CRYSTAL SYMMETRY OF THE CHLORATE ANION IN HOST STRUCTURES

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The infrared spectra were studied for the pyramidal ClO_3^- anion (C_{3v}) embedded in host structures of various symmetries. Small amounts of $NaClO_3$ or $KClO_3$ were incorporated in $NaBrO_3$ (T^4), $NaIO_3$ (D_{16}^{2h}), $KBrO_3$ (C_{3v}^5), and KIO_3 (C_1^1) structures. The ClO_3^- anion was found to assume the site symmetry of the host structure anion, *i.e.* C_3 C_s, C_{3v}, and C_1, respectively, in accordance with the results of group analysis.

Interpretation of the infrared spectra of inorganic polycrystalline substances from the point of view of their crystal symmetry is complicated by the mutual vibrational interaction of the particles in the elementary cell. This dynamic effect can be eliminated by diluting the particle studied in a host crystal structure. Isostructural substances give rise to mixed crystals. For substances with different crystal structures, the mixed crystal formation is not feasible, small amounts of foreign ions, however, can be embedded in the host structure. Their site symmetry can be studied by vibrational spectroscopy. The aim of this work was to investigate site symmetry of the ClO_3^- anion in host structures of the T^4, D_{2h}^{16}, C_{3v}^5 and C_1^1 symmetries.

EXPERIMENTAL

Samples of $NaBrO_3$, $NaIO_3$, $KBrO_3$, and KIO_3 containing $NaClO_3$ or $KClO_3$ in concentrations of 5 and 7 mol.% were prepared by mixing the chemicals of reagent grade purity in the appropriate proportions, dissolving them in water, and concentrating the solution for crystallization.

The infrared spectra were measured over the region of $200-4\,000\ cm^{-1}$ on a Perkin–Elmer 325 spectrophotometer in KBr disks 13 mm in diameter.

RESULTS AND DISCUSSION

The crystallographic data of the pure starting substances were taken from the literature[1–5]. The own symmetry of the ClO_3^-, BrO_3^-, and IO^- pyramidal anions is C_{3v}. The space groups, numbers of formula units in the elementary cells (Z), and the site symmetries of the XO_3^- anions in the substances used are given in Table I. $NaClO_3$ and $NaBrO_3$ crystallize in the cubic system, $NaIO_3$, $KBrO_3$, and $KClO_3$ in the

orthorhombic, trigonal, and monoclinic systems, respectively. KIO_3 crystallizes in several modifications[6] in dependence on temperature over the region of -190 to $+212°C$; the C_{3v}^5 and C_1^1 structures have been reported[3-5] at room temperature.

The infrared spectra of the ClO_3^-, BrO_3^-, and IO_3^- anions in their sodium and potassium salts were interpreted by Sterzel and Shnee[7], who used the ^{18}O substitution for the study. Lowering in the mutual influencing of the anions and its manifestation in the Raman spectra were studied on $NaClO_3$–$NaBrO_3$ mixed crystals[8]. Present in concentrations as low as about 1 mol %, BrO_3^- exhibited the C_3 symmetry. ^{79}Br–^{81}Br isotopic splitting was observed in the spectra. The spectral patterns over the $v_1 - v_3$ vibrational region was examined for the BrO_3^- anion embedded in an $NaClO_3$ host crystal in various concentrations[9]. The results were compared with those derived from the Raman spectra of $RbClO_3$–$RbBrO_3$ mixed crystals[10]. Also in this system the anions exhibited the C_3 symmetry. The occurrence of two absorptions in the region of the v_3 vibration were explained by the isotopic effect. The vibrations of ClO_3^- were found more sensitive to environmental changes than those of BrO_3^-. The isotopic effects in the Raman spectra of $NaClO_3$, $KClO_3$, $NaBrO_3$, and $KBrO_3$ were discussed also in refs[11,12].

Infrared Spectra

The crystallographic data given in Table I show that the possible symmetries of XO_3^- anions accomodated in T^4, D_{2h}^{16}, C_{2h}^2, C_{3v}^5, and C_1^1 lattices are C_3, C_{3v}, C_s, and C_1. The six normal vibrations of the XO_3^- anion of the own symmetry C_{3v} divide into the irreducible representations $2A_1 + 2E$, all infrared-active. The vibrational correlation between the own symmetry of the anions and their site symmetries in the

TABLE I

Crystallographic data of salts of XO_3^- anions

Compound	Space group	Z	Anion site symmetry	Ref.
$NaClO_3$	T^4-$P2_13$	4	C_3	1
$NaBrO_3$	T^4-$P2_13$	4	C_3	1
$NaIO_3$	D_{2h}^{16}-$Pnma$	4	C_s	1, 2
$KClO_3$	C_{2h}^2-$P2_1/m$	2	C_s	1
$KBrO_3$	C_{3v}^5-$R3m$	1	C_{3v}	1
KIO_3^a	C_{3v}^5-$R3m$	1 or 8	C_{3v}	3, 4
KIO_3^a	C_1^1-$P1$	4	C_1	5

^{a} At room temperature.

structures in question, along with their IR activity, is shown in Table II. The wavenumbers for the ClO_3^- anion of $NaClO_3$ and $KClO_3$ each embedded in $NaBrO_3$, $NaIO_3$, $KBrO_3$ and KIO_3 crystals are given in Table III.

Taking into account the theoretical correlations $C_{3v} \rightarrow C_3$, $C_{3v} \rightarrow C_s$, and $C_{3v} \rightarrow C_1$ (Table II), the absorption bands of the ClO_3^- anion of $NaClO_3$ in $NaBrO_3$ matrix (Table III) where both the host and the doping substance possess the T^4 structure indicate that the ClO_3^- anion occupies sites of C_3 symmetry. The infrared-active ν_1, ν_2, ν_3, and ν_4 vibrations appear at 935, 610, 955 and 965, and 480 cm^{-1}, respectively. The splitting of the ν_3 vibration is due to the isotopic effect (Table IV).

TABLE II

Correlation table[a]

C_{3v}	C_3	C_s	C_1
$2A_1$	$2A$	$2A'$	$2A$
$2E$	$2E$	$2(A' + A'')$	$2(A + A)$

[a] All vibrations are infrared-active.

TABLE III

Band position (cm^{-1}) in the infrared spectra of the ClO_3^- anion of $NaClO_3$ and $KClO_3$ in host crystals

Host crystal	ν_1	ν_2	ν_3	ν_4
		$NaClO_3$		
$NaBrO_3$	935	610	955 sh, 965	480
$NaIO_3$	935 sh, 940	615 sh, 620	960 sh, 970, 990 sh, 1 005	490, 495
$KBrO_3$	925 sh, 930	605 sh, 610	955 sh, 965	480 sh, 490
KIO_3	935 sh, 940	620	960 sh, 970, 1 000	490
		$KClO_3$		
$NaBrO_3$	930 sh, 940	610 sh, 615	955 sh, 970	485
$NaIO_3$	930 sh, 940	620	960 sh, 970, 990 sh, 1 005	485 sh, 495
$KBrO_3$	925 sh, 930	605 sh, 610	955 sh, 965	490
KIO_3	935 sh, 940	620	960 sh, 970, 1 005	490 sh, 495

A similar result is obtained for KClO$_3$, with the C_{2h}^2 symmetry, embedded in the NaBrO$_3$ host lattice (T^4); the spectral patterns for the ClO$_3^-$ ion again show that the anion assumes the C_3 site symmetry of the space group T^4, hence, the site symmetry of the host lattice which is higher than that in the lattice of KClO$_3$ itself. The v_1, v_2 and v_3 vibrational bands are split due to the isotopic effect; for the v_4 vibration the possible splitting is obscured by the near-by v_4 vibration of BrO$_3^-$.

Fig 1 shows the infrared spectra of the ClO$_3^-$ anion over the region of its v_1 and v_3 vibrations for the NaClO$_3$–NaIO$_3$ and KClO$_3$–NaIO$_3$ systems; the spectra display

TABLE IV

Values of the ^{37}Cl—^{35}Cl isotopic effect for the ClO$_3^-$ anion (C_{3v})

Symmetry species	Theoretical value	Experimental values			
		NaClO$_3$–NaBrO$_3$ C_3 site	NaClO$_3$–KBrO$_3$ C_{3v} site	KClO$_3$–NaBrO$_3$ C_3 site	KClO$_3$–KBrO$_3$ C_{3v} site
A_1	0·990		0·986 (−0·6%)	0·981 (−0·8%)	0·986 (−0·6%)
E	0·982	0·990 (+0·8%)	0·970 (−2·2%)	0·985 (+0·3)	0·990 (+0·8%)
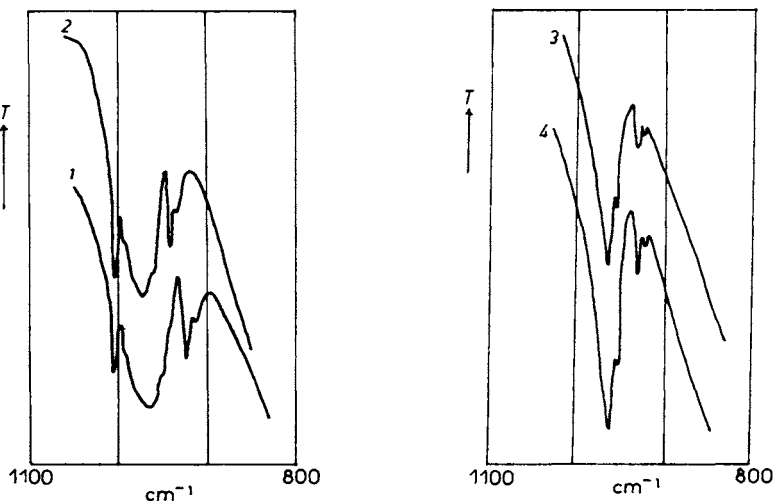
FIG. 1

v_1 and v_3 vibrations of the ClO$_3^-$ anion, *1* NaClO$_3$–NaIO$_3$, *2* KClO$_3$–NaIO$_3$, *3* KClO$_3$–KBrO$_3$, *4* NaClO$_3$–KBrO$_3$

the active v_1, v_2 (A') and split degenerate v_3 and v_4 $(A' + A'')$ vibrations. The v_1 vibrational bands again are split due to the isotopic effect. The v_2 vibration in the $NaIO_3$ samples is not very marked. The split v_3 vibrational bands exhibit additional splitting by the isotopic effect (Table III). The experiments give evidence that in both cases the site symmetry of the ClO_3^- anion is C_s, which is the site symmetry of the IO_3^- ion in the $NaIO_3$ host structure (D_{2h}^{16}), although the crystal symmetries of $NaClO_3$ and $KClO_3$ themselves are different. Similarly, the ClO_3^- anion in the $KBrO_3$ host lattice assumes the site symmetry of the latter, namely, C_{3v} (Fig. 1). The v_1, v_2, and v_3 vibrational bands are markedly split on account of the isotopic effect.

In the $NaClO_3$–KIO_3 and $KClO_3$–KIO_3 systems the ClO_3^- anion exhibits the v_1 vibration $(935\text{ sh}, 940\text{ cm}^{-1})$ with isotopic splitting, and the v_2 vibration which is not very marked due to the low concentration of the minority component. The v_3 vibrational band is split into a broad band at 970 cm^{-1} with an indistinct shoulder at 960 cm^{-1}, and a sharp band at $1\,000$ and $1\,005\text{ cm}^{-1}$, respectively. These facts indicate the C_1 symmetry for the ClO_3^- anion.

For KIO_3, two structures, viz. C_{3v}^5 and C_1^1, have been reported at room temperature. Assuming that as before, ClO_3^- in KIO_3 matrix will respect the site symmetry of the host lattice, the C_{3v}^5 space group $(C_{3v}$ site$)$ can be ruled out; the C_1^1 space group thus suits for KIO_3.

The theoretical ^{37}Cl–^{35}Cl spectral isotopic effect for the ClO_3^- anion was evaluated by the product rule in terms of the kinematic G matrix, hence, as $(|G^*|/|G|)^{1/2}$ where G^* and G refer to $^{37}ClO_3^-$ and $^{35}ClO_3^-$, respectively. The matrix elements were calculated from the formula given for the XY_3 (C_{3v}) grouping[13] using the geometry of ClO_3^- reported in ref.[14]. The theoretical values (Table IV) are in a good agreement with the experimental values derived from the data of Table III.

The infrared spectra of the ClO_3^- anion in all the systems studied give evidence that this anion always adopts the site symmetry of the anion of the host crystal, which can be lower or higher than the site symmetry of the ion in the parent $NaClO_3$ and $KClO_3$ crystals themselves. This result is analogous to that obtained previously for tetrahedral XO_4^{2-} anions[15].

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Translated by P. Adámek.