Structural Studies of Matrix-isolated Alkali Metal Chlorates; an Example of Tridentate Co-ordination by the Chlorate Ion

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The vapours from heated alkali metal chlorates isolated in nitrogen and argon matrices have been studied by infrared spectroscopy. The use of ^{16}O–^{18}O partial isotopic substitution demonstrates the presence of a C_3 axis for the molecule $CsClO_3$ isolated in an argon matrix. This is interpreted as the ClO_3^- ion showing a tridentate interaction with the caesium ion.

The vapours above alkali metal salts of oxo-anions can be studied conveniently by trapping in inert gas matrices at cryogenic temperatures. Subsequent infrared spectroscopy coupled with partial ^{16}O–^{18}O substitution can lead to rigorous determination of the symmetry of the oxo-anion, and hence to an understanding of the nature of the interaction with the alkali metal ion. The species NO_2^-;[1] PO_2^-, AsO_2^-, SbO_2^-;[2] NO_3^-;[3] PO_3^-;[4] CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-} [5] all appear to co-ordinate to the alkali metal ion *via* two oxygens. The oxo-anions thus behave as bidentate ligands. In the case of XO_2^- (X = N, P, As, or Sb) the idealised free ion is of C_{2v} symmetry, while for XO_3^- (X = N or P) the free ion has idealised D_{3h} symmetry. This behaviour is quite unlike that of a variety of van der Waals molecules such as $Ar(Kr)SO_3$[6,7] isoelectronic with $K(Rb)PO_3$, $ArBF_3$ [8] isoelectronic with KNO_3, or $ArSO_2$ [9] isoelectronic with KPO_2, all of which can be described as based on an inert gas atom lying on a line perpendicular to the plane of the molecular component and approximately above the centre of mass.[10] It is interesting, however, that in $ArCH_3Cl$ [11] the argon is not situated on the C_3 axis and the molecule (in a similar way to ArClCN [12]) can be loosely described as T-shaped. The related ' ionic ' molecule KCN has been shown to be T-shaped in the gas phase,[13] by using nozzle-beam electric-dipole techniques. This result is perhaps not so surprising when it is remembered that species such as KO_2 [14] have equivalent oxygen atoms and hence are also T-shaped.

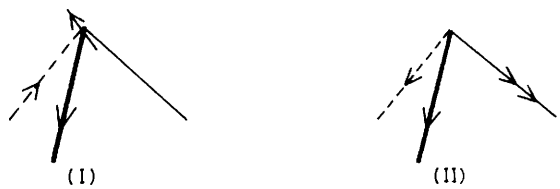
In the case of XO_4^{2-} (X = Cr, Mo, or W), at first sight the possibility of tridentate co-ordination to the alkali metal ion (M^+) might look attractive. However the change from tridentate co-ordination (alkali metal atoms in *necessarily* adjacent *faces*) to bidentate co-ordination (alkali metal atoms on opposite *edges* of the XO_4^{2-} tetrahedron) leads to a considerable reduction in $M^+ \cdots M^+$ interactions.

We were interested in attempting to obtain an example of tridentate co-ordination. As long ago as 1968, Andrews and Carver [15] showed that in $LiCCl_3$ the lithium lay on the C_3 axis. As recently as 1979 it was pointed out [16] that the correct structural interpretation requires the lithium to be adjacent to the carbon. There are many calculations on the structures of related lithiated organics.[17] Bearing in mind the relationship between CCl_3^- and SiF_3^-, we decided to look at ClO_3^-, which is isoelectronic with SiF_3^- and has the advantage of the possibility of isotopic substitution at the oxygen. We knew from previous experience that the splitting patterns derived from partial $^{16}O/^{18}O$ substitution are normally of high quality. Further, use of the caesium salts minimises lattice energies and also minimises $Cs^+ \cdots$ central atom repulsion terms.

Results and Discussion

Preliminary infrared matrix-isolation experiments on $CsClO_3$ in argon in the region 450—1 000 cm^{-1} showed principal bands at 963.7, 925.6, and 618.4 cm^{-1} which correspond closely to the positions expected [18] for $\nu_3(e)$, $\nu_1(a_1)$, and $\nu_2(a_1)$ of $^{35}ClO_3^-$. Further experiments using other cations are summarised in Table 1 and show that the bands are cation dependent, suggesting that the molecule under study is $CsClO_3$. Bands whose relative intensity varied with matrix deposition conditions or annealing are recorded as footnotes to Table 1. The band observed at 1 020 cm^{-1} for $KClO_3$ and previously [19] assigned to one component of (a split) ν_3 did not appear in our spectra where a superheater was used during matrix deposition. The fact that the *e* mode is unsplit in $CsClO_3$ is a very strong indication that C_{3v} symmetry is retained, and suggests that the previous assignment [19] of a bidentate interaction is incorrect. It is likely that the ClO_3^- is acting as a tridentate ligand. Proof of the correctness of the assumption of C_{3v} symmetry comes from partial isotopic substitution using ^{18}O. The Figure shows the infrared spectrum of $Cs^{35}Cl^{16/18}O_3$ isolated in a matrix. The calculated frequencies and intensities (for a 50 : 50 ^{16}O : ^{18}O mixture) are given for ν_1, ν_2, and ν_3 of the ion. The patterns can easily be understood by considering the vibrations of the isotopomers.[20]

The ClO_3^- ion is pyramidal and of C_{3v} symmetry. The ν_3 vibration may be represented by the two components (I) and



(I) (II)

(II). Assuming that the ClO_3^- ion in $CsClO_3$ retains C_{3v} symmetry, the degeneracy of the *e* vibration is not resolved. However for the partially substituted ions (16 16 18 or 16 18 18) the symmetry falls to C_s. The plane of symmetry in this case passes through the chlorine and the unique 18 or 16 oxygen atom. Thus the resolution of the degeneracy leads to an *a'* mode and an *a''* mode. In the *a''* modes the unique oxygen atom does not move. Thus to a first approximation these components from the partially substituted species will occur at the same frequencies as the *e* modes of the corresponding all 16 or all 18 ions.

For 50% ^{18}O substitution the statistical occurrence of the four isotopomers will be in the ratio 1 : 3 : 3 : 1. This is approximately the intensity distribution found for ν_1 and ν_2 (see Figure). By contrast for ν_3 because the degeneracy is removed for the two partially substituted isotopomers the intensity distribution in this case is $(1 + 1\frac{1}{2}) : 1\frac{1}{2} : 1\frac{1}{2} : (1 + 1\frac{1}{2})$ or 5 : 3 : 3 : 5, which again is the approximate intensity distribution. Finally we note that ν_1 occurs in the same region

Table 1. Infrared bands (cm^{-1}) and assignments for matrix-isolated $MClO_3$ (M = K, Rb, or Cs)

Argon matrix			Nitrogen matrix			
$CsClO_3$	$RbClO_3$	$KClO_3$	$CsClO_3$	$RbClO_3$	$KClO_3$	Assignment
963.7s	967.2s	969.4s	978.2s, 973.8s	980.9s, 976.6s	981.2s, 979.0s, 977.0s	ν_3 $^{35}ClO_3^-$
953.8m	957.6m	957.4m	967.8m, 964.0m	971.0m, 967.2m	971.4m, 969.6m, 968.0m	ν_3 $^{37}ClO_3^-$
925.6m	926.8m	927m	934.7m	935.8m	937.2m	ν_1 $^{35}ClO_3^-$
917.3w	919.6w		927.7w	928.8w	934.4w	ν_1 $^{37}ClO_3^-$
618.4m	623.5m	628.0m	619.8m	623.4m	626.0m	ν_2 $^{35}ClO_3^-$
614.0w	618.6w	623.0w	614.8w	618.4w	620.8w	ν_2 $^{37}ClO_3^-$
474w	478.2w	481.5w	481.2w, 479.1w	483.8w, 482.0w	484w	ν_4 $^{35}ClO_3^-$
*						ν_4 $^{37}ClO_3^-$
986.0	987.4	976.4				Bands of variable intensity
984.0	976.0	961.0				
977.0	952.4					
974.6						
967.6						
936.0	936.4					
625.0						
1 020.5	1 021.5	1 020.5	1 014.5	1 015.8	1 016.0	Bands not observed in superheater experiments
1 017.5	1 018.5	1 018.0	1 011.0	1 013.2	1 013.7	
1 015.0	1 017.3		1 008.5	1 010.5		
	1 015.5					
	1 014.5					

* Note that the calculated isotope splitting ($^{35}Cl/^{37}Cl$) for $\nu_4(e)$ is only 1.1 cm^{-1}.

Table 2. Observed (argon matrix) and calculated * infrared bands (cm^{-1}) for isotopically labelled $CsClO_3$

	Observed	Calculated	Assignment
ν_3	963.7	963.7	e $^{35}Cl^{16}O_3^-$
		963.4	a'' $^{35}Cl^{16}O_2{}^{18}O^-$
	949.4	949.5	a' $^{35}Cl^{16}O_2{}^{18}O^-$
	957.2	957.1	a' $^{35}Cl^{16}O^{18}O_2^-$
	931.5	932.5	a'' $^{35}Cl^{16}O^{18}O_2^-$
		932.1	e $^{35}Cl^{18}O_3^-$
	953.8	952.8	e $^{37}Cl^{16}O_3^-$
		952.5	a'' $^{37}Cl^{16}O_2{}^{18}O^-$
	940.0	938.9	a' $^{37}Cl^{16}O_2{}^{18}O^-$
	947.5	946.3	a' $^{37}Cl^{16}O^{18}O_2^-$
	921.2	921.1	a'' $^{37}Cl^{16}O^{18}O_2^-$
		920.7	e $^{37}Cl^{18}O_3^-$
ν_1	925.6	925.6	a_1 $^{35}Cl^{16}O_3^-$
	906.9	907.8	a' $^{35}Cl^{16}O_2{}^{18}O^-$
	897.2	898.7	a' $^{35}Cl^{16}O^{18}O_2^-$
	891.2	891.5	a_1 $^{35}Cl^{18}O_3^-$
	917.3	917.1	a_1 $^{37}Cl^{16}O_3^-$
	898.7	898.5	a' $^{37}Cl^{16}O_2{}^{18}O^-$
	889.4	889.4	a' $^{37}Cl^{16}O^{18}O_2^-$
	—	882.3	a_1 $^{37}Cl^{18}O_3^-$
ν_2	618.4	618.4	a_1 $^{35}Cl^{16}O_3^-$
	610.0	609.5	a' $^{35}Cl^{16}O_2{}^{18}O^-$
	601.5	600.4	a' $^{35}Cl^{16}O^{18}O_2^-$
	592.8	591.0	a_1 $^{35}Cl^{18}O_3^-$
	614	614.3	a_1 $^{37}Cl^{16}O_3^-$
	606	605.6	a' $^{37}Cl^{16}O_2{}^{18}O^-$
	597	596.5	a' $^{37}Cl^{16}O^{18}O_2^-$
	—	587.3	a_1 $^{37}Cl^{18}O_3^-$

* Force constants (mdyn $Å^{-1}$; 1 dyn = 10^{-5} N): f_r = 5.541; f_{rr} = 0.247; f_α = 1.033; $f_{\alpha\alpha}$ = 0.306.

of the spectrum as ν_3 (930 and 960 cm^{-1}, respectively). The a' components deriving from ν_3 for the C_s point group clearly have the same symmetry as the a' vibrations deriving from ν_1. These two vibrations will interact with one another for each of the two partially substituted chlorate ions. Thus the two central components of ν_3 will be pushed to higher frequencies while the two central components of ν_1 will correspondingly be pushed to lower frequencies. Table 2 summarises our isotopomer data in a more formal manner.

From Tables 1 and 2 it is apparent that in argon $KClO_3$, $RbClO_3$, and $CsClO_3$ contain a chlorate unit of essentially C_{3v} symmetry. The $CsClO_3$ data are clear-cut within the normal limitations of the technique, but the quality of the spectra for $KClO_3$ were not as high as those for $RbClO_3$ and $CsClO_3$. In nitrogen the bands were generally narrower and there appeared to be less tendency towards aggregation. However a doubling of ν_3 occurred for $RbClO_3$ and $CsClO_3$, while for $KClO_3$ three bands occurred in the region of ν_3. It is interesting that for $CsClO_3$ the a' components of the mixed $^{16}O/^{18}O$ isotopomer showed no doubling (while as indicated both the ^{16}O parent and the all-^{18}O species showed a doubling). The situation with the a'' components of the mixed isotopomer is unclear owing to overlap with (doubled) bands from the all-^{16}O and all-^{18}O species. Nonetheless our results suggest that the doubling of the ν_3 bands for $RbClO_3$ and $CsClO_3$ is due to a lifting of the degeneracy.

This study demonstrates, within the limitations of the 'natural' half width of the bands and the resolution of the infrared spectrometer used, that in argon $CsClO_3$ has a three-fold symmetry axis. Of the two possible positions for Cs^+ on the C_3 axis, it is reasonable to propose that the one adjacent to the three oxygens is preferred. The caesium ion then sits in the tripod provided by the chlorate ion.

We thus have the perhaps unexpected result that for $CsClO_3$

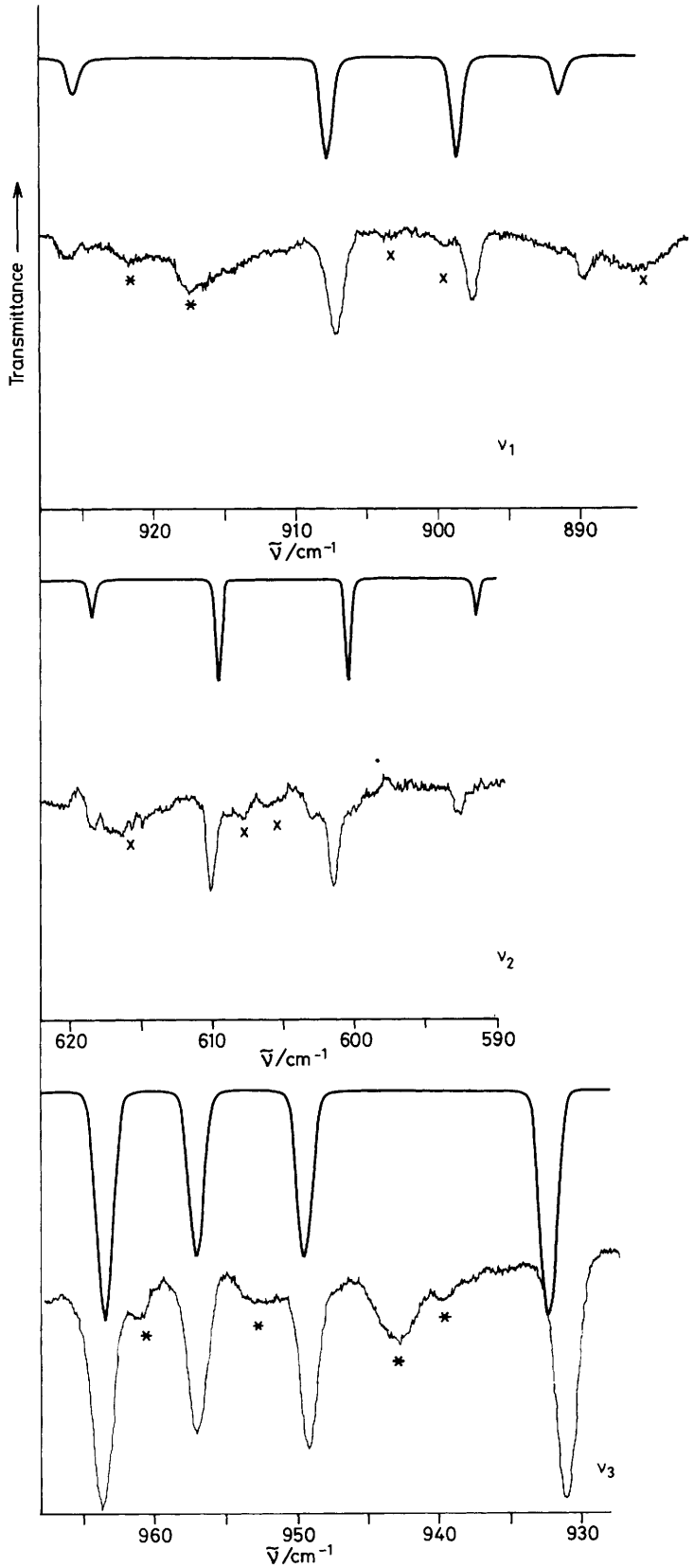


Figure. High resolution infrared spectrum of isotopically pure ^{35}Cl in $Cs^{35}ClO_3$ (with partial ^{18}O substitution) isolated in an argon matrix. The upper pattern in each case is that calculated on the basis of C_{3v} symmetry for the $^{35}ClO_3^-$ ion (50% ^{18}O enrichment) (bands marked with an asterisk are of variable relative intensity)

the molecule retains the C_3 axis but for $CsClO_4$ a bidentate or C_{2v} co-ordination is apparently preferred.[21] The major difference between the two is addition of an oxygen. There have been recent structural studies on crystalline $KClO_3$ [22] and $KClO_4$.[23]

$KClO_3$: shortest K–O 2.804 Å; average angle 106.4°; average Cl–O 1.497 Å

$KClO_4$: shortest K–O 2.862 Å; average angle 109.2°; average Cl–O 1.433 Å

(The K–O distance on the basis of the sum of Pauling ionic radii is 2.73 Å.)

Use of the bond lengths given above for $KClO_4$ with tetrahedral angles gives the following:

C_{3v}	K–Cl	3.00 Å	C_{2v}	K–Cl	3.44 Å
	K–(3)O	2.86		K–(2)O	2.86
	K–(1)O	4.43		K–(2)O	4.42

In essence the difference between the tridentate (C_{3v}) and the bidentate (C_{2v}) $KClO_4$ models is a reduction in the K–O attraction term by change of one oxygen distance from 2.86 to 4.42 Å (the other at 4.43 changing almost negligibly to 4.42 Å), coupled with a decrease in the K–Cl repulsion term (3.00 to 3.44 Å). Clearly it is extremely finely balanced on this simple ionic model. This is further exemplified by the observed change from C_{3v} $CsClO_3$ to C_{2v} $CsClO_4$, which in this case involves a change in the formal charge on chlorine from +5 to +7.

Experimental

The sample of $KClO_3$ (AR grade; Hopkins and Williams) was used without further purification. Samples of $RbClO_3$ and $CsClO_3$ were prepared by electrolysis of hot saturated aqueous solutions of the corresponding chlorides, using platinum electrodes.[24] The product was recrystallised from water and fused under vacuum before use. Enriched samples of $Cs^{35}ClO_3$ were prepared by the foregoing method using ^{18}O-enriched water (50 atom % ^{18}O) and enriched $Cs^{35}Cl$ (90 atom % ^{35}Cl NaCl exchanged with caesium-enriched Dowex 50-X8 cation resin). High purity nitrogen and argon were supplied by B.O.C. Vaporisation was accomplished from borosilicate or silica sample holders heated by a resistive electrical furnace to *ca.* 750 K. Deposition times were typically *ca.* 1 h and during this period the CsI window on the cryostat was maintained at *ca.* 12 K. Spectra were recorded (200—5 000 cm^{-1}) on a Perkin-Elmer 225 spectrometer calibrated in the normal way.

Vibrational Analysis.—The model used for the interpretation of these data is based on a C_{3v} ClO_3^- ion with an OClO bond angle of 106° and a Cl–O distance of 1.48 Å. The force constant data [25] and results of calculations based on the SOTONVIBP [26] program are summarised in Table 2 for $CsClO_3$.

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