Spectroscopic Studies of Metal Carbonyl Complexes. Part II.[1] Dicobalt Octacarbonyl

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Dicobalt octacarbonyl has been studied by i.r. spectroscopy in solution at various temperatures and CO pressures. The nature of the species occurring in solution at temperatures greater than 150 °C and at CO pressures greater than 150 atm is discussed, and a CO-bridged $[Co_2(CO)_9]$ complex, previously suggested, is considered unlikely. The force field for the non-bridged isomer of $[Co_2(CO)_8]$ has been calculated from solution Raman data.

SEVERAL spectroscopic studies have been made on dicobalt octacarbonyl due to the structural changes which occur in solution. At low temperatures and in the solid state a bridged structure occurs whereas at higher temperatures a non-bridged form (presumably of D_{3d} symmetry) predominates.[2-6] We report the Raman spectra of solutions of $[Co_2(CO)_8]$ and use the data, with a treatment previously developed in Part I,[1] to evaluate the force field of the non-bridged structure. The behaviour of $[Co_2(CO)_8]$ at high pressures of carbon monoxide and high temperatures (150—200 °C) has been reinvestigated. Spectral changes were previously assigned to the formation of $[Co_2(CO)_9]$,[7] with a $[(OC)_4Co(CO)Co(CO)_4]$ structure related to that of the non-bridged form of $[Co_2(CO)_8]$.

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[1] E. E. Ernstbrunner and M. Kilner, *J.C.S. Dalton*, 1975, 2598.

[2] K. Noack, *Spectrochim. Acta*, 1963, **19**, 1925.

[3] G. Bor, *Spectrochim. Acta*, 1963, **19**, 1209, 2065.

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[5] K. Noack, *Helv. Chim. Acta*, 1964, **47**, 1555.

[6] G. Bor and K. Noack, *J. Organometallic Chem.*, 1974, **64**, 367.

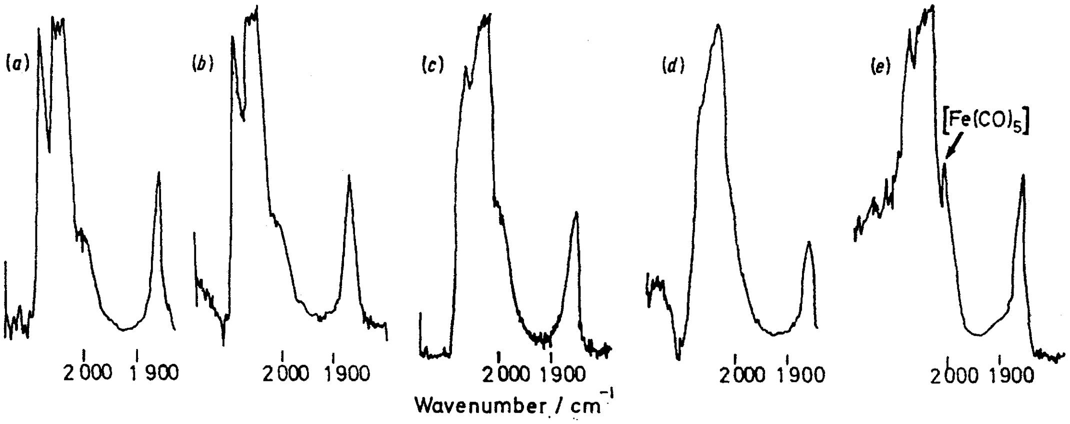
[7] R. Whyman, *Nature*, 1971, **230**, 139.

EXPERIMENTAL

Dicobalt octacarbonyl was used as donated by I.C.I. Petrochemicals Division, Billingham. Raman spectra were recorded in a rotating solution cell on the instrument previously described;[1] specifically, excitation was by a He–Ne laser, with polarisation measurements made by rotating the plane of the incident light, yielding the quotient $\rho_n = I_T(\text{obs.}\|)/I_T(\text{obs.}\perp)$. Infrared spectra at high pressures and temperatures were obtained using a modified Perkin-Elmer SP 257 spectrophotometer and a pair of balanced, specially constructed, high-pressure solution cells.[8] The 2,2,4-trimethylpentane (AnalaR) used as solvent for the Raman spectra was first degassed, then saturated with CO to reduce decomposition of the complex. The 632.8 nm line of the He–Ne laser was used for excitation.

RESULTS AND DISCUSSION

High-pressure Studies.—The results of our high-temperature–high-pressure i.r. studies are broadly in agreement with those of Whyman[7] who used Nujol as the solvent, but our conclusions are at variance with the proposed formation of $[Co_2(CO)_9]$ at high CO pressures. First, the absorption frequencies quoted (at 2 067, 2 042, 2 030, 2 023, and 1 860 cm^{-1}) can all, with the exception of the band at 2 030 cm^{-1}, be assigned to $[Co_2(CO)_8]$; they differ by no more than 3 cm^{-1} from room-temperature solution data. Also the band at 1 860 cm^{-1} cannot be confidently ascribed to only one vibration. All the bands of $[Co_2(CO)_8]$ became broader on warming under a CO pressure of 260 atm * and at greater than 100 °C the weak absorption at 1 862 cm^{-1} merely appeared as a shoulder, becoming less distinct at higher temperature. At 185 °C this band appeared only as a slight asymmetry of the band at 1 860 cm^{-1}. Secondly, we observed the absorption at 2 030 cm^{-1} at pressures of up to 150 atm (>100 °C) and its intensity was not strongly dependent on CO pressure, contrary to what is to be expected for $[Co_2(CO)_9]$.[7] In 2,2,4-trimethylpentane at high temperatures rather different results were obtained; the band at 2 067 cm^{-1} degenerated to a shoulder (Figure), another new shoulder was observed at 2 053 ± 3 cm^{-1}, and the absorption maximum of the broad main band occurred at 2 032 ± 2 cm^{-1}. The presence of the band at 1 860 cm^{-1} showed that a substantial amount of residual $[Co_2(CO)_8]$ (bridged form) remained. Finally, Cotton's generalisation,[9] that 'bridging carbonyl groups never occur unless the bridged metal atoms are formally bonded to each other,' renders questionable the interpretation in terms of $[Co_2(CO)_9]$.



I.r. spectral changes observed for $[Co_2(CO)_8]$ in 2,2,4-trimethylpentane solution under carbon monoxide (270 atm): at 100 (*a*), 140 (*b*), 170 (*c*), 185 (*d*), and when cooled to 140 °C (*e*). The complex $[Fe(CO)_5]$ resulted from prolonged heating (48 h, >200 °C) of the equipment, particularly the high-pressure steel pipework, under pressure of carbon monoxide

Three possible alternative interpretations are presented here since an unequivocal explanation of all the experimental data is not possible. The species considered are $[Co(CO)_4H]$, $[Co(CO)_4]^{\bullet}$, and $[Co(CO)_5]^{\bullet}$.

(*i*).—The complex $[Co(CO)_4H]$ could form either from hydrogen gas in the carbon monoxide used, or from hydrogen abstraction from the solvent. Precautions were taken to avoid contamination of the solvent and the equipment by water vapour, so this seems unlikely as a source of hydrogen. The two strongest absorptions for $[Co(CO)_4H]$ (2 052m and 2 030s cm^{-1})[10] are very similar to those recorded [2 053 (sh) and 2 032s cm^{-1}], and the presence of the hydride thus appears to be a strong possibility. Support for this conclusion was obtained on addition of 5% hydrogen gas (125 °C, 300 atm total pressure) which caused the main absorption band to sharpen (220 °C, over 48 h) and produced the eventual disappearance of the absorption at 1 860 cm^{-1}. Considerable excess of hydrogen is required to effect extensive conversion of $[Co_2(CO)_8]$ into $[Co(CO)_4H]$;[10] *ca.* 80% conversion is reported in heptane (290 atm, 1 : 1 CO–H_2 mixture, 150 °C). Using data[11,12]

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* 1 atm = 101 325 Pa, 1 dyn = 10^{-5} N.

[8] W. Rigby, R. Whyman, and K. Wilding, *J. Phys.* (*E*), *Sci. Instr.*, 1970, **3**, 572.

[9] F. A. Cotton and D. L. Hunter, *Inorg. Chem.*, 1974, **13**, 2044.

[10] R. Whyman, *J. Organometallic Chem.*, 1974, **66**, C23, and personal communication.

[11] M. van Boven, N. Alemdaroğlu, and J. M. L. Penninger, *J. Organometallic Chem.*, 1975, **84**, 65.

[12] S. Peter and M. Weinert, *Z. phys. Chem.*, 1955, **5**, 114; S. K. Lachowicz, D. M. Newitt, and K. E. Weale, *Trans. Faraday Soc.*, 1955, **51**, 1198; M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, 1957, **26**, 748.

for equilibrium (1), we estimate that a pressure of hydrogen of at least 5 atm or 2.5% hydrogen in the

$$[Co_2(CO)_8] + H_2 \rightleftharpoons 2[Co(CO)_4H] \qquad (1)$$

carbon monoxide used is required to produce the observed changes.

The source of the hydrogen poses a problem. The determined hydrogen content (by mass spectroscopy) of the carbon monoxide used amounted to $<0.1\%$, and corresponds to about one-tenth that required to effect quantitative conversion. A possible additional source of hydrogen is the solvent, but abstraction from alkanes is rare. Interestingly, abstraction of hydrogen from tertiary carbons of paraffins by Ag^I–H_2SO_4–CO systems[13] occurs much more readily than abstraction from CH_3 and CH_2 groups, and may be relevant to the differences in spectral changes occurring in Nujol and 2,2,4-trimethylpentane. More extensive reaction occurred in 2,2,4-trimethylpentane which has a tertiary carbon atom, but this may arise from the solubility of hydrogen in 2,2,4-trimethylpentane which is about three times that in Nujol.[12] Water could be a contributary source of hydrogen, through the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$, but is not a major source since the required amount of water (*ca.* 70 mg) is considerably in excess of that estimated as a contaminant.

(*ii*).—The radical $[Co(CO)_4]^\bullet$ is expected to have two absorptions in the 2 000—2 050 cm^{-1} region in the approximate intensity ratio that we observe. No direct evidence is available for this species in solution at room temperature,[2,14] but in the vapour phase it clearly exists and can be generated in a matrix[15] or formed by sublimation of $[Co_2(CO)_8]$.[16] The matrix-generated radical[11] has absorptions *ca.* 22—23 cm^{-1} lower than those recorded in this study. Since positional changes relating to a change in matrix material and non-polar solvent are normally less than 5 cm^{-1}, it is unlikely that this radical is the species present.

(*iii*).—The radical $[Co(CO)_5]^\bullet$ is a 19-electron system with one electron in a π^* orbital, and consequently the carbonyl-stretching frequencies are expected to be lower than those of $[Co(CO)_4]^\bullet$ and $[Fe(CO)_5]$, in contrast to those recorded. An apparently related radical $[Co(CO)_4(O_2)]^\bullet$ is known, but the unpaired electron is considered to be confined to the two oxygen atoms despite the possibility of π delocalisation.

It must be concluded that no straightforward explanation exists for the spectral data recorded under high CO pressures, but, although none of the possible species considered allows a satisfactory interpretation of all the data, the formation of $[Co(CO)_4H]$ seems to present the most satisfactory explanation.

Raman Studies.—Attempts to obtain the Raman spectrum of a $[Co_2(CO)_8]$ solution were complicated both by photochemically- and thermally -induced decomposition (no cooling was possible). When a saturated solution was employed rapid decomposition occurred and absorption of the exciting line was almost total, even at grazing incidence. However, spectra were obtained at a dilution of 1 : 3, but it was necessary to replace the solutions every 30 min. The results are shown in Table 1.

TABLE 1

Raman spectrum of $[Co_2(CO)_8]$ in 2,2,4-trimethylpentane

Wavenumber/ cm^{-1}	I_T(obs. ⊥)[a]	I_T(obs. ‖)[a]	ρ_n	Assignment (h.t.f.)[b]
2 110	25 ± 2	0.5 ± 0.5	0.02 ± 0.02	ν_1 + l.t.f.
2 068	15 ± 2	4 ± 2	0.80 ± 0.25	l.t.f.
ca. 2 040(sh)	?	?		l.t.f.
2 035	100[c]	80 ± 3[c]	0.80 ± 0.03	ν_2 or ν_3
2 000	32 ± 2	25 ± 2	0.78 ± 0.08	ν_3 or ν_2

[a] Intensity relative to the band at 2 035 cm^{-1}, obs. ⊥. [b] See text. [c] Total intensity, including the shoulder at 2 042 cm^{-1}.

Fortunately the assignment of the bands to the bridged (l.t.f.) * and non-bridged structure (h.t.f.) * respectively is possible without temperature-variation studies, since the two lower frequencies of the h.t.f. are observed at wavenumbers (2 035 and 2 000 cm^{-1}) which can be ruled out as l.t.f. fundamentals.[6] On the other hand, the highest Raman band at 2 180 cm^{-1} must be attributed to both the h.t.f. (A_{1g}) and the l.t.f. (A_1) (for the latter the highest i.r. fundamental is assigned[3,6] at 2 111 cm^{-1}).

In the following treatment, the same approximations have been employed as before;[1] for a discussion see Part I[1] and, in particular, ref. 17. From the data in Table 1 the coupling parameter $\cos\beta_g$ necessary to calculate the force field can be obtained as outlined previously.[1] The angle δ (defined as before[1]), indicating the deviation of the equatorial CO groups from a plane perpendicular to the Co–Co bond, has been taken as 5°, D_{3d} symmetry being assumed.[6] First, $\nu_2(A_{1g})$ and $\nu_3(E_g)$ have to be assigned. Depolarisation ratios and intensities would indicate ν_2 at 2 000 and ν_3 at 2 035 cm^{-1}, similar to $Hg[Co(CO)_4]_2$, since $(I_3 > I_1 + I_2)$(obs.‖).[1] On the other hand, for the quotient $[I_3/(I_1 + I_2)]$(obs.‖) we find 3.2 instead of the expected 1.4; this indicates that the intensity of the band at 2 035 cm^{-1} is enhanced by fundamentals of the l.t.f., in particular by that giving rise to the strong i.r. absorption at 2 040 cm^{-1} (a very strong band in the Raman spectrum of the solid is observed at 2 030 cm^{-1}).[18] As this intensity is therefore unreliable, the reverse assignment (ν_2 at 2 035, ν_3 at 2 000 cm^{-1}) cannot be ruled out. The calculation of $\cos\beta_g$ from Raman intensities is also less reliable in this case because of the larger uncertainties in the intensities.

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* The low-temperature form is abbreviated as l.t.f. and the high-temperature form as h.t.f. as used by Bor.[3]

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[14] D. J. Keeley and R. E. Johnson, *J. Inorg. Nuclear Chem.*, 1959, **11**, 33.

[15] O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J.C.S. Dalton*, 1973, 1321.

[16] S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567.

[17] J. R. Miller, *J. Chem. Soc.* (*A*), 1971, 1885.

[18] W. P. Griffith and A. J. Wickham, *J. Chem. Soc.* (*A*), 1969, 834.

If we use the quotient $(I_1/I_2)_{\text{obs.}}$ as in the previous study,[1] a value of $\cos\beta_g = 0.35 \pm 0.21$ is obtained. A more accurate calculation is possible by using the depolarisation ratio of ν_1 as follows. From $\rho_n = 6\gamma^2/(45\bar{\alpha}^2 + 7\gamma^2)$ we obtain (2), and with the relations

$$\bar{\alpha}^2/\gamma^2 = (6 - 7\rho_n)/45\rho_n \qquad (2)$$

for $\bar{\alpha}_{Q_1}{}^2$ and $\gamma_{Q_1}{}^2$ (Table 1, ref. 1) this becomes (3). If a

$$\left(\frac{\alpha_l + 2\alpha_p}{\alpha_l - \alpha_p}\right)^2 \cdot \frac{2 + \cos\beta_g + \sin\beta_g 3^{\frac{1}{2}}}{\frac{3}{4}(1 + \cos\beta_g)(1 - 3\sin^2\delta)^2 + 1 - \cos\beta_g - 3^{\frac{1}{2}}(1 - 3\sin^2\delta)\sin\beta_g} = (12 - 14\rho_n)/5\rho_n \qquad (3)$$

value of $x = (\alpha_l + 2\alpha_p)^2/(\alpha_l - \alpha_p)^2$ can be found, $\cos\beta_g$ can be calculated from (3). The best approximation for x is obtained by making the calculation for $Hg[Co(CO)_4]_2$, with $\rho_n = 0.125$ and $\cos\beta_g = 0.55$,[1] and transferring the value to $[Co_2(CO)_8]$ (h.t.f.). This yields $x = 0.135$ {compared to 0.196 in $[Mo(CO)_6]$ [19]} and $\cos\beta_g = 0.24 \pm 0.10$. An average value of $\cos\beta_g = 0.30$ was used subsequently.

TABLE 2

Force field (mdyn Å^{-1}) of $[Co_2(CO)_8]$ for alternative assignments (I) and (II)

	(I), $A_{1g} > A_{1g} > E_g$			(II), $A_{1g} > E_g > A_{1g}$		
	(A)	(B)	(C)	(D)	(E)	(F)
$\cos\beta_g$	0.30	0.30	0.30	0.30	0.30	0.30
$\cos\beta_u$	−0.20	0.20	0.60	−0.20	0.20	0.60
F_t	17.094	17.031	16.968	16.918	16.855	16.792
F_e	16.630	16.651	16.672	16.795	16.816	16.837
f_{ee}	0.294	0.315	0.336	0.166	0.187	0.208
f_{et}	0.262	0.262	0.245	0.340	0.340	0.324
$f_{tt'}$	0.060	0.123	0.186	−0.116	−0.052	0.010
$f_{et'}$	0.082	0.082	0.100	0.162	0.162	0.179
$f_{ee'}$	−0.022	−0.043	−0.064	0.143	0.122	0.101
$f_{ee''}$	0.167	0.146	0.125	0.039	0.018	−0.003

In order to evaluate $\cos\beta_u$, i.r. intensities have to be determined; some uncertainty in the intensities arises from the overlap between bands due to the h.t.f. and l.t.f. The results are $I_4(2\,069) = 2.3 \pm 0.5$, $I_5(2\,031) = 2.3 \pm 0.3$, and $I_6(2\,023) = 10$ (relative intensities). Thus $K = (\mu_{ax}'/\mu_{eq}') = 1.16 \pm 0.08$ and $\cos\beta_u = -0.20 \pm 0.10$, from (5a) and (5b) in ref. 1.

Force constants were calculated in the way outlined before[1] from $Y_1 = (4\pi^2\nu_i{}^2/\mu_{CO})$, giving $Y_1 = 17.989$, $Y_2 = 16.733$ or 16.163, $Y_3 = 16.163$ or 16.733, $Y_4 = 17.285$, $Y_5 = 16.656$, and $Y_6 = 16.525$ mdyn Å^{-1}. Since no definitive choice can be made between the two possible assignments of ν_2 and ν_3 (see above), the results for both cases ($A_{1g}^{(1)} > A_{1g}^{(2)} > E_g$ and $A_{1g}^{(1)} > E_g > A_{1g}^{(2)}$) are shown in Table 2. As before, $\cos\beta_u$ was varied over a range of 0.8 to take account of electronic-interaction effects affecting i.r. intensities.

In a ^{13}CO-enrichment study of $[Co_2(CO)_8]$, bands at 2 011, 1 994, and 1 975 cm^{-1} were assigned tentatively to the non-bridged h.t.f.,[6] and set (C) (Table 3) approximates to these observed wavenumbers most closely. On the other hand, it is not possible to improve this fit much further by varying $\cos\beta_g$ and $\cos\beta_u$ within reasonable limits for either $A_{1g}^{(1)} > A_{1g}^{(2)} > E_g$ or $A_{1g}^{(1)} > E_g > A_{1g}^{(2)}$, since for all the sets in Table 3 the two lowest frequencies of ^{13}CO equatorially-substituted h.t.f. are almost insensitive to variation of both $\cos\beta_g$ and $\cos\beta_u$. A decision between (I) and (II) (Table 2) cannot be therefore made with certainty, but we consider (II) to be more likely for several reasons: first, on the basis of the intensity data (Table 1) previously mentioned; secondly, on the basis that in all sets of (I) $f_{ee'}$ is negative and smaller than $f_{ee''}$ in magnitude; thirdly, the fact that only (II) accurately reproduces the only reasonably certain ^{13}C satellite wavenumber (1 975 cm^{-1}) of the h.t.f. There is little to choose between sets (D)—(F); force-field (F) might be preferred because it shows a positive *trans–trans*-interaction constant as predicted for such complexes[20] and because f_{ee} in (D) and (E) appears somewhat low.

TABLE 3

Calculated ^{13}C satellite wavenumbers for force fields (A)—(F) of $[Co_2(CO)_7(^{13}CO)]$ (see text for the observed wavenumbers)

	Equatorial						Axial			
(A)	2 106,	2 067,	2 035,	2 029,	2 014,	1 971	2 105,	2 061,	2 032,	2 001
(B)	2 106,	2 066,	2 034,	2 030,	2 014,	1 971	2 104,	2 064,	2 033,	1 997
(C)	2 106,	2 066,	2 033,	2 031,	2 014,	1 971	2 104,	2 067,	2 034,	1 993
(D)	2 107,	2 067,	2 032,	2 029,	2 005,	1 983	2 104,	2 059,	2 024,	1 976
(E)	2 107,	2 066,	2 031,	2 029,	2 005,	1 983	2 104,	2 063,	2 021,	1 975
(F)	2 107,	2 066,	2 030,	2 028,	2 005,	1 983	2 104,	2 067,	2 018,	1 974

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