Solid-state Studies. Part V.[1] Raman- and Infrared-active Carbonyl Stretching Vibrations of Three Triphenyltin Complexes

By **H. J. Buttery** and **S. F. A. Kettle,*** School of Chemical Sciences, University of East Anglia, Norwich NOR 88C
G. Keeling, School of Chemistry, The University, Bristol BS8, 1TS
I. Paul, Department of Chemistry, Queen Elizabeth College, London W.8
P. J. Stamper, Department of Chemistry, The University, Southampton SO9 5NH

The solid-state Raman- and i.r.-active carbonyl stretching vibrations of pentacarbonylmanganese-, π-cyclopentadienyldicarbonyliron-, and triphenylphosphinetetracarbonylmanganese-triphenyltin have been analysed by use of a new type of symmetry group, called the *situs* group. Three methods of modifying the crystallographic unit cell to give the vibrational unit cell are outlined. It is shown that even the crystal class of a compound cannot, in general, be inferred from vibrational data.

IN comparison with other vibrations, carbonyl stretching vibrations of transition-metal carbonyl complexes exhibit large factor-group splittings. Previously, it was established that a formal factor-group approach by use of the crystallographic unit cell is frequently at variance with the observed i.r. and Raman spectra of crystalline powders.[1-5] This occurs when both

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[1] Part IV, H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1971, 3148.

[2] Part III, H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1970, 471.

[3] Part II, H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1969, 2224.

[4] Part I, H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1969, 2077.

[5] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *Discuss. Faraday Soc.*, 1969, **47**, 48.

specific interactions between relatively remote vibrational units are effectively zero and symmetry-unrelated nearest-neighbour interactions are essentially equal. Under these circumstances, some of the peaks distinguishable in a full factor-group analysis become superimposed. In particular, it was demonstrated that this situation arises when molecular orientation within the crystallographic unit cell is such that additional symmetry elements ' nearly ' exist, and that selection rules appropriate to a space group containing the new symmetry operation(s) provide a very good first approximation.

In previous papers [1-5] only the solid-state spectra of molecules containing a *cis*-M(CO)$_3$ moiety were considered. In the present work, the solid-state i.r. and Raman spectra of the carbonyl stretching vibrations of pentacarbonylmanganese-, π-cyclopentadienyldicarbonyliron-, and *trans*-triphenylphosphinetetracarbonylmanganese-triphenyltin are analysed. To do so, it is convenient to introduce a new approach which involves the use of vibrational units intermediate to the crystallographic site and factor groups. These vibrational units represent a local environment within the lattice and are associated with symmetry groups which it seems appropriate to call *situs* groups. Any particular example of this type of group can only be associated with an analysis of the vibrational modes of a specific set of internal molecular co-ordinates (in the present context, carbonyl stretching vibrations). The *situs* group describes an isolated pocket containing a small number of molecules and is a solid-state analogue of the idealised local point group.[6] Since the latter concept is widely known and has, in fact, been the fulcrum of the i.r. and Raman spectroscopy of transition-metal carbonyl complexes in dilute solutions,[7] it is to be expected that the former will be useful for the corresponding studies of the solid state.

EXPERIMENTAL

π-$C_5H_5Fe(CO)_2SnPh_3$, $Ph_3SnMn(CO)_5$, and $Ph_3SnMn(CO)_4PPh_3$ were prepared and purified by the method of Gorsich.[8] All gave satisfactory analyses. The i.r. spectra were recorded on Unicam SP 100 (Mark II) and Perkin-Elmer 521 spectrometers. Samples were finely ground before being pressed as KBr discs. Spectra of several analysed samples were recorded. The Raman spectra were recorded by a Spex 1401 spectrometer with He–Ne

TABLE 1

Crystal data for the triphenyltin complexes

Complex	Space group	Unit-cell dimensions/Å *a*	*b*	*c*	β	*Z*
π-$C_5H_5Fe(CO)_2SnPh_3$	$P2_1/c$	17·27	32·86	7·69	95° 10′	8
$Ph_3PMn(CO)_4SnPh_3$	$P2_1/n$	10·45	26·48	12·65	99° 34′	4
$Ph_3SnMn(CO)_5$	$P2_1$	12·17	32·22	11·39	90° 33′	8

TABLE 2

Vibrational frequencies/cm^{-1} of Raman- and i.r.-active solid-state CO vibrations for the triphenyltin complexes

Complex	Raman	I.r.	
π-$C_5H_5Fe(CO)_2SnPh_3$	2002	1989	
	1990	*ca.* 1986	
	1947	1937	
	1933	1927	
$Ph_3PMn(CO)_4SnPh_3$	2046	2040	
	1991	1984	
	1957	*ca.* 1950	
	1951	1941	
		Room temp.	Liq. N_2 temp.
$Ph_3SnMn(CO)_5$			*ca.* 2096
	2094		2094
	ca. 2091	2091 *	
	ca. 2086 *	*ca.* 2087 *	*ca.* 2088 *
	2026	*ca.* 2028	2032
	2022		
	2014	2014	2016
	2011		
	ca. 2004	*ca.* 2000	2001
	1992	1996	1997
	1987		*ca.* 1989
		1981	1981
	1975	1976	1975
			ca. 1968
	1958	1954	1954

* Weak peaks which are not explained by a simple factor-group model.

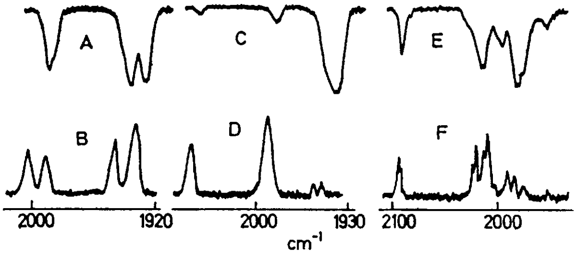

FIGURE 1 Solid-state spectra of the triphenyltin complexes: A, i.r. of π-$C_5H_5Fe(CO)_2SnPh_3$; B, Raman of π-$C_5H_5Fe(CO)_2SnPh_3$; C, i.r. of $Ph_3PMn(CO)_4SnPh_3$; D, Raman of $Ph_3PMn(CO)_4SnPh_3$; E, i.r. of $Ph_3SnMn(CO)_5$ (room temperature); and F, Raman of $Ph_3SnMn(CO)_5$

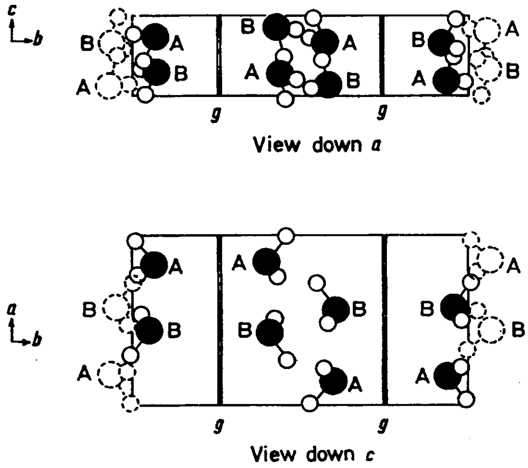

FIGURE 2 π-$C_5H_5Fe(CO)_2SnPh_3$ showing the packing in the unit cell. The projection is down the *c**-axis. Only Fe–O vectors are shown

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[6] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

[7] S. F. A. Kettle and I. Paul, *Adv. Organometallic Chem.*, 1972, **10**, 199.

[8] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.

laser excitation (632·8 nm). Samples were mounted in glass capillary tubes. No spectrum from the glass was recordable. Neon discharge lines were used for calibration. Before spectra were run, all samples were either recrystallised or sublimed. Solid-state i.r. and Raman spectral data are presented in Table 2 and Figure 1. Space-group and unit-cell parameters are in Table 1.

RESULTS AND DISCUSSION

π-Cyclopentadienyldicarbonylirontriphenyltin crystallises with eight molecules in a monoclinic unit cell[9] with space-group $P2_1/c$ (Table 1, Figure 2). This structure is of particular interest in that each asymmetric unit contains two independent molecules with different conformation (A and **B** in Figure 2), which are not related by any symmetry operation. Although the arrangement of ligands around the iron atom is the same for each molecule of the asymmetric unit, A and B differ both in the orientation of the phenyl rings with respect to the metal–metal axis, and also in the relative orientation of the groups around this axis.[9] The $Fe(CO)_2$ fragments of each molecule, however, are very similar (*ca.* 5% difference between C–Fe–C angles, with individual A and B C–Fe and C–O distances being almost identical) and, for the purpose of a vibrational analysis, may be assumed to be identical.

The maximum symmetry that the molecule may show in solution is C_s, for which two coincident i.r.- and Raman-active modes are expected. In the solid state, four peaks are observed in both the i.r. and Raman spectra with, most probably, no coincidences (Table 2, Figure 1). A site-group analysis, which predicts two coincident i.r.- and Raman-active modes (or four coincident bands if it is assumed that peaks associated with molecules A and B are not superimposed), is evidently inadequate. Alternatively, on the basis of a full factor-group analysis (C_{2h}^5) eight non-coincident bands are to be expected in each spectrum (i.r., $4A_u + 4B_u$; Raman, $4A_g + 4B_g$). This is also unsatisfactory. Low-temperature i.r. studies did not produce any additional bands in the spectrum, although the shoulder at *ca.* 1986 cm^{-1} was further resolved.

As with previous cases,[1,3,5] a detailed study of the molecular packing within the crystal helps to resolve the difficulty. The crystal may be described as consisting of chains of molecules interrelated by glide planes (Figure 2). Since intermolecular interactions decrease rapidly with increasing internuclear distance, only those carbonyl groups which are in close proximity are expected to interact strongly. In addition, from a knowledge of the crystal structure[9] it appears reasonable to assume that intermolecular coupling of carbonyl groups *via* other non-carbonyl ligands is negligible. Consequently, on the basis of these two assumptions and for the purpose of the present discussion, it is only necessary to find a primitive unit of any one of these chains of molecules. Figure 2 shows that this unit consists of two pairs of molecules, one of type A and the other of type B, and represents the vibrational unit cell for this system. This description is strongly supported by the appropriate interatomic distances. Between neighbouring carbonyl sets within any chain, interoxygen distances lie in the range 3·10—3·25 Å whereas those between chains are greater than 13 Å. The molecules of each pair are symmetry-related by a centre of inversion. Therefore, the vibrational factor group is isomorphous to the point group C_i, and an analysis based upon it leads to the prediction of four bands in each spectrum with no coincident frequencies (i.r., $4A_u$; Raman, $4A_g$), in agreement with the observed spectra (Figure 1).

In that the volume of the vibrational unit cell is half that of the crystallographic unit cell, this analysis is similar to that of hexamethylbenzenetricarbonylchromium.[3] However, the reduction in volume results from quite different sources. The salient difference is that specific nearest-neighbour carbonyl interactions are effectively zero in this system whereas with the chromium complex similar carbonyl interactions are essentially equal. In cases such as the latter, these conditions are concisely accounted for by incorporating additional symmetry elements within the lattice.[1-3,5] In contradistinction, effectively zero nearest-neighbour interactions can only be accounted for, in the present analysis, by the isolation of units within the crystal. This is equivalent to removing symmetry elements from the lattice (*viz.*, glide planes) and considering only the immediate locality of the relevant molecules. This reasoning is closely related to that which led to the introduction of the idealised local point group,[6] extensively and successfully used in spectroscopic studies of transition-metal carbonyl complexes.[7] It seems appropriate, therefore, to refer to this new type of isomorphous point group as the *situs* group.

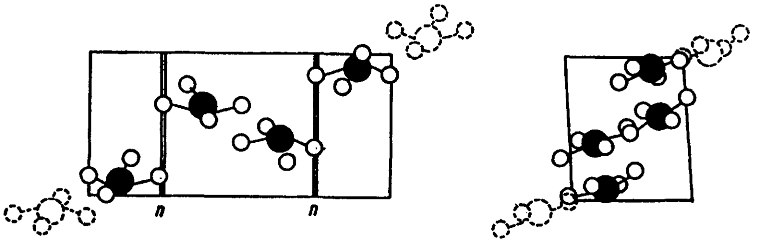
The space group of *trans*-triphenyltintriphenylphosphinetetracarbonylmanganese is $P2_1/n$ with four molecules per unit cell[10] (Table 1, Figure 3). The four symmetry-related molecules are required, therefore, to occupy general positions of site symmetry C_1. As each asymmetric unit posseses only one molecule, an analysis based upon the site group leads to the prediction of four coincident i.r.- and Raman-active carbonyl stretching vibrations ($4A$). From a formal factor-group analysis (C_{2h}^5), 16 vibrational modes either i.r.- ($4A_u + 4B_u$) or Raman- ($4A_g + 4B_g$) active are to be expected. In practice, the two spectra are non-coincident and four peaks are observed in both. Clearly, neither the site-group nor the factor-group analysis is appropriate.

Once again a detailed examination of the molecular packing within the crystal sheds some light upon the problem. The crystal can be described as consisting of pairs of molecules interrelated by the presence of glide planes (Figure 3). If the two conditions applicable to the previous example are also relevant to the present system, as appears to be the case, a primitive vibrational unit cell can be chosen such that it contains two pairs of

[9] R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 192.

[10] R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 172.

molecules which lie, for the purposes of the present discussion, in isolated pockets. Consequently, the vibrational unit cell can be assumed to consist of two molecules symmetry related by a centre of inversion. The corresponding *situs* group is C_i^1 and an analysis based upon it leads to the prediction of four bands in both the i.r. and Raman spectra with no common frequencies (i.r., $4A_u$; Raman, $4A_g$). This is in excellent agreement with the observed spectra (Figure 1). The relatively broad absorption at *ca.* 1946 cm^{-1} was further resolved into two bands at lower temperature (Figure 1).



Projection onto *bc* plane

Projection onto *ac* plane

FIGURE 3 The arrangement of molecules in the unit cell of $Ph_3PMn(CO)_4SnPh_3$. Only Mn–O vectors are shown

Previous studies [10,11] indicate that the local molecular symmetry of this complex is approximately C_{4v} for which two i.r.-active stretching vibrations are expected in solution ($A_1 + E$). However, even in solution a weak peak arising from the formally i.r.-inactive $B_1(C_{4v})$ mode is observed, indicating that distortion from the idealised C_{4v} geometry is small but significant. In addition, the A_1 vibration, although formally allowed, has a low i.r. intensity since the net dipole-moment change along the molecular *z*-axis is small. In solution, peaks observed to be strong in the i.r. spectrum are weak in the Raman and *vice versa.* Further, these features persist into the solid state indicating that there is little mixing of the free-molecule modes under the lower symmetry in the crystal lattice.

Triphenyltinpentacarbonylmanganese crystallises with eight molecules in a non-centrosymmetric monoclinic unit cell [12] (Table 1, Figure 4). Its space group $P2_1$ requires that the molecules occupy four sets of general positions of site symmetry C_1. That is, each asymmetric unit possesses four symmetry-unrelated molecules.[13] In order to simplify the discussion, the asymmetric unit we have chosen differs from that used by Weber and Bryan.[12] A site-group analysis leads to a prediction of 20 peaks which are both i.r.- and Raman-active ($20A$). A formal factor-group analysis (C_2^2) leads to an expectation of no fewer than 40 peaks, active in both processes ($20A + 20B$). Although it is difficult to assess the total number of bands, owing to their concentration into such a small frequency range, at least eight i.r. and eight Raman bands are observed at room temperature (Table 2). On cooling the sample with liquid nitrogen, additional peaks are detected in the i.r. spectrum. In certain regions (*e.g., ca.* 2025 cm^{-1}) non-coincident frequencies are observed possibly indicating a centrosymmetric vibrational unit cell. However, with such a large number of peaks occurring within *ca.* 150 cm^{-1}, it is impossible to be conclusive, although it is obvious that neither the site-group nor a formal factor-group analysis leads to predictions which are consistent with the experimental data.

In order to resolve this problem, it is necessary to consider again the molecular packing within the unit cell. Figure 4 shows that the eight $Mn(CO)_5$ moieties of each unit cell fall into two distinct pockets, each containing four molecular fragments. Since the intermolecular separation within each pocket or asymmetric unit is small in comparison with that between pockets, the molecular interactions within the asymmetric unit are most probably the significant ones in determining the vibrational unit cell. In other words, for our purposes, the presence of the crystallographic two-fold screw axes can be ignored. Apart from slight differences in the orientation of one phenyl group, which makes them identical in pairs, the four molecules in the asymmetric unit are equivalent. Indeed, the dispositions of molecules within each pocket is such that considerable non-crystallographic symmetry exists. A complete list of the relevant symmetry elements is given in Table 3.

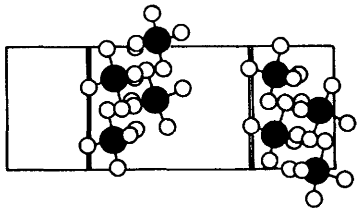


FIGURE 4 The unit cell of $Ph_3SnMn(CO)_5$ in the (001) projection

As the role of such elements in the analysis of vibrational spectra has been discussed at length,[1-3,5] it is sufficient to incorporate them and conclude that, for the present case, the locality of the four molecules of

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[11] L. M. Bower and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 706.

[12] H. P. Weber and R. F. Bryan, *Acta Cryst.*, 1967, **22**, 822.

[13] 'International Tables for *X*-Ray Crystallography,' vol. I, eds. N. F. M. Henry and K. Lonsdale, Kynoch Press, Birmingham, 1965.

each asymmetric unit can be associated with the vibrational unit cell. Because of the slight deviations of these unit-cell axes from orthogonality, the non-crystallographic symmetry elements are not propagated throughout the lattice by primitive translations.[12] When the *situs* group approach is used, however, this feature is irrelevant so that the presence of a two-fold screw axis parallel to *c*, an *a*-glide plane perpendicular to *c*, and a centre of inversion can be assumed. The resulting *situs* group C_{2h}^5 leads to a prediction of only ten bands in each spectrum (i.r., $5A_u + 5B_u$; Raman, $5A_g + 5B_g$; no coincidence) in very good agreement with experimental data.

TABLE 3

Orientation of the real and pseudo-symmetry elements of $Ph_3SnMn(CO)_5$

Symmetry element	Orientation
Axial glide plane ($t_x = \frac{1}{2}$)	$\perp c$
Diagonal glide plane ($t_y = \frac{1}{2}$, $t_z = \frac{1}{4}$)	$\parallel bc$
Diagonal glide plane ($t_x = \frac{3}{4}$, $t_z = \frac{3}{4}$)	$\perp b$
Two-fold screw axis ($t_x = \frac{1}{4}$)	$\perp bc$
Two-fold screw axis ($t_z = \frac{1}{2}$)	$\parallel c$
Centres of symmetry	
Two-fold screw axis *	$\parallel b$

* Crystallographic symmetry element (t_i represents the translational operation).

As in the previous example, the vibrational spectra of solid triphenyltinpentacarbonylmanganese can be tentatively assigned by correlation of the relative intensities of the crystal vibrations with those of the parent molecular vibrations. The local symmetry of the $Mn(CO)_5$ fragment is C_{4v}, for which three i.r.- ($2A_1 + E$) and four Raman- ($2A_1 + B_1 + E$) active modes are expected in solution. In fact, of those in the i.r. spectrum the higher-energy $A_1(A_1^{(2)})$ and B_1 vibrations are weak, and the lower energy $A_1(A_1^{(1)})$ and E modes are strong; in the Raman spectrum, the B_1 vibration is strong and the E mode very weak.[11,14-18] Assuming negligible interaction of the free-molecule modes under the lower symmetry in the crystal lattice, we also expect crystal vibrations derived from weak molecular vibrations to be weak and *vice versa*.

The crystal modes derived from the high-energy $A_1^{(2)}$ molecular vibration (*ca.* 2094 cm^{-1}) are relatively easy to assign. The two bands expected in both the i.r. and Raman spectrum are observed.[19,20] Although it is expected that these bands will all have different frequencies, the energy separation is not sufficient to be conclusive. Definite resolution of the main i.r. absorption only occurs at lower temperatures.

The lower-energy region is much more complex and the crystal modes occurring in this region (*ca.* 2040—1950 cm^{-1}) are more difficult to assign. The parent molecular vibrations (B_1, E, $A_1^{(1)}$) are expected to generate 16 peaks, consisting of eight non-coincident i.r. and Raman-active carbonyl modes. The observed spectra are in agreement with these predictions with regard to numbers of bands, but the frequencies are too close to make conclusions about coincidences. For both the i.r. and Raman spectra, the relative intensities of the band sets indicate that crystal vibrations derived from the molecular E vibration occur in the range 2005—1950 cm^{-1} and those derived from the molecular B_1 vibration are found in the region 2040—2005 cm^{-1}, since the relative intensities in these regions approximately correspond to the intensities of the parent molecular vibrations. Within the context of this interpretation, the small frequency separations between the i.r.- and Raman-active vibrations probably indicate small intermolecular coupling constants.

Conclusion.—Although with improved resolution, or for single-crystal studies with polarised radiation, a formal factor-group approach may be necessary, the current approaches appear to have the merit of allowing a rationalisation of the vibrational spectra of molecular species in the solid state.

It is evident that the crystallographic unit cell can be modified for vibrational purposes in at least three ways. First, owing to the near-equality of specific nearest-neighbour interactions simulating the existence of additional symmetry elements, a vibrational unit cell of higher symmetry than the crystallographic unit cell can result. In some cases, it may even be of smaller volume. Secondly, if appropriate nearest-neighbour interactions approximate to zero, some crystallographic symmetry elements may not be apparent in the vibrational spectra. Consequently, a vibrational unit cell of lower symmetry than that of the crystallographic unit cell may result. Where it does, it may be convenient to work in terms of an approximate group, which we have called the *situs* group, describing the symmetry of the relevant crystal locality. Invariably, this vibrational unit cell will be of smaller volume than its crystallographic counterpart. Thirdly, owing to the concurrent existence of the two types of nearest-neighbour interaction, a vibrational unit cell of higher symmetry but of smaller volume than that of the crystallographic unit cell may result.

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[14] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.

[15] J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1195.

[16] N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, 1968, **7**, 94.

[17] F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, 1967, **6**, 1357.

[18] R. J. H. Clark and B. C. Crosse, *J. Chem. Soc.* (*A*), 1969, 224.

[19] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 2844.

[20] B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc.* (*A*), 1968, 522.