592. *The Infrared Spectra of Some Transition-metal Perchlorates.*

By B. J. HATHAWAY and A. E. UNDERHILL.

The infrared spectra of some hydrated transition-metal perchlorates, some transition-metal perchlorate–methyl cyanide complexes, and anhydrous copper perchlorate are reported. The spectra are interpreted in terms of ionic perchlorate and perchlorato-groups.

As a result of the observation that anhydrous cupric perchlorate is volatile [1] the infrared spectrum of this and some transition-metal perchlorate complexes have been examined to obtain evidence of the formation of the metal–perchlorate bond in the solid state.

The infrared spectra of a number of ionic perchlorates are listed by Miller and Wilkins.[2] The Raman spectrum of the perchlorate ion has been studied by several investigators,[3,4] and apart from minor differences in the numerical values accepted for its fundamentals their assignments have been established. The perchlorate ion has a regular tetrahedral structure and belongs to the point group T_d, having nine vibrational degrees of freedom distributed between four normal modes of vibration. The assignments of these modes are listed in Table 1. In general the triply degenerate frequencies ν_3 and ν_4 are observed

TABLE 1. *Vibrations of the ClO₄ group as a function of symmetry.†*

State of ClO₄	Symmetry						
−O*−ClO₃	C_{3v}	ν_2 A₁(I,R) ClO str.	ν_6 E(I,R) rocking.	ν_1 A(I,R) s.str. ClO₃	ν_4 E(I,R) a.bend. ClO*	ν_3 A(I,R) s.bend. ClO₃	ν_5 E(I,R) a.bend. ClO₃

(correlation arrows)

ClO₄⁻	T_d	ν_1 A(R) s.str. 932	ν_2 E(R) s.bend. 460	ν_3 F₂(I,R) a.str. 1110	ν_4 F₂(I,R) a.bend. 626

(correlation arrows)

−O* ClO₂ −O*	C_{2v}	ν_2 A₁(I,R) Cl–O₂* s.str.	ν_4 A₁(I,R) ClO₂* s.bend.	ν_5 A₂(R) torsion	ν_1 A₁(I,R) ClO₂ s.str.	ν_6 B₁(I,R) Cl–O₂ a.str.	ν_8 B₂(I,R) Cl–O₃* a.str.	ν_3 A₁(I,R) ClO₂ s.bend	ν_7 B₁(I,R) rocking	ν_9 B₂(I,R) rocking

† A and B, non-degenerate. E, doubly degenerate. F, triply degenerate. I, infrared active. R, Raman active. s., symmetric. a., antisymmetric. O* refers to oxygen co-ordinated to copper.

in the infrared spectra of ionic perchlorates, the former appearing as a very broad strong band with a poorly defined maximum, which is occasionally split.[2] The non-degenerate frequency ν_1, which is theoretically forbidden in the infrared, usually occurs as a very weak absorption at 930 cm.⁻¹. This absorption becomes weakly allowed owing to distortion of the ion in a crystal field of lower symmetry than itself.

If the perchlorate group changes from an ionic to a perchlorato-group, *i.e.*, is involved in partial covalent bonding between one of its oxygen atoms and a cation, this oxygen atom is no longer equivalent to the other three and the original T_d symmetry of the perchlorate ion is lowered to C_{3v}. Table 1 illustrates the correlation between the vibrations of a molecule with T_d symmetry and those of its derivative of C_{3v} symmetry. The numerical values of the fundamental frequencies in a perchlorato-group with C_{3v} symmetry

[1] Hathaway, *Proc. Chem. Soc.*, 1958, 344.
[2] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[3] Landolt–Börnstein, " Zahlenwerte und Funktion," Springer-Verlag, Berlin, 1951, I Band, 2 Teil, Molekeln I, pp. 152, 259.
[4] Cohn, *J.*, 1952, 4282.

cannot be predicted with accuracy. However, the values for anhydrous perchloric acid [5] and perchloryl fluoride,[6] both of which have C_{3v} symmetry, can be taken as a useful guide. These values are given as follows:

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$HClO_4$	1032	739	574	1312	585	426
ClO_3F	1061	715	549	1315	589	405
$O \cdot SO_3{}^{2-}$	1038	970	645	1130	604	438

The shift from 932 cm.$^{-1}$ (ν_1) of the ionic perchlorate to 739 and 715 cm.$^{-1}$ (ν_2) of perchloric acid and perchloryl fluoride, respectively, is rather large but is consistent with the radical differences between the symmetrical ClO stretching vibration of the ionic perchlorate and that of the ClF and ClOH bonds. Such a radical shift in this frequency would not be expected in the perchlorato-group, as the oxygen atom involved in co-ordination is similar to the remaining three oxygen atoms because it is not involved in a complete covalent bond to a cation. Evidence to support this is found in the case of the sulphate ion,[7] the corresponding shift being 981 (T_d) to 970 cm.$^{-1}$ (C_{3v}).

If the perchlorate group occupies a position in a crystal lattice where two of its oxygen atoms are involved in partial covalent bond formation to a cation, or, more probably, to two separate cations, the symmetry of the perchlorate group is lowered to C_{2v}. Table 1 illustrates the correlation between the vibrations of a molecule with T_d symmetry and its C_{2v} derivative. These correlations have been determined by analogy with the sulphate ion when this group is acting as a monodentate (C_{3v}) and bidentate (C_{2v}) ligand.[7] The modes of vibration were assigned by comparison with the assignment for sulphuryl difluoride,[8] and a guide to their numerical values was obtained by comparison with the known values of a bidentate sulphate ion [7] and sulphuryl difluoride,[8] as follows:

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
$SO_4{}^{2-}$	1055	995	641	462	*	1105	610	1170	571
SO_2F_2	1269	848	544	~300	*	1502	553	885	539

* Raman active only.

The analogy between the bidentate sulphate group and the bidentate perchlorate group should be very close, and the figures for the sulphate should be a much better guide than those of the sulphuryl difluoride.

While the effect of co-ordination of the perchlorate group is likely to bring about major differences in the infrared spectra, minor shifts or splittings may result from a lowering of the site symmetry of the group, from coupling of vibrations between perchlorate groups in the same unit cell, or by a purely isotopic effect within the group.

RESULTS AND DISCUSSION

Normal Hydrated Transition-metal Perchlorates.—In Table 2 are recorded the infrared spectra of some hydrated transition-metal perchlorates. They consist of a strong broad

TABLE 2. *Some hydrated transition-metal perchlorates.*

$Fe(ClO_4)_2,9H_2O$	2040wb			1200—1030s, b	935
$Ni(ClO_4)_2,6H_2O$				1190—1030s, b	930w
$Cu(ClO_4)_2,6H_2O$	2020w			1160—1085s, b	947w, sh	800vw
$Ag(ClO_4),H_2O$	2037s	1985s	1320m	1160—1030s, b	930w
$Th(ClO_4)_4,6H_2O$	2030w		1310m	1160—1105s, b	940w, sh	800vw

v = very. s = strong. b = broad. m = medium. w = weak. sh = shoulder. sp = sharp.

absorption at 1200—1030 cm.$^{-1}$ (ν_3), a very weak absorption at 950—930 cm.$^{-1}$ (ν_1), and a rising absorption at 650 cm.$^{-1}$ due to a peak at about 620 cm.$^{-1}$ (ν_4) which lies outside

[5] Ref. 3, pp. 551, 153.
[6] Lide and Mann, *J. Chem. Phys.*, 1956, **25**, 1128; Powell and Lippincott, *J. Chem. Phys.*, 1960, **32**, 1883.
[7] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[8] Perkins and Kent Wilson, *J. Phys. Chem.*, 1952, **20**, 1792.

the region studied. The spectra are consistent with a simple perchlorate ion in these salts.

Transition-metal Perchlorate–Methyl Cyanide Complexes.—In Table 3 are recorded the infrared spectra of some transition-metal perchlorate–methyl cyanide complexes. A broad strong absorption still occurs in the region 1200—1000 cm.$^{-1}$ but its width increases in the sequence cobalt, copper, manganese, and zinc. In the last case it is just resolved

TABLE 3. *Transition-metal perchlorate–methyl cyanide complexes.*

Cu(ClO$_4$)$_2$,4MeCN	Co(ClO$_4$)$_2$,6MeCN	Mn(ClO$_4$)$_2$,4MeCN	Zn(ClO$_4$)$_2$,4MeCN
2325s	2310s	2300s	2320s
2315s	2285s	2285s	2290s
2040w	2030vw		2060vw
	1725		1728w
	1641w	1628w	1628w
1370m	1370m	1370m	1370m
1312vw	1312vw	1315vw	1305vw
	1285vw		
			1200sh
	1143s	1148vs	1150vs
1125vs	1103vs	1130sh	
1065w, sh	1050sh	1060vs	
1038vs		1038sh	1028vs
958w, sp	948w	940m, sp	954w
937w, sp	937vw		948w
			927s, sp
800w	800w	800w	800w
	740w	787w	
671vw	675vw	675vw	658m

into two broad strong peaks at 1150 and 1029 cm.$^{-1}$. The absorption at 950—925 cm.$^{-1}$ increases in intensity and in its degree of splitting in the same sequence. This suggests that the perchlorate group in these complexes may be present not as an ionic species, but as a weakly co-ordinated group, the extent of co-ordination increasing in the above sequence until at zinc the ionic v_3 band is just resolved into the v_4 and v_1 vibrations of the monodentate perchlorate group. The cobalt complex is the least covalent of these four complexes as it contains six methyl cyanide molecules per cobalt ion, in contrast to four in the other complexes. These are probably arranged octahedrally around the cobalt ion and prevent co-ordination by the perchlorate group. In the zinc, copper, and manganese complexes the four methyl cyanide molecules are almost certainly arranged in a square-coplanar configuration around the metal ion, with the perchlorate groups above and below this plane. In the copper complex the otherwise regular octahedral arrangement will be distorted by the Jahn–Teller effect [9] to give a slightly longer bond between the perchlorate groups and the copper ion. This will result in less covalent character in the copper–oxygen bond, and the perchlorate group will be more ionic than in the zinc and manganese complexes. In the zinc and manganese complexes a regular octahedral configuration is likely as they have a d^{10} and d^5 electron configuration, respectively, neither of which is distorted by the Jahn–Teller effect. It is not understood why the zinc compound should contain a perchlorate group with more covalent character than the manganese compound. In the zinc complex the T_d symmetry of the perchlorate group is lowered slightly towards a C_{3v} symmetry, indicating that the bonding between the oxygen of the perchlorate group and the zinc ion is only weak.

The split absorption at 2300 cm.$^{-1}$ in the methyl cyanide complexes is due to the $-C\equiv N$ vibration, which is shifted to slightly higher frequencies than the normal absorption at 2248 cm.$^{-1}$ in methyl cyanide. A similar shift has been observed for co-ordinated methyl cyanide.[10]

Transition-metal Perchlorates: Lower Hydrates.—In Table 4 are listed the main infrared

[9] Orgel and Dunitz, *Nature*, 1957, **179**, 462.
[10] Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

absorption frequencies in the sodium chloride region of the lower hydrates of iron, nickel, and copper perchlorate, and of copper perchlorate dihydrate in the potassium bromide region. The spectra are completely different from those of the normal hydrates shown in Table 2. They all contain two very strong, well-resolved, peaks between 1200 and 1000 cm.$^{-1}$ and an equally strong peak between 940 and 890 cm.$^{-1}$. From these spectra

TABLE 4. *Transition-metal perchlorates: lower hydrates.*

Sodium chloride region

$Fe(ClO_4)_3,4H_2O$	2010w			1310w, sh	1160s	1025s	898—865mb	672w
$Ni(ClO_4)_2,2H_2O$	2025w	1915w		1298w, sh	1135s	1035s	937m	660sh
$Cu(ClO_4)_2,2H_2O$	2057w	1930w	1820w		1158vs	1030vs	920vs	660w

Potassium bromide region

$Cu(ClO_4)_2,2H_2O$	648s	620s	605s		480m	460w

it seems that the T_d symmetry of the ionic perchlorate present in the normal hydrate has been lowered almost completely to that of C_{3v}, and that the perchlorate groups are co-ordinated through a single oxygen atom to the transition-metal ion. The strong absorption, for example, of copper perchlorate dihydrate at 920 cm.$^{-1}$ can be assigned to the non-degenerate Cl–O* symmetrical stretching frequency ν_2, that at 1158 cm.$^{-1}$ as the doubly degenerate ClO* antisymmetrical bending frequency ν_4, and that at 1030 cm.$^{-1}$ as the non-degenerate ClO_3 symmetrical stretching frequency ν_1 of the monodentate perchlorate group. To obtain confirmation of this interpretation, copper perchlorate dihydrate was also examined in the potassium bromide region, and showed three strong bands, at 648, 620, and 605 cm.$^{-1}$, a medium band at 480 cm.$^{-1}$, and a weak band at 460 cm.$^{-1}$. The absorption at 648 cm.$^{-1}$ can be assigned to the non-degenerate ClO_3 symmetrical bending frequency ν_3, those at 620 and 605 cm.$^{-1}$ to the doubly degenerate ClO_3 antisymmetrical bending frequency ν_5 which is split, and that at 480 cm.$^{-1}$ to the doubly degenerate rocking frequency ν_6, of the monodentate perchlorato-group. It is uncertain why the ν_5 vibration should be split, but a similar effect was obtained with anhydrous copper perchlorate and is discussed below. The three strong bands in the potassium bromide region, in contrast to the single absorption of an ionic perchlorate, support the interpretation of the bands in the sodium chloride region as due to a covalently bonded perchlorate group with C_{3v} symmetry.

The change in the spectra of the dihydrates compared with hexahydrates is too large to be interpreted as a change of site symmetry of the perchlorate group in the crystal lattice. As water is removed from the crystal lattice of the hexahydrate the holes left must allow the perchlorate groups to move so that they can co-ordinate to the metal ions. If the perchlorate groups are monodentate in the dihydrate lattice the copper ions are four-co-ordinated by two oxygen atoms from water molecules and two from perchlorate groups. This type of four co-ordination for copper is unusual, as cupric copper is usually octahedral with four equivalent short bonds and two slightly longer bonds.[9] However, in the dihydrate crystal factors may not allow the perchlorate groups to rearrange and act as bidentate ligands to give the preferred distorted octahedron.

Copper perchlorate dihydrate, prepared by the action of anhydrous perchloric acid on anhydrous copper nitrate,[11] has the same spectra as that prepared by dehydration.

Anhydrous Transition-metal Perchlorates.—In Table 5 are listed the main infrared absorption frequencies of sublimed copper perchlorate and anhydrous ferric perchlorate. The spectrum of copper perchlorate in the sodium chloride region has three strong absorptions, at 1270—1245, 1130, and 948—920 cm.$^{-1}$, and a weak one at 1030 cm.$^{-1}$. This spectrum differs radically from that of the normal hydrated perchlorate (Table 2) and significantly from those of the lower hydrates. For comparison the three types of spectra

[11] Hathaway and Underhill, *J.*, 1960, 648.

for the copper salts are shown in the Figure. It seems that the symmetry of the perchlorate groups has been lowered to C_{2v} and indicates that they are acting as bidentate ligands through two of their oxygen atoms. The completeness of this transition suggests

TABLE 5. *Anhydrous transition-metal perchlorates.*

	$Cu(ClO_4)_2$	$Fe(ClO_4)_{2\cdot6}(NO_3)_{0\cdot4},0\cdot2NO_2ClO_4$*			$Cu(ClO_4)_2$	$Fe(ClO_4)_{2\cdot6}(NO_3)_{0\cdot4},0\cdot2N_2ClO_4$*
	1350vw	1605vw	ν_3	$\{$ 665m		662m
ν_8	1270—1245sb	1285sb		647m		—
ν_6	1130s	1160s	ν_7	$\{$ 624m		—
ν_1	1030w	1018w		600s		—
ν_2 $\{$	948s	922s	ν_9	497m		—
	920s	893sh	ν_4	466w		—

* See Experimental section, p. 3096.

that the perchlorate groups are quite strongly co-ordinated to the transition-metal ion. For anhydrous copper perchlorate with C_{2v} symmetry, the absorption at 948—920 cm.$^{-1}$ is assigned to the non-degenerate ClO_2* symmetrical stretching frequency ν_2, that at 1270—1245 cm.$^{-1}$ to the non-degenerate ClO_2* antisymmetric stretching frequency ν_8, that at

Infrared spectra of hydrated and anhydrous copper perchlorate.
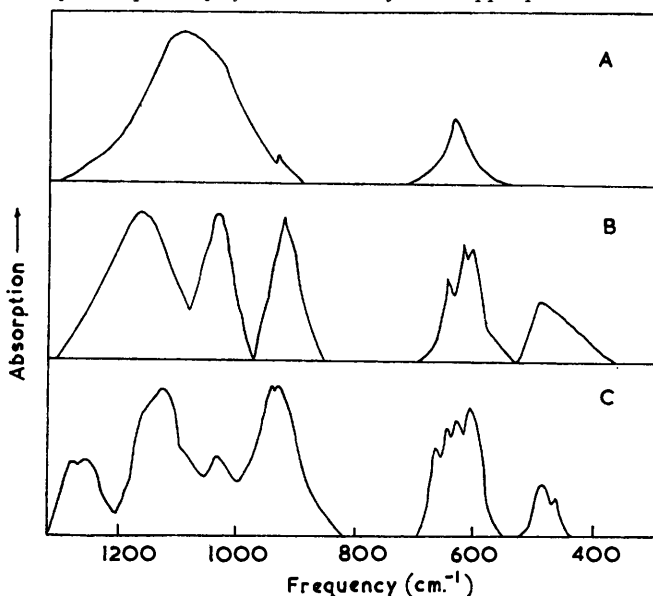
(A) $Cu(ClO_4)_2,6H_2O$.   (B) $Cu(ClO_4)_2,2H_2O$.   (C) $Cu(ClO_4)_2$.

1130 cm.$^{-1}$ to the non-degenerate ClO_2 antisymmetric stretching frequency ν_6, and that at 1030 cm.$^{-1}$ to the non-degenerate ClO_2 symmetrical stretching frequency ν_1. Similar assignments can be made for ferric perchlorate in this region. It is not known why the vibration ν_1 should be so weak compared with the corresponding one of the monodentate perchlorate group. The infrared absorption frequencies in the potassium bromide region of anhydrous copper perchlorate are shown in Table 5 and consist of one strong, four medium, and one weak band. For a bidentate perchlorate group four bands would be expected theoretically in this region, but as there are six some must involve splitting. The two bands at 665 and 647 cm.$^{-1}$ are tentatively assigned to the non-degenerate ClO_2 symmetrical bending frequency ν_3, those at 624 and 600 cm.$^{-1}$ to the non-degenerate rocking frequency ν_7, and that at 497 cm.$^{-1}$ to the non-degenerate rocking frequency ν_9. The weak absorption at 466 cm.$^{-1}$ is assigned to the non-degenerate ClO_2* symmetrical bending

frequency ν_4. The assignment of these vibrations has been made mainly by comparison with the corresponding vibration of the bidentate sulphate ion [7] and sulphuryl difluoride.[8]

The splitting which occurs with anhydrous copper perchlorate and to a smaller extent for the dihydrate may be due to the presence of the ^{35}Cl and ^{37}Cl isotopes of chlorine although in this case it would be expected to be less than 10 cm.$^{-1}$. Alternatively, it may be due to coupling of vibrations between two separate perchlorate ions. A similar coupling occurs with uranyl nitrate hydrate.[12]

EXPERIMENTAL

Determination of Spectra.—A Unicam S.P. 100 infrared spectrophotometer was used for measurements in the sodium chloride region, and a Perkin–Elmer 21 instrument for those in the potassium bromide region. All spectra were for mulls in Nujol (5000—400 cm.$^{-1}$) or hexachlorobutadiene (regions obscured by Nujol).

The mull plates were protected from the mull by thin films of polythene,[13] which was necessary for work with perchlorates as these compounds react with the windows to give the spectrum of the perchlorate ion.

The mull samples were prepared and placed between the potassium bromide plates, and the plates mounted in the plate holder, in a dry box.

Preparation of Compounds.—The normal hydrated transition-metal perchlorates were obtained by standard procedures. The lower hydrates were obtained by heating the normal hydrates under a vacuum to constant weight, at $\sim100°$, with care to avoid decomposition to the basic salt.

Anhydrous copper perchlorate was prepared [1] by the repeated reaction under a vacuum of nitrosyl perchlorate on copper perchlorate dihydrate, followed by fractional vacuum-sublimation of the product at 200° under a vacuum between each reaction. The hygroscopic pale green crystals of anhydrous copper perchlorate were separated from the emerald-green crystals of copper nitrate perchlorate, by hand in a dry box [Found: Cu, 24·1; ClO_4, 75·7. Calc. for $Cu(ClO_4)_2$: Cu, 24·1; ClO_4, 75·9%]. Impure ferric perchlorate was obtained by reaction of nitrosyl perchlorate on anhydrous ferric chloride at 200°: it could not be purified by fractional sublimation but was heated at 180° under a vacuum to decompose the excess of nitronium perchlorate. The residue was a red-brown solid which contained 85% of ferric perchlorate. Analysis gave the formula $Fe(ClO_4)_{2·6}(NO_3)_{0·4},0·2NO_2ClO_4$.

The methyl cyanide complexes of copper,[14] cobalt, manganese, and zinc perchlorate were obtained by treating a suspension of nitrosyl perchlorate in methyl cyanide with the respective metal under reduced pressure for 4—6 hr. The resulting solution of the metal perchlorate in methyl cyanide was then evaporated to dryness under a vacuum to yield the metal perchlorate–methyl cyanide *complexes* [Found: Co, 11·3; ClO_4, 38·0. $Co(ClO_4)_2,C_{12}H_{18}N_6$ requires Co, 11·7; ClO_4, 39·5. Found: Zn, 15·0; ClO_4, 45·5. $Zn(ClO_4)_2,C_8H_{12}N_4$ requires Zn, 15·38; ClO_4, 46·4. Found: Mn, 13·2; ClO_4, 46·7. $Mn(ClO_4)_2,C_8H_{12}N_4$ requires Mn, 13·1; ClO_4, 47·6%].

THE UNIVERSITY, HULL.

[12] Gatehouse and Comyns, *J.*, 1958, 3965.
[13] Vratny, *Appl. Spectroscopy*, 1959, **13**, 59.
[14] Hathaway and Underhill, *J.*, 1960, 3705.