

Solid State Studies.

Part XIII. Tris(diphenylacetylene)tungsten Monocarbonyl, a Species Showing no $\nu(\text{CO})$ Factor Group Splitting

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In orthorhombic tris(diphenylacetylene)tungsten monocarbonyl the coincidence between infrared and Raman features, ^{13}C CO enrichment studies and peak intensities indicate the absence of factor group effects in the $\nu(\text{CO})$ region. The $\nu(\text{CO})$ features associated with crystallographically non-equivalent molecules are separated by ca. 9 cm^{-1} .

Introduction

It is now clear that in the $\nu(\text{CO})$ region crystalline metal carbonyl species exhibit factor group splitting (*i.e.* intermolecular vibrational coupling occurs) [1]. In high-symmetry situations a particular molecular mode may be vibrationally uncoupled from its neighbours [2], but there is to date no example known in which the absence of factor group splitting has been unambiguously established for the entire $\nu(\text{CO})$ region. It must be recognised that the observation that a spectrum can be interpreted on a site-group basis may not be conclusive evidence of the absence of intermolecular vibrational coupling. Thus, for crystalline $\text{M}_2(\text{CO})_{10}$, $\text{M} = \text{Mn}, \text{Re}$, site and factor group analyses lead to identical spectral predictions. In this case, however, detailed mixed crystal and isotopic studies demonstrated the applicability of the factor group model [3].

Intuitively, the most favourable situation for the absence of factor group effects will be that in which the CO units are spatially dilute and well separated. In the present communication we present what we believe to be the first conclusive example of the absence of factor group coupling in such a situation.

Results and Discussion

A particularly convenient molecule for study will be one that contains only one CO group in each

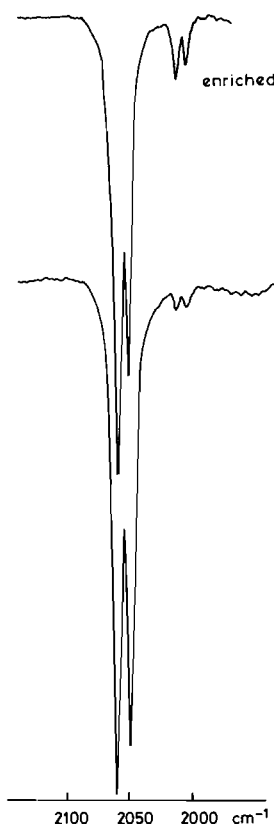


Figure 1. Infrared room temperature KBr disc spectra of unenriched and enriched $[\text{C}_2(\text{C}_6\text{H}_5)_2]_3\text{W}(\text{CO})$ in the 2000 cm^{-1} region.

molecule. In such a case any splitting observed in the solid state spectra must be factor group in origin (by choice of a molecule crystallising in a centrosymmetric unit cell L.O.–T.O. splittings can be disregarded). We have therefore studied the infrared and Raman spectra of the compound $[\text{C}_2(\text{C}_6\text{H}_5)_2]_3\text{W}(\text{CO})$ [4]. This is known to crystallise in at least three different crystal forms [5]; we obtained and studied the orthorhombic modification crystallising in P_{bca} with $Z = 16$. For such a unit cell occupancy

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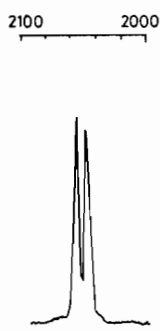


Figure 2. Raman spectra of polycrystalline $[\text{C}_2(\text{C}_6\text{H}_5)_2]_3\text{W}(\text{CO})$ in the 2000 cm^{-1} region.

no less than eight Raman and non-coincident six infrared features are predicted by a formal factor group analysis. In contrast, the absence of factor group effects will be manifest by the presence of either one or two features, coincident in infrared and Raman spectra. Two peaks would be expected if the two crystallographically distinct sites that are occupied are also vibrationally distinct.

We find that the $\nu(\text{CO})$ infrared spectra of crystalline $[\text{C}_2(\text{C}_6\text{H}_5)_2]_3\text{W}(\text{CO})$ consist of two bands of comparable intensity (Figure 1) suggesting an explanation based on the existence of site differences and the absence of vibrational coupling.

The observation that the Raman frequencies are, within error, identical to the infrared and also show two peaks of similar intensity (Figure 2) is extremely strong evidence that intermolecular coupling is not occurring. It is not, however, conclusive evidence. The obvious 1:1 correspondence between infrared and Raman peaks may be too facile – it is not impossible that a ‘crossing-over’ occurs, so that the high frequency infrared peak is to be associated, factor-group-wise, with the low frequency Raman and *vice versa* (and so the coincidence fortuitous). One method of testing for this possibility lies in the study of both infrared and Raman single crystal spectra; ideally, a knowledge of the crystal structure should also be available to enable a comparison between experimental and calculated band intensity ratios.

In practice, like the triclinic modification, the orthorhombic crystals are rhombic with no $\{100\}$ faces developed (those appearing are largely $\{110\}$), and so considerable crystal cutting would be needed to obtain single crystal spectra. Since inferior spectra are usually obtained from multiply cut and polished crystals we decided not to carry out such measurements.

Fortunately, an alternative, simpler, but definitive test exists. In the presence of strong intermolecular vibrational coupling partial ^{13}C substitution leads to crystal spectra in which isotopic bands do not

TABLE. The Raman and Infrared Frequencies (cm^{-1}) of Tris(diphenylacetylene)tungsten Monocarbonyl.

Raman	Solid State Infrared (KBr disc)	Solution CCl_4 Infrared	
		unexchanged	exchanged
2058.5	2060	2065	2065
2050	2050		2019 ^a
	2014*		
	2004*		

^a ^{13}C CO frequencies, enhanced on ^{13}C CO enrichment.

appear. Rather, the host, $\nu(^{12}\text{CO})$, frequencies decrease smoothly with substitution and usually are somewhat broadened for comparable isotopic abundances. In the presence of weak coupling separate isotopic features occur but these are broadened compared with those of the isotopically pure lattice. In the present case, in the infrared spectra (Figure 1) there are two weak, low frequency, peaks which could well be isotopic in origin. Exchange with ^{13}C CO confirms this assignment (Figure 1). This observation, combined with the comparable peak half-widths of $\nu(^{12}\text{CO})$ and $\nu(^{13}\text{CO})$ features, is sufficient to completely establish that $\nu(\text{CO})$ intermolecular vibrational coupling is of negligible magnitude in this compound. Frequency data associated with Figures 1–2 are detailed in the Table.

Although the crystal structure of the orthorhombic form of this compound was not refined, approximate atomic coordinates are known [6]. These reveal that the distance of closest approach of two carbonyl C atoms is over 10 Å, consistent with the expectation that the absence of factor group splitting is to be associated with spatial isolation.

Experimental

Preparation of Tris(diphenylacetylene)tungsten Monocarbonyl

The compound was prepared by the method of Tate *et al.*, involving reaction between diphenylacetylene and tris(acetonitrile tungsten tricarbonyl) under nitrogen.

For this work the tricarbonyl was not prepared by refluxing $\text{W}(\text{CO})_6$ in excess acetonitrile, because in our hands this method gave a complicated product, in which spectroscopic evidence revealed the existence of other carbonyls *i.e.* $(\text{CH}_3\text{CN})\text{W}(\text{CO})_5$, $(\text{CH}_3\text{CN})_2\text{W}(\text{CO})_4$ and species with bridging carbonyl groups. The preparative method we adopted was to use spectroscopic grade ethane as a solvent and an exact 1:3 molar ratio of tungsten hexacarbonyl and acetonitrile. The system was kept under nitrogen and

was refluxed gently for about ten days. After the completion of the reaction, the product was precipitated with oxygen-free water. The product was contaminated with $\text{W}(\text{CO})_6$ but could be used as an intermediate for the preparation of $[\text{C}_2(\text{C}_6\text{H}_5)_2]\text{W}(\text{CO})$ without purification.

The second step of the preparation for monocarbonyl was straightforward. Diphenylacetylene (5.4 g) and tris(acetonitrile)tungsten tricarbonyl (3.9 g) in 50 ml of oxygen free ethanol were refluxed under nitrogen for 20 hours. The product crystallised out as bright yellow crystals, in a yield of 80%. Recrystallisation from CH_2Cl_2 gave the orthorhombic modification of the compound. Found C, 69.7; H, 4.2%. Calculated C, 69.3; H, 4.0%.

¹³Co-enrichment

Ca. 20 ml (760 nm) carbon monoxide enriched to ca. 70% ¹³CO (Pro. Chem) was contacted with tris(diphenylacetylene)tungsten monocarbonyl (50 mg) in benzene (20 ml) for 10 days. At the end of this time the solvent was removed and the enriched product recrystallised.

Infrared spectra were recorded on a Perkin-Elmer model 325 infrared spectrometer. The quoted infrared frequencies are estimated to be reproducible to $\pm 1 \text{ cm}^{-1}$.

The Raman spectra of a polycrystalline sample was recorded at room temperature on a Spex 1401 spectrometer, and Spectra-Physics model 165-02 Argon/Krypton ion laser. The 6471 Å line was used with an incident power of ca. 20 mW.

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References

- 1 S. F. A. Kettle, "The Vibrational Spectral of Metal Carbonyls", *Topics in Current Chemistry*, 71, 111 (1977).
- 2 D. N. Kariuki and S. F. A. Kettle, *Inorg. Chem.*, 17, 141 (1978).
- 3 M. Arif, A. M. Cartner, D. N. Kariuki and S. F. A. Kettle, *J. Chem. Phys.*, in press.
- 4 D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross and J. G. Grasselli, *J. Am. Chem. Soc.*, 86, 3261 (1964).
- 5 R. M. Laine, R. E. Moriarty and R. Bau, *J. Am. Chem. Soc.*, 94, 1402 (1972).
- 6 R. Bau, personal communication.