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Solid State Studies.
Pt. XVI. The ν(CO) Vibrational Spectra of η^5-$C_5H_5Fe(CO)_2M(C_6H_5)_3$, M = Sn, Ge

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Pure and mixed crystal studies and intensity calculations have been carried out on the ν(CO) features of η^5-$C_5H_5Fe(CO)_2M(C_6H_5)_3$, M = Sn, Ge. This work demonstrates the presence of intermolecular vibrational coupling and supports the proposal that the vibrational unit cell of the tin compound is one half of the crystallographic.

Introduction

The interpretation of the vibrational spectra of crystalline η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ in the 2000 cm^{-1} region poses a fascinating problem. The symmetric and antisymmetric ν(CO) features are well separated in solution spectra and so the interpretation of the crystal spectra would be expected to be straightforward. In practice, the interpretation is far from simple and is the subject of the present communication.

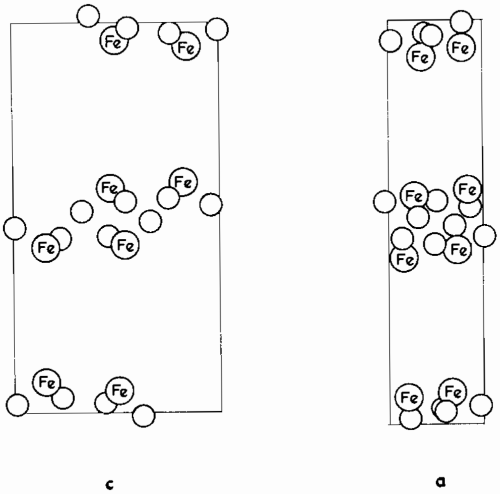

Figure 1. The unit cell of η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ viewed down the *c* and *a* axes. Each CO group is represented by a single circle.

TABLE I. Correlation of Idealised Molecular, Site and Factor Group for η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$.

Molecular Point Group C_2	Site Group C_1	Factor Group C_{2h}^5
A (I.r. Raman)	A (I.r. Raman)	A_g (Raman) B_g (Raman) A_u (I.r.) B_u (I.r.)
B (I.r. Raman)		

Firstly, in the crystal structure it is found that the CO groups are layered (Figure 1) [1]. Secondly, the CO groups are oriented in rather special ways, which are such that some allowed crystal modes are expected to be of rather low intensity. Thirdly, there are two types of non-crystallographically equivalent molecules in each unit cell.

Results and Discussions

The molecule crystallises in the $P2_1/C$ space group with Z = 8 [1]. The factor group predictions and correlations with both site and molecular point group are detailed in Table I. A full factor group analysis predicts eight infrared and eight non-coincident Raman bands. A site group analysis, on the other hand, predicts either two coincident infrared and Raman peaks or four coincident features depending on whether or not the two crystallographically distinct molecules are also vibrationally distinct. The explanation previously advanced was that the vibrational unit cell is one half of the crystallographic [2]. The basis of this explanation is evident from Figure 1.

The infrared and Raman spectra of crystalline samples are shown in Figures 2 and 3; frequencies are detailed in Table II. Of the four strong features in each spectrum, two are clearly coincident and one

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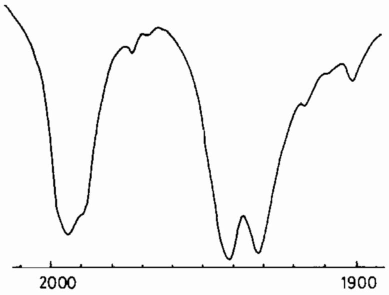

Figure 2. 95 K temperature ν(CO) KBr disc I.R. spectrum of η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$.

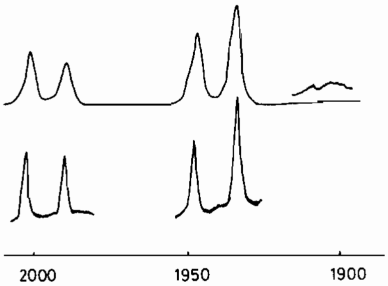

Figure 3. Room temperature (upper trace, 2 cm^{-1} resolution) and 95 K (lower trace, 0.8 cm^{-1} resolution) ν(CO) Raman spectra of polycrystalline η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$.

TABLE II. (CO) Vibrational Spectra (cm^{-1}) of η^5-C_5H_5-$Fe(CO)_2Sn(C_6H_5)_3$. Relative intensities are given in brackets.

Room temperature		95 ± 5 K	
I.r.	Raman	I.r.	Raman
	2002 (5.8)		2004 (4.5)
		1998 sh	
1995 (8.3)		1995 (5.8)	
~1990 sh	1990 (4.6)	1900 (5.8)	1900 (4.6)
1973 (0.8)		1974 (0.8)	
1967 (0.4)		~1967 (0.4)	
	1946 (8.4)		1947 (5.7)
1942 (10)		1941 (10)	
1934 (9.6)	1934 (10)	1932 (9.6)	1933 (10)
1916 (0.8)		1916 (0.8)	
			1913 vw
1908 (0.4)			
1902 (1.2)		1902 (1.2)	1903 vw
	Solution (CH_2Cl_2)		
		I.r.	Raman
		1995	1996
		1944	1945

in each is clearly non-coincident*. Irrespective of whether the coincidences are accidental or not, the observations are in accord with neither the factor nor site group models.

The apparent absence of any model which can account for the observations prompted us to consider a variety of possibilities. Is it possible, for instance, that factor group effects occur for one set of crystallographically related molecules but not for the other? If this occurs it would go at least some way towards an acceptable explanation. Further, detailed examination of the crystal structure revealed an interesting pseudo-symmetry which might be responsible for a low intensity in what are formally allowed bands.

The present paper therefore falls into two sections. Firstly, an account of an experimental study aimed at determining whether or not all bands are affected by factor group effects. Secondly, a study of the consequences of the pseudo-symmetry.

In previous papers in this series we have demonstrated that vibrational coupling can occur between ν(CO) vibrators in mixed crystals of metal carbonyl derivatives [3]. Strong coupling is indicated by one mode behaviour, in which a single feature, similar in profile to that of the corresponding band of either pure component, occurs at a composition-dependent frequency. Two mode behaviour, in which the individual molecular features appear little changed in profile or frequency, typifies the absence of intermolecular vibrational coupling. Broadened peaks typify the intermediate-mode region, in which intermolecular coupling is comparable to zeroth order molecular frequency differences.

In the present study we have prepared and studied the effects of the incorporation of the compound η^5-$C_5H_5Fe(CO)_2Ge(C_6H_5)_3$ in the lattice of the tin compound. The crystal structure of the germanium compound is very similar to that of the tin [4], with the exception that all molecules in the lattice are symmetry-related. X-ray powder studies show that mixed tin–germanium crystals crystallise in the lattice of the tin compound. Whilst our mixed crystal technique is applicable to the interpretation of infrared spectra, its application to ν(CO) Raman spectra is usually much more productive. This is because the band-widths of Raman spectral bands of metal carbonyls in the 2000 cm^{-1} region are almost always much less than that of their infrared counterparts, enabling frequency and profile changes to be more accurately studied.

In Figures 4 and 5 we give the infrared and Raman spectrum of η^5-$C_5H_5Fe(CO)_2Ge(C_6H_5)_3$. Figure 6 shows the spectrum of an approximately 50–50 mixture of pure crystals of the tin and germanium compounds. The two spectra are very similar and accidental coincidences occur (Table III). The Raman spectrum of a mixed crystal containing *ca.* 5% of the

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*The present work using calibrated spectra, has revealed a systematic error in previous infrared data.

Figure 4. Room temperature ν(CO) Raman spectra of polycrystalline η^5-$C_5H_5Fe(CO)_2Ge(C_6H_5)_3$.

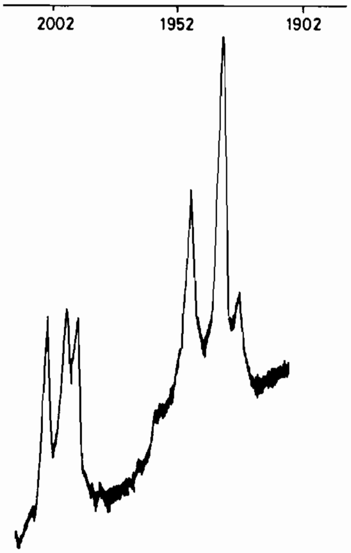

Figure 5. Room temperature ν(CO) KBr disc i.r. spectrum of η^5-$C_5H_5Fe(CO)_2Ge(C_6H_5)_3$.

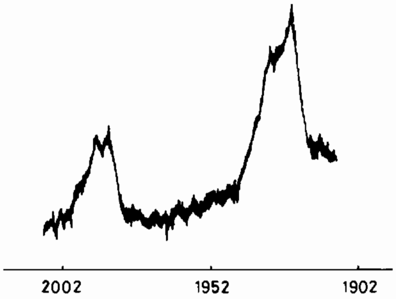

Figure 6. Room temperature ν(CO) Raman spectrum of a *ca.* 1:1 mixture of polycrystalline samples of η^5-$C_5H_5Fe(CO)_2M(C_6H_5)_3$ (M = Sn, Ge).

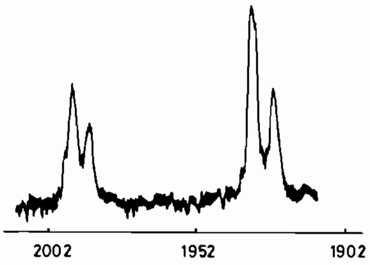

Figure 7. Room temperature ν(CO) Raman spectrum of a mixed crystal containing *ca.* 5% η^5-$C_5H_5Fe(CO)_2Ge(C_6H_5)_3$ in η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$.

TABLE III. Comparison of ν(CO) Raman Spectral Frequencies of Pure, Mixture and Mixed Crystals of η^5-$C_5H_5Fe(CO)_2M(C_6H_5)_3$, M = Sn, Gr.

M = Sn (Fig. 3)	M = Ge (Fig. 4)	Mixture of crystals M = Sn, Ge (Fig. 6)	Mixed crystal M = Sn, Ge (Fig. 7)
2002		2002	
	1994	1994	1996 (sh,br)
1990	1989	1990	1990 (br)
			1985
1946		1946	
1933	1933	1933	1931 (br)
	1926	1926	1924 (br)

germanium compound is shown in Figure 7. A comparison of Figures 6 and 7 clearly demonstrates the band broadening which has occurred, typical of intermediate mode behaviour, and leads us to conclude that all of the ν(CO) vibrators in the lattice are involved in intermolecular vibrational coupling. Evidently, the observed spectrum is not to be explained in terms of isolated molecular vibrations; in the lattice of the tin compound the molecules on non-crystallographic related sites are sufficiently similar for vibrational coupling to occur between them. Indeed, this would be expected, for the major geometric difference between the two independent molecules lies in the orientation of their phenyl groups.

Because of the previous indictment of the molecular separations as responsible for the observed spectral pattern we built a scale model of the unit cell. From this model it was clear that the positions of the CO units are related in a way beyond that required by the space group.

Within the crystal it is possible to define two sets of planes such that each CO group in the crystal lies approximately in one of them, both types of molecule contributing to each plane. Further, within any one unit cell, the disposition of CO groups is such that they approximately define a diagonal plane of a cube within the plane.

These patterns mean that no combination of CO group vibrations from groups within any one set of parallel planes has a non-zero component out of the plane. Not surprisingly, this situation manifests itself in spectral simplifications.

The oriented gas model was used, using the crystal structure data with dipoles along each CO axis, to predict relative infrared intensity patterns, using x and y axes indicated by vector addition of molecular contributors to the factor group mode. The predicted

TABLE IV. Predicted ν(CO) Relative Infrared Intensities.

A mode-derived region		B mode-derived region	
A_u	0.0	A_u	0.0
A_u	7.3	A_u	0.5
B_u	5.7	B_u	6.1
B_u	1.6	B_u	10.0

relative intensities are given in Table IV; just four strong bands are predicted.

As in the previous paper we have made Raman intensity calculations for the present compounds. Unlike the infrared case for which axial directions are evident, the intensities varied with assumed coupling model and, in general, gave indifferent predictions. It is to be noted, however, that the relative total intensities in the A-mode and B-mode-derived regions were independent of the model employed and, by appropriate choice of b/a could be made to give agreement with experiment. This b/a value was similar to that found in the previous paper (−0.85).

Conclusions

Several lines of evidence must be assembled to enable a qualitative rationalisation of the ν(CO) spectra of crystalline η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$.

1) Mixed crystal data demonstrate that intermolecular vibrational coupling occurs.

2) The presence of just four infrared features occurs as a result of a pseudo symmetry in the unit cell which is in addition to the division of the unit cell into two disparate vibrational units.

3) The corresponding germanium compound with a crystallographic unit cell which is, essentially, one half of that of the tin compound has very similar infrared and Raman spectra.

The original postulate that the vibrational unit cell of the tin compound is one half of that of the crystallographic is consistent with all of these pieces of evidence (although it is not *required* by the infrared calculations). However, it is evident that the additional symmetry revealed in our infrared calculations may also be important; unlike the 'half cell' model the additional symmetry feature does not require an infrared and Raman exclusion. Nonetheless, a problem which remains is that of the coincidence of two infrared and Raman features; however, the data from the germanium compound, showing a different pattern of near-coincidences, suggest that this may be accidental.

Experimental

The compound η^5-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ was prepared by the literature methods [4], the germanium compound was prepared in an analogous manner. Spectra were recorded on a P.E. 325 in 0.1% KBr discs at *ca.* 0.6 cm^{-1} resolution and on a Spex 1401 Raman spectrometer with either 15.454 kK or 17.599 kK radiation at *ca.* 10 mW incident power and 2 cm^{-1} resolution.

Acknowledgement

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References

1 R. F. Bryan, *J. Chem. Soc. A*, 192 (1967).
2 H. J. Buttery, S. F. A. Kettle, G. Keeling, I. Paul and P. J. Stamper, *J. Chem. Soc. Dalton*, 2487 (1972).
3 D. N. Kariuki and S. F. A. Kettle, *Inorg. Chem., in press.*
D. N. Kariuki and S. F. A. Kettle, *J. Chem. Soc. Dalton*, in press.
D. N. Kariuki and S. F. A. Kettle, *J. Raman Spec.*, *6*, 319 (1977).
4 C. C. Tso (personal communication).
5 D. S. Field and M. J. Newlands, *J. Organometal. Chem.*, *27*, 213 (1971).