest the wider use of resonance Raman spectroscopy as a technique for the assignment of electric-dipole-allowed transitions.

There have been a number of recent reports of the observation of resonance Raman spectra from various inorganic molecules and ions.[1] Such spectra are characterized, among other things, by a very large enhancement to the intensity of a band arising from a totally symmetric fundamental of the molecule, together with the appearance of high intensity overtone progressions in this same mode. Several metal-metal bonded species which belong, or to a first approximation belong, to the D_{4h} point group, viz. the $Mo_2Cl_8{}^{4-}$ ion,[2] the $Re_2Cl_8{}^{2-}$ and $Re_2Br_8{}^{2-}$ ions,[3] and the carboxylate-bridged species $Ru_2(O_2CR)_4Cl$ (R = CH_3 or n-C_4H_9),[4] have been particularly spectacular in this respect; irradiation within the contour of the lowest allowed transition of these formally multiply metal-metal bonded species has led, in each case, to the observation of long progressions in the (axial) metal-metal stretching fundamental, clearly demonstrating that the resonant electronic transition is also axially polarized, and thus of the $\delta^* \leftarrow \delta$ sort (${}^1A_{2u} \leftarrow {}^1A_{1g}$).

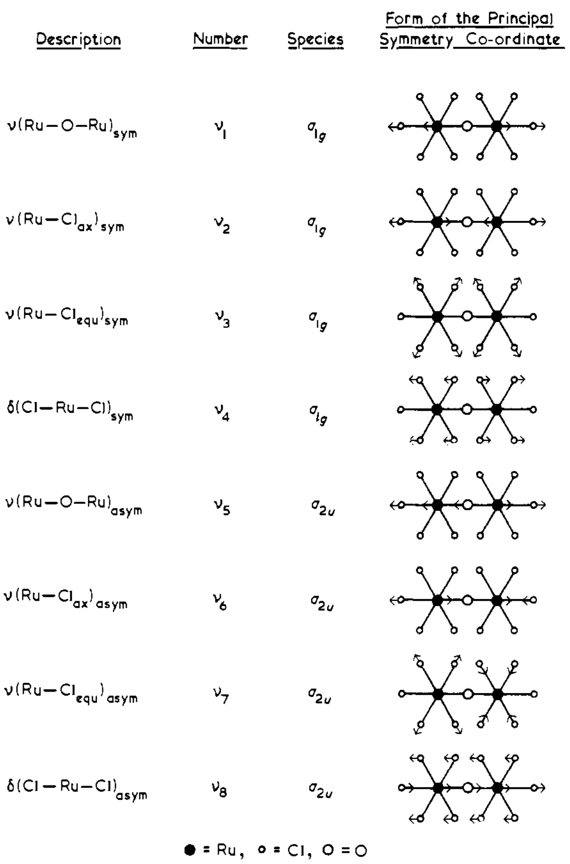

Figure 1. The a_{1g} and a_{2u} symmetry coordinates of the $Ru_2OCl_{10}^{4-}$ ion.

The $M_2OX_{10}^{4-}$ ions (X = Cl or Br) represent another class of inorganic species which, where linear, belong to the point group D_{4h}, and which also possess multiple bonds (in this case in the M-O-M part of the ion). The high polarizability of the axial π-bond system should thus render it suitable for Raman and resonance Raman studies. One such species is the $Ru_2OCl_{10}^{4-}$ ion, which is known from early x-ray crystallographic work[5] to be linear and which has already been the subject of some rather restricted infrared and Raman spectral studies.[6,7] No attempt has yet been made to assign the visible absorption spectrum of the ion, in which two strong bands (presumably electric dipole allowed) occur at ca. 20 000 and ca. 23 000 cm^{-1} (the exact frequencies depend slightly on the cation). Overtone progressions have only been observed,[1] and are only expected to be observed,[8] under conditions in which the electronic transition with which the exciting frequency is brought into coincidence is electric dipole allowed. In view of the close relationship between resonance Raman and electronic spectroscopy it seemed possible that if a resonance Raman spectrum could be excited from the $Ru_2OCl_{10}^{4-}$ ion, and the progression forming mode identified, the assignment of the absorption bands in the visible region of the spectrum of the ion might be deduced. Accordingly the infrared, Raman, and electronic spectra of the ion have been investigated, as well as the resonance Raman spectra with a variety of exciting lines whose frequencies are in the vicinity of 20 000 cm^{-1}. The ion is, under these conditions, found to display the resonance Raman effect, most spectacularly by the potassium salt; the characteristic feature of the spectra is the observation of (at most) nine progressions, in each of which the ν_1(Ru-O-Ru) a_{1g} fundamental is the progression forming mode. These observations have not only permitted the determination of the various spectroscopic constants ω_1, x_{11}, and x_{1n}, but also permitted the resonant electronic transition to be assigned.

Experimental Section

Preparation of Samples. The most widely used method for the synthesis of the $Ru_2OCl_{10}^{4-}$ ion is based on that of Woodhead and Fletcher,[9] who employed ruthenium(VIII) oxide as starting material. It is also possible to prepare different salts of the $Ru_2OCl_{10}^{4-}$ ion from the more readily available commercial ruthenium(III) chloride.

Ruthenium(III) chloride (0.5 g) was suspended in concentrated hydrochloric acid (12 M). The solution was gently heated for a few minutes and any undissolved solid was filtered off. To the warm solution was added a solution of potassium chloride (0.5 g) in concentrated hydrochloric acid. The resulting solution was allowed to cool, and the red-brown microcrystalline product was separated by suction filtration, washed with absolute ethanol (two 10-cm^3 portions), and dried in vacuo, yield 0.45 g (60%). Anal. Calcd for $K_4[Ru_2OCl_{10}]$: Cl, 48.69. Found: Cl, 48.5$_5$.

The rubidium and cesium salts were prepared similarly using the calculated amount of alkali halide. Anal. Calcd for $Rb_4[Ru_2OCl_{10}]$: Cl, 37.67. Found: Cl, 36.7$_5$. Calcd for $Cs_4[Ru_2OCl_{10}]$: Cl, 32.10. Found: Cl, 31.6.

Instrumental Details. Raman spectra were recorded using a Spex 1401 double spectrometer in conjunction with Coherent Radiation Model CR12 Ar^+ and Model 52 Kr^+ ion lasers. The powers of all lines used were in the range 100 mW-2 W. Detection was by means of a cooled RCA C31034 phototube (Grade 1) with linear response; further details of the system are described elsewhere.[2]

Spectra were calibrated by reference to the emission lines of neon, which were superimposed directly onto the spectra while they were recorded. Band areas were determined by the trace, cut-and-weigh procedure and then corrected for the spectral response of the instrument. Relative intensities were measured with respect to the 981-cm^{-1} band of potassium sulfate as internal standard. Samples were rotated at ca. 1400 rpm in order to minimize thermal decomposition of the sample at the beam focus.[1] There was no evidence of irradiation-produced decomposition. The frequencies are accurate to ±0.5 cm^{-1} for sharp bands, ±1 cm^{-1} for broader bands, and ±5 cm^{-1} for the broadest bands (given in parentheses). Raman spectra at liquid nitrogen temperatures were recorded by scanning the laser beam with a rotating glass block across a KCl disk of the compound mounted on a copper finger attached to a Dewar flask. The finger was contained in an evacuated glass envelope.

The diffuse reflectance spectra were recorded by use of a Cary 14 spectrometer.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer down to 200 cm^{-1} and on a FS720 interferometer below 200 cm^{-1}; Nujol mulls were used in each case. The results are accurate to ±2 cm^{-1}.

Results and Discussion

Vibrational Analysis. The vibrational representation of the $Ru_2OCl_{10}^{4-}$ ion, in terms of the D_{4h} point group to which it belongs, is as follows:

$$\Gamma_{vib} = 4a_{1g} + 2b_{1g} + b_{2g} + 4e_g + a_{1u} + 4a_{2u} + b_{1u} + 2b_{2u} + 5e_u$$

Thus the 33 normal modes of vibration of the ion give rise to 11 Raman bands (the g modes) and nine infrared bands (the a_{2u} and e_u modes). The axial fundamentals of the ion are of particular importance in the subsequent discussion, and accordingly the symmetry coordinates which principally contribute to each normal coordinate of a_{1g} and a_{2u} symmetry are sketched in Figure 1. The mode numbering scheme which has been adopted in this paper is also made explicit in Figure 1. The observed infrared and normal (i.e., off-resonance, λ_0 = 647.1 nm) Raman bands of the ion, as they occur in the potassium, rubidium, and cesium salts, are given in Table I, together with (as far as is possible) the band assignments. The rule of mutual exclusion is seen to apply, consistent with the centrosymmetric nature of the complex ion. Three of the a_{1g} fundamentals have been identified by measurements of the band depolarization ratios (see later). These are ν_1, $\nu(Ru-O-Ru)_{sym}$ at 256.2-249.5 cm^{-1} (the strongest Raman band); ν_2, $\nu(Ru-Cl_{ax})_{sym}$ at 293.1-286.4 cm^{-1}; ν_3, $\nu(Ru-Cl_{eq})_{sym}$ at 357.2-345.7 cm^{-1}.

Table I. Infrared and Raman Bands Observed in the Spectra of Different Salts of the $Ru_2OCl_{10}{}^{4-}$ Ion (cm^{-1})[a]

	$K_4[Ru_2OCl_{10}]$		$Rb_4[Ru_2OCl_{10}]$		$Cs_4[Ru_2OCl_{10}]$	
Assignment	IR	R	IR	R	IR	R
ν_5, $\nu(Ru\text{-}O\text{-}Ru)_{asym}$	887 w		887 w		888 w	
ν_3, $\nu(Ru\text{-}Cl_{eq})_{sym}$[b]		357.2 s		349.8 s		345.7 s
ν_7, $\nu(Ru\text{-}Cl_{eq})_{asym}$	327 vs,br		322 vs,br		324 vs,br	
ν_9, $\nu(Ru\text{-}Cl_{eq})$		312.6 w		320.8 vw		323.3 w
	298 w		302 w?		312 s	
ν_2, $\nu(Ru\text{-}Cl_{ax})_{sym}$[b]		293.1 s		286.4 s		288.8 s
ν_6, $\nu(Ru\text{-}Cl_{ax})_{asym}$	278 s		278 s		275 s	
ν_1, $\nu(Ru\text{-}O\text{-}Ru)_{sym}$		256.2 vs	253 w	254.0 vs		249.5 vs
ν_4, $\delta(ClRuCl)_{sym}$		209.8 w		218.3 w		210.2 vw
		191.2 w		192.5 w		
	186 m				183 m	
	178 m	178.2 w				178.0 m
		145.0 m		145.0 m		148.2 w
	123 w					
	106 m		106 w			
	76 wm		84 m		74 m	
	67 w					

[a] Raman bands observed with 514.5 and/or 647.1-nm excitation. Qualitative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. [b] Cl_{ax} and Cl_{eq} are axial and equatorial, respectively.

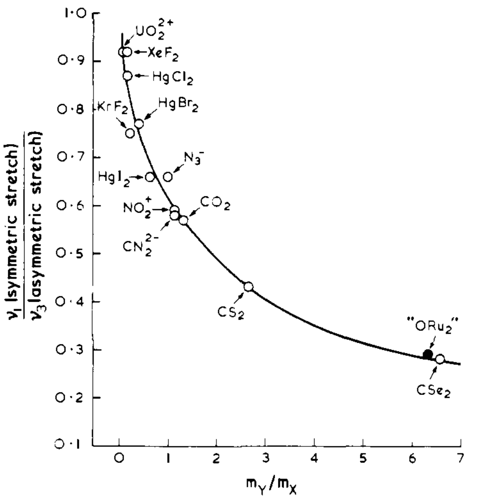

Figure 2. Plot of ν_1 (symmetric stretch)/ν_3 (asymmetric stretch) for linear XY_2 type molecules vs. the mass ratio m_Y/m_X (XY_2 nomenclature, ref 11).

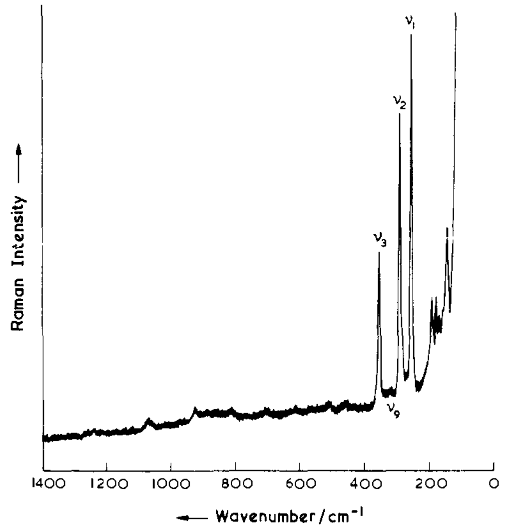

Figure 3. Raman spectrum of the complex $K_4[Ru_2OCl_{10}]$ obtained with the 647.1-nm exciting line of the Kr^+ ion laser. Slit widths 200/300/200 μm (spectral slit width 3 cm^{-1}).

The assignment $\nu_3 > \nu_2$ is consistent with the fact that, from the newly determined x-ray structure of the $Os_2OCl_{10}{}^{4-}$ ion, $r_{OsCl_{eq}} < r_{OsCl_{ax}}$ (2.370 vs. 2.433 Å).[10]

The fourth a_{1g} fundamental is the symmetric bend ν_4, which, owing to its similarity in form to that of the t_{1u} bending mode of an octahedral ion, would be expected near 200 cm^{-1} (cf. for the $RuCl_6{}^{2-}$ ion this band occurs in the infrared spectrum at ca. 185 cm^{-1}). There is a very large difference between the symmetric (ν_1) and antisymmetric (ν_5) Ru-O-Ru stretching frequencies (256.2 and 887 cm^{-1}, respectively, for the potassium salt). Although this may seem surprising at first sight, it is fully consistent with all known data on linear XY_2 species.[11] Thus the ratios of the symmetric to the antisymmetric stretching frequencies of all such molecules, including "Ru_2O", when plotted against the mass ratios m_Y/m_X, give rise to a single smoothly varying curve (Figure 2).

Resonance Raman Spectra. (a) Room Temperature. The Raman spectrum of each salt of the $Ru_2OCl_{10}{}^{4-}$ ion is found to display a marked dependence on the frequency of the exciting line.[12] With the Kr^+ ion 647.1-nm exciting line, as indicated above, a normal Raman spectrum is observed (Figure 3). However, with the Kr^+ ion 530.9, 520.8, and 482.5-nm lines and the Ar^+ ion 514.5, 501.7, 496.5, 488.0, 476.5, 472.7, 465.8, and 457.9-nm lines, all of which are fairly close to the maximum of the 20 000-cm^{-1} electronic band of the complex ion (Figure 4), a resonance Raman spectrum is obtained. This spectrum is characterized by a large increase in the intensity of the $\nu_1(Ru\text{-}O\text{-}Ru)_{sym}$ band and the appearance of an overtone progression involving ν_1 which reaches $7\nu_1$, $5\nu_1$, and $4\nu_1$ for the potassium, rubidium, and cesium salts, respectively. The overtone bands display the usual features characteristic of the resonance Raman effect,[1,8] viz. continuous increase in half bandwidth and continuous decrease in intensity with increase in the vibrational quantum number, v_1.

In addition to the $v_1\nu_1$ progression (progression (i)), further progressions are also observed in the resonance Raman spectrum of each salt; the progression forming mode is again ν_1 in each case. The additional progressions are as follows: (ii) $v_1\nu_1 + \nu_2$, which reaches at most $v_1 = 3$, 1, and 1 for the K^+, Rb^+, and Cs^+ salts, respectively; (iii) $v_1\nu_1 + \nu_3$, which reaches at most $v_1 = 4$, 3, and 2 for the K^+, Rb^+, and Cs^+ salts, respectively; (iv) $v_1\nu_1 + \nu_4$, which was observed only for the potassium and rubidium salts, and reached $v_1 = 4$ and 1, respectively; (v)

Table II. Wave Numbers and Half Bandwidths of the Members of the $v_1\nu_1$ and other Progressions Observed in the Resonance Raman Spectrum of the Complex $K_4[Ru_2OCl_{10}]$ with 514.5 or 488.0-nm Excitation

	Max, cm^{-1}		$\Delta\nu_{1/2}$, cm^{-1}			Max, cm^{-1}		$\Delta\nu_{1/2}$, cm^{-1}	
Band	RT[a]	LT[b]	RT[a]	LT[b]	Band	RT[a]	LT[b]	RT[a]	LT[b]
ν_1	256.2	258.3	8	8	ν_4	209.8	205.0	8	≈20?
$2\nu_1$	512.2	518.7	14	11	$\nu_1 + \nu_4$	464.5	467.4	15	≈20?
$3\nu_1$	768.0	778.4	22	14	$2\nu_1 + \nu_4$	719	728.2	25	14
$4\nu_1$	1023	1037	31	19	$3\nu_1 + \nu_4$	973	988	36	24
$5\nu_1$	1278	1298	42	21	$4\nu_1 + \nu_4$	1227	1242	50	28
$6\nu_1$	1533	1558	55	27	$5\nu_1 + \nu_4$		(1500)		
$7\nu_1$	1787	1815	70	26					
$8\nu_1$		2075		29	$2\nu_5$		1779		12
$9\nu_1$		2335		30	$\nu_1 + 2\nu_5$		2036		16
$10\nu_1$		2595							
$11\nu_1$		2846			ν_9	312.6	322.1	10	
$12\nu_1$		(3120)			$\nu_1 + \nu_9$	567		18	
ν_2	293.1	295.2	10	9	ν_{10}	927.6	935	19	10
$\nu_1 + \nu_2$	547.4	553.9	16	15	$\nu_1 + \nu_{10}$	1184	1194	25	12
$2\nu_1 + \nu_2$	801.4	814.3	30	18	$2\nu_1 + \nu_{10}$	1439	1453	32	14
$3\nu_1 + \nu_2$	1055	1072	40		$3\nu_1 + \nu_{10}$	(1695)	1712	42	18
$4\nu_1 + \nu_2$		1333			$4\nu_1 + \nu_{10}$		1977		21
$5\nu_1 + \nu_2$		(1594)			$5\nu_1 + \nu_{10}$		2227		28
					$6\nu_1 + \nu_{10}$		2483		28
					$7\nu_1 + \nu_{10}$		(2740)		
ν_3	357.2	361.1	10	9					
$\nu_1 + \nu_3$	612.5	623.1	18	12					
$2\nu_1 + \nu_3$	867.8	882	26	15	$2\nu_{10}$		1865		13
$3\nu_1 + \nu_3$	1122	1142	37	21	$\nu_1 + 2\nu_{10}$		2117		16
$4\nu_1 + \nu_3$	1377	1400	50	27	$2\nu_1 + 2\nu_{10}$		2374		18
$5\nu_1 + \nu_3$		1659		26	$3\nu_1 + 2\nu_{10}$		2635		21
$6\nu_1 + \nu_3$		1921			$4\nu_1 + 2\nu_{10}$		(2896)		
$7\nu_1 + \nu_3$		2180							
$8\nu_1 + \nu_3$		(2441)			ν_{11}	159.0	152.0	9	
					$\nu_1 + \nu_{11}$	416.0	410.0	11	
					$2\nu_1 + \nu_{11}$	672.1	666	15	

[a] RT = room temperature (≈295 K). [b] LT = liquid nitrogen temperature (≈100 K).

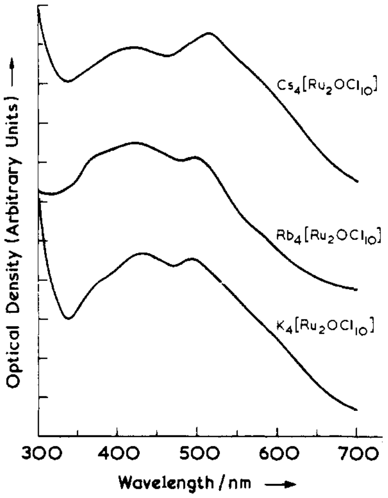

Figure 4. Diffuse reflectance spectra of the complexes $K_4[Ru_2OCl_{10}]$, $Rb_4[Ru_2OCl_{10}]$, and $Cs_4[Ru_2OCl_{10}]$.

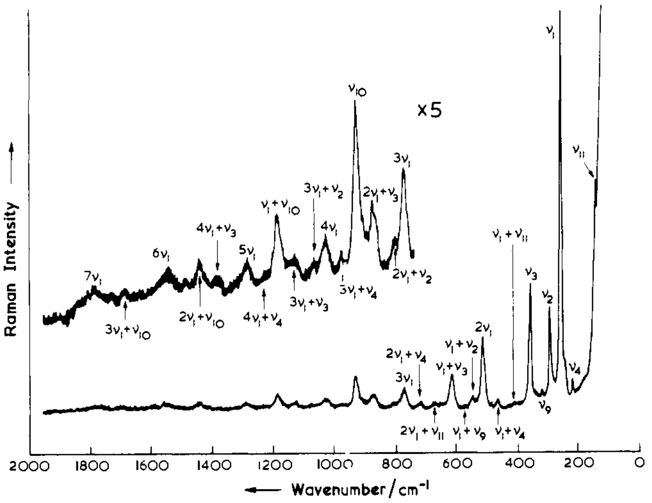

Figure 5. Resonance Raman spectrum of the complex $K_4[Ru_2OCl_{10}]$ obtained with the 514.5-nm exciting line of the Ar^+ ion laser. Slit widths 100/200/100 μm (spectral slit width 2 cm^{-1}).

$\nu_1 + \nu_9$, which was observed only for the potassium salt; ν_9 is the 312.6-cm^{-1} Raman-active fundamental (belonging to the irreducible representations b_{1g} or e_g); (vi) $v_1\nu_1 + \nu_{10}$, which reaches at most $v_1 = 3, 2$, and 2 for the K^+, Rb^+, and Cs^+ salts, respectively; the nature of the mode responsible for ν_{10} is not known, but it is unlikely that it arises from an impurity[12] in view of the progression with ν_1 and the fact that its excitation profile peaks at the 20 000-cm^{-1} absorption band; (vii) $v_1\nu_1 + \nu_{11}$, which reaches at most $v_1 = 2$, 1, and 1 for the K^+, Rb^+, and Cs^+ salts, respectively. The wave numbers and half bandwidths of the members of each progression are given in Table II for the potassium salt and Table III for the rubidium and cesium salts.

The main progression, $v_1\nu_1$, and progressions $v_1\nu_1 + \nu_2$, $v_1\nu_1 + \nu_3$ and $v_1\nu_1 + \nu_4$, all involve solely totally symmetric fundamentals, and all seven progressions apparently involve ν_1 as the progression forming mode. This is accordingly the most richly structured resonance Raman spectrum yet observed (Figure 5). The dominance of the a_{1g} modes indicates that the

Table III. Wave Numbers and Half Bandwidths for the Members of the $v_1\nu_1$ and Other Progressions Observed in the Resonance Raman Spectra of $Rb_4[Ru_2OCl_{10}]$ and $Cs_4[Ru_2OCl_{10}]$ with 514.5-nm Excitation

	$Rb_4[Ru_2OCl_{10}]$				$Cs_4[Ru_2OCl_{10}]$			
	Max, cm^{-1}		$\Delta\nu_{1/2}$, cm^{-1}		Max, cm^{-1}		$\Delta\nu_{1/2}$, cm^{-1}	
Band	RT	LT	RT	LT	RT	LT	RT	LT
ν_1	254.0	254.8	9	8	249.5	251.0	10	10
$2\nu_1$	507.0	511.3	14	13	498.6	502.5	15	16
$3\nu_1$	758.6	766.9	22	18	747.4	753.5	22	24
$4\nu_1$	1011	1021	32	22	996	1006	36	30
$5\nu_1$	1262	1284	48	28		1261		48
$6\nu_1$		1538		32		1529		58
$7\nu_1$		1792		32		(1798)		
$8\nu_1$		2052		35				
ν_2	286.4	292.1	10	10	288.8	290.8	11	11
$\nu_1 + \nu_2$	539.5	547.8	15	17	537	541.6	16	15
$2\nu_1 + \nu_2$		802.8			785	793	22	
$3\nu_1 + \nu_2$		1055						
ν_3	349.8	356.1	9	9	345.7	351.0	9	13
$\nu_1 + \nu_3$	603.6	613.4	17	16	594.3	603.4	16	19
$2\nu_1 + \nu_3$	856.1	869	24	18	842.2	854	22	25
$3\nu_1 + \nu_3$	1109	1122	36	25		1106		28
$4\nu_1 + \nu_3$		1381		24		1357		25
$5\nu_1 + \nu_3$		1637				1611		
$6\nu_1 + \nu_3$		1891				1854		
ν_4	218.3		11					
$\nu_1 + \nu_4$	471.5	467.1	16			466.3		
$2\nu_1 + \nu_4$		719.8				712.6		
$3\nu_1 + \nu_4$		972				960		
$4\nu_1 + \nu_4$		1223				1214		
$5\nu_1 + \nu_4$		1479						
ν_{10}	926.6	923	18	12	924.4	933	19	18
$\nu_1 + \nu_{10}$	1180	1188	24	13	1172.4	1183	24	21
$2\nu_1 + \nu_{10}$	(1433)	1442	26	20	1420	1437	34	32
$3\nu_1 + \nu_{10}$		1700		28		1689		33
$4\nu_1 + \nu_{10}$		1955		33				
$\nu_2 + \nu_3$		652.9				642.3		
$\nu_1 + \nu_2 + \nu_3$		902				891		
$2\nu_1 + \nu_2 + \nu_3$						1140		
ν_{11}		145.6				145.6		
$\nu_1 + \nu_{11}$		403.7				394.3		

enhancement is, in Albrecht's nomenclature,[13] primarily of the *A* term type, i.e., of the type in which the nuclear coordinate dependence of the energy of the resonant electronic state is responsible for the resonance enhancement.

A single combination band only of the sort $v_1\nu_1 + \nu_9$ has been observed; the shortness of this progression is undoubtedly because ν_9 is very weak and not totally symmetric; cf. the situation of the $AuBr_4^-$ ion,[14,15] where short progressions in the a_{1g} fundamental have been observed based on one quantum of a nontotally symmetric, but nevertheless Raman-active vibration.

(b) Liquid Nitrogen Temperatures. We have also recorded the resonance Raman spectra of the three salts at ≈100 K. The spectra obtained with 514.5 or 488.0 nm exhibited considerably more structure than those recorded at room temperature. In particular for the K^+ salt (Figure 6) nearly all the progressions showed further members; in addition, short progressions were observed based on $2\nu_5$ and on $2\nu_{10}$, in both of which ν_1 again acts as the progression forming mode. For the Rb^+ and Cs^+ salts short progressions were also observed of the type $v_1\nu_1 + \nu_2 + \nu_3$.

In general all the bands are narrower at 100 K than at room temperature, partly because the contributions of hot bands has been decreased. Most bands occur at very slightly higher frequencies in the low temperature (KCl disk) spectrum of the complex as compared with the room temperature (pure solid) one. This is a consequence of compressing the solid into a KCl disk and not of the temperature change. Both wave numbers and half bandwidths for the 100 K spectra are given in Tables II (K^+) and III (Rb^+ and Cs^+).

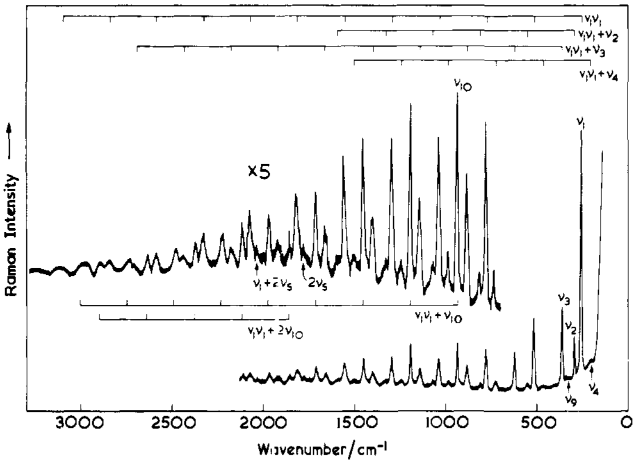

Figure 6. Resonance Raman spectrum (100 K) of the complex $K_4[Ru_2OCl_{10}]$ obtained with the 488.0-nm exciting line of the Ar^+ ion laser (spectral slit width 4 cm^{-1}).

We have considered the possibility of calculating the change in the Ru-O bond length on excitation of the ion from the ground to the excited state from the observed overtone progressions.[16,17] However neither the state of the theory nor the

Table IV. Wave Numbers, Half Bandwidths, and Depolarization Ratios of Bands Observed in the Resonance Raman Spectrum of an 8 M HCl Solution of $K_4[Ru_2OCl_{10}]$ with 514.5-nm Excitation[a]

Band	Max, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ρ 514.5 nm	ρ 647.1 nm
ν_1	251.1 ± 0.5	14	0.34	0.73
ν_2	292.5 ± 0.5	16	0.33	0.71
ν_3	350.7 ± 0.5	14	0.36	0.65
ν_{10}	938.0 ± 0.5	23	0.33	
$2\nu_1$	501 ± 1	21	0.30	
$2\nu_{10}$	1874 ± 1	46	0.31	
$\nu_1 + \nu_3$	600 ± 1	25	0.30	
$\nu_1 + \nu_{10}$	1188 ± 1	40	0.28	

[a] The $K_4[Ru_2OCl_{10}]$ was 6.7×10^{-3} mol dm^{-3}.

available data seem to be sufficient at present to make a reliable estimate of this change.

The Raman spectrum of the $Ru_2OCl_{10}{}^{4-}$ ion has also been observed in 8 M hydrochloric acid solution with a range of different exciting lines. With 514.5-nm excitation a resonance Raman spectrum is observed, although this is less richly structured than for the ion in the solid state; this is partly because the absorption bands of the ion are shifted in solution to higher wave numbers (21 050 and 26 700 cm^{-1}, ϵ 4200 and 8800 dm^3 mol^{-1} cm^{-1}, respectively)[18] than for the solid material, leading to less effective resonance with this exciting line, and partly because of solute-solvent interactions which lead to larger half bandwidths in solution. The wave numbers, half bandwidths, and depolarization ratios of each observed band in solution are listed in Table IV. None of the bands is strongly polarized off resonance, but with 514.5-nm excitation several have depolarization ratios close to the value one-third, which is characteristic of that expected for a_{1g} modes of D_{4h} molecules in the circumstances in which the resonant electronic transition is axially polarized ($\alpha_{zz} \neq 0$, all other α_{ii} and $\alpha_{ij} = 0$).[19] This point will be returned to in the later discussion.

(c) Harmonic Frequencies and Anharmonicity Constants. The observation of overtone progressions in which the progression forming mode is $\nu_1(a_{1g})$ makes it possible to determine the harmonic frequency ω_1, the anharmonicity constant x_{11}, and certain cross terms x_{1n}. The observed wavenumber $\nu(v_1)$ of any overtone of a nondegenerate anharmonic oscillator is given by the equation[1,20]

$$\nu(v_1) = G(v_1) - G(0)$$
$$= \omega_1 v_1 + x_{11}(v_1{}^2 + v_1) + \text{higher terms}$$

where $G(v_1)$ is the term value of the v_1th vibrational level. A plot of $\nu(v_1)/v_1$ vs. v_1 therefore has (ignoring the higher terms) an intercept $\omega_1 + x_{11}$ and a slope of x_{11}. Least-squares analyses of the room temperature $v_1\nu_1$ data in Tables II-IV lead, therefore, to the ω_1 and x_{11} values[21] given in Table V. Corresponding considerations[1] of the other progressions lead to the conclusion that plots of $\{[\nu_n + \nu(v_1)] - \nu_n\}/v_1$ vs. v_1 should likewise have slopes of x_{11}, but that they should differ in their intercepts from that obtained for the $\nu(v_1)/v_1$ vs. v_1 plot by the cross term x_{1n} in each case. Similar least-squares analyses of the data in Tables II-IV for progressions (ii) to (vi) lead to x_{11} and x_{1n} values which are also included in Table V. The ω_1 values decrease slightly with increasing size of the cation, viz. 256.5 (K^+), 254.7 (Rb^+), and 249.9 (Cs^+) cm^{-1}; this may be due in part to the smaller lattice forces present in each complex with the larger cations.[22]

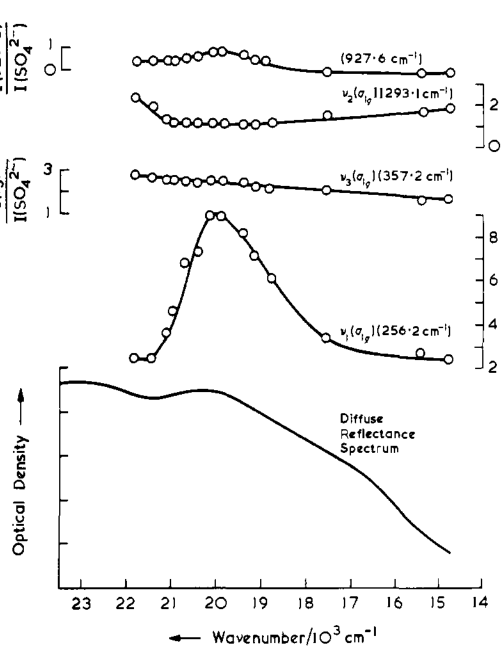

Figure 7. Excitation profiles of the ν_1, ν_2, ν_3, and 927.6-cm^{-1} bands of the complex $K_4[Ru_2OCl_{10}]$ together with its diffuse reflectance spectrum.

The anharmonicity constant x_{11} is very small in every case, and this appears to be a common feature of fundamentals whose bands display the resonance Raman effect.[1,23-25]

Excitation Profiles. The excitation profiles of four bands, viz. ν_1, ν_2, ν_3, and ν_{10}, of the complex $K_4[Ru_2OCl_{10}]$ in the solid state have been determined with reference to the $\nu_1(a_1)$ band of potassium sulfate as internal standard; the results are given in Table VI. The excitation profiles are plotted in Figure 7 together with the diffuse reflectance spectrum of the complex. The excitation profile of ν_1 maximizes at ca. 20 000 cm^{-1}, clearly demonstrating[8,13] that the electronic band of the ion which reaches a maximum at the same wave number must, like ν_1, be intimately associated with the ruthenium-oxygen rather than the ruthenium-chlorine bonds; i.e., the resonant electronic transition must be internal to the Ru-O-Ru π system.

Of the other excitation profiles plotted, that of ν_3 shows virtually no frequency dependence, consistent with its assignment as an equatorial Ru-Cl stretching mode, whereas that of ν_2 shows a marked increase on approaching 23 500

Table V. Harmonic Frequencies and Anharmonicity Constants for Different Salts of the $Ru_2OCl_{10}{}^{4-}$ Ion (cm^{-1}) at Room Temperature[a]

Progression	$K_4[Ru_2OCl_{10}]$ ω_1	$K_4[Ru_2OCl_{10}]$ x_{11}	$Rb_4[Ru_2OCl_{10}]$ ω_1	$Rb_4[Ru_2OCl_{10}]$ x_{11}	$Cs_4[Ru_2OCl_{10}]$ ω_1	$Cs_4[Ru_2OCl_{10}]$ x_{11}
$v_1\nu_1$	256.5 ± 0.5	−0.16 ± 0.03	254.7 ± 0.6	−0.40 ± 0.06	249.9 ± 0.6	−0.17 ± 0.04
$v_1\nu_1 + \nu_2$	256.4 ± 0.6	−0.16 ± 0.03				
$v_1\nu_1 + \nu_3$	255.7 ± 0.5	−0.15 ± 0.03	254.5 ± 0.6	−0.40 ± 0.06		
$v_1\nu_1 + \nu_4$	255.0 ± 0.6	−0.14 ± 0.03				
$v_1\nu_1 + \nu_{10}$	256.4 ± 0.8	−0.15 ± 0.04	254.7 ± 0.8	−0.34 ± 0.06	249.7 ± 0.8	−0.26 ± 0.06

[a] The values listed for "ω_1" for the $v_1\nu_1 + \nu_n$ progressions are strictly values for $\omega_1 - x_{1n}$ in each case. Thus for the potassium salt $x_{12} = 0.1$, $x_{13} = 0.8$, $x_{14} = 1.5$, and $x_{1,10} = 0.1$ cm^{-1}; for the rubidium salt, $x_{13} = 0.2$ and $x_{1,10} = 0.0$ cm^{-1}; for the cesium salt $x_{1,10} = 0.2$ cm^{-1}. In each case the values, being small differences between large quantities, are subject to substantial but not readily determinable errors.

Table VI. Intensities[a] of the ν_1, ν_2, ν_3, and ν_{10} Bands of the Complex $K_4[Ru_2OCl_{10}]$ Relative to the 981-cm^{-1} Band of the Sulfate Ion as Internal Standard for Various Exciting Wavelengths

Exciting wavelength, nm	$I(\nu_1)/I(SO_4^{2-})$	$I(\nu_2)/I(SO_4^{2-})$	$I(\nu_3)/I(SO_4^{2-})$	$I(\nu_{10})/I(SO_4^{2-})$
457.9	2.49	2.29	2.78	0.43
465.8	2.41	1.90	2.57	0.49
472.7	3.62	1.29	2.55	0.49
476.5	4.58	1.08	2.49	0.44
482.5	6.79	1.09	2.42	0.58
488.0	7.24	1.16	2.37	0.56
496.5	8.94	1.15	2.62	0.81
501.7	8.90	1.10	2.58	0.86
514.5	8.17	1.08	2.57	0.74
520.8	7.15	1.09	2.43	0.56
530.9	6.09	1.19	2.20	0.54
568.2	3.37	1.55	1.86	0
647.1	2.75	1.72	1.64	0
676.4	2.34	1.94	1.77	0

[a] Corrected for the spectral response of the instrument.

cm^{-1}, the wave number of the next higher electronic transition of the ion. Unfortunately, we are not in a position to scan the profile as far as this maximum, owing to lack of suitable exciting lines. However, the results are consistent with the assignment of the 23 500-cm^{-1} band to a Ru(π) $\leftarrow$ Cl(π) transition of the axial chlorine atoms; cf. the corresponding transition ($t_{2g} \leftarrow \pi$) of the ruthenium(IV) ion $RuCl_6^{2-}$ at ca. 20 000 cm^{-1} ($\epsilon \approx 4400$ dm^3 mol^{-1} cm^{-1}, $f \approx 0.036$).[26]

Molecular Orbital Scheme and Detailed Assignment of the Resonant Electronic Transition. A molecular orbital scheme for the $Ru_2OCl_{10}^{4-}$ ion was proposed by Dunitz and Orgel[27] to account for the facts that (a) the ion is diamagnetic, (b) the Ru-O-Ru bonds are linear, (c) the Ru-O bond lengths (1.80 Å) are less than the sum of the single bond radii (1.98 Å), and (d) the Ru-Cl bond lengths are normal (2.34 Å). Each ruthenium(IV) ion is in a field of C_{4v} symmetry. After consideration of the six σ-bond orbitals on each ruthenium(IV) ion, only the d_{xz}, d_{yz}, and d_{xy} orbitals are nonbonding; these transform in the C_{4v} point group as e and b_2, respectively. With two ruthenium(IV) ions per complex ion, molecular orbitals can then be formed which transform as e_g, e_u, b_{2g}, and b_{1u} in the D_{4h} point group of the complex ion, and, since the metal ions are relatively far apart from each other, these orbitals would be expected to be nearly degenerate, pair by pair. However, interaction of the e_u orbitals on the ruthenium ions with the π orbitals on the oxygen atom (which also transform as e_u) leads to the situation in which one of the e_u molecular orbitals becomes strongly bonding and the other strongly antibonding. With 12 electrons in π orbitals (four from each ruthenium(IV) ion, and four from the oxygen atom), the electronic configuration of the complex ion is therefore expected to be

$$(e_u^b)^4[(e_g)^4(b_{2g})^2(b_{1u})^2](e_u^*)^0$$

The lowest allowed electronic transitions of this ion (Figure 8) therefore involve excitation of one of the nonbonding electrons to the e_u^* orbital, viz. (i) $e_u^* \leftarrow b_{1u}$ ($e_u \times b_{1u} = e_g$), (ii) $e_u^* \leftarrow b_{2g}$ ($e_u \times b_{2g} = e_u$), and (iii) $e_u^* \leftarrow e_g$ ($e_u \times e_g = a_{1u} + a_{2u} + b_{1u} + b_{2u}$). The first of these transitions is electric dipole forbidden, the second is allowed in x,y polarization, and the third is allowed (via the a_{2u} component) in z (i.e., axial) polarization. From the axial nature of the progression forming mode (ν_1) in the resonance Raman spectrum, and from the value of the depolarization ratio of the ν_1 band at resonance (⅓), it follows therefore that the resonant electronic transition must be axial. Hence the only possibility for the resonant electronic transition at 20 000 cm^{-1} is $^1A_{2u} \leftarrow {}^1A_{1g}$

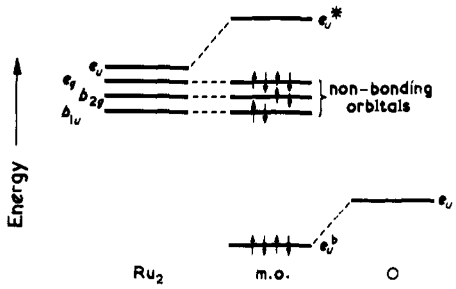

Figure 8. Molecular orbital scheme for the π-bond system of the $Ru_2OCl_{10}^{4-}$ ion.

$$(e_u^b)^4[(e_g)^3(b_{2g})^2(b_{1u})^2](e_u^*)^1 \leftarrow (e_u^b)^4[(e_g)^4(b_{2g})^2(b_{1u})^2](e_u^*)^0$$

This is a metal-localized transition within the Ru-O-Ru π system.

Conclusion

The resonance Raman effects observed when the $Ru_2OCl_{10}^{4-}$ ion is irradiated within the contour of the 20 000-cm^{-1} band are spectacular, nine progressions in the $\nu_1(\text{Ru-O-Ru})_{sym}$ stretching mode being observed for the potassium salt. These observations permit the determination of a number of spectroscopic constants of the ion. The excitation profiles of the a_{1g} Raman bands indicate that the 23 500-cm^{-1} electronic band of the ion is a ruthenium $\leftarrow$ chlorine transition (of the $t_{2g} \leftarrow \pi$ sort), whereas the 20 000-cm^{-1} transition is the $^1A_{2u} \leftarrow {}^1A_{1g}$ transition ($e_u^* \leftarrow e_g$) of the Ru-O-Ru π-bond system. Resonance Raman spectroscopy would thus seem to be a valuable new tool with which to assign charge transfer transitions.

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Influence of Copper(II) on Proton Nuclear Relaxation Rates of Poly-L-histidine

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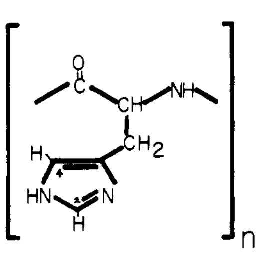
Abstract: Proton NMR chemical shifts and nuclear relaxation rates have been measured for the C_2 and C_4 protons of poly-L-histidine (PLH) as a function of pH. The NMR titration curves of chemical shift indicate a pK_a value of 6.1 for the imidazole groups. The C_4 proton is relaxed more efficiently than the C_2 proton at all values of pH due to its proximity to the C_β protons. The relaxation rates are not affected appreciably by changes in pH. In the presence of Cu(II) the relaxation rates show a pronounced maximum at ca. pH 3.5. Above this pH value, temperature dependence studies indicate that slow exchange is occurring between Cu(II) and PLH. On the basis of this and other evidence, we conclude that the maximum in the relaxation rates appears to represent the pH of most rapid exchange of Cu(II) ions between the ligand sites.



I

Poly-L-histidine (PLH) (I) forms complexes with Cu(II),[2a] the nature of which have been examined by a variety of physical techniques.[2b] Maximum binding occurs at pH 5 and the binding constant at this pH is 10^{19} M^{-1}.[2b] It has been suggested that three of the four ligands which bind Cu(II) at this pH are imidazole nitrogens while the fourth ligand may be a peptide nitrogen.[2b] Part of the interest in the Cu(II)-PLH complex arises from the observation that it is effective in catalyzing the oxidation of ascorbic acid, *p*-hydroquinone, and several other organic substrates.[3,4]

In the present study we have measured both transverse ($1/T_2$) and longitudinal ($1/T_1$) proton NMR relaxation rates to study the nature of the Cu(II)-PLH complex as a function of pH. Transverse relaxation rates have previously been determined from resonance line widths by several workers to investigate Cu(II)-amino acid and Cu(II)-peptide interactions.[5,6] The danger of measuring only transverse relaxations rates, to determine metal-ligand distances, has been discussed previously.[7-11]

At low pH, PLH is an extended chain or at least possesses segments of extended chains; however, at pH values above the imidazolium pK_a value the polymer undergoes a conformational transition to a more ordered state.[12-16] PLH is quite insoluble in aqueous solutions when in this relatively ordered conformation (pH 6.3 to 13). Potentiometric titration data[2a] indicate a pK_a of 6.15 for the imidazolium groups of the polymer, essentially the same value observed for histidine.[17,18] In this study we have also used proton chemical shifts to estimate the pK_a of the imidazolium groups in PLH.

Experimental Section

PLH was obtained from Schwartz-Mann (degree of polymerization, dp, = 45), lot U3821, and from Miles-Yeda, mol wt $\simeq$ 11 100 (dp = 81), lot HS36. A stock solution of 0.075 M copper sulfate in D_2O was prepared and analyzed for Cu(II) by atomic absorption spectroscopy.

All PLH solutions were 10 mg/ml (7.3×10^{-2} M in histidine residues) in 0.1 M NaCl-D_2O. The amount of the standard copper sulfate solution added gave ratios of imidazole groups to Cu(II) ion of 100:1 and 50:1, except that for the variable temperature work a ratio of 775:1 was used.

Measurements of pH were made on a Radiometer pH meter with an Ingold long thin combination electrode inserted directly into the NMR tube. Adjustments of pH were made directly in the NMR tubes with standard solutions of NaOD (0.5 M) and DCl (1 M) in hand-held burets. Values reported are direct pH meter readings in D_2O.

NMR spectra were recorded at 220 MHz on a Varian Associates HR220 spectrometer equipped with an accessory for pulse Fourier transform spectroscopy. Measurements were carried out at 20 ± 1°, except where temperature was adjusted to higher values with a Varian Variable Temperature Controller, and the temperature was determined with a standard ethylene glycol sample.

Transverse relaxation times (T_2) were determined by measurement of line width at half-height ($W_{1/2}$) with an expanded recorder scale, using the relationship $T_2 = (1/\pi W_{1/2})$. Longitudinal relaxation times (T_1) were determined by the inversion recovery method,[19] with delay times always $>5 \times T_1$. A 180° pulse was 90 μs and a 90° pulse was 45 μs.

Theoretical Section

Before presenting and discussing our experimental results it will be useful to briefly present the theory of NMR relaxation