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Transition Metal Nuclear Quadrupole Resonance. IV. Manganese-55 Nuclear Quadrupole Resonance in π-Pyrrolenylmanganese Tricarbonyl and π-Cyclopentadienylmanganese Tricarbonyl and π-Pyrrolenyl–Metal Bonds

BY M. D. FAYER AND C. B. HARRIS[1]

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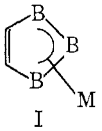
The ^{55}Mn nuclear quadrupole resonance in π-pyrrolenylmanganese tricarbonyl is reported. The temperature-dependent ^{55}Mn nuclear quadrupole resonance of π-pyrrolenylmanganese tricarbonyl and π-cyclopentadienylmanganese tricarbonyl was studied. The data suggest that the π-pyrrolenyl–manganese bond is significantly distorted *via* a pyrrole slippage such that the manganese to nitrogen and α-carbon bond distances are shorter than the manganese to β-carbon bond distances. The π-pyrrolenyl–manganese bond might be described as a four-electron metal–heterocyclic allylic and a two-electron metal–olefin bond rather than a six-electron π-cyclopentadienyl-type bond. A fast-sweep nqr spectrometer is also described.

Introduction

The interpretation of the spectra, magnetic properties, and the electronic structure and bonding of transition metals with cyclopentadienyl and related ligands such as substituted cyclopentadienyls, carborane anions, pyrrolenyl, etc., have been problems of considerable importance in coordination chemistry. In spite of the past and continuing interest in these compounds several unresolved questions related to both the electronic and molecular structures still exist. In particular, the observations of Hawthorne[2] and Wing[3] that transition metal–1,2 carborane complexes of Cu(II), Cu(III), Ni(II), Pt(II), Au(II), and Pd(II) exhibit bonds more characteristic of allylic (I) rather than π-cyclopentadienyl (II) type of interactions suggest that substituted cyclopentadienyl–metal bonds in certain cases may likewise be distorted. Recently,[4] it has been suggested that substituted cyclopentadienyl tricarbonyl complexes of the form π-RC$_5$H$_4$M(CO)$_3$ (M = Mn or Re) can be distorted from the ideal π-C$_5$H$_5$Mn(CO)$_3$, CpMn(CO)$_3$, structure *via* an induction or conjugative interaction of the substituent, R, with the cyclopentadienyl moiety. It is possible, however likely or unlikely, to envision a more allylic cyclopentadienyl (III) resulting from the inductive effect of the substituent R and a fulvene-like structure (IV) of the substituted cyclopentadienyl in the limit of high conjugation of R with the π electrons of the C$_5$ ring. From a structural point of view, the existence of III or IV should result in a distorted metal–cyclopentadienyl bond. Unfortunately no crystallographic data are available for these compounds. However, data available [5-7] for 1,2-carborane complexes with d^6 transition metals show little, if any, evidence of distorted C$_3$B$_2$–M (M = Fe(II), Co(III), Re(I)) bonds. Moreover a recent investigation[8] of the Co(III) field gradient in Cs(1,2-C$_2$B$_9$H$_{11}$)$_2$Co$^{\text{III}}$ established a maximum difference of only ~4% between the borons and carbons bonded to Co. It is of interest therefore to determine if distortions in RC$_5$H$_4$Mn(CO)$_3$, d^6, complexes exist if and when differences in the electron density of various carbons of the C$_5$ ring exceed 4%.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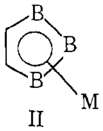
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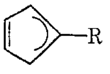
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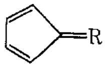
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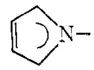
For our investigation the ^{55}Mn nuclear quadrupole resonance of π-pyrrolenylmanganese tricarbonyl, PyMn(CO)$_3$, rather than substituted π-cyclopentadienylmanganese tricarbonyl was compared to π-cyclopentadienylmanganese tricarbonyl, CpMn(CO)$_3$, for several reasons. First, there can be no conjugative effect in the sense that no reasonable olefinic resonance structure exists for carbons and nitrogen in the pyrrolenyl ring. Second, the known distortions[2,3] in transition metal–1,2-carborane complexes are allylic in nature and an allylic resonance structure (V) can be postulated for pyrrolenyl. Finally, since a temperature-dependent nqr investigation of ^{55}Mn relates to vibrational frequencies and *moments of inertia,*[9] it is necessary to have the molecular weights of six-electron donors (C$_5$H$_5^-$, MW = 65.095; NC$_4$H$_4^-$, MW = 66.083) as close as possible to facilitate the comparison.


V

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(1) To whom correspondence should be addressed.

(2) L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 4823 (1968).

(3) R. M. Wing, *ibid.*, **90**, 4828 (1968).

(4) A. N. Nesmeyanov, G. K. Semin, E. V. Bryuchova, T. A. Babushkina, K. N. Anisimov, N. E. Kolobova, and Yu. V. Makarov, *Tetrahedron Letters*, **37**, 3987 (1968).

(5) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Am. Chem. Soc.*, **87**, 3988 (1965).

(6) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967).

(7) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *ibid.*, **5**, 1189 (1966).

(8) C. B. Harris, *ibid.*, **7**, 1517 (1968).

(9) T. P. Das and E. L. Hahn, *Solid State Phys. Suppl.*, **1**, 44 (1958).

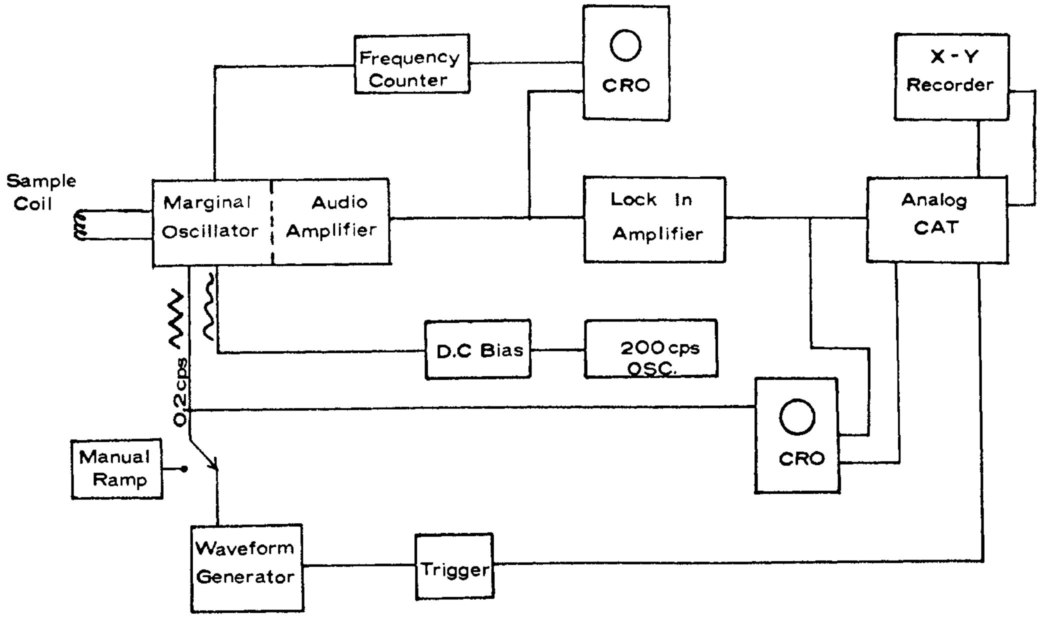

Figure 1.—Fast-sweep nqr spectrometer.

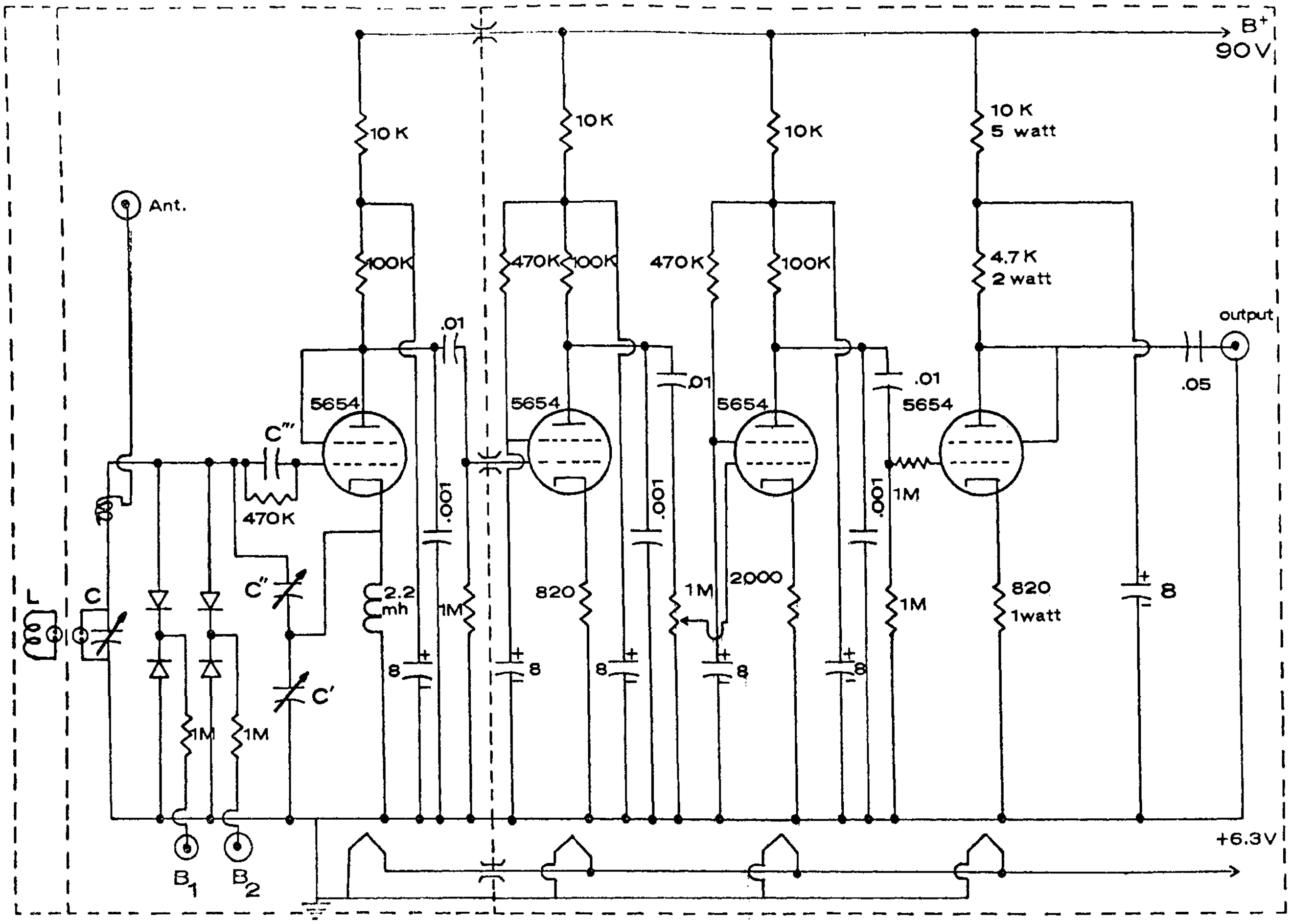

Figure 2.—Marginal oscillator and audioamplifier circuits.

Experimental Section

Spectrometer.—Because very accurate frequency measurements are required in temperature-dependent nqr experiments, it was necessary to construct a versatile frequency-modulated regenerative or marginal oscillator. The spectrometer shown in Figure 1 has sweep capabilities of 20–80 kHz/sec in 100–500-kHz increments from 5 to 50 MHz. The circuit in Figure 2 is a modified Colpitts[10] oscillator followed by an audioamplifier identical with that used by Gutowsky, *et al.*[11]

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[10] E. V. Malmstadt, C. G. Enke, and E. C. Toren, Jr., "Electronics for Scientists," W. A. Benjamin, Inc., New York, N. Y., 1963.

[11] H. S. Gutowsky, L. H. Meyer, and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

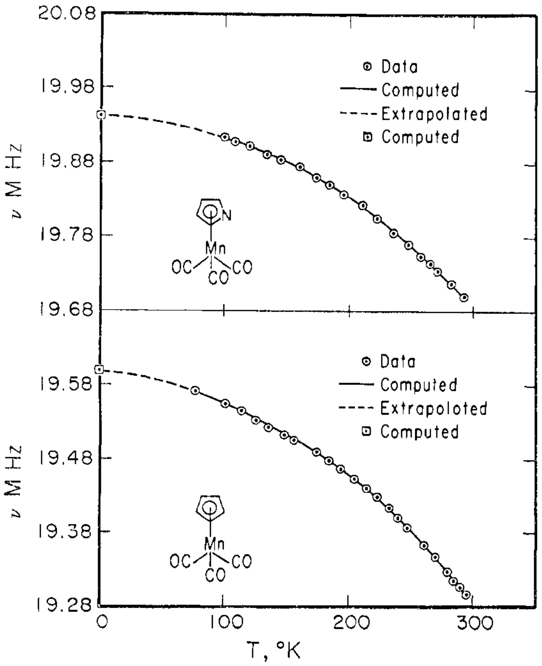

Figure 3.—Temperature-dependent nqr ±$^3/_2$ → $^5/_2$ transitions in PyMn(CO)$_3$ and CpMn(CO)$_3$.

The radiofrequency energy absorbed by the sample at resonance lowered the oscillation amplitude by lowering the LC impedance of the tank circuit. This change manifested itself as an increased audiocomponent at the modulation frequency. After audioamplification the signal was detected by a phase-sensitive narrow-banded amplifier, a PAR HR-8. Because the frequency was swept at a high rate, it was necessary to use a very low RC time constant (10–100 msec). The high rate of sweep, *e.g.*, 50 kHz/sec, accomplished two purposes. First, it prevented saturation of the nqr resonance under saturation conditions, $H_1 > 1/\gamma(T_1T_2)^{-1/2}$, provided the time required for passage through resonance was less than T_2, where H_1 is the radiofrequency field, γ is the gyromagnetic ratio, and T_1 and T_2 are the spin–lattice and spin–spin relaxation times, respectively. Furthermore, it allowed one efficiently to time-average the signal output from the lock-in amplifier. This increased the over-all sensitivity from the lock-in by the $\sqrt{n}$ where n is the number of sweeps through resonance. Allowing time for manual readjustment of the oscillator level every 200–500 kHz, the spectrometer was capable of scanning 3–4 MHz every hour.

In principle large signal-to-noise ratios could be obtained in phase-sensitive detection methods using slow sweep rates and long time constants, *e.g.*, 10 kHz/min and 3 sec or longer. This assumed, however, that saturation was not a problem at these slow sweep rates. In practice, however, the signal-to-noise ratio was not a linear function of the square root of the time constant. At some given value of the lock-in amplifier time constant, characteristic of each instrument, the signal-to-noise ratio became nonlinear. This was primarily due to the increased low-frequency noise component.[12] For most marginal and superregenerative oscillators the nonlinearity began at a time constant on the order of 1–10 sec. Analog or digital averaging on the other hand was linear to infinite "effective time constants," *i.e.*, number of repetitive sweeps.

When signal recovery required long characteristic time constants, as is generally the case in nqr, it is better to decrease the lock-in detection time, increase the frequency sweep rate, and analog or digitally average repetitive sweeps.

In order simultaneously to frequency-modulate and frequency-sweep, two varactor bridges, B$_1$ and B$_2$, were connected across the tank circuit. It was important to dc-bias[13] both bridges so that the varactors operated in their low-capacitance region. In this manner the circuit Q was high and it was not limited by the lower varactor Q at low voltages.

The oscillator was frequency-modulated by a dc-biased 1-V (peak-to-peak) 200-Hz/sec sine wave across B$_1$. An Exact Model 250 waveform generator supplied the ramp voltage, 30–50 V, necessary for frequency sweeping at B$_2$. It also triggered a dc-coupled PAR-TDH-9 Waveform Eductor which served as an analog memory in which the signal was accumulated.

The radiofrequency was continually monitored by an HP 5245L frequency counter. Two turns of insulated wire wrapped around the "hot" terminal of C served as an effective antenna. Utilizing an HP 5261A videoamplifier the radiofrequency level could be conveniently set such that the oscillator operated at optimum marginality, *e.g.*, about 1 mV on the HP 5261A. The disadvantage of such a monitor system was that the antenna introduced stray capacitance in parallel with the tank circuit. This had the effect of lowering the Q about 5–10%. Such a loss, however, did not visibly decrease the over-all sensitivity of the instrument.

To ensure adequate shielding against radio stations and spurious radiofrequency signals, the sample coil, the radiofrequency oscillator, and the audioamplifier were placed in three compartments of a brass box.

A simple method has been devised for measuring the resonance frequency and half-width. When the ramp voltage at B$_2$ was used to sweep a storage oscilloscope in the external horizontal mode and the PAR-TDH-9 readout was used as the signal input, the oscilloscope became x–y in frequency and amplitude, respectively. After a sufficient signal had accumulated in the analog memory, one replaced the ramp voltage with a manually adjustable dc bias and simply centered the CRT electron beam at the appropriate position on the x axis and read the frequency from the frequency counter. An accuracy of ±0.1 kHz could easily be obtained in this manner.

Finally, the variable-temperature cell used was that described in an earlier paper.[14]

Sample Preparation.—C$_5$H$_5$Mn(CO)$_3$ (Strem Chemical) was purified twice by sublimation and sealed in a glass vial under N$_2$. NC$_4$H$_4$Mn(CO)$_3$ was prepared according to the literature,[15] sublimed twice for purification, and sealed under N$_2$. About 2.5-g samples of the compounds were used in the nqr spectrometer.

Results

The temperature-dependent ^{55}Mn $\omega = \pm{}^3/_2 \rightarrow \pm{}^5/_2$ nuclear quadrupole transitions are presented graphically in Figure 3 for both CpMn(CO)$_3$ and PyMn(CO)$_3$.[16] The ^{55}Mn $\omega = \pm{}^1/_2 \rightarrow \pm{}^3/_2$ transition for PyMn(CO)$_3$ was also found at 10.1317 MHz for 295°K. The room-temperature[17] and the liquid N$_2$ data[4] have been reported for CpMn(CO)$_3$ as well as various substituted RC$_5$H$_5$Mn(CO)$_3$'s.[4] The CpMn(CO)$_3$ and PyMn(CO)$_3$ $\omega = \pm{}^1/_2 \rightarrow \pm{}^3/_2$ transitions and $\omega = \pm{}^3/_2 \rightarrow \pm{}^5/_2$ transitions were measured at room temperature and at liquid N$_2$ temperature. The data and the calculated asymmetry parameters η are presented in Table I.

From Table I it can be seen that the asymmetry parameter η is virtually temperature independent over the temperature range under consideration. The tem-

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[12] M. P. Klein and G. W. Barton, Jr., *Rev. Sci. Instr.*, **34**, 754 (1963).

[13] The value of the dc bias across B$_1$ and B$_2$ apply to Microwave Associates Types MA-4273C and MA-4273E varactors, respectively.

[14] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8**, 763 (1969).

[15] K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. H. Stubbs, *J. Organometal. Chem.* (Amsterdam), **1**, 471 (1963).

[16] To our knowledge the ^{55}Mn nqr signal in NC$_4$H$_4$Mn(CO)$_3$ has never been reported.

[17] J. Voitländer, H. Klocke, R. Longino, and H. Thieme, *Naturwissenschaften*, **49**, 491 (1962).

TABLE I

	$CpMn(CO)_3$		$PyMn(CO)_3$	
	298°K	77°K	298°K	77°K
$\omega(\pm{}^1/_2 \rightarrow \pm{}^3/_2)$, MHz	9.6520	9.8030	10.1331	10.2287
$\omega(\pm{}^3/_2 \rightarrow \pm{}^5/_2)$, MHz	19.2957	19.5724	19.6952	19.9355
η	0.0185	0.0340	0.1490	0.1425

perature-dependent data were fit by a least-squares program to Bayer's equation[9,18] and extrapolated to 0°K. In both molecules excellent agreement with Bayer's theory is observed, presumably because the effect of the ^{55}Mn vibrations in the lattice are small compared to the librational and vibrational motion of cyclopentadienyl or pyrrolenyl ligands.

Discussion

The salient features of temperature-dependent nuclear quadrupole resonance in molecular crystals have been derived by Bayer[18] and are represented by

$$\omega(T) = \omega_0\left\{1 - {}^3/_2h\left[\frac{1 + (\eta/3)}{2A_x\nu_x} + \frac{1 - (\eta/3)}{2A_y\nu_y}\right] - {}^3/_2h\left[\frac{1 + (\eta/3)}{A_x\nu_x(\exp(h\nu_x/kT) - 1)} + \frac{1 - (\eta/3)}{A_y\nu_y(\exp(h\nu_y/kT) - 1)}\right]\right\} \quad (1)$$

where $\omega(T)$ is the temperature-dependent nqr frequency, *i.e.*, ^{55}Mn $\omega(\pm{}^3/_2 \rightarrow \pm{}^5/_2)$, ω_0 is the zero-point frequency, η is the asymmetry parameter defined in terms of the field gradient tensor, $\eta = (q_{xx} - q_{yy})/q_{zz}$, A_x and A_y are the moments of inertia in the x and y directions, and ν_x and ν_y are the vibrational frequencies around the x and y directions. The x, y, and z directions are defined by the coordinate system, shown in Figure 4a, that diagonalized the field gradient tensor. At low temperatures librations of the molecule or parts of the molecule (*i.e.*, the cyclopentadienyl or pyrrolenyl anion) are especially effective in linearly averaging the field gradient tensor. At higher temperatures this effect manifests itself in the curvature of the field gradient. In order to simplify the analysis Table II lists parameters and ratios of the various parameters calculated from a least-squares fit of the data to Bayer's equation.[9,18]

TABLE II

Parameter	$PyMn(CO)_3$/ $CpMn(CO)_3$ parameter ratio	Parameter	$PyMn(CO)_3$/ $CpMn(CO)_3$ parameter ratio
A_x	2.1 ± 0.1	ν_x	0.9 ± 0.2
A_y	1.0 ± 0.1	ν_y	1.2 ± 0.2

Parameter	$PyMn(CO)_3$	$CpMn(CO)_3$
ω_0, MHz	21.3309	22.0495
ω(0°K), MHz	19.9415	19.5965
$\omega_0 - \omega$(0°K), MHz	1.3894	2.4530

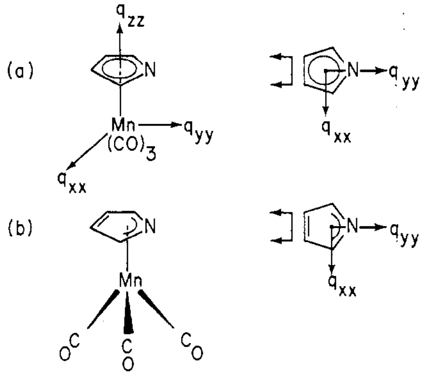

Figure 4.—The relation of the field gradient tensor to the molecular geometry of (a) "normal" $PyMn(CO)_3$ and (b) "slipped" $PyMn(CO)_3$.

At the lower temperature, $\omega_0 - \omega$(0°K) is a measure of zero-point vibration contribution to the field gradient. It can be seen that the $PyMn(CO)_3$ zero-point vibrational contribution is a full 1 MHz lower than that of $CpMn(CO)_3$ in spite of the larger η. This amounts to 5% of the total field gradient and can only be accounted for by the larger A_x since the A_y, ν_x, and ν_y values appear to be practically identical for the two molecules. Furthermore, the high-temperature curvature differences result almost entirely from the twofold difference in the x moment of inertia, A_x.

The implication of the data to the nature of the π-pyrrolenyl–manganese bond is self-evident assuming Bayer's theory is representative of temperature-dependent nqr effects. Consider first the vibrational frequency ratios in the x and y directions. The fact that the vibrations or, more accurately, rocking frequencies around the q_{xx} and q_{yy}, respectively, appear to be practically identical in the two complexes means that the pyrrolenyl should be nearly orthogonal to the threefold axis of the CO's. Distortions larger than about 10–15° would cause the ν_x and ν_y ratios ($PyMn(CO)_3/CpMn(CO)_3$) to deviate significantly from 1 since the cyclopentadienyl group is orthogonal to the threefold axis in $CpMn(CO)_3$.[19]

Finally, and by far the most interestingly, a slippage of the pyrrole anion with respect to the $Mn(CO)_3$ can be postulated to account for the twofold difference in A_x, $PyMn(CO)_3$ *vs.* $CpMn(CO)_3$. This is illustrated in Figure 4b. Assuming all of the differences in the x moments of inertia result from a slippage of the pyrrole anion, one can calculate the amount of distortion. A slippage of 0.6–0.7 Å is necessary to account for the data. It should be emphasized that the magnitude of this number is maximum since other distortions, *i.e.*, carbonyl distortions on the order of 0.2–0.5 Å, could reduce it substantially. Furthermore, the hypothesis of a slippage in $PyMn(CO)_3$ is only consistent within the basic validity of Bayer's theory. If the slippage is real, the bonding of the Mn to the pyrrole anion can be described in valence-bond terms as a 4e$^-$ heterocyclic allylic bond and a 2e$^-$ olefin

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(18) H. Bayer, *Z. Physik*, **130**, 227 (1961).

(19) A. F. Berndt and R. E. Marsh, *Acta Cryst.*, **16**, 118 (1963).

bond (*cf.* Figure 4b). Although one cannot distinguish between a cyclopentadienyl group bonded in the allylic manner and one bonded as a six-electron donor,[20] it is entirely reasonable that the nitrogen in a pyrrolenyl ligand causes enough electron asymmetry to produce a distortion. It is noteworthy that the E mode of C≡O stretch is split by 11 cm^{-1} in PyMn(CO)$_3$. This reflects the electronic asymmetry at the Mn *via* the loss of the fivefold symmetry of the ring (*e.g.*, Cp$^-$ *vs.* Py$^-$). Moreover in substituted RCpMn(CO)$_3$[21] molecules where R equals C(O)CH$_3$, C(O)C$_6$H$_5$, etc., splittings of the same order of magnitude are observed. Whether or not the pyrrole slippage is real, the pyrrolenyl affects the Mn 3d orbitals by removing the degeneracy of the 3d$_{xz}$ and 3d$_{yz}$ orbitals.

The similarity in the properties, particularly the ν_x and ν_y's, of PyMn(CO)$_3$ and CpMn(CO)$_3$ as displayed in Table I, indicate that the direction of the field gradient tensor in the PyMn(CO)$_3$ is essentially the same as in CpMn(CO)$_3$. The major factor contributing to the asymmetry parameter, η, is therefore the population difference of the 3d$_{xz}$ and 3d$_{yz}$ orbitals. The difference can be calculated from η. In terms of a molecular orbital interpretation[22] of the field gradient an equation for η

$$\eta = \frac{{}^3/_2\,(\#3\mathrm{d}_{xz} - \#3\mathrm{d}_{yz})eq_{3\mathrm{d}_{z^2}}Q}{eq_{zz}Q} \qquad (2)$$

can be derived where #3d$_{xz}$ and #3d$_{yz}$ are the orbital populations and $eq_{3\mathrm{d}_{z^2}}Q$ and $eq_{zz}Q$ are the quadrupole coupling constants for one 3d$_{z^2}$ electron and for PyMn(CO)$_3$, respectively. Using eq 2 the difference #3d$_{xz}$ − #3d$_{yz}$ is 0.03 ± 0.01 electron.[23] This difference arises from the donation of pyrrolenyl π electrons to the manganese in predominantly ligand molecular orbitals since the metal molecular orbitals having 3d$_{xz}$ and 3d$_{yz}$ character would be empty.

In summary, the temperature-dependent ^{55}Mn nqr data are consistent with a slipped pyrrolenyl–manganese bond (*cf.* Figure 4b), although final confirmation of such a distortion must come from a crystallographic study of PyMn(CO)$_3$.

Acknowledgments.—M. D. F. acknowledges the NSF for an undergraduate fellowship. This work was supported by the Inorganic Materials Research Division, Lawrence Radiation Laboratory, under the auspices of the United States Atomic Energy Commission.

[20] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **91**, 2528 (1969).

[21] J. Kozikowski, R. E. Maginn, and M. S. Klove, *ibid.*, **81**, 2995 (1959).

[22] F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

[23] The error of ±0.01 electron is due to the 25% uncertainty in Q for ^{55}Mn.

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Vibrational Spectra and Structure of Organophosphorus Compounds. VIII. Tetramethylbiphosphine[1]

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The infrared spectra of gaseous, liquid, and solid tetramethylbiphosphine have been recorded from 4000 to 33 cm^{-1}. The Raman spectra of the liquid and the solid have also been recorded and depolarization values have been measured. A comparison of the Raman spectra of the liquid and the solid indicates that the liquid consists of a mixture of *trans* and *gauche* conformers with the *gauche* structure slightly predominant. A similar comparison of the infrared and Raman bands of solid tetramethylbiphosphine below 750 cm^{-1} shows the mutual exclusion principle is operative, and it is concluded from this alternate forbiddeness that the *trans*-P$_2$(CH$_3$)$_4$ isomer of C$_{2h}$ symmetry gives rise to these mutually exclusive bands. Assignments of the observed frequencies based on depolarization values, band positions, and relative intensities are presented for the molecule in both the C$_2$ and C$_{2h}$ configurations. It is also shown that the two isomers may differ little in energy in the liquid state.

Introduction

The symmetry of molecules which have the general formula X$_2$Y$_4$ has been the subject of several recent vibrational studies. The possible structures for X$_2$Y$_4$-type molecules include planar (D$_{2h}$ symmetry), staggered (D$_{2d}$), *trans* (C$_{2h}$), *gauche* (C$_2$), and *cis* (C$_{2v}$). It has been found that, for molecules in which the central pair of atoms is nitrogen or phosphorus, the structures determined have been either *trans* or *gauche.* These structures correspond to a pyramidal arrangement of neighboring atoms and nonbonded electron pairs about the central group V atoms. The relative amounts of the *trans* or *gauche* isomers will depend upon the interactions of the two nonbonded electronic clouds and the steric repulsions of the substituent atoms as

[1] Part VII: J. R. Durig and J. S. DiYorio *J. Mol. Struct.*, **3**, 179 (1969).

[2] Taken in part from the thesis submitted by J. S. DiYorio to the Department of Chemistry in partial fulfillment of the Ph.D. degree.