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Single-crystal Vibrational Spectra of Hexaquonickelhexachlorostannate

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A complete assignment is established for $[Ni(H_2O)_6][SnCl_6]$ *from single-crystal Raman and i.r.-reflectance evidence.*

Introduction

The vibrational spectra of hydrated materials are of considerable spectroscopic interest for the variety of degrees of orientational disorder they may display, and for the accompanying problems in lattice dynamics. Of more direct chemical concern is the need to establish reliably a fully-proven assignment for a hexa-aquo species $[M(H_2O)_6]^{n+}$ and, surprisingly, this has not yet been done. The crystal form of the title compound is ideal for our purpose: the high symmetry more than compensates for the high degree of aquation. In an earlier report[1] of the powder i.r. spectra of this complex we indicated an outline assignment for the metal–ligand region but it was not then possible to interpret the lower-frequency features.

Experimental

Crystals of the title compound were grown by slow evaporation of aqueous solutions of $NiCl_2 \cdot 6H_2O$ and $SnCl_4 \cdot 4H_2O$. These usually formed as large, green, deliquescent rhombohedra. However, if a few drops of hydrochloric acid are added to the solution truncated rhombohedra are obtained (Figure 1) which exhibit faces parallel to the *c*-axis; these were used for the spectroscopic measurements. $[Ni(D_2O)_6][SnCl_6]$ was prepared by repeated crystallisation of the protiated complex from heavy water, but none of the crystals were of high enough optical quality for work in polarised light. Faces were ground and polished in a dry-box.

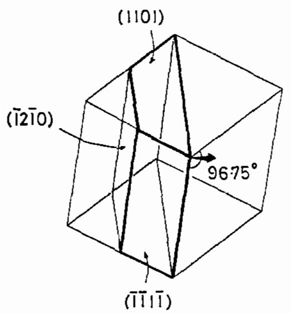

Figure 1. Morphology of $[Ni(H_2O)_6][SnCl_6]$ crystals.

Raman spectra were obtained using a Coderg T800 triple monochromator instrument with 514.5 nm excitation from a CRL model 52A laser delivering 500mW at the sample. For the single-crystal work the spectral slit width was 3 cm^{-1} for most spectra. The crystals were coated with paraffin and mounted in an evacuated 'cryocirc' cold cell for runs both at ambient and liquid nitrogen temperatures.

I.r. reflectance spectra were obtained at near-normal incidence using a Beckman–RIIC FS–720 fourier spectrometer with an RS7F reflectance module and a wire-grid polariser.

Selection Rules

The title compound crystallises in the trigonal system[2] with the symmetry of space group $R\bar{3} \equiv C_{3i}^2$ ($\equiv S_6^2$) and z = 1. Since both complex ions are on sites of symmetry S_6 and the cell is unimolecular, there can be no correlation coupling, and the only mechanism causing the spectrum of each ion to differ from that of its solutions is the site field. This crystal is therefore an excellent case for testing the strength of the site field. Table I shows the factor group analysis for the unit cell, and the correlation with O_h symmetry for each complex ion. Each triply degenerate mode in O_h is site split into A and E components, retaining the activities of O_h, but the inactive ν_6, t_{2u} is now allowed in the i.r. spectrum.

Results and Discussion

In this study we are chiefly concerned with the low-frequency part of the spectra, below 400 cm^{-1}. Lock[1,3] has located the i.r.-active external modes of water in $[Ni(H_2O)_6][SnCl_6]$, by deuteriation, at 630 and

TABLE I. Factor Group Analysis for $[Ni(OH_2)_6][SnCl_6]$ (Omitting Hydrogen Atoms).

S_6	N_T	T_A	T	R	N_i	Activities
A_g	6			2	4	x^2+y^2, z^2
E_g	6			2	4	$(x^2-y^2, xy), (xz, yz)$
A_u	8	1	1		6	I.r. (z)
E_u	8	1	1		6	I.r. (x, y)

N_T = total number of modes of primitive cell; T_A = acoustic modes; T = translatory lattice modes; R = rotatory lattice modes; N_i = internal modes of complex ions.

ML_6 ion, O_h	Site, S_6[a]
ν_1 a_{1g} Raman	A_g
ν_2 e_g Raman	E_g
ν_3 t_{1u} I.r.	$A_u + E_u$
ν_4 t_{1u} I.r.	$A_u + E_u$
ν_5 t_{2g} Raman	$A_g + E_g$
ν_6 t_{2u} Inact.	$A_u + E_u$

[a] All g-modes Raman-active, all u-modes i.r.-active.

430 cm^{-1}; in the Raman spectrum they are extremely weak. Raman and i.r. data are collected in Tables II and III and represent modes due to skeletal and lattice vibrations only. The i.r. reflectance spectra were analysed by the Kramers–Krönig method with the results shown in Figure 2. It is not uncommon for this method to yield TO frequencies which are shifted from the theoretical position, *i.e.* at the low-frequency side of each reflectance peak: this is one such case. We also give in Table II the visually estimated frequency values and consider these more reliable than those from Kramers–Krönig analysis.

All six A_g modes predicted by factor group analysis were observed, and four of the six E_g modes. One of the missing E_g modes is of the rotatory type and is either vanishingly weak or is accidentally coincident with the other E_g rotatory mode at 66 cm^{-1}. No sign of it was found down to 10 cm^{-1} shift from the exciting line. The other missing E_g mode corresponds to ν_2, e_g of the (NiO_6) complex. Extinctions between Raman spectra from the various derived tensor com-

TABLE II. Raman Frequencies/cm^{-1} and Intensities (Arbitrary Units) for Single-crystal $[Ni(H_2O)_6][SnCl_6]$ at Liquid Nitrogen Temperature, and for Powdered $[Ni(D_2O)_6][SnCl_6]$ at Liquid Nitrogen Temperature.

Assignment	cm^{-1}	x(zz)y	x(zx)y	x(yz)y	x(yx)y	$[Ni(D_2O)_6][SnCl_6]$
$\nu_R(SnCl_6)$	66 E_g		20	28	10	(60)[a]
	68 A_g	93	*ca.* 5	*ca.* 5	3	
ν_R (NiO_6)	103 A_g	55				(90)
$\nu_5(SnCl_6)$	157 A_g	135	3	8		
	169 E_g	20	55	80	110	168
$\nu_5(NiO_6)$	192 E_g		5	10	25	(183)
	212 A_g	140	10	8	5	203
$\nu_2(SnCl_6)$	246 E_g	17	50	70	30	243
$\nu_1(SnCl_6)$	315 $A_g(?+E_g)$[b]	>500	80	100	80	316
$\nu_1(NiO_6)$	383 A_g	28				375

[a] Figures in parentheses ± 5 cm^{-1}. [b] $\nu_2(NiO_6)$ may be coincident, see text.

TABLE III. I.r. Frequencies/cm^{-1} at Room Temperature for Single-crystal $[Ni(H_2O)_6][SnCl_6]$ Obtained by Kramers–Krönig Analysis of Reflectance Spectra, and Corresponding Data for the Aquo- and Deuterio-complexes as Powders at Ambient and Liquid Nitrogen Temperatures.

Single-crystal[a]		Assignment	$[Ni(H_2O)_6][SnCl_6]$[b]		$[Ni(D_2O)_6][SnCl_6]$[b]	
A_u	E_u		Ambient	L.N.	Ambient	L.N.
	73s(68)	Translatory	73s	78s	83vw	
88s(86)		lattice modes	88wm	97m	92vw	93ms
108w(103)	120sh(107)	$\nu_6(NiO_6)$	116w	112w	108w	112w
138w(134)	147vs(141)	$+\nu_6(SnCl_6)$	145*s*	146*s*	145*s*	142*s*
170vs(167)	177wm(168)	$\nu_4(SnCl_6)$	174s	178s	171*s*	176*s*
204w(198)	206w(193)	$\nu_4(NiO_6)$	202s	212s	194*s*	197*s*
306vs(301)	318s(304)	$\nu_3(SnCl_6)$	305vs	307vs	303ms	305s
		$\nu_3(NiO_6)$	327vs	327*s*	274s	276s
			340sh	340s	288m	290m

[a] Figures in parentheses are visually estimated values. [b] From reference 3. Mull spectra.

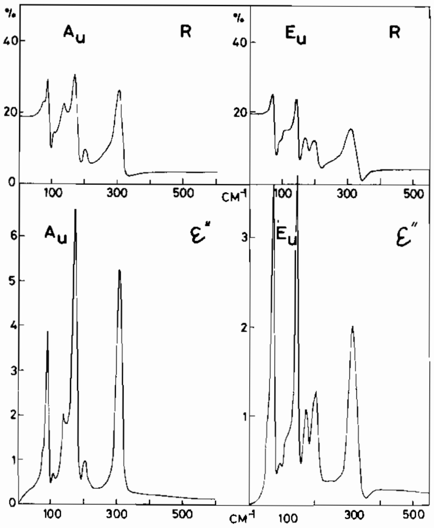

Figure 2. The i.r. reflectance spectrum (R) of $[Ni(H_2O)_6]$ $[SnCl_6]$, and the imaginary (ε'') part of the complex dielectric constant $\varepsilon^* = \varepsilon'-i\varepsilon''$ as computed by Kramers–Krönig analysis.

ponents were good, with some slight residuals. The 315 cm^{-1} A_g band is exceedingly intense in comparison with the rest of the spectrum and it is probable that the intensity at 315 cm^{-1} shift in the (zx), (yz), and (yx) spectra is due to residual scattering from it: nevertheless, the possibility exists that this is not residual scatter but a coincident band of E_g symmetry due to ν_2, $\nu(Ni–OH_2)$, e_g. If this were true, deuteriation should result in a small downward shift of the E_g component, but this was not found. The deuteriation shift of ν_1 of $[Ni(OH_2)_6]^{2+}$ is not large and that of ν_2, e_g might be smaller. On balance, we consider that the most probable situation is that the missing E_g band is of vanishingly low intensity. ν_5, t_{2g} is split by the site field by 12 and 20 cm^{-1} for $[SnCl_6]^{2-}$ and $[Ni(OH_2)_6]^{2+}$ respectively.

The i.r.-active ν_3, t_{1u} $\nu(Ni–OH_2)$ mode was located by Lock[3] at 327, 340 cm^{-1} (A_u and E_u site-split components) from deuteriation experiments. Our crystals showed negligible reflectivity in this region, but below 320 cm^{-1} the reflectance results greatly assist the i.r. assignment. Lock's deuteriation work also showed[1,3] that the ν_4, t_{1u}, $\delta(Ni–O)$ mode is at 202 cm^{-1} (protiate); our reflectance spectra show that what appeared as a single band in the mull spectra is a site-split doublet, Table III. ν_3 and ν_4 of $[SnCl_6]^{2-}$ are also site-split and occur at the frequencies expected from earlier work on alkali metal hexachlorostannates.[4]

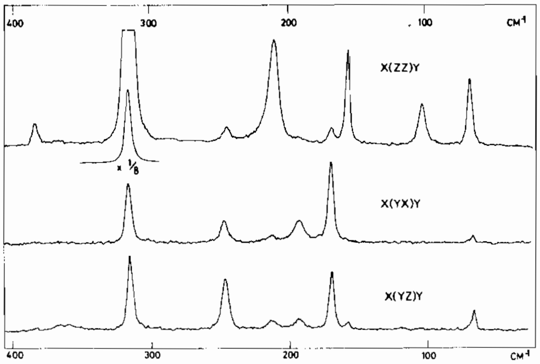

Figure 3. Single-crystal Raman spectra of $[Ni(H_2O)_6][SnCl_6]$.

Below 150 cm^{-1} the i.r. spectra show exactly the number of bands predicted by factor group analysis, *viz.*, $3A_u + 3E_u$, thereby showing that ν_6 for both ions has become i.r.-active. The 138/147 cm^{-1} pair develop quite remarkable intensity and may therefore be associated with the anion rather than the cation. Finally, we note that the translatory modes at 73, 88 cm^{-1} are close to those for K_2SnCl_6, despite the presence of a heavier cation. We conclude that this is due to the strengthening of the lattice by O–H---Cl bonding.

An assignment of the skeletal modes of the cation in $[Mg(H_2O)_6]SO_4$ was recently deduced[5] from single-crystal experiments. They found: ν_1 374, ν_2 318, ν_3 418, ν_4 210/190, ν_5 250/240/233 cm^{-1}, where multiples represent site-splitting. These values are comparable with ours for $[Ni(OH_2)_6]^{2+}$ with the exception of ν_3 which appears to us to be unreasonably high: it is possible that an external mode of water (*cf.* 430 cm^{-1} in our crystal) has been mistaken for ν_3 in $[Mg(OH_2)_6]^{2+}$, or perhaps overlays it. Deuteriation studies could resolve the question.

Acknowledgement

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References

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