Solid-state Studies. Part VI.[1] A Single-crystal Raman Study of the Vibrations of the Tricarbonylchromium Unit in Benzenetricarbonylchromium and Tricarbonyl(1,3-dimethylbenzene)chromium

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The single-crystal Raman spectra of the isomorphous, monoclinic, title compounds are reported. In the 2000 cm^{-1} region a factor group analysis is appropriate. The 500 cm^{-1} region is more complex but the data obtained enable a distinction between alternative assignments to be made.

In recent years we have studied the solid-state vibrational spectra in the 2000 cm^{-1} region of a variety of metal carbonyl species.[2] In general, we have found that vibrational coupling between different molecules is sufficient to require a factor group, rather than a site symmetry approach to the problem. So, in the case of benzenetricarbonylchromium,[3] where the observation of three bands in the i.r. spectra might indicate the applicability of the site symmetry approach, the observation of three *non-coincident* bands in the Raman spectra clearly indicates that the factor group method should be used. This particular compound provides an excellent example because of the existence of a centre of symmetry in the unit cell, leading to a prediction of non-coincidence of Raman and i.r. bands by the factor group method as opposed to the coincidence predicted by the site symmetry approximation. In addition to making qualitative spectral predictions, the factor group method also specifies the symmetry species of the observed bands. We have shown elsewhere, by a simple normal co-ordinate analysis of the benzenetricarbonylchromium problem, that only one assignment of the bands in the 2000 cm^{-1} region is acceptable (the alternative leading to unacceptable values for force and/or interaction constants). The factor group and normal co-ordinate analysis predictions may be simultaneously tested by recording the single crystal polarised i.r. and Raman spectra of the compound. We have not succeeded in making the i.r. measurements although it is possible to obtain polarised data for the weak peaks observed on the lower frequency side of the main peaks. However, discussion of these spectra must await confirmation of the assignment of the bands as due to ^{13}C–O. In contrast, single-crystal Raman data are relatively easily obtained, despite the fairly low oxidative and thermal stability of the compound, and are reported in the present paper. An additional motivation for this work was our recognition that for many metal carbonyl species it is useful to introduce the concept of a vibrational unit cell either of the same volume but of higher symmetry than, or smaller than, the crystallographic primitive unit. Since the bands studied are almost invariably broader than our spectral slit width, single-crystal studies provide the simplest test of our approximation. Single-crystal measurements on some of these compounds will be the subject of future communications; the present work provides, for comparison, data on a system for which such approximations are not needed.

We report high resolution single-crystal Raman studies of the vibrational spectra of the tricarbonylchromium fragments of benzenetricarbonylchromium[3] and tricarbonyl(1,3-dimethylbenzene)chromium.[4] Of these, the latter crystallises in two forms, one monoclinic and one tetragonal. Our crystal-growing conditions produced almost entirely the monoclinic crystals, which were of two different forms, both being identical with the corresponding two crystal forms of benzenetricarbonylchromium except for an angle of 21° between the crystal and indicatrix axes for the 1,3-dimethylbenzene complex as compared with the 23° for the benzene complex (Figure 1). Only one or two extremely thin plates of the tetragonal form, identified by the optic axis conoscopic interference figure, were found. These plates were too fragile to be handled so their single-crystal spectra could not be obtained. Benezenetricarbonylchromium crystallises in the monoclinic space group $P2_1/m$ (C_{2h}^2) with two molecules in a unit cell of dimensions $a = 6{\cdot}17$, $b = 11{\cdot}07$, $c = 6{\cdot}57$ Å and $\beta = 101{\cdot}5°$.[5]

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The space group of the monoclinic form of tricarbonyl(1,3-dimethylbenzene)chromium is either $P2_1/m$ (C^2_{2h}) or $P2_1$ (C^2_2) with two molecules in a unit cell of dimensions $a\sin\beta^* = 6{\cdot}09$, $b = 13{\cdot}07$, $c = 6{\cdot}91$ Å, $\beta = 101{\cdot}5°$. The choice of $P2_1/m$ as the correct space group is suggested by the similarity between both the crystal shape and the spectra of this complex and those of benzenetricarbonylchromium. However, it is instructive to consider both space group possibilities in the spectral analysis, although the similarity of spot pattern and intensities in Weissenberg photographs of the two complexes also suggests that they are isomorphous.

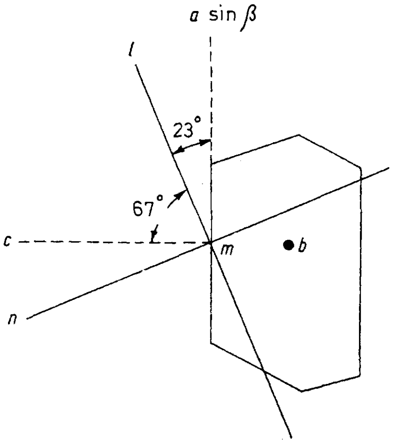

FIGURE 1 Type B single crystal of benzenetricarbonylchromium at extinction (along *l* and *n*)

The vibrational spectra of these complexes have been studied by a number of authors. The solution and solid state i.r. spectra in the carbonyl stretching region have been recorded by Fischer[6] and by Fritz and Manchot.[7,8] Reassignments were made by Adams[9] and Brown and Carroll,[10] the latter authors also discussing the far-i.r. spectra in terms of a simple molecular orbital theory. These complexes have also been the subject of solution[11,12] and solvent effects studies,[13] intensity measurements,[13-15] and further molecular orbital calculations.[16,17] A normal co-ordinate analysis has been reported,[18] as have Raman and far-i.r. data for the solid state.[19] Also, the changes in the vibrational spectra of the co-ordinated arene upon incorporation into the complex have been investigated.[20]

EXPERIMENTAL AND DISCUSSION

Raman spectra were recorded with a Spex 1401 spectrometer and a Spectra-Physics 125 He–Ne gas laser. The power incident on the crystals was usually less than 10 mW and the spectral slit width was *ca.* 2 cm^{-1}. Single crystals were oriented by optical microscopy and the crystallographic axes were identified from Weissenberg *X*-ray photographs.

Both arenetricarbonylchromium compounds were prepared by the method of Nicholls and Whiting;[21] single crystals were grown by slow evaporation from solution in 1 : 1 diethyl ether–di-isopropyl ether. (In this solvent mixture very little oxidation of the compounds occurs on exposure to air.) In the case of benzenetricarbonylchromium two types of crystal were obtained: regular hexagonal plates with edges *ca.* 3 mm and thickness *ca.* 1 mm (type A), and irregular hexagonal plates of similar size (type B). Conoscopic examination indicated that type B crystals are the more suitably oriented; they showed a principal optical indicatrix axis interference figure, whereas type A crystals exhibited an inclined bisectrix figure. We therefore used solely type B crystals for the single-crystal Raman measurements. Figure 1 shows the results of an orthoscopic and *X*-ray examination of a type B crystal. The developed (0*l*0) face contains the *a* and *c* crystal axes and the *l* and *n* optical indicatrix principal axes (the orthogonal, *m* indicatrix axis corresponds to the *b* crystal axis for the monoclinic system). Since no dispersion of the indicatrix *l* and *n* axes was observed under the conoscope in white light, the crystal was cut (and then polished) along *l* and *n*, and these principal optical indicatrix axes (*l, m, n*) were used to define the experimental scattering axes.

In the primitive unit cell each benzenetricarbonylchromium molecule lies on a mirror plane, *i.e.* on a site of C_s symmetry. We have elsewhere detailed a factor group analysis for this compound.[3] For the present purpose it is convenient to choose axes in conformity to crystallographic convention and we therefore take the unique axis in the isomorphous point group (C_{2h}) as y, rather than z.

Considering, initially, only a factor group analysis of the six carbonyl group stretching vibrations, and using the above convention, we obtain the irreducible representations in the isomorphic point group:

$$2A_g{}^0 + B_g{}^0 + A_u{}^0 + 2B_u{}^0$$

The Cartesian axes and products of axes transform as follows:

x^2, y^2, z^2, and xz as A_g
xy and yz as B_g
y as A_u
x and z as B_u

It follows that three Raman-active ($2A_g + B_g$) and three i.r.-active ($A_u + 2B_u$) bands are predicted on the

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basis of the factor group analysis. The vibrational correlations from molecule (C_{3v}) to site (C_s) to factor group (C_{2h}^2) are given in Table 1. The observed spectra (Figure 2 and Table 2) are in agreement with the factor group predictions. The derived polarisability tensor elements (*ll*), (*mm*), (*nn*), and (*ln*) should admit only of modes of A_g symmetry, whilst for the elements (*ml*) and (*mn*) the B_g modes should be active. There is no requirement that the relative intensity of the allowed peaks in, for instance, the (*ll*) spectra should be identical to those in, say, the (*ln*). Recognising the possibility of breakthrough (weak peaks appearing which are formally forbidden for a particular derived polarisability tensor element) we assign peaks as of the symmetry species appropriate to the spectrum in which they, qualitatively, attain maximum intensity. We thus assign the bands at 1864 and 1944 cm^{-1} to the totally symmetric A_g vibrations and the band at 1887 cm^{-1} to the B_g vibration. Very weak bands occur at *ca.* 1829 cm^{-1} in the i.r. and *ca.* 1844 cm^{-1} in the Raman spectra. As mentioned above, such bands may be attributable to ^{13}CO vibrations, although overtone and combination bands may also occur in this region.

TABLE 1

Correlation table for benzenetricarbonylchromium

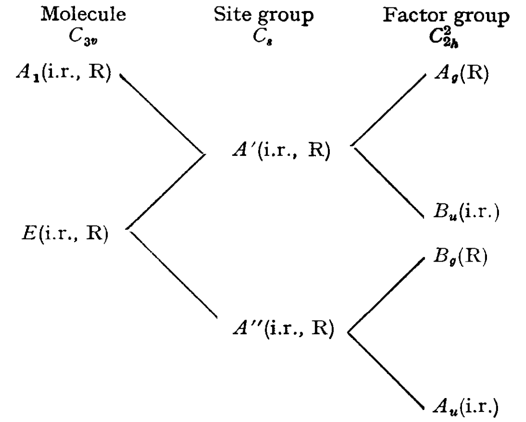

TABLE 2

I.r. and single-crystal Raman frequencies (cm^{-1}) for the carbonyl stretching vibrations of benzenetricarbonylchromium

I.r.		Raman							
			Intensities *						
Solid state	Solution (CCl_4)	Δν	*n*(*ll*)*m*	*n*(*mm*)*l*	*m*(*nn*)*l*	*n*(*ln*)*m*	*n*(*ml*)*m*	*n*(*mn*)*m*	Assignment
1964	1976	1944	28	18	12	3	(3)	(2)	A_g
1878		1887	4	28	19	6	30	65	B_g
	1907								
1860		1864	91	90	37	100	18	13	A_g
ca. 1829 †		*ca.* 1844 †	2			2			

* Peak heights (arbitrary units). † ^{13}CO.

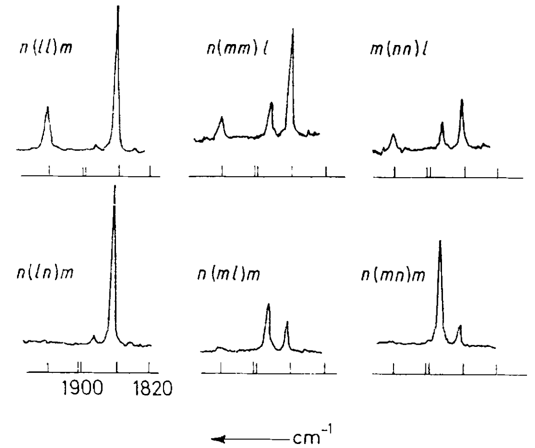

FIGURE 2 Single-crystal Raman spectra of benzenetricarbonylchromium

There are grounds for believing that, despite the observation of no dispersion of the indicatrix axes, these axes may not be entirely appropriate. In the isolated molecule of benzenetricarbonylchromium the molecular indicatrix must be symmetric about the three-fold axis. This axis persists, to a first approximation, in the crystal. Since there are two molecules in a unit cell, related by a centre of symmetry, all of these pseudo-three-fold axes are parallel in the crystal (and are almost coincident with the crystallographic *c* axis). It would therefore seem reasonable to suppose that one axis of the derived polarisability tensors should approximate to the crystallographic *c* (another being symmetry-determined). However, the effect of a rotation about the *b* axis would be to change relative band intensities in the different spectra appropriate to each symmetry species and not to change assignments. In particular, it provides no explanation for the ' breakthrough ' obtained in the present study. From our experience with compounds which crystallise with a morphology such that no cutting is needed, we believe the dominant cause of breakthrough is the errors introduced by cutting (which include partial depolarisation of the laser beam).

For the case of tricarbonyl(1,3-dimethylbenzene)-chromium, if we assume that the space group is $P2_1/m$, the site group and factor group predictions are identical with those for benzenetricarbonylchromium. The spectra are also very similar (Figure 3 and Table 3) and the analyses equivalent, with breakthrough being less pronounced. The bands at 1865 and 1942 cm^{-1} in the Raman spectra are assigned to the totally symmetric A_g vibrations, and the band at 1882 cm^{-1} to the B_g vibration. There appears to be an additional Raman band at *ca.* 1937 cm^{-1} of A_g symmetry which is difficult to assign.

Many of the $M(CO)_3$ complexes we have studied exhibit a similar low frequency shoulder on a high frequency molecular A_1-derived Raman band. In the present case it is not a carbonyl stretching fundamental since all the factor group allowed modes have been assigned. The A_g symmetry suggests that it may be a Fermi resonance-enhanced overtone of the ring breathing mode at 980 cm^{-1} or a combination band from two modes of the same symmetry. There are intense A_g and B_g bands at *ca.* 100 cm^{-1} (see later), and the *ca.* 1973 cm^{-1} peak may be a combination band of one of these modes with a carbonyl stretching fundamental. Yet a further explanation is that the ' peak ' originates in the form of the dispersion relationship for $k \neq 0$, the transition also involving a low frequency lattice mode of the same $|k|$ value but of opposite sign (to preserve the overall $k \approx 0$ condition).

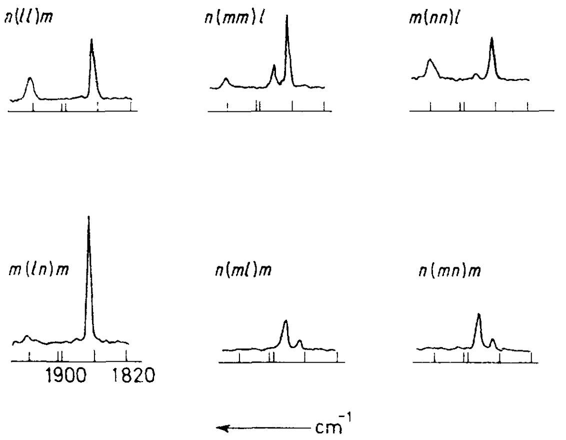

FIGURE 3 Single-crystal Raman spectra of tricarbonyl-(1,3-dimethylbenzene)chromium

TABLE 3

I.r. and single-crystal Raman frequencies (cm^{-1}) for the carbonyl stretching vibrations of tricarbonyl(1,3-dimethylbenzene)chromium

I.r.		Raman							
			Intensities *						
Solid state	Solution (CCl_4)	$\Delta\nu$	$n(ll)m$	$n(mm)l$	$m(nn)l$	$n(ln)m$	$n(ml)m$	$n(mn)m$	Assignment
1954	1970	1942	19	8	18	6			A_g
		1937 †	9	6	12				A_g
1879									
		1882	2	19	15	3	24	29	B_g
1857	1900								
		1865	48	62	35	100	8	9	A_g
ca. 1840 ‡									
		1844 ‡		1		2			
ca. 1824 ‡									

* Peak heights (arbitrary units). † Overtone or combination band. ‡ ^{13}CO.

For the $P2_1$ space group, the C_2^2 factor group analysis predicts six Raman- and i.r.-active bands ($3A + 3B$) with coincidences. This prediction is clearly not in agreement with the observed spectra. A possible complication in $P2_1$ is the occurrence of LO–TO effects, a phenomenon which we have observed in other studies. However, it does not appear in Figure 3. On the other hand, if the tricarbonylchromium unit had pseudo-C_s symmetry, the appropriate factor group becomes isomorphous with the $C_2 \times C_s = C_{2h}$ point group and the factor group analysis is identical with that for $P2_1/m$. The alternative of a C_{2v} factor group may be discarded because of its failure to predict the observed exclusion between i.r. and Raman spectra. An approximate local (molecular) mirror plane is all that is needed to provide the ascent in symmetry to a C_{2h} factor group, provided that these pseudo-mirror planes are parallel or near-parallel; it is not required that they propagate throughout the lattice.

Low-frequency Spectra (4—700 *cm*$^{-1}$).—Although the main objective of the present work was to provide a more critical test of our interpretation of the spectra in the 2000 cm^{-1} region than has hitherto been possible, we have also taken the opportunity to study the low frequency region (4—700 cm^{-1}). The data are given in Table 4. In view of the coupling which may occur between internal modes and of internal lattice modes, together with the added complication of breakthrough effects, no attempt is made at a detailed assignment. The low-frequency powder Raman spectrum of benzenetricarbonylchromium has been reported by Adams and Squire,[19] who proposed an assignment based on a factor group analysis. Their assignment differs from the one suggested by the low-frequency i.r. spectrum and normal co-ordinate analysis of Cataliotti [18] *et al.*, especially in the assignment of the ' metal–carbon ' stretching vibrations. The single-crystal Raman data enable comments on these different assignments to be made.

The correlation table for the relevant modes of the tricarbonylchromium unit is given in Table 5 together with the frequencies assigned to these modes by Adams and Squire.[19] These frequencies are in agreement with those obtained in the present single-crystal study (Table 4). The single-crystal spectra show intense A_g and B_g modes at *ca.* 100—150 cm^{-1}, possibly arising from lattice C–Cr–O, and ring Cr–C bending vibrations. Uncertainty in the total number of bands in the *ca.* 100—150 cm^{-1} region exists because of the breakthrough effects. Adams and Squire have assigned the bands at 486 and 490 cm^{-1} to Cr–CO stretching modes arising from the A_1 and E parent molecular modes respectively and the bands at 537 and 543 cm^{-1} to Cr–C–O bending modes of E parentage. However, Cataliotti *et al.* from their KBr disc i.r. data assigned a band at 537 cm^{-1} to the Cr–CO stretching mode of A_1 molecular origin and bands at 492 and 487 cm^{-1} to the Cr–CO stretching mode of E molecular origin. The single-crystal Raman data reported in Table 4 allow the bands at 487, 491, and 535 cm^{-1} to be assigned to A_g factor group modes, and the band at 545 cm^{-1} to a B_g factor group mode. These polarisation data support the assignment of the 535 and 545 cm^{-1} bands as arising from an E parent molecular mode. Further, the bands at 487 and 491 cm^{-1} must arise from two parent molecular modes, since they are both of A_g symmetry.

TABLE 4

(*a*) Single-crystal Raman spectrum of benzenetricarbonylchromium (below 700 cm^{-1})

	Intensities *					
$\Delta\nu$	$m(ll)n$	$n(mm)l$	$m(nn)l$	$m(nl)n$	$m(lm)n$	$m(nm)n$
42	15	1	32	24		
44					20	
51			26	31	27	119
67	19	22	59	77		
69					35sh	39
72		24			53	25sh
111					268	49
114	310	321	79	109		
135	131	302	480	66	46	114
148	26sh	44sh	53sh	54	20	34sh
299	188	198	314	39	46	71
330						29
333	5	29	21		11	25
335				48		
432						9
487	190		197	37	60	75
491		193	200	36	26sh	58sh
535	8	61	12			
545	8	32			24	17
616	11					
663	5					
665	4	7	115	11		25
668						

(*b*) Single-crystal Raman spectrum of tricarbonyl(1,3-dimethylbenzene)chromium (below 750 cm^{-1})

	Intensities *					
$\Delta\nu$	$n(ll)m$	$n(mm)l$	$m(nn)l$	$n(ln)m$	$n(ml)m$	$n(mn)m$
36		39			44	44
38				22		
42		56			42	
62	9		41	34	5	12
82	9					12
96					168	118
98	61	140		64		
110	195	246	166	110	61	83
117	190	160sh	521	110	48	95
125				41	17	
128	33	30				16
136	13			12		11
202			78	23		
206	11	11	58			16
212					12	10
268		61				
270				8	12	13
316	114	91	197	42	25	39
352		14				17
360	8	15	37	40	8	13
445	7					
462	4					
485	89	53	268	47	27	53
492	38	84	166	45	26	46
520	4	14		7	16	11
538	5	62	20	9	12	14
555					9	
640		10				9
645						8
664			71	9		12
672		14	183	15		25
728	117	25	24	26	13	14

* Peak heights (arbitrary units).

Assignment of the B_g mode in this region cannot be made because of breakthrough, so that A_1 or E parentages remain unknown. However, our data support the suggestion of Adams and Squire rather than that of Cataliotti *et al.* Strong bands at *ca.* 300 cm^{-1} remain unassigned but are presumably to be associated with modes involving the co-ordinated benzene ring.

TABLE 5

Correlations and assignments (Raman) for the low-frequency vibrations of the tricarbonylchromium unit of benzenetricarbonylchromium

Description	Molecule C_{3v}	Site group C_s	Factor group $C_{2h}^2(2)$	Frequencies * (cm^{-1})
ν(Cr–CO)	A_1	A'	$A_g + B_u$	487 (486)
	E	A'	$A_g + B_u$	491 (490)
		A''	$B_g + A_u$	
δ(CrCO)	A_1	A'	$A_g + B_u$	663, 665 668, (664)
	A_2	A''	$B_g + A_u$	(658)
	E	A'	$A_g + B_u$	(640)
		A''	$B_g + A_u$	
	E	A'	$A_g + B_u$	545 (543)
		A''	$B_g + A_u$	535 (537)
δ(CCrC)	A_1	A'	$A_g + B_u$	148, 135 (131) †
	E	A'	$A_g + B_u$	114, 111 (108) †
		A''	$B_g + A_u$	

* Data in brackets are from ref. 8. † Together with δ(ring CrC) and lattice modes.

The low-frequency spectra for tricarbonyl(1,3-dimethylbenzene)chromium are similar to those of benzenetricarbonylchromium. The bands at *ca.* 90—120 cm^{-1} may contribute to the presumed combination band at 1937 cm^{-1}. The comments above on the various assignments of the 'metal–carbon' stretching frequencies are supported by the data for tricarbonyl(1,3-dimethylbenzene)chromium. That is, the bands at 485, 492, and 538 cm^{-1} arise from A_g factor group modes, and the band at 520 cm^{-1} arises from a B_g mode. Although we have not made a detailed study of the 700—1800 cm^{-1} region, an intense benzene ring breathing mode is observed at 980 cm^{-1}.

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