

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF LEICESTER, LE1 7RH, ENGLANDSingle-Crystal Raman and Far-Infrared Study of
Tetramethylammonium Trichloromanganate(II)

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All of the infrared-active and nearly all of the Raman-active fundamentals of $(\text{CH}_3)_4\text{NMnCl}_3$ below 300 cm^{-1} have been observed for single crystals using polarized radiation. An unambiguous assignment is given.

Introduction

Although many spectroscopic studies have been reported for perovskite fluorides, $\text{M}^1\text{M}'\text{F}_3$, and related oxides, no work has been reported for compounds of the type $\text{M}^1\text{M}'\text{Cl}_3$. Many of these complex chlorides adopt a hexagonal structure in which the M' atoms are in octahedral sites formed by chlorine atoms only, thereby differing considerably from the perovskite structure. These sites are so arranged that chains of MCl_6 octahedra sharing opposite faces run through the crystal.¹ In order to emphasize the chain nature of the structure, we chose to work with a tetramethylammonium salt.

$(\text{CH}_3)_4\text{NMnCl}_3$ crystallizes in the hexagonal system with symmetry $P6_3/m (C_{6h}^2)$, $z = 2$.² Thus, there is one chain per primitive cell, with the repeat unit $\text{Mn}_2\text{Cl}_6^{2-}$, which considerably simplifies the spectra. A factor group analysis, carried out using the tables of Adams and Newton,³ is given in Table I. Since the internal vibrations of the cations were of secondary interest to us, we restricted our study to the region below 300 cm^{-1} .

TABLE I
FACTOR GROUP ANALYSIS^a FOR $(\text{CH}_3)_4\text{NMnCl}_3^b$

C_{6h}	Total	A	T	R_+	R_{chain}	N_i	Activity
A_g	3			1	1	1	$xx + yy, zz$
B_g	2		1			1	
E_{1g}	2			1		1	(yz, zx)
E_{2g}	3		1			2	$(xx - yy, xy)$
A_u	3	1	1			1	z
B_u	4			1		3	
E_{1u}	4	1	1			2	(x, y)
E_{2u}	3			1		2	

^a Excluding cation internal modes. ^b A, acoustic modes; T, translatory lattice modes; R_+ , rotatory modes of cations; R_{chain} , rotatory mode of chain; N_i , internal modes of chain.

Experimental Section

Large rose-pink hexagonal rods of $(\text{CH}_3)_4\text{NMnCl}_3$ were grown from concentrated hydrochloric acid solutions of stoichiometric amounts of tetramethylammonium chloride monohydrate and manganous chloride tetrahydrate. For infrared absorption measurements thin slices of crystal cut parallel to the (100) face were polished to a thickness of a few tens of microns.

Raman spectra were obtained with 488.0-nm radiation from a Coherent Radiation Laboratories Model 52A laser. Infrared spectra were obtained using a Beckman-RIIC FS-720 interferometer fitted with a step drive. Infrared reflectance spectra were obtained using a reflectance module FS7RF with the interferometer.

(1) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 374.

(2) B. Morosin and E. J. Graeber, *Acta Crystallogr.*, **23**, 766 (1967).

(3) D. M. Adams and D. C. Newton, *J. Chem. Soc. A*, 2822 (1970); D. M. Adams and D. C. Newton, "Tables for Factor Group Analysis," Beckman-RIIC Ltd., Sunley House, Croydon CR9 4LG, England, 1970.

Results

Infrared Spectra.—The predicted numbers of bands (Table I) were observed (Table II) for both z -polarized ($2 A_u$) and x -polarized ($3 E_{1u}$) radiation. While the lowest frequency bands were sharp in each case (Figure 1), those at *ca.* 170 (z) and 220 (x) cm^{-1} were very

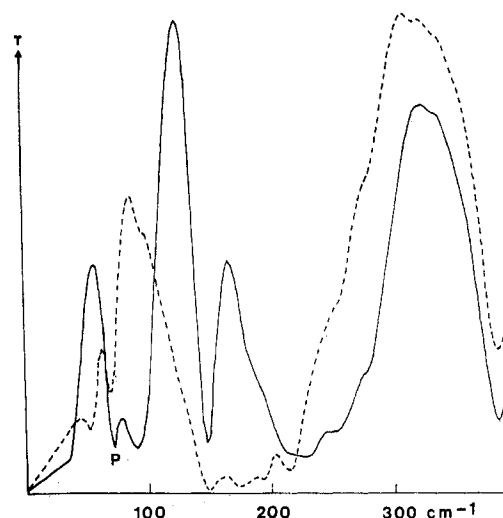


Figure 1.—Infrared absorption spectrum of single-crystal $(\text{CH}_3)_4\text{NMnCl}_3$ at room temperature: ---, electric vector parallel to crystal c axis; —, electric vector perpendicular to c axis; P, absorption due to polythene.

broad. Their appearance is in part due to our inability to obtain sufficiently thin crystal sections, leading to total radiation absorption in the regions of these bands. Some of the structure is probably associated with combination bands and perturbations due to the finite size of the crystal perpendicular to the plane of the slice.

TABLE II
INFRARED VIBRATIONAL FREQUENCIES (CM^{-1}) OF A
SINGLE CRYSTAL OF $(\text{CH}_3)_4\text{NMnCl}_3$

Polarization	Absorption ^a	Reflection	Assignment
x	220 vs, b	224	E_{1u}
z	170 vs, b	170	A_u
x	148 s	148	E_{1u}
x	91 m	91	E_{1u}
z	52 w	52	A_u

^a Abbreviations: vs, very strong; s, strong; m, medium; w, weak; b, broad.

The above complications are absent from the reflectance spectra (Figure 2) which, in each case, show the equivalent number of maxima. (The weak 52-cm^{-1} band was only found clearly in absorption.)

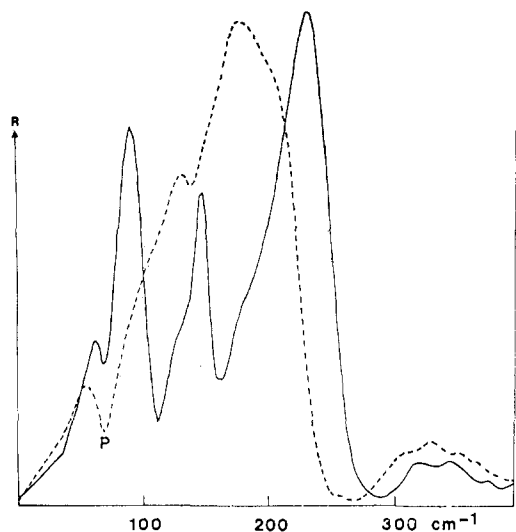


Figure 2.—Infrared reflectance spectrum of single-crystal $(\text{CH}_3)_4\text{NMnCl}_3$ at room temperature: ----, electric vector parallel to crystal c axis; —, electric vector perpendicular to c axis; P, absorption due to polythene.

Raman Spectra.—Initially we examined this crystal at room temperature with 632.8-nm excitation but without success due to very strong fluorescence emission. It proved possible to obtain spectra at liquid nitrogen temperature due to the shift of the fluorescence maximum. However, much better quality spectra were obtained with 488.0-nm excitation (*ca.* 200 mW at the sample) as this line falls at a minimum in the absorption spectrum of the crystal.⁴ No decomposition was noted.

The crystals are strongly dichroic; the intensity of the scattered light was particularly low in those experiments in which the electric vector was parallel to the crystallographic c axis. The Raman frequencies are in Table III. Spectra were recorded at 120°K (488.0 nm) to avoid possible decomposition due to heating by the focused laser beam.

TABLE III
RELATIVE PEAK INTENSITIES IN THE RAMAN
SPECTRUM OF $(\text{CH}_3)_4\text{NMnCl}_3$ AT 120°K^a

Peak, cm^{-1}	$x(zz)y$	$x(zx)y$	$x(yz)y$	$x(yx)y$	Assignment
256	100	14	20	20	A_g
182	10	20	35	100	E_{2g}
129	89	E_{2g}
118	20	100	100	...	E_{1g}
88	40	11	10	38	E_{2g}

^a Spectral slit width 4 cm^{-1} .

Discussion

Assignment of the observed bands or lines to symmetry species of C_{6h} follows clearly from the selection rules. From Table I and the results, it is evident that all of the predicted translatory lattice modes have been observed, *viz.*, E_{2g} at 88 cm^{-1} , A_u at 52 cm^{-1} , E_{1u} at 91 cm^{-1} . The E-type modes are largely due to motion of the cations in a plane normal to the chain axis and, for the E_{2g} mode, will not involve motion of the chain at all. For comparison, the T_{1u} lattice mode associated with cation translation in $[(\text{CH}_3)_4\text{N}]_2[\text{PtCl}_6]$ is at 90 cm^{-1} .⁵

(4) K. E. Lawson, *J. Chem. Phys.*, **47**, 3627 (1967).

(5) D. M. Adams and D. M. Morris, *J. Chem. Soc. A*, 1686 (1967).

While no rotatory lattice modes are predicted in the infrared spectrum, three are required in the Raman spectrum. We have no evidence for them and it is probable that the polarizability changes accompanying cation rotation are small. Thus, in the $x(zz)y$ experiment only one strong line was observed, its frequency being such that it can only be the A_g internal mode of the chain (basically $\nu(\text{Mn}-\text{Cl})$). Other (weak) lines were also found in this experiment but as they are coincident with peaks strong in other orientations, we take them to be residuals.

The only ambiguity lies in the assignment of the single observed E_{1g} line at 118 cm^{-1} , which might be either an internal mode of the chain (see Figure 3) or

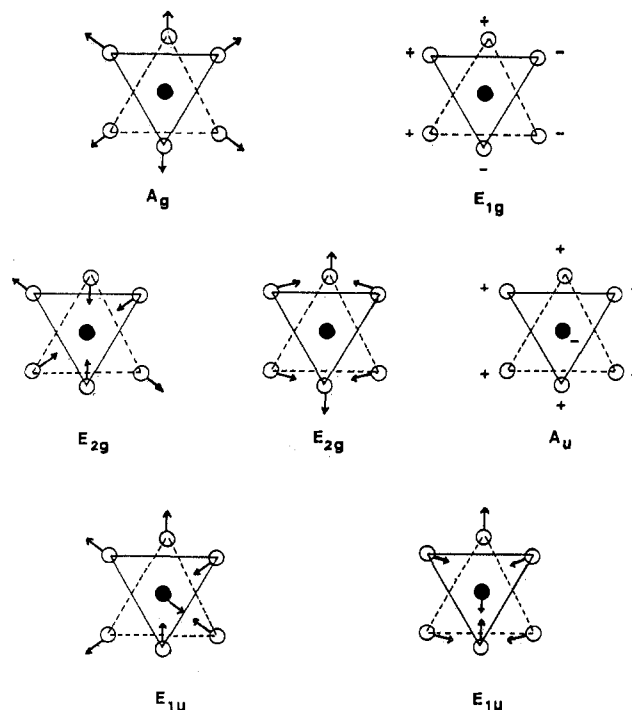


Figure 3.—Approximate form of the normal modes of the $(\text{MX}_3^-)_n$ chain.

the rotatory lattice mode. However, CsNiCl_3 (powder) shows a set of Raman lines at room temperature (267 (m), 196 (vs), 142 (w), 138 (w), 57 cm^{-1} (s)) close to those of $(\text{CH}_3)_4\text{NMnCl}_3$ and clearly cannot exhibit cation rotatory modes. From the crystal structure⁶ the selection rules (Table IV) follow³ and

TABLE IV
FACTOR GROUP ANALYSIS FOR CsNiCl_3^a

D_{6h}	Total	A	T	Rehain	N_i	Activity
A_{1g}	1				1	$xx + yy, zz$
A_{2g}	1			1	0	
B_{1g}	2		1		1	
B_{2g}	0				0	
E_{1g}	1				1	(yz, zx)
E_{2g}	3		1		2	$(xx - yy, xy)$
A_{1u}	0				0	
A_{2u}	3	1	1		1	z
B_{1u}	1				1	
B_{2u}	2				2	
E_{1u}	4	1	1		2	(x, y)
E_{2u}	2				2	

^a Nomenclature as in Table I.

(6) G. N. Tishchenko, *Tr. Inst. Kristallogr., Akad. Nauk SSSR*, **11**, 93 (1955).

show that the same number of Raman- and infrared-active internal modes of the chain are expected for both CsNiCl₃ and (CH₃)₄NMnCl₃. Further, the chain rotatory mode is now inactive. In view of the close correspondence between the Raman spectra of the two compounds we assign the 118-cm⁻¹ line to the E_{1g} internal chain mode of the manganese compound.

Assuming that the corresponding bands in CsNiCl₃ have the same assignment as for (CH₃)₄NMnCl₃ the frequency differences between them are readily explained. The E_{2g} translatory mode falls (88 to 57 cm⁻¹) due to the increased mass of cesium over tetramethyl-

ammonium. The A_g mode can be taken as a measure of M-Cl bond strength because the metal atoms do not move in this vibration. The increase from 256 (Mn) to 267 (Ni) cm⁻¹ can be attributed to ligand field stabilization energy, which is only operative for the nickel complex.

We conclude that all of the internal modes of the (MnCl₃)_n chain have been observed and correctly assigned.

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Vibrational Spectra of Lithium Tetramethylaluminate and Lithium Tetramethylzincate

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Infrared and Raman spectra of lithium tetramethylzincate, Li₂Zn(CH₃)₄, and lithium tetramethylaluminate, LiAl(CH₃)₄, and their isotopic analogs as solids have been measured and assigned. In both complexes, Li-C stretching modes have been observed at around 300 cm⁻¹ in the ir spectra. The local symmetries of Zn(CH₃)₄²⁻ and Al(CH₃)₄⁻ ions are T_d and V_d (D_{2d}), respectively, LiAl(CH₃)₄ seems to form a linear chain analogous to LiAl(C₂H₅)₄.

Introduction

There are several reports concerned with X-ray diffraction studies of -ate complexes.¹⁻⁵ These studies have suggested that the cation-anion interaction is largely ionic. Mach⁶ has reported the infrared spectra of several aluminum anions and has concluded that LiAl(CH₃)₄ and NaAl(CH₃)₄ have C_{2v} symmetry in the solid state.

This paper presents the complete infrared and Raman spectra of LiAl(CH₃)₄ and Li₂Zn(CH₃)₄. These spectra indicate T_d symmetry around both Zn and Li in Li₂Zn(CH₃)₄; LiAl(CH₃)₄ showed V_d symmetry around both Al and Li.

Results and Discussion

Lithium Tetramethylaluminate.—The ir and Raman frequencies of ⁷LiAl(CH₃)₄, ⁶LiAl(CH₃)₄, and ⁶LiAl(CD₃)₄ are given in Table I. Spectra in the pertinent region are shown in Figures 1-3.

In the C-H stretching region, four ir bands arise all of which are Raman active. Three of these are assigned to C-H stretching modes. The band at 2810 cm⁻¹ (unless otherwise noted, the frequencies refer to those for ⁷LiAl(CH₃)₄) is assigned to ν_s(CH₃). The two other bands arise from the splitting of the degenerate ν_{as}(CH₃). These C-H stretching frequencies are low and

comparable to those of methyl groups bonded to electropositive metals such as Li and K and suggest carbanionic character of the methyl groups in LiAl(CH₃)₄.^{7,8} The fourth band (2894 cm⁻¹) is assigned as an overtone of the absorption at 1445 cm⁻¹ in the Raman. In the ir spectrum a weak band was observed at 2166 cm⁻¹. This ir band is absent in the deuterated compound and is absent in the Raman spectrum and is probably due to an impurity.

In the C-H deformation region three ir bands arise; these are also Raman active. The ir band at 1100 cm⁻¹ is split, as observed by Mach.⁶ This band may be assigned to δ_{as}(CH₃).

In the region 500-800 cm⁻¹, four ir bands are observed. The two at 632 and 567 cm⁻¹ are also Raman active and shift to 619 and 526 cm⁻¹, respectively, on substitution of protium with deuterium. The isotopic frequency ratios, ν_H/ν_D, of these bands are 1.02 and 1.08, respectively; these are comparable to 1.06 calculated for Al-CH₃, using a diatomic harmonic oscillator approximation, considering CH₃ as an atom. These are assigned to the Al-C stretching modes in accord with Mach.⁶ The band at 526 cm⁻¹ in the ir spectrum of ⁶LiAl(CD₃)₄ shows a splitting in the Raman spectrum (498 and 518 cm⁻¹) possibly due to a crystal field effect. In the Raman spectrum an intense line appears at 493 cm⁻¹ which shifts to 441 cm⁻¹ (ν_H/ν_D = 1.12) in LiAl(CD₃)₄ and may be assigned to an Al-C stretching mode.

Mach suggested C_{2v} symmetry for LiAl(CH₃)₄,⁶ *i.e.*

(1) R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3**, 872 (1964).

(2) E. Weiss and R. Wolfrum, *Chem. Ber.*, **101**, 35 (1968).

(3) E. Weiss and R. Wolfrum, *J. Organometal. Chem.*, **12**, 257 (1968).

(4) R. Wolfrum, S. Sauerman, and E. Weiss, *ibid.*, **13**, 27 (1969).

(5) J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 2538 (1969).

(6) K. Mach, *J. Organometal. Chem.*, **2**, 410 (1964).

(7) J. Goubeau and K. Walter, *Z. Anorg. Allg. Chem.*, **322**, 58 (1963).

(8) P. Kraemer and J. Goubeau, *ibid.*, **369**, 238 (1969).