

**Vibrational Frequencies of the Encapsulated Carbon Atom of the
Carbido Carbonyl Cluster $\text{Co}_6\text{C}(\text{CO})_{12}\text{S}_2$ determined through
Selective ^{13}C Labelling**

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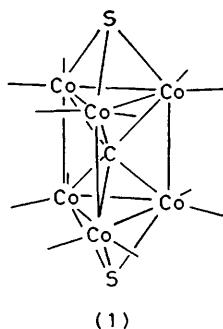
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Summary $\text{Co}_6\text{C}(\text{CO})_{12}\text{S}_2$ containing 90% ^{13}C in the central carbide position has been prepared and its i.r. spectrum compared with that of an unlabelled sample; the bands at 819 and 548 cm^{-1} (at 790 and 535.5 cm^{-1} , respectively,

for ^{13}C) have been identified as belonging to the vibrations A_2' and E' , respectively, of the encapsulated carbon atom.

THE structure determination of $\text{Co}_6\text{C}(\text{CO})_{12}\text{S}_2$ (**1**)¹ invalidated the earlier assignment² of an absorption band at 819 cm^{-1} (which was the only band observed in the medium wavenumber region of the i.r. spectrum of this compound) as a 'C-S stretching mode'. The structure permitted only



one re-assignment of this absorption, *viz.* to the vibration of the carbido C-atom in the centre of the trigonal prism formed by the six cobalt atoms. This suggestion, however, required experimental confirmation since no vibrational frequency had been observed for the encapsulated carbon atom in transition metal carbido clusters. We now report the successful verification of this assignment through ¹³C labelling.

Selectively ¹³C labelled (**1**) was obtained by t.l.c. as the main product of the reaction between $\text{Co}_2(\text{CO})_8$ and ¹³CS₂ (90% ¹³C content) in hexane solution at room temperature.¹ The i.r. spectrum of the labelled compound not only shows the expected isotopic shift of the 819 cm^{-1} band to 790 cm^{-1} but also permits the identification, at 548 cm^{-1} , of the second carbido vibrational mode that is predicted by group theory: this frequency is shifted to 535.5 cm^{-1} by ¹³C substitution (Figure). The elongated form of the Co₆ prism¹ requires that the higher $\nu(\text{C})$ frequency should belong to a vibration along the threefold symmetry axis *z* (species *A*'₂) and the lower one should be the perpendicular vibration in the *x-y* plane (species *E*'₂).

The intensity ratio of the bands at 819 and 790 cm^{-1} in the spectrum of the 90% ¹³C labelled sample proves unequivocally that the carbido atom of (**1**) arises entirely from the CS₂ and not from a CO-group of the $\text{Co}_2(\text{CO})_8$.

The only significant spectral change, besides these frequency shifts, is the considerable loss in intensity of the band at 517 cm^{-1} for the ¹³C containing sample relative to the ¹²C-carbido molecule. Since this band must be assigned to a Co-C-O deformation mode, this intensity decrease points to quite a strong coupling between such a mode and the *E*' carbido vibration; consequently this deformation mode must also belong to the same species.

These ¹³C substitution results indicate that the only previously suggested assignment for metal-carbido vibrations, *viz.* that of Braye *et al.*³ for $\text{Fe}_5\text{C}(\text{CO})_{15}$ (at 790 and 770 cm^{-1}), is probably correct. Although it is tempting, it

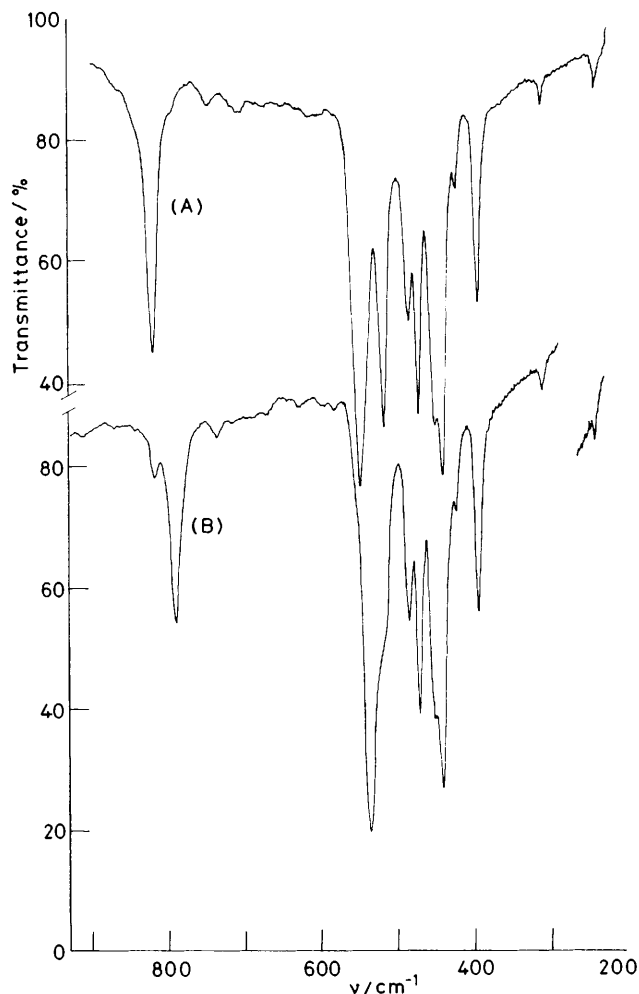


FIGURE. I.r. spectra, between 920 and 220 cm^{-1} , in KBr pellets (with compensation), of $\text{Co}_6\text{C}(\text{CO})_{12}\text{S}_2$ (**1**), showing the $\nu(\text{Co-C-Co})$, $\delta(\text{Co-C-O})$, $\nu(\text{Co-CO})$, and $\nu(\text{Co-S})$ absorptions; A: natural sample; B: sample with 90% carbide-¹³C content.

seems unsafe to make predictions for the frequencies of carbido vibrations in other types of carbido clusters until more ¹³C enrichment studies have been done. However, it is certain that the negative charge of anionic carbido carbonyl metallate clusters shifts this type of vibration towards lower energies, since in the low-frequency part of the i.r. spectrum of $\text{K}_2[\text{Rh}_6\text{C}(\text{CO})_{15}]$,⁴ the highest band (a probable candidate for one of the carbido vibrations) occurs at 694 cm^{-1} . Hence the combined effect of the double negative charge and the increased metal-carbon distances is a decrease in the i.r. frequency of at least 125 cm^{-1} . Thus in these cases a much stronger coupling of the carbido vibration with the M-C-O deformation modes than that found for (**1**) is to be expected.

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³ E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4663.

⁴ V. G. Albano, P. Chini, S. Martinengo, D. J. A. McCaffrey, D. Strumolo, and B. T. Heaton, *J. Amer. Chem. Soc.*, 1974, **96**, 8106; the spectrum was taken with an unenriched sample kindly donated by Professor P. Chini.