Determination of structural parameters for the half-sandwich compounds cyclopentadienyl thallium and cyclopentadienyl indium and indium quadrupole coupling for cyclopentadienyl indium using microwave spectroscopy

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Microwave rotational transitions for $J' \leftarrow J = 2 \leftarrow 1$ and $3 \leftarrow 2$ were measured in the 7–11 GHz range for three isotopomers of $(C_5H_5)In$. Similar transitions (up to $J' \leftarrow J = 5 \leftarrow 4$) for eight isotopomers of $(C_5H_5)Tl$ were measured in the 5–15 GHz range. The rotational constants of the most abundant isotopomers are $B(Cp\ ^{203}Tl) = 1467.9730(11)$ MHz, $B(Cp\ ^{205}Tl) = 1465.0723(14)$ MHz, $B(Cp\ ^{113}In) = 1809.9785(30)$ MHz, and $B(Cp\ ^{115}In) = 1800.8199(18)$ MHz $(Cp = C_5H_5)$. The quadrupole coupling strengths for the indium compounds are $eQq(Cp\ ^{113}In) = -118.397(69)$ MHz and $eQq(Cp\ ^{115}In) = -119.981(31)$ MHz. Spectra for single-substitution ^{13}C isotopomers were seen in natural abundance. Deuterated samples of CpTl were prepared to obtain spectra for deuterium-substituted isotopomers. Analysis of the spectra allowed the determination of the following structural parameters; for $(C_5H_5)Tl$, $r(Tl-C_5) = 2.413(3)$ Å, $r(C-C) = 1.421(10)$ Å, $r(C-H) = 1.082(9)$ Å and $\angle C_5-H = 0.9(2)°$ (C_5 represents the planar, 5-carbon ring of C_5H_5), and for $(C_5H_5)In$, $r(In-C_5) = 2.314(4)$ Å and $r(C-C) = 1.426(6)$ Å. A Kraitchman analysis was performed on the available isotopomers for comparison of r_0 and r_s values. Both structural analyses indicate that the hydrogen atoms in $(C_5H_5)Tl$ are bent slightly out of the carbon plane away from the coordinated metal atom. © *1997 American Institute of Physics.* [S0021-9606(97)01234-8]

I. INTRODUCTION

Cyclopentadienyl thallium and cyclopentadienyl indium are relatively stable examples of the interesting and unusual ''half-sandwich'' complexes. The open coordination geometry suggests that these complexes could be quite reactive, but both complexes can be easily prepared and readily sublimed without decomposition. CpIn ($Cp = \eta^5 - C_5H_5$) is light sensitive and CpTl only slightly light sensitive. The preparation of CpTl was reported by Fischer[1] and the preparation of CpIn by Fischer and Hofmann.[2] CpTl is useful as a donor of the Cp ligand, and CpIn for the preparation of other indium complexes. The π-bonded, half-sandwich geometry was proposed by Cotton and Reynolds,[3] on the basis of infrared spectra. Some of the earliest studies of microwave spectra of transition metal complexes include the reports of transitions for Cp ^{203}Tl, and Cp ^{205}Tl, along with other symmetric top complexes.[4] Since only two isotopomers were observed in the earlier work, only approximate structural parameters could be obtained, but it was determined that the complex is a symmetric top. The previous structure for CpIn was obtained from gas-phase electron diffraction work.[5] The results of the present analysis of microwave data for three isotopomers of CpIn are in excellent agreement with the electron diffraction results. The C–H bonds were found to be bent out of the C_5 plane by slightly different amounts in the two complexes.

II. EXPERIMENT

The CpTl sample was obtained from Strem Chemicals(81-0300) and used after sublimation at about 80 °C and 10 mTorr pressure. The CpIn sample was also obtained from Strem(97-3425) and used after sublimation at about 40 °C and 10 mTorr pressure. Deuterated isotopomers of CpTl were prepared via the method outlined by A. Emad and M. D. Rausch.[6] Attempts were made to synthesize deuterated isotopomers of CpIn from $InCl_3$ and deuterated CpTl, following the general scheme of Fischer and Hofmann,[2] but only the $In(III)Cp_3$ complex was formed, and attempts to convert this to $In(I)Cp$ were not successful. The microwave spectrum was scanned in the 5–15 GHz range for CpTl and in the 7–11 GHz range for CpIn using a Flygare–Balle type spectrometer system.[7] For CpTl, the sample and pulse valve (General Valve 9-181) were maintained at 85–105 °C to produce sufficient vapor pressure. For CpIn, they were maintained at 50–60 °C. The samples, mixed with neon at 0.6–0.9 atm, were pulsed into the Fabry–Perot microwave cavity for observation of the spectra. Spectra typical for a symmetric top were seen for $J' \leftarrow J = 2 \leftarrow 1$ through $5 \leftarrow 4$ for CpTl and spectra expected for a symmetric top with quadrupole coupling due to a 9/2 spin were observed for $J' \leftarrow J = 3 \leftarrow 2$ and $2 \leftarrow 1$ for CpIn. The measured transition frequencies are listed in Tables I–VIII and XII–XIV.

III. DATA ANALYSIS

A. Cyclopentadienyl thallium

Sixty seven lines were measured for eight isotopomers. Symmetric top spectra were observed for the two Tl isotopic species and the perdeuterated samples. Simple asymmetric top spectra were observed for the remaining species. More

TABLE I. Measured and calculated microwave transition frequencies (MHz) for the CpTl doubly deuterated isotopomer, meta-D_2- $^{205}TlC_5D_2H_3$. The calculated frequencies are from a least-squares fit to the data with parameters listed in Table IX. The ''Difference'' column is ''Measured''-''Calculated'' frequency. ''Intensity'' is the approximate, relative measured intensity of the transition.

Measured	Calculated	Difference	Intensity	J'	K'_p	K'_0	J	K_p	K_0
5628.2954(30)	5628.2941	0.0013	10	2	1	2	1	1	1
5661.9871(40)	5661.9840	0.0031	13	2	0	2	1	0	1
5696.2616(44)	5696.2503	0.0113	16	2	1	1	1	1	0
8442.2186(24)	8442.2217	−0.0031	30	3	1	3	2	1	2
8492.1399(18)	8492.1387	0.0012	35	3	0	3	2	0	2
8493.4469(26)	8493.4458	0.0011	10	3	2	2	2	2	1
8544.2614(29)	8544.2712	−0.0098	16	3	1	2	2	1	1

TABLE II. Measured and calculated microwave transition frequencies (MHz) for the singly deuterated isotopomer $^{205}TlC_5DH_4$.

Measured	Calculated	Difference	Intensity	J'	K'_p	K'_0	J	K_p	K_0
5737.6094(11)	5737.6057	0.0037	35	2	1	2	1	1	1
5758.7011(25)	5758.6993	0.0018	55	2	0	2	1	0	1
5780.1115(11)	5780.1031	0.0084	30	2	1	1	1	1	0
8606.3160(16)	8606.3179	−0.0019	120	3	1	3	2	1	2
8637.7904(11)	8637.7901	0.0003	220	3	0	3	2	0	2
8638.2537(56)	8638.2462	0.0075	150	3	2	2	2	2	1
8670.0598(10)	8670.0641	−0.0043	165	3	1	2	2	1	1
11 474.9211(19)	11 474.9211	0.0000	300	4	1	4	3	1	3
11 516.4598(25)	11 516.4616	−0.0018	150	4	0	4	3	0	3
11 517.5352(78)	11 517.5386	−0.0034	75	4	2	3	3	2	2
11 517.8281(26)	11 517.8283	−0.0002	70	4	3	2	3	3	1
11 518.7424(36)	11 518.7448	−0.0024	55	4	2	2	3	2	1
11 559.9135(22)	11 559.9141	−0.0006	300	4	1	3	3	1	2

TABLE III. Measured and calculated microwave transition frequencies (MHz) for the natural abundance ^{13}C isotopomer $^{203}Tl^{13}CC_4H_5$.

Measured	Calculated	Difference	Intensity	J'	K'_p	K'_0	J	K_p	K_0
5797.4460(38)	5797.4439	0.0021	20	2	1	2	1	1	1
5803.4611(17)	5803.4598	0.0013	20	2	0	2	1	0	1
5809.4864(21)	5809.4874	−0.0010	20	2	1	1	1	1	0
8696.1442(51)	8696.1453	−0.0011	40	3	1	3	2	1	2
8705.1494(22)	8705.1508	−0.0014	50	3	0	3	2	0	2
8714.2104(37)	8714.2105	−0.0001	50	3	1	2	2	1	1
11 594.8199(48)	11 594.8201	−0.0002	5	4	1	4	3	1	3
11 606.7957(83)	11 606.7953	0.0004	30	4	0	4	3	0	3
11 618.9077(51)	11 618.9071	0.0006	15	4	1	3	3	1	2

TABLE IV. Measured and calculated microwave frequencies (MHz) for $^{205}Tl^{13}CC_4H_5$.

Frequency	Calculated	Difference	Intensity	J'	K'_p	K'_0	J	K_p	K_0
5785.8729(37)	5785.8717	0.0012	8	2	1	2	1	1	1
5791.8630(13)	5791.8620	0.0010	20	2	0	2	1	0	1
5797.8666(25)	5797.8668	−0.0002	20	2	1	1	1	1	0
8678.7831(18)	8678.7841	−0.0010	70	3	1	3	2	1	2
8687.7525(10)	8687.7534	−0.0009	85	3	0	3	2	0	2
8696.7765(26)	8696.7769	−0.0004	80	3	1	2	2	1	1
11 571.667(16)	11 571.6670	−0.0000	25	4	1	4	3	1	3
11 583.5983(48)	11 583.5975	0.0008	35	4	0	4	3	0	3
11 583.6673(47)	11 583.6675	−0.0002	25	4	2	3	3	2	2
11 583.7500(48)	11 583.7497	0.0003	25	4	3	2	3	3	1

TABLE V. Measured and calculated microwave frequencies (MHz) for ^{205}TlC$_5$H$_5$.

Measured	Calculated	Difference	Intensity	J'	K'	J	K
5860.2811(7)	5860.2812	−0.0001	1000	2	0	1	0
8790.3542(33)	8790.3592	−0.0050	1000	3	1	2	1
8790.4103(12)	8790.4067	0.0036	1000	3	0	2	0
11 720.5159(34)	11 720.5139	0.0020	100	4	0	3	0
14 650.5207(49)	14 650.5177	0.0030	15	5	1	4	1
14 650.5931(47)	14 650.5968	−0.0037	15	5	0	4	0

TABLE VI. Measured and calculated microwave frequencies (MHz) for ^{203}TlC$_5$H$_5$.

Measured	Calculated	Difference	Intensity	J'	K'	J	K
5871.8816(9)	5871.883	−0.0018	330	2	0	1	0
8807.7658(26)	8807.769	−0.0028	500	3	1	2	1
8807.8107(22)	8807.809	0.0020	500	3	0	2	0
11 743.7174(28)	11 743.714	0.0032	30	4	0	3	0
14 679.5284(68)	14 679.527	0.0017	10	5	1	4	1
14 679.5904(43)	14 679.593	−0.0030	10	5	0	4	0

TABLE VII. Measured and calculated microwave frequencies (MHz) for ^{205}TlC$_5$D$_5$.

Measured	Calculated	Difference	Intensity	J'	K'	J	K
5390.5500(45)	5390.550	0.000	10	2	0	1	0
8085.8007(16)	8085.809	−0.0083	135	3	0	2	0
10 780.8720(50)	10 780.872	0.000	25	4	2	3	2
10 781.0553(28)	10 781.049	0.0063	50	4	0	3	0

TABLE VIII. Measured and calculated microwave frequencies (MHz) for ^{203}TlC$_5$D$_5$.

Measured	Calculated	Difference	Intensity	J'	K'	J	K
5401.5414(18)	5401.538	0.0034	10	2	0	1	0
8102.2870(10)	8102.291	−0.0040	65	3	0	2	0
10 802.8075(12)	10 802.806	0.0015	10	4	2	3	2
10 802.9605(44)	10 802.968	−0.0075	10	4	1	3	1
10 803.0296(49)	10 803.023	0.0066	50	4	0	3	0

TABLE IX. Parameters from the least-squares-fit analyses of the various CpTl isotopomers. The listed uncertainties are 2σ. The σ values are the standard deviations for the fits.

Parameter	^{203}TlC$_5$H$_5$	^{205}TlC$_5$H$_5$	^{203}Tl^{13}CC$_4$H$_5$	^{205}Tl^{13}CC$_4$H$_5$	^{205}TlC$_5$H$_4$D	m-^{205}TlC$_5$H$_3$D$_2$	^{203}TlC$_5$D$_5$	^{205}TlC$_5$D$_5$
A (MHz)			4400(400)	4700(106)	4250(19)	4050(55)		
B (MHz)	1467.9730(11)	1465.0723(14)	1453.8802(9)	1450.9689(5)	1450.3412(14)	1432.5888(45)	1350.3868(42)	1347.6397(14)
C (MHz)	1467.9730(11)	1465.0723(14)	1447.8584(9)	1444.9713(5)	1429.0923(1)	1398.5716(45)	1350.3868(42)	1347.6397(14)
D_J (kHz)	0.27(3)	0.25(3)	0.25(4)	0.32(2)	fixed	fixed	0.28(16)	fixed
D_{JK} (kHz)	6.6(8)	7.9(10)	0.82(56)	0.18(14)	1.1(3)	0.3(12)	6.8(7)	5.5(6)
σ (kHz)	3.6	4.7	1.7	1.0	4.6	9.1	8.3	7.6

TABLE X. Measured transition frequencies believed to be due to the ortho-D_2-^{205}Tl($C_5H_3D_2$)(o-205) isotopomer and the D_2– ^{203}Tl($C_5H_3D_2$)(o-203, m-203) isotopomers.

Frequency	Intensity	Isotopomer	J'	K'_p	K'_0	J	K_p	K_0
5660.4764(9)	10	o-205	2	0	2	1	0	1
8472.8472(46)	25	o-205	3	1	3	2	1	2
8490.5965(8)	25	o-203	3	1	3	2	1	2
8507.6114(17)	30	o-203	3	0	3	2	0	2
8508.6028(36)	35	o-205	3	1	2	2	1	1
8509.1485(36)	35	m-203	3	0	3	2	0	2

lines are included in the asymmetric top spectral analysis simply because the K states are no longer degenerate. In each case, the data was fit to a Hamiltonian consisting of rotational constants and the distortion constants D_J and D_{JK}. For the deuterated isotopomers, the value of D_J was fixed at the values from the ^{13}C data because this parameter had remained relatively constant during the other spectral analyses but was highly correlated with the A rotational constant in these spectral line fits. The seven measured transitions for the meta-D_2, ^{205}Tl isotopomer, listed in Table I, were fit to obtain molecular parameters. The measured and ''best fit'' calculated frequencies for other isotopomers for CpTl are given in Tables II–VIII. The centrifugal distortion terms are small for this complex so for some lines listed in Tables V and VI, the transitions for different K-values were not resolved. The approximate values listed for relative intensities include contributions from the unresolved components, so $J(K) = 3(2)\leftarrow 2(2)$, and $2(1)\leftarrow 1(1)$, and similar unresolved components are not listed separately. The parameters determined in these spectral line fits are given in Table IX. The listed error limits are 2σ. A few lines for the ortho form of

the doubly deuterated ^{205}Tl isotopomer were recorded along with a few lines for the doubly deuterated ^{203}Tl isotopomers, but there was not enough data to obtain reasonable spectral fits for these species. The transition frequencies and the probable assignments for the quantum numbers are listed in Table X.

Twelve rotational constants from eight isotopomers were used in a least-squares structure fit to determine the four parameters that completely describe the CpTl structure. These parameters are the distance from the C_5 plane to Tl (Tl–C_5), the Cp C–C bond length, the C–H bond length and the angle between the C–H bond and the Cp carbon plane ($\angle C_5$–H). The results are listed in Table XI. The standard deviation of the fit was 44.4 kHz, indicating a good fit to the data.

A Kraitchman analysis was performed using the singly substituted isotopomers of ^{203}Tl, ^{13}C, and ^{2}H(D) with the ^{205}Tl isotopomer as the parent molecule. This analysis provided the distance of the substituted atom to the center-of-mass of the parent molecule. We have used the four isoto-

TABLE XI. Structural parameters for cyclopentadienyl thallium and comparison to previous microwave results (Ref. 4). The structural parameters were obtained from a least-squares fit to the measured rotational constants given in the lower part of this table. Standard deviation for least squares fit was 44.4 kHz, listed errors are 2σ. Differences between measured and calculated parameters are shown in second part of the table. The propagated errors from rotational constants for the Kraitchman values for bond lengths were less than 0.0008 Å, but uncertainties in the Kraitchman values are likely to be 0.002 Å, or larger.

Parameter	Least-squares fit (r_0)	Kraitchman (r_s)	Cox *et al.* (Ref. 4)
Tl–C_5 (Å)	2.4134(28)	2.409	2.41(1)
C–C (Å)	1.421(11)	1.424	1.43(2)
C–H (Å)	1.082(9)	1.080	fixed at 1.08
$\angle C_5$–H	0.89(19)°	1.20(2)°	assumed 0°

Parameter	Measured value (MHz)	Calculated (MHz)	Difference (MHz)
$B(^{205}$Tl)	1465.0723	1465.1119	-0.0396
$B(^{203}$Tl)	1467.9730	1468.0161	-0.0431
$B(^{205}$Tl$C_5D_5)$	1347.6397	1347.6164	0.0233
$B(^{203}$Tl$C_5D_5)$	1350.3868	1350.3672	0.0196
$B(^{205}$Tl^{13}C)	1450.9689	1450.9151	0.0556
$C(^{205}$Tl^{13}C)	1444.9713	1444.9421	0.0311
$B(^{203}$Tl^{13}C)	1453.8802	1453.8302	0.0519
$C(^{203}$Tl^{13}C)	1447.8584	1447.8333	0.0273
$B(D_1)$	1450.3412	1450.3770	-0.0359
$C(D_1)$	1429.0923	1429.1299	-0.0377
$B(D_2$-meta)	1432.5888	1432.6057	-0.0227
$C(D_2$-meta)	1398.5716	1398.5996	-0.0276

TABLE XII. Measured and calculated microwave transition frequencies (MHz) for $^{115}InC_5H_5$. In the "2F" column is listed twice the total angular momentum ($\mathbf{F}=\mathbf{I}+\mathbf{J}$).

Measured	Calculated	Difference	Intensity	J'	K'	$2F'$	J	K	$2F$
7187.2690(10)	7187.272	−0.003	190	2	0	11	1	0	11
7190.2608(15)	7190.268	−0.007	400	2	1	9	1	1	9
7190.2972(17)	7190.292	0.005	560	2	1	11	1	1	9
7192.9811(09)	7192.984	−0.003	205	2	0	7	1	0	7
7195.6532(07)	7195.657	−0.004	218	2	1	7	1	1	9
7201.3117(06)	7201.289	0.022	241	2	1	9	1	1	11
7203.7982(10)	7203.797	0.001	125	2	1	9	1	1	7
7205.8424(08)	7205.843	0.001	450	2	0	13	1	0	11
7207.9800(04)	7207.984	−0.004	200	2	0	5	1	0	7
7209.1844(48)	7209.186	−0.002	200	2	1	7	1	1	7
7209.3012(11)	7209.301	0.000	200	2	0	9	1	0	9
7210.5612(10)	7210.563	−0.002	550	2	1	13	1	1	11
7216.6447(08)	7216.647	−0.002	180	2	1	5	1	1	7
7219.9826(12)	7219.987	−0.004	80	2	0	7	1	0	9
10 785.3149(43)	10 785.319	−0.004	50	3	0	11	2	0	13
10 789.6356(23)	10 789.638	−0.002	75	3	0	13	2	0	13
10 789.8316(14)	10 789.833	−0.001	55	3	0	7	2	0	5
10 792.3441(53)	10 792.347	−0.003	30	3	1	11	2	1	13
10 794.8462(65)	10 794.852	−0.006	900	3	2	13	2	2	11
10 798.9873(29)	10 798.984	0.003	220	3	1	9	2	1	7
10 799.1633(44)	10 799.160	0.003	170	3	0	5	2	0	5
10 801.5852(19)	10 801.597	−0.012	250	3	1	11	2	1	11
10 801.6309(14)	10 801.621	0.010	500	3	1	11	2	1	9
10 804.3771(77)	10 804.373	0.004	250	3	1	9	2	1	9
10 804.5402(90)	10 804.519	0.021	150	3	1	5	2	1	5
10 804.8472(73)	10 804.846	0.001	400	3	1	13	2	1	11
10 804.9902(90)	10 804.985	0.005	320	3	1	7	2	1	7
10 805.5761(26)	10 805.577	−0.001	200	3	2	7	2	2	7
10 806.3043(22)	10 806.304	0.000	400	3	0	15	2	0	13
10 807.4765(29)	18 807.493	−0.017	50	3	0	3	2	0	5
10 807.5310(35)	10 807.525	0.006	80	3	0	9	2	0	9
10 808.0833(23)	10 808.083	0.000	370	3	1	15	2	1	13
10 808.2136(20)	10 808.209	0.005	350	3	0	13	2	0	11
10 810.3715(09)	10 810.373	−0.002	60	3	1	7	2	1	9
10 810.7618(17)	10 810.762	0.000	120	3	1	3	2	1	5
10 811.9759(38)	10 811.981	−0.005	130	3	1	5	2	1	7
10 813.4054(18)	10 813.408	−0.003	350	3	2	15	2	2	13
10 814.160(06)	10 814.161	−0.001	120	3	0	5	2	0	7
10 815.5143(30)	10 815.519	−0.005	70	3	0	7	2	0	9
10 820.557(10)	10 820.556	0.001	130	3	2	3	2	2	5

TABLE XIII. Measured and calculated microwave frequencies in MHz for $^{113}InC_5H_5$.

Measured	Calculated	Difference	Intensity	J'	K'	$2F'$	J	K	$2F$
7224.1313(21)	7224.125	0.007	5	2	0	11	1	0	11
7227.0804(10)	7227.099	−0.019	5	2	1	11	1	1	9
7240.4353(37)	7240.425	0.010	5	2	1	9	1	1	7
7242.4511(11)	7242.451	0.000	5	2	0	13	1	0	11
7244.5606(08)	7244.564	−0.003	5	2	0	5	1	0	7
7245.7507(19)	7245.742	0.009	5	2	1	7	1	1	7
7245.8656(19)	7245.863	0.003	5	2	0	9	1	0	9
7253.1064(05)	7253.106	0.000	5	2	1	5	1	1	7
7256.4007(04)	7256.408	−0.007	5	2	0	7	1	0	9
10 854.0334(46)	10 854.031	0.002	5	3	1	9	2	1	7
10 856.6406(57)	10 856.632	0.009	5	3	1	11	2	1	9
10 859.8114(49)	10 859.816	−0.005	5	3	1	13	2	1	11
10 865.6466(41)	10 865.653	−0.006	5	3	1	3	2	1	5

TABLE XIV. Measured and calculated microwave frequencies in MHz for ^{115}In^{13}C^{12}C$_4$H$_5$.

Measured	Calculated	Difference	Intensity	J'	K'	$2F'$	J	K	$2F$
7125.4408(05)	7125.448	−0.007	10	2	1	9	1	1	9
7125.4792(21)	7125.472	0.007	10	2	1	11	1	1	9
7127.5715(08)	7127.571	0.001	60	2	−1	13	1	−1	11
7130.8358(17)	7130.834	0.002	10	2	1	7	1	1	9
7131.9104(10)	7131.913	−0.003	20	2	0	13	1	0	11
7135.3315(17)	7135.337	−0.006	15	2	0	11	1	0	9
7135.3712(09)	7135.370	0.001	15	2	0	9	1	0	9
7145.7329(09)	7145.731	0.002	25	2	1	13	1	1	11
7151.8142(16)	7151.812	0.002	10	2	1	5	1	1	7
10 680.3576(43)	10 680.354	0.004	5	3	−1	13	2	−1	11
10 683.5858(31)	10 683.589	−0.004	10	3	−1	15	2	−1	13
10 695.3485(45)	10 695.349	0.001	10	3	0	15	2	0	13
10 697.2568(07)	10 697.252	0.005	10	3	0	13	2	0	11
10 707.5905(40)	10 707.594	−0.004	5	3	1	13	2	1	11
10 710.8283(31)	10 710.829	−0.001	5	3	1	15	2	1	13

pomers listed above to obtain substitution (r_s) coordinates for all atoms. The results of this analysis are given in Table XI for comparison with the (r_0) bond lengths obtained from the least-squares fit. All substitution coordinates except the C$_5$–H angle show excellent agreement with the r_0 values. This angle was observed to change depending on how many isotopomers were included in the study. In order to average over zero-point vibrational changes in the isotopically substituted species, all of the available isotopic data were included in the least-squares structure fit. The initial value was 1.0(2)° using the singly and doubly deuterated isotopes in a least-squares structure fit. When the data set for the structure fit was expanded to include the perdeuterated isotopes a slightly smaller value was obtained 0.89(19)°. The r_s value is slightly larger, 1.20(2)°. The r_s values are expected to be closer to ''equilibrium'' values, therefore, they might be expected to be slightly different from the r_0 parameters.

B. Cyclopentadienyl indium

Sixty eight lines were measured in two relatively dense areas of the microwave spectrum of this complex. These areas contain transitions due to the three naturally abundant isotopomers. The measured transition frequencies are listed in Tables XII–XIV. For the two indium isotopic species, a normal quadrupole splitting was observed in the symmetric top spectrum. The $I=9/2$ spin for each In nucleus results in a multitude of observed microwave transitions. The natural abundance of ^{13}C was sufficient to observe asymmetric top quadrupole splitting patterns for the singly substituted ^{13}C, ^{115}In isotopomer. Most of the $J=2\leftarrow1$ and $3\leftarrow2$ transitions were located for the most abundant isotopomer, ^{115}In, whereas only about fourteen of the strongest lines were measured for each one of the less abundant ^{113}In and ^{13}C isotopomers. Each set of measured lines was fit to a five parameter Hamiltonian which included the quadrupole coupling strength eQq, the rotational constant B (and C for the ^{13}C isotopomer) and the distortion constants D_J and D_{JK}. The final values of these parameters are listed in Table XV. The A rotational constants were fixed at values calculated from the GED structure.[5]

Structural parameters for CpIn were obtained using four rotational constants in a two parameter least-squares fit. This structure fit was used to determine the C$_5$ ring to In perpendicular distance (In–C$_5$) and the C–C bond length. A weak correlation between $\angle$C$_5$–H (the angle between the C–H bond and the plane of the Cp carbon atoms) and the In–C$_5$ distance was observed. No data was available for deuterated isotopomers, so this angle was fixed at the value found in the gas phase electron diffraction (GED) study. Since these parameters are correlated, the error limits on the In–C$_5$ distance include the propagated uncertainty in the GED $\angle$C$_5$–H value. Resulting error limits are only slightly larger than 2σ from the structure fit. The C–H bond length was also fixed at the GED determined value and the fit results obtained for the two variable parameters are in excellent agreement with the

TABLE XV. Final values of parameters obtained from the least-squares fits to measured transitions listed in Tables XII–XIV. The A rotational constant was fixed at 4300 MHz for the fit to ^{13}C data (third column).

Parameter		^{115}InC$_5$H$_5$	^{113}InC$_5$H$_5$	^{115}In^{13}C^{12}C$_4$H$_5$
B	(MHz)	1800.8199(18)	1809.9785(30)	1786.8838(18)
C	(MHz)	1800.8199(18)	1809.9785(30)	1777.8040(24)
eQq	(MHz)	−119.981(31)	−118.397(69)	−119.913(41)
D_1	(kHz)	0.42(11)	0.18(28)	0.31(10)
D_{JK}	(kHz)	1.91(35)	3.3(31)	3.8(10)
σ	(kHz)	7.20	9.10	4.55

TABLE XVI. Structural parameters for CpIn and comparison with electron diffraction results. The parameters were obtained using a least-squares fit to the rotational constants listed in the lower part of this table. The standard deviation for the least-squares fit was 53 kHz. The propagated error from rotational constants for the Kraitchman values was less than 0.0001 Å, but uncertainties in the Kraitchman values are likely to be 0.002 Å, or larger.

Parameter	Least squares (r_0)	Kraitchman (r_s)	GED values (Ref. 5)
C_5–In (Å)	2.314(4)	2.312	2.312(4)
C–C (Å)	1.426(6)	1.424	1.426(7)
C–H (Å)	fixed	n.a.	1.10(6)
$\angle C_5$–H (°)	fixed	n.a.	4.5(20)

Rotational constant	Measured (MHz)	Calculated (MHz)	Difference (MHz)
$B(^{115}\text{In})$	1800.8199	1800.7665	0.0534
$B(^{113}\text{In})$	1809.9785	1810.0280	−0.0495
$B(^{115}\text{In}^{13}\text{C})$	1786.8838	1786.8979	−0.0141
$C(^{115}\text{In}^{13}\text{C})$	1777.8040	1777.7935	0.0105

GED results. The results are compared to the GED results in Table XVI. The structure is shown in Fig. 1.

Additional Kraitchman calculations were done in order to determine two r_s structural parameters for the (C_5H_5)In molecule. Since only the indium and carbon 13 isotopomers were available, only the In–C_5 and C–C bond lengths could be determined. These values are shown in Table XVI for comparison with the least-squares fit r_0 values.

The indium quadrupole coupling splittings due to the $I = 9/2$ nuclei were well resolved. The quadrupole coupling terms, eQq (or eQq_{aa}) were determined quite accurately from the spectral fits for the two symmetric top species. For the asymmetric top ^{13}C isotopomer, the quadrupole asymmetry parameter $\sqrt{1/6}(eQq_{bb} - eQq_{cc})$ was included in the initial spectral fits, but could not be well determined, due to the small angle of rotation of the ''a'' axis from the C_5 symmetry axis. This term was calculated from preliminary structural and quadrupole parameters to be 5.5 kHz and then fixed during the final spectral fit. Although we would expect a relatively anisotropic charge distribution for this half-sandwich complex, the quadrupole coupling strength of $eQq_{aa}(^{115}\text{In}) = -119.98$ MHz is relatively small. A much larger indium quadrupole coupling strength of $eQq(^{115}\text{In}) = -723.8$ MHz was reported recently[8] for the diatomic molecule, InF. The ratio of nuclear quadrupole moments, $Q(^{113}\text{In})/Q(^{115}\text{In})$ from the InF work[8] is 0.9862(2), in good agreement with the ratio 0.9868(6) from the present data on CpIn.

IV. DISCUSSION

Accurate and precise structural parameters were obtained from the microwave spectra for CpTl and CpIn. The new rotational constants are in good agreement with the values from the earlier microwave work on CpTl, but an accurate structure can now be reliably determined since a much larger group of isotopomers was measured in the present work. The accuracy of the structural parameters is significantly improved for CpTl. In the case of CpIn, the structural parameters are in excellent agreement with the electron diffraction values.[5] This agreement seems to justify the assumption made by Schibata and co-workers[5] that the failure of the Born approximation does not significantly lower the accuracy of the results. It is desirable to determine the level of agreement between the microwave and GED work since in many cases, not enough isotopomers will be studied in the microwave measurements to determine the complete structure.
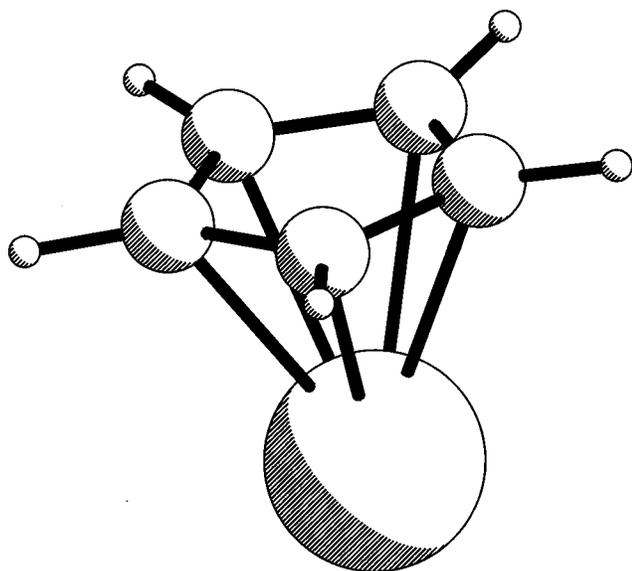

FIG. 1. Structure of the cyclopentadienyl indium complex. The structure for cyclopentadienyl thallium is very similar. For both cases the ''a'' principal axis is coincident with the C_5 symmetry axis, and the C–H bonds are slightly bent out of the carbon plane, away from the metal atom.

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