376. *High-resolution Infrared Spectra and Structures of Cobalt Carbonyls.*

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The infrared spectra of $Co_2(CO)_8$ and $[Co(CO)_3]_n$ in the CO stretching region have been re-examined, a calcium fluoride prism being used. They are found to be much richer than previously believed, and previously proposed structures of these molecules must be abandoned in favour of others. The spectrum of $Co_2(CO)_8,AlBr_3$ is also reported. The advisability of using optics affording better resolution than does sodium chloride, and certain other pitfalls are illustrated and discussed.

THE practice of inferring structures or partial structures of metal carbonyl compounds by comparing observed spectra in the CO stretching region with the spectra expected (*i.e.*, the number of terminal and bridge bands) for various models, on the basis of group-theoretically derived selection rules, has become increasingly common in the past few years. The reliability of this procedure depends on, *inter alia*, the authenticity of the observed spectrum, in particular on whether the spectrum is sufficiently well resolved to disclose all the bands.

Under optimum conditions currently available commercial spectrometers give resolution of 6—10 cm.$^{-1}$ with a rock-salt prism and 2—3 cm.$^{-1}$ with a calcium fluoride prism in the region of C=O and C≡O stretching frequencies.[1] Under the sub-optimum conditions often prevailing, it is our experience that the resolution may be no better than 10—20 and 4—6 cm.$^{-1}$ respectively. Thus, in some cases, closely spaced bands may fail to be resolved and a spectrum of misleading simplicity obtained when sodium chloride optics are used. One instance of this is already on record.[2] We report here two other cases, *viz.*, $Co_2(CO)_8$ and $Co_4(CO)_{12}$, in which the use of calcium fluoride optics allows observation of additional CO bands, thus changing the inferences as to structure.

For $Co_2(CO)_8$, the spectrum obtained with sodium chloride optics has been reported [3,4]

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[1] Gore, McDonald, Williams, and White, *J. Opt. Soc. Amer.*, 1947, **37**, 23.

[2] Cotton and Wilkinson, *J. Amer. Chem. Soc.*, 1957, **79**, 752.

[3] Cable, Nyholm, and Sheline, *J. Amer. Chem. Soc.*, 1954, **76**, 3373.

[4] Friedel, Wender, Shufler, and Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

to consist of four bands, at ~2070, ~2042, ~2025, and ~1859 cm.$^{-1}$. Fig. 1*a* shows such a spectrum obtained by us, and on such a basis structures of C_{2h} or D_{2h} symmetry have been proposed.[3,4] Using a calcium fluoride prism, we find the spectrum shown in Fig. 1*b*, with maxima at 2075, 2064, 2047, 2035, 2028, 1867, and 1859 cm.$^{-1}$. The appearance of four and possibly five terminal fundamentals, and especially of two bridge bands rules out unequivocally all structures previously proposed. The highest likely symmetry compatible with our results is C_{2v}. Two types of C_{2v} models appear possible. (1) Those with two terminal CO's necessarily in the Co(CO)$_2$Co plane: structure XI-a of Friedel *et al.*[4] is

FIG. 1. *The spectrum of* $Co_2(CO)_8$ *obtained* (*a*) *for hexane solution with a rock-salt prism, and* (*b*) *for pentane solution with a calcium fluoride prism.*

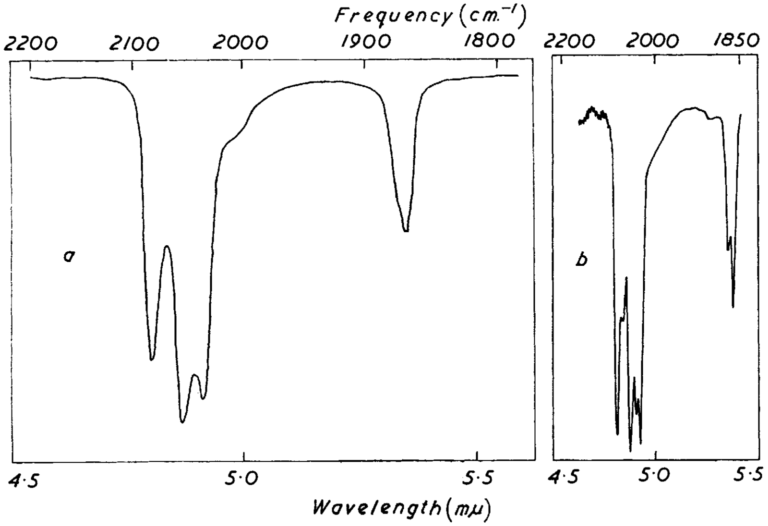


FIG. 2. *The infrared spectrum obtained for* $Co_2(CO)_8,AlBr_3$ *in Nujol mull with a calcium fluoride prism.*

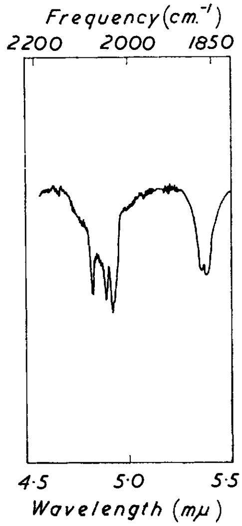


FIG. 3. *The infrared spectrum obtained for* $Co_4(CO)_{12}$ *in pentane with* (*a*) *a rock salt and* (*b*) *a fluorite prism.*

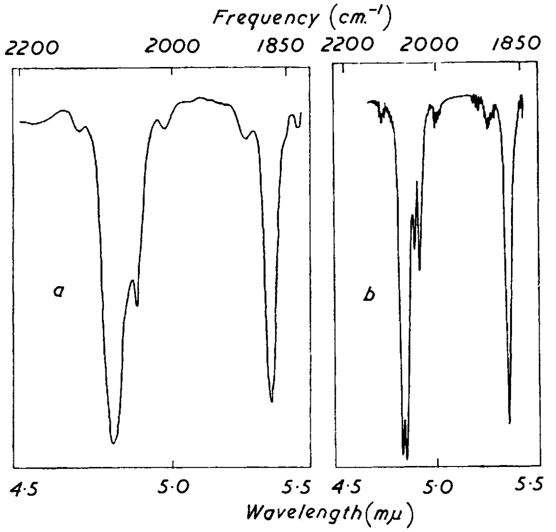
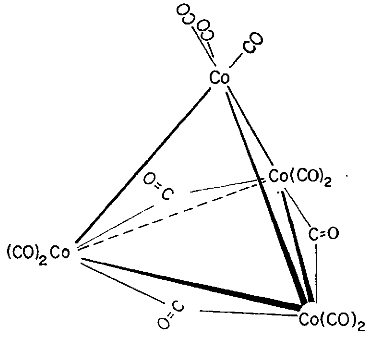


FIG. 4. *The structure of* $Co_4(CO)_{12}$ *according to Corradini and Ercoli.*[9]



representative of this type. (2) Those with no three CO's necessarily coplanar: structure IV-a of Cable *et al.*[3] is an example, the coplanarity of six CO's being non-essential to the symmetry. The bent structure suggested by Mills and Robinson [5] is also of type (2). The non-planarity of the $Co(CO)_2Co$ ring is an example of a chemically and structurally significant geometrical feature which is, however, of no significance to the point group symmetry. Any of the above-mentioned or other C_{2v} models or models of lower symmetry are compatible with our spectral data.

We have also measured the spectrum of the adduct $Co_2(CO)_8,AlBr_3$ recently reported by Chini and Ercoli.[6] The spectrum is shown in Fig. 2; the peaks occur at 2073s, 2064?sh, 2074s, 2028s, 2023sh, 1864m, and 1859m cm.$^{-1}$. The similarity to the spectrum of $Co_2(CO)_8$ is obvious. It is in excellent accord with the structure proposed for this adduct by Chini and Ercoli, and it may be observed that on removing the $AlBr_3$ from the Chini and Ercoli structure for $Co_2(CO)_8,AlBr_3$ one obtains the kind of structure suggested by Mills and Robinson for $Co_2(CO)_8$ itself.

$Co_4(CO)_{12}$, studied with rock-salt optics, has been reported [4,7] to have only three bands, at ~2060, ~2035, and ~1870 cm.$^{-1}$. Our results with a rock-salt prism (Fig. 3*a*) are in agreement. However, using a fluorite prism afforded the spectrum shown in Fig. 3*b*, with absorption maxima at 2070, 2062, 2045, 2033, and 1869 cm.$^{-1}$. The appearance of at least three fundamentals in the terminal region vitiates Cable and Sheline's contention [7] that a tetrameric formula originally reported by Hieber *et al.*[8] should be abandoned because of the simplicity of the spectrum. On the contrary, the complexity of the spectrum requires that Cable and Sheline's dimeric structure be abandoned.

As soon as these studies were complete it was learned that the structure of $Co_4(CO)_{12}$ had been determined by *X*-ray studies by Corradini and Ercoli.[9] The *X*-ray work is said to give the structure depicted in Fig. 4. This structure apparently has C_{3v} symmetry, and the CO groups fall into three equivalent sets: (1) three $CO^{(1)}$ groups bonded to the unique cobalt atom; (2) three $CO^{(2)}$ groups, the bridging groups around the base, and (3) six $CO^{(3)}$ groups, two attached to each of three equivalent Co atoms. Group theoretical methods readily yield the following results for the number of infrared-active C–O stretching modes due to each set of CO's:

Terminal	$CO^{(1)}$:	2	(A_1,E)
	$CO^{(3)}$:	4	$(2A_1,2E)$
Bridging	$CO^{(2)}$:	2	(A_1,E)

Clearly the observed spectrum is rather simpler than this. This is perhaps the most extreme example so far encountered in infrared studies of metal carbonyls where the observed spectrum is simpler than that expected in principle.

There are three possible reasons for such a phenomenon: (1) Some of the "allowed" bands may, by chance, be very weak so that they are undetected or at least recognised as fundamentals. (2) There may be accidental degeneracies of bands arising from different sets of equivalent oscillators. (3) There may be only unresolvably small splittings between the modes arising out of the same set of equivalent oscillators if the members of the set are only negligibly coupled. All these effects may occur simultaneously.

Clearly, one or more of them could be responsible for the observation of only four instead of six terminal absorption bands, but it is somewhat surprising that the three bridging carbonyl groups do not give rise to two observable and resolvable peaks.

In conclusion two points seem worthy of emphasis. First, irrespectively of other difficulties in interpreting spectra of metal carbonyl compounds in terms of molecular

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[5] Mills and Robinson, *Proc. Chem. Soc.*, 1959, 156.

[6] Chini and Ercoli, *Gazzetta*, 1958, **88**, 1171.

[7] Cable and Sheline, *Chem. Rev.*, 1956, **56**, 1.

[8] Hieber, Muhlbauer, and Ehmann, *Ber.*, 1932, **65**, 1090.

[9] Corradini and Ercoli, Abs. XVIIth Internat. Congress, Pure and Applied Chemistry, Munich, 1959, Vol. I, p. 25; Corradini, personal discussions.

symmetry, it is very dangerous to draw conclusions from the relatively poorly resolved spectra obtainable in this region with a rock-salt prism. Secondly, $Co_4(CO)_{12}$ provides a striking example of how failure to observe as many bands as are *in principle* " required " for a structural model is by no means conclusive evidence against that model.

[*Added in proof.*] Bor and Markó recently (*Spectrochem. Acta*, 1959, 747, made a preliminary report of a few results similar to ours. All our results were received for publication as a preliminary note on August 10th, 1959, but at the Editor's suggestion were withdrawn and resubmitted in their present form.

Experimental.—Samples of the cobalt carbonyls were received from Dr. H. W. Steinberg, U.S. Bureau of Mines, Pittsburg, Pa. $Co_2(CO)_8$ was recrystallized and handled in a gloved box flushed with dry nitrogen. $Co_4(CO)_{12}$ was manipulated entirely in a vacuum-line. The solution was made up and the infrared cell filled with liquid entirely in a vacuum. $Co_2(CO)_8,AlBr_3$ was prepared and handled entirely in a nitrogen atmosphere, according to the directions of Chini and Ercoli; [6] our product was green-yellow rather than yellow. The spectra were measured on a Baird spectrometer equipped with a fluorite prism. Subsequently the resolution was checked by using gaseous carbon monoxide. The rotational fine structure of the carbonyl band was clearly resolved, indicating resolution at least as good as $\sim 3{\cdot}5$ cm.$^{-1}$.

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