

Figure 5 as a function of  $\theta$ , the angle between the phenyl rings and the  $xz$  plane.

The planar  $C_{2v}$  conformation,  $\theta = 0$ , does not give a satisfactory interpretation of the spectrum in solution. Of the nonplanar conformations, both  $\theta = 15^\circ$  and  $\theta = 30^\circ$  give a reasonable interpretation of the ultraviolet spectrum with essentially the same band assignments. The computed transition energies, oscillator strengths polarizations, and wave functions for  $\theta = 30^\circ$  are collected in Table VI.

The main component of the A band in *cis*-stilbene is  ${}^1B \leftarrow {}^1A$  and the main component of the B band is  ${}^1H^+ \leftarrow {}^1A$ , just as in the *trans* isomer. Again the *plus* state falls below the minus state for the  ${}^1H$  states, and an argument analogous to that presented for the *trans* isomer applies. A third band  ${}^1G^+ \leftarrow {}^1A$  is indicated just above  $200 m\mu$ , but the spectrum of *cis*-stilbene has not yet been reported in this region. As in *trans*-stilbene a number of forbidden components appear, with the  ${}^1G^- \leftarrow {}^1A$  transition likely to be the most intense. A summary of band assignments proposed for *cis*-stilbene is given in Table VII and term level diagrams indicating the correlation between the states of *trans*-stilbene and the states of *cis*-stilbene are presented in Figure 6.

A study of the spectrum of *cis*-stilbene in dibenzyl crystal<sup>18</sup> indicates the 0-0 band of *cis*-stilbene lies at slightly lower energy than the *trans* isomer in the same phase. In dibenzyl crystal, *cis*-stilbene presumably

Table VII. Summary of Band Assignments for *cis*-Stilbene

Absorption region	Obsd. $\lambda_{max}$ ( $m\mu$ ) <sup>a</sup>	Transition	Symmetry	Calcd. $\lambda$ ( $m\mu$ )
A band	272	${}^1B \leftarrow {}^1A$	B	270 <sup>b</sup>
		${}^1G^- \leftarrow {}^1A$	A	263
		${}^1G^+ \leftarrow {}^1A$	B	262
		${}^1(H,C) \leftarrow {}^1A$	A	243
B band	219	${}^1H^+ \leftarrow {}^1A$	B	225 <sup>b</sup>
C band ?	...	${}^1G^+ \leftarrow {}^1A$	B	203 <sup>b</sup>
		${}^1G^+ \leftarrow {}^1A$	A	201

<sup>a</sup> See ref. 7. <sup>b</sup> Principal allowed component.

would assume a nearly planar conformation. From Figure 5 it may be seen that the  ${}^1B \leftarrow {}^1A$  transition energy for *cis*-stilbene at  $\theta = 0^\circ$  and  $\theta = 15^\circ$  is lower than the  ${}^1B \leftarrow {}^1A$  transition energy for *trans*-stilbene and thus, although the calculation is not parametrized to give 0-0 transition energies, the trend is observed in accord with experimental results. For the conformation corresponding to  $\theta = 30^\circ$ , the energy of the  ${}^1B \leftarrow {}^1A$  transition in *cis*-stilbene is greater than in *trans*-stilbene.

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## The Vibrational Spectra and Structure of Cyclooctatetraeneiron Tricarbonyl<sup>1</sup>

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The infrared ( $4000-110 \text{ cm.}^{-1}$ ) and Raman (up to  $1650 \text{ cm.}^{-1}$ ) spectra of cyclooctatetraeneiron tricarbonyl are reported. The Raman spectra were excited by the rubidium resonance line at  $7800 \text{ \AA}$ . obtained from a radiofrequency-powered rubidium plasma arc. The spectra indicated a low symmetry ( $C_2$ ) for the complex, with identical structures in the solid and solution states, and no free rotation between the hydrocarbon ring and the  $\text{Fe}(\text{CO})_3$  group. The results were also consistent with the presence of some  $\pi$ -electron delocalization in the uncoordinated part of the cyclooctatetraene ring system.

### Introduction

Several structures based on a variety of physical and chemical evidence have been postulated for cyclooctatetraeneiron tricarbonyl,  $(\text{COT})\text{Fe}(\text{CO})_3$ .<sup>2-6</sup> The pres-

ence of a single, sharp proton resonance in the nuclear magnetic resonance spectrum and the absence of a strong infrared absorption attributable to an olefinic  $\text{C}=\text{C}$  stretching vibration were widely interpreted as strong evidence for a planar cyclooctatetraene (COT) ring in the complex. Chemical evidence, indicating the absence of free olefinic double bonds, also influenced workers toward this conclusion. Two molecular orbital calculations, based upon a planar configuration of the COT ring claimed to have rationalized the bonding in the complex.<sup>5,6</sup> Recent X-ray diffraction data, however, clearly established that in the crystalline solid, at least, the  $\text{Fe}(\text{CO})_3$  group is bonded to the butadiene-like residue in the COT ring.<sup>7</sup> The structure is shown in Figure 1. The dihedral COT ring lies in two planes, the angle between which is  $41^\circ$ . The  $\text{Fe}(\text{CO})_3$  group is associated with only one pair of conjugated double bonds, with the remaining

(1) This work has been supported in part by the U. S. Atomic Energy Commission, the U. S. Public Health Service, and the Advanced Research Projects Agency, Department of Defense.

(2) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, 82, 336 (1960).

(3) M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959).

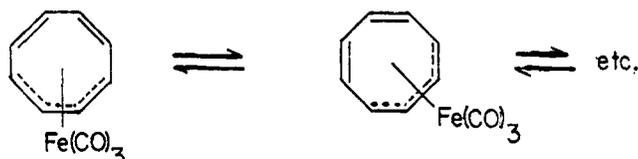
(4) A. Nakamura and N. Hogihara, *Bull. Chem. Soc. Japan*, 32, 880 (1959).

(5) D. A. Brown, *J. Inorg. Nucl. Chem.*, 10, 39, 49 (1959).

(6) F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

(7) (a) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, 83, 4062 (1961); (b) *J. Chem. Phys.*, 37, 2084 (1962).

pair forming a second plane and having relative positions very similar to those in butadiene. This structure, however, leaves unexplained the presence of the single sharp proton resonance in  $\text{CS}_2$  solution; such a structure should give rise to a more complicated n.m.r. spectrum. This anomaly can be resolved in one of three ways: by assuming a negligible relative chemical shift, a different geometry in the solid and solution states, or a dynamical effect. Dickens and Lipscomb<sup>7b</sup> concluded that a dynamical effect, resulting in the equivalence of all the protons in the COT ring, was the most plausible explanation. To accomplish this, the  $\text{Fe}(\text{CO})_3$  group is assumed to be rapidly rotating around the COT ring, *i.e.*



This mechanism has also been invoked to account for the single proton resonance observed in iron tricarbonyl complexes of the tropylium ion.<sup>8</sup>

In this work, the infrared and Raman spectra of  $(\text{COT})\text{Fe}(\text{CO})_3$  have been studied in an attempt to gain a better insight into the structure and chemical bonding involved in this compound. The Raman spectra were of particular interest in the  $\text{C}=\text{C}$  stretching region, where the infrared data were inconclusive, and also below  $250\text{ cm}^{-1}$ , where the low-lying fundamentals can be detected. Several partial infrared investigations have been reported,<sup>2,3,6</sup> and Fritz and Keller<sup>9,10</sup> measured the infrared spectra of the solid complex in KBr pellets from  $4000$  to  $250\text{ cm}^{-1}$ . No Raman data have previously been available for this compound since it is completely opaque to visible radiation.

### Experimental Section

$(\text{COT})\text{Fe}(\text{CO})_3$  was prepared by the photochemical reaction between COT and iron pentacarbonyl<sup>2,3</sup> and purified by recrystallization from *n*-hexane followed by vacuum sublimation. It was obtained as dark red crystals, m.p.  $94^\circ$ , stable in air and soluble in organic solvents to give dark red-brown solutions.

**Raman Spectra.** The Raman spectra were obtained on solutions of  $(\text{COT})\text{Fe}(\text{CO})_3$  in benzene and carbon disulfide. The spectra were excited in all cases by the rubidium resonance line at  $7800\text{ \AA}$ , isolated by two primary filter solutions. A saturated solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  removed radiation below  $6000\text{ \AA}$ , while a  $0.25\text{ M}$  solution of  $\text{NdCl}_3$  in 6-mm. thickness effectively suppressed the intensity of the other Rb resonance line so that it did not excite Raman spectra. A radio-frequency-powered rubidium plasma discharge in a toroidal lamp provided the exciting radiation. Details of the plasma arcs and of their use in Raman spectroscopy have been published previously.<sup>11-15</sup> Photo-

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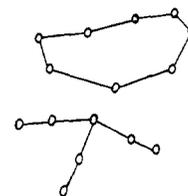


Figure 1. The structure of  $(\text{COT})\text{Fe}(\text{CO})_3$ .

graphic recording was employed using a Jarrell-Ash 75-000 F6.3 grating spectrograph. A plane grating ruled with 15,000 grooves/in. and blazed for  $7500\text{ \AA}$  was used to give a dispersion of  $20\text{ \AA./mm.}$  in the first order. Hypersensitized Eastman Kodak 1-N photographic plates were used to record the spectra. With a slit width of  $200\text{ }\mu$ , exposure times of up to 30 hr. were required. The Raman spectra were not observed beyond  $1650\text{ cm}^{-1}$  owing to the rapid decrease in sensitivity of the photographic plates beyond  $9000\text{ \AA}$ . Polarization measurements were possible only for the strong lines due to the very long exposure times required. The plates were calibrated by means of a superimposed neon spectrum and measured using standard techniques. The strong Raman lines are estimated to be accurate to  $\pm 2\text{ cm}^{-1}$ , but for weak or diffuse features the error may be greater.

**Infrared Spectra.** The infrared spectra of  $(\text{COT})\text{Fe}(\text{CO})_3$  were recorded as solutions in  $\text{CS}_2$ ,  $\text{CCl}_4$ , and  $\text{C}_2\text{Cl}_4$  in the frequency range  $4000$ – $240\text{ cm}^{-1}$ , on a Perkin-Elmer 421 grating spectrometer equipped with low-frequency interchange, and in the range  $250$ – $110\text{ cm}^{-1}$  as a solution in benzene on a grating spectrometer designed and built at Royal Holloway College. The spectra of the solid complex were obtained in Nujol mulls and KBr pellets. The observed infrared and Raman spectra are listed in Table I.

In general, the infrared data are in reasonable agreement with those published by Fritz and Keller.<sup>9</sup> Some discrepancies were apparent but most of these can probably be ascribed to calibration errors; the strong band reported at  $1019\text{ cm}^{-1}$  was not, however, observed in this work.

### Discussion

The excellent agreement between the infrared spectra of  $(\text{COT})\text{Fe}(\text{CO})_3$  in the solid state and in solution is strong evidence for identical structures in both states. Thus one possible explanation of the single proton resonance observed in solution is eliminated. The assumption of a negligible relative chemical shift is also rendered unlikely by the appearance of two proton resonance frequencies in the disubstituted complex  $(\text{COT})\text{Fe}[(\text{CO})_2]_2$ , in which there is very little  $\pi$ -orbital overlap between the complexed portions of the COT ring. We are therefore led to the conclusion, reached previously by Dickens and Lipscomb,<sup>7b</sup> that tautomerism of the COT ring relative to the  $\text{Fe}(\text{CO})_3$  group is the most probable explanation of the single proton resonance. It should be noted, however, that the time scales required for n.m.r. equivalence and for equivalence in the vibrational spectra are totally dif-

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(14) R. T. Bailey and E. R. Lippincott, *ibid.*, **21**, 389 (1965).

Table I. Observed Vibrational Spectra of (COT)Fe(CO)<sub>3</sub><sup>a</sup>

Infrared, cm. <sup>-1</sup>		Raman, cm. <sup>-1</sup>
Soln.	Solid	Soln.
3075 w		
3040 vs		
3022 s, sh		
~2925 w		
2879 w		
2061 vs	2062 vs	
1993 vs	1998 vs	
1976 vs	1982 vs	
1942 s	1947 w	
~1895 m		
1845 w		
1768 w		
1750 w		
1708 w		(1639)
1562 m		1563 m, p
1490 m		
1460 m		1460 s
1431 w		1431 m, p
1419 s	1418 w	(1406)
1401 vw		
1383 w		
1314 m	1313 w	1312 vw
1298 m	1299 w	1303 vw
1252 m	1256 vw	1255 w, br
1235 w, sh	1244 vw	1230 w, p
1177 m	1172 w	1180 m
	1150 vw	1147 m
1122 m	1125 w	1129 s
~1090 w		
1075 vw		(1080)
		1057 w
		1042 w
~1040 w, br		1024 vw, br
995 w, sh		
984 m	987 w	984 w
955 w	~945 w	951 m
922 m	918 w	924 m
898 s	898 m	889 w
864 s	868 m	875 w, br
846 m	845 w	849 w
		827 w
804 m	806 vw	
777 m	778 m	782 w
765 m, sh	765 w	766 w
743 m	741 vw	(730)
	715 vs	
707 vs	708 vs	716 vw
698 s, sh	698 vs	690 w, p
672 vw		
		643 vw
628 s, sh	627 s, sh	
607 vs	610 vs	607 s
597 vs, sh	597 vs	
561 vs	563 vs	563 m
537 vs	538 s	538 w
498 vs	498 s	498 w
485 s, sh		
461 vs	458 s	456 w
404 w	400 vw, sh	
	417 w	
389s	388m	391 m, vbr
362 w, sh	356 w, sh	
330 m	329 w, br	330 vs, br, p
	275 w	279 w
263 m	262 w	262 s, p
224 m		(238)
174 s		176 s
		137 m
		100 vs, vbr

<sup>a</sup> p, polarized; v, very; s, strong; m, medium; w, weak; sh, shoulder; br, broad. Values in parentheses indicate strong source lines which probably obscure Raman lines. N.M. designates no measurement.

ferent. Thus it does not necessarily follow that equivalence of the protons in the COT ring implies a high molecular symmetry with respect to the normal vibrational modes.

The vibrational spectra of the (COT)Fe(CO)<sub>3</sub> complex will now be considered in relation to its molecular structure. It is at once apparent from the large number of observed frequencies and coincidences between infrared and Raman bands that structures of high symmetry are precluded. Thus, structures having a planar COT ring and C<sub>3v</sub> symmetry are not consistent with the observed data.

The observed vibrational frequencies can be conveniently divided into three groups: (1) those belonging to the Fe(CO)<sub>3</sub> group, (2) those associated with COT ring modes, and (3) those arising from vibrations between the COT ring and the Fe(CO)<sub>3</sub> group. These three groups will be considered separately. Descriptive assignments of some of the observed frequencies are given in Table II.

Table II. Descriptive Assignments of Frequencies

Assign-ment, cm. <sup>-1</sup>	Descriptive assignment
3075	CH stretch
3040	
3022	
2061	CO stretch
1993	
1976	
1562	
1490	Sym. C=C stretch
1460	C=C stretch
1431	C=C stretch
1419	Ring deformation
1400	
to	CH deformation
1100	
750-500	Fe-C-O angle bending
475-350	Fe-CO stretch
404	Ring tilt
330	Ring metal stretch
137	C-Fe-C angle bend
100	

(1) *The Fe(CO)<sub>3</sub> Group.* Assuming identical structures in the solid and solution states, the highest possible symmetry for (COT)Fe(CO)<sub>3</sub> is C<sub>s</sub>. In many organometallic compounds containing metal-carbonyl groups M(CO)<sub>x</sub> bonded to an organic ring system, the observed spectroscopic data can be readily interpreted by considering only the local symmetry of the M(CO)<sub>3</sub> group and of the organic residue.<sup>15-17</sup> This approximation would<sup>16,17</sup> be valid only, however, if the M(CO)<sub>x</sub> group is rotating freely with respect to the ring system and there is no strong coupling between the vibrational modes of the two groups. On this basis, the Fe(CO)<sub>3</sub> group would belong to the C<sub>3v</sub> point group. The distribution of normal modes among

(15) R. T. Bailey and E. R. Lippincott, *J. Chem. Phys.*, **42**, 1121 (1965).

(16) F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 301.

(17) F. A. Cotton, A. O. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).

the various symmetry species for the  $C_{3v}$  point group is:  $4a_1 + a_2 + 5e$ . All species are infrared and Raman active except  $a_2$  which is Raman active only. The normal modes can be described approximately as follows: two C=O stretching ( $a_1 + e$ ), two Fe-CO stretching ( $a_1 + e$ ), four Fe-C-O angle bending ( $a_1 + a_2 + 2e$ ), and two C-Fe-C angle bending ( $a_1 + e$ ). Thus, two infrared-active C=O stretching vibrations would be expected, whereas, in fact, three frequencies at 2061, 1993, and 1976  $\text{cm}^{-1}$  are observed in the CO stretching region. This indicates a lower symmetry than  $C_{3v}$  (*i.e.*,  $C_3$ ) resulting in the splitting of the degenerate e-class CO stretching vibration. Thus, an asymmetric  $\text{Fe}(\text{CO})_3$  group not freely rotating in space is implied, contrary to the conclusions of Cotton.<sup>6</sup> This is supported by the X-ray data which show the  $\text{Fe}(\text{CO})_3$  to be slightly asymmetric.<sup>7b</sup> However, the vibrational data do not rule out a hindered or restricted rotation of the  $\text{Fe}(\text{CO})_3$  group. The reduction in symmetry will also result in a splitting of the other degenerate  $\text{Fe}(\text{CO})_3$  modes. In the case of the low-frequency modes, however, this may be too small to be observed under the present experimental conditions. A broadening of the degenerate modes should, however, be observed. The metal-carbonyl stretching frequencies are significantly lower than the corresponding modes in  $\text{Fe}(\text{CO})_5$  at 2117, 2034, and 2014  $\text{cm}^{-1}$ .<sup>18</sup> This is principally caused by back-donation from the filled d orbitals on the iron atom to vacant antibonding  $\pi$  orbitals on CO. This compensates for the formal negative charge imposed on the iron atom by coordination to the butadiene-like residue. There is also the possibility of some  $\pi$ -electron donation from bonding CO to vacant d orbitals on the metal atom, but this should be relatively small. This mechanism is consistent with the observed Fe-CO bond length which is about 0.17 Å. shorter than the normal single bond distance.<sup>7b</sup> The assignment of the other  $\text{Fe}(\text{CO})_3$  modes is rendered rather difficult owing to overlapping with COT and ring-metal modes. Several C-H deformation and ring deformation modes of COT are found below 700  $\text{cm}^{-1}$ .<sup>19</sup> In general, M-C-O angle bending modes lie at higher frequencies than M-CO stretching modes, but they sometimes overlap.<sup>20</sup> In  $(\text{COT})\text{Fe}(\text{CO})_3$ , the M-C-O angle bending modes probably lie in the range 500–750  $\text{cm}^{-1}$  and the M-CO stretching modes in the range 350–475  $\text{cm}^{-1}$ . The M-CO stretching modes generally fall within a shorter frequency interval than M-C-O bending modes and in the neutral species rarely rise above 500  $\text{cm}^{-1}$ . The C-M-C angle bending modes generally are found near 100  $\text{cm}^{-1}$ . The frequencies at 176 and 100  $\text{cm}^{-1}$  probably belong to these modes. Since the 100- $\text{cm}^{-1}$  band is very broad, it is assigned to an unresolved splitting of the degenerate vibration. It is possible, however, that the  $\text{COT-Fe}(\text{CO})_3$  bending modes will also occur in this region and overlap the C-Fe-C bending modes.

(2) *The COT Ring Modes.* Assuming  $C_s$  symmetry for the COT ring, eight infrared-active C-H stretching modes should be observed. Only two strong bands are found in the C-H stretching region in the infrared

(18) W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963).

(19) E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.*, **73**, 3370 (1951).

(20) D. M. Adams, *J. Chem. Soc.*, 1771 (1964).

spectra of the complex. This implies a higher symmetry than  $C_s$  for the COT ring. Cyclooctatetraene has two strong bands in the C-H stretching region at 2955 and 3004  $\text{cm}^{-1}$ .<sup>19</sup> The corresponding frequencies in  $(\text{COT})\text{Fe}(\text{CO})_3$  are found at 3002 and 3040  $\text{cm}^{-1}$ , a shift toward the benzene frequencies at 3047, 3062, and 3099  $\text{cm}^{-1}$  implying an increase in aromatic character of the C-H stretching vibration. The strong infrared bands at 1609 and 1635  $\text{cm}^{-1}$  in cyclooctatetraene, characteristic of the stretching of conjugated double bonds, are not observed in the complex. The Raman data for  $(\text{COT})\text{Fe}(\text{CO})_3$  in this region are somewhat uncertain owing to the presence of a strong cesium resonance line at 1639  $\text{cm}^{-1}$ , but no Raman lines could be detected in this region. Manual and Stone<sup>2</sup> and Cotton<sup>6</sup> assigned the strong infrared band at 1416  $\text{cm}^{-1}$  to the C=C stretching vibration since no other strong bands were found in this region. This was cited as evidence for a planar regular octagonal structure for the COT ring. Fritz and Keller,<sup>9,10</sup> from infrared measurements on solid  $(\text{COT})\text{Fe}(\text{CO})_3$  in KBr, assigned a band at 1464  $\text{cm}^{-1}$  to the C=C stretching mode and frequencies at 1414 and 1372  $\text{cm}^{-1}$  to the C-H deformation modes.

In this work, bands at 1562, 1490, and 1460  $\text{cm}^{-1}$  were found in the solution spectra, and it is probable that these are attributable to C=C stretching modes. The highest frequency at 1562  $\text{cm}^{-1}$  is polarized in the Raman spectrum and may result from symmetric stretching of the conjugated double bonds in the uncomplexed portion of the COT ring. This band has a somewhat lower infrared intensity than is normally associated with bands derived from C=C stretching modes, but this may be due in part to the planarity of this part of the ring which has also acquired some aromatic character. Some delocalization in the uncomplexed portion of the COT ring would also explain the lower C=C stretching frequency observed, compared to free COT. The existence of partial delocalization over the dihedral form of the ring is supported by the calculation of overlap integrals between SCF carbon  $\pi$  orbitals.<sup>7b</sup> The calculated overlap integral of 0.25 between C-1 and C-3 indicates an appreciable  $\pi$ -orbital interaction between the complexed butadiene-like residue and the remainder of the ring. Furthermore, the free half of the ring is almost planar as required for maximum overlap. There is a continuous  $\pi$ -electron overlap of 0.16 or more around the dihedral COT ring.

The assignment of the bands at 1414 and 1372  $\text{cm}^{-1}$  to C-H deformation modes<sup>9,10</sup> seems questionable since the corresponding modes in COT are found at 1221 and 1202  $\text{cm}^{-1}$ .<sup>19</sup> The highest in-plane C-H deformations in ferrocene and benzene are found at 1178  $\text{cm}^{-1}$ . It appears probable that the frequencies found at 1431 and 1419  $\text{cm}^{-1}$  in this work are derived from ring deformation modes.

(3) *Ring Metal Modes.* The ring-metal modes will consist of a ring-metal stretch, a ring-tilt,  $\text{COT-Fe}(\text{CO})_3$  bending modes, and an internal rotation of the  $\text{Fe}(\text{CO})_3$  group relative to the COT ring. The latter mode should give rise to a fairly high frequency in view of the strength of the ring-metal bonding which is sufficient to distort the COT ring. The exact location of this frequency is, however, uncertain. The ring-metal

stretch, found at 303  $\text{cm}^{-1}$  in ferrocene,<sup>21</sup> 298  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ,<sup>22</sup> and 279  $\text{cm}^{-1}$  in  $(\text{C}_6\text{H}_6)_2\text{Cr}$ ,<sup>23</sup> is expected around 300  $\text{cm}^{-1}$ . This vibration would also involve a large change in polarizability and should, therefore, give rise to a strong Raman shift. The

(21) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 10, 307 (1958).

(22) H. P. Fritz and J. Manchot, *ibid.*, 18, 171 (1962).

(23) H. P. Fritz, W. Lüttke, H. Stammreich, and R. Forneris, *ibid.*, 17, 1068 (1961).

very strong polarized band at 330  $\text{cm}^{-1}$  is most likely derived from this mode. This line is, however, broad and so may overlap a COT mode. In ferrocene,  $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ , and  $(\text{C}_6\text{H}_6)_2\text{Cr}$ <sup>23</sup> the ring-tilt is found at 388, 330, and 333  $\text{cm}^{-1}$ , respectively. The weak band at 404  $\text{cm}^{-1}$  may belong to this mode. The COT-Fe-(CO)<sub>3</sub> bending modes should be very low, below 100  $\text{cm}^{-1}$ , and were probably not observed in this work.

## Electron Spin Density Distribution and Structure of Nickel(II) and Cobalt(II) Acetylacetonate Complexes with Pyridine N-Oxides by Nuclear Magnetic Resonance Isotropic Shifts<sup>1</sup>

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*Pyridine N-oxide and its monomethyl derivatives form a series of isolable 2:1 complexes with nickel(II) and cobalt(II) acetylacetonates. Electron spin density distribution in the ligands was studied by n.m.r., and the data were compared with other experimental and calculated values. From pseudo-contact n.m.r. shifts it was ascertained that the pyridine N-oxide complexes have a M-O-N angle of 114–125° in solution. Evidence for hydrogen bonding with chloroform and the presence of other than 2:1 complexes in solution was also obtained.*

### Introduction

Nuclear magnetic resonance has been used in the determination of unpaired spin density distribution in the ligands of paramagnetic metal complexes in which the effective electron spin relaxation time is short.<sup>2–7</sup> More recently n.m.r. data on pairs of paramagnetic complexes, one essentially magnetically isotropic and the other anisotropic, have provided some details on the geometric structure of these complexes in solution.<sup>2–4</sup> Convenient systems for the study of these effects are the metal acetylacetonates of nickel(II) and cobalt(II) [bis(2,4-pentanedionato)nickel(II) and -cobalt(II), hereafter referred to as Ni(AA)<sub>2</sub> and Co(AA)<sub>2</sub>]. In solution these chelates exist as octahedrally coordinated polymeric species, but upon addition of

basic ligands an equilibrium mixture is formed in which the added ligand coordinates with the metal and reduces the degree of polymerization. With increasing ligand concentration there is generally formed a 2:1 complex in which the two acetylacetonate groups define an equatorial plane which includes the metal atom, and the two added ligands occupy positions axial to this plane.<sup>8</sup> The exchange rate of these ligands with the metal acetylacetonates has been found to be rapid. This results in a proton n.m.r. spectrum in which the observed chemical shifts are a number-average of the shifts of the coordinated and uncoordinated ligand. The deviations from the diamagnetic positions of the coordinated ligand proton resonances are dependent on the electron spin density at the proton and, in a magnetically anisotropic complex, the position of the proton relative to the molecular axis. Using the M(AA)<sub>2</sub> system, previous workers have determined that electron spin density is distributed by a  $\sigma$  mechanism in pyridine<sup>4</sup> and by a  $\pi$  mechanism in phenylisocyanide<sup>2</sup> and triphenylphosphine.<sup>2</sup> Furthermore all of these ligands form complexes in which the major ligand axis is coincident with the complex axis.

The present work is concerned with a study of the coordination of pyridine N-oxide and some of its methyl derivatives with Ni(AA)<sub>2</sub> and Co(AA)<sub>2</sub>. These aromatic N-oxides are weakly basic substances<sup>9</sup> which coordinate readily with metal salts.<sup>10</sup> Several calculations of the  $\pi$ -electronic structures of these ligands have been published.<sup>11,12</sup> These ligands are shown to

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