Calculations and measurements for the rotational spectrum and structure of the cyclopentadienyl thallium – benzene complex.

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Abstract

Calculations on the structure of the cyclopentadienyl thallium – benzene complex were made using gaussian-G16 and Spartan programs. Calculations converged to symmetric top and asymmetric top structures. Rotational transition frequencies for the cyclopentadienyl thallium – benzene complex were measured in the 4.5-8.3GHz range using a Flygare-Balle pulsed beam microwave spectrometer. The basic spectrum from the preliminary experiments exhibited splittings of the observed transitions which would not be expected for a rigid symmetric top molecule. 10 of the measured transitions were assigned to an asymmetric top structure and fit, yielding rotational constants A = 1137.0(6) B = 378.6(1)MHz and C = 375.3(1)MHz.

1. INTRODUCTION

Cyclopentadienyl thallium is an unusual and relatively stable ‘‘half-sandwich’’ complex which can be sublimed at about 40 °C and 10 mTorr pressure.[1,2] The π-bonded, half-sandwich geometry was proposed by Cotton and Reynolds[2] 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.[3,4] The open coordination geometry suggests that this complex could be reactive and readily accept additional ligands, but it is observed to be quite stable.[2] Microwave spectra and structural parameters for many isotopologues of cyclopentadienyl thallium and cyclopentadienyl indium were reported by Drouin, Cassak, Briggs, and Kukolich.[5]

It would be expected that cyclopentadienyl thallium with the open coordination geometry would readily form weakly-bound complexes with other ligands. Cyclopentadienyl thallium was observed to form polymer chains with the thallium atom fo one molecule weakly bound the the cyclopentadienyl group of the next molecule in the chain.[6] The rotational spectrum and structure for the argon-cyclopentadienyl thallium complex were reported by Tanjaroon, Daly, and Kukolich.[7] It was surprising that the Ar was bound on the Cp side rather the to the thallium atom. The MP2 calculations predicted a bound structure in reasonably good agreement with the experimental parameters. The DFT calculations (B3LYP, B3PW91) predicted no binding for Ar-CpThallium.

DFT and MP2 calculations were used to predict the structural parameters and rotational constants for the cyclopentadienyl thallium – benzene complex. The basic structure of the complex is shown in Figure 1. This is a weakly bound complex between a transition metal and benzene. For many transition metal catalyzed reactions, the reaction intermediates are weakly-bound complexes between the transition metal and the reactant, but these complexes are very difficult to observe spectroscopically. This makes the current project for CpTl-benzene a potential useful model for these interactions and a test of theoretical methods.

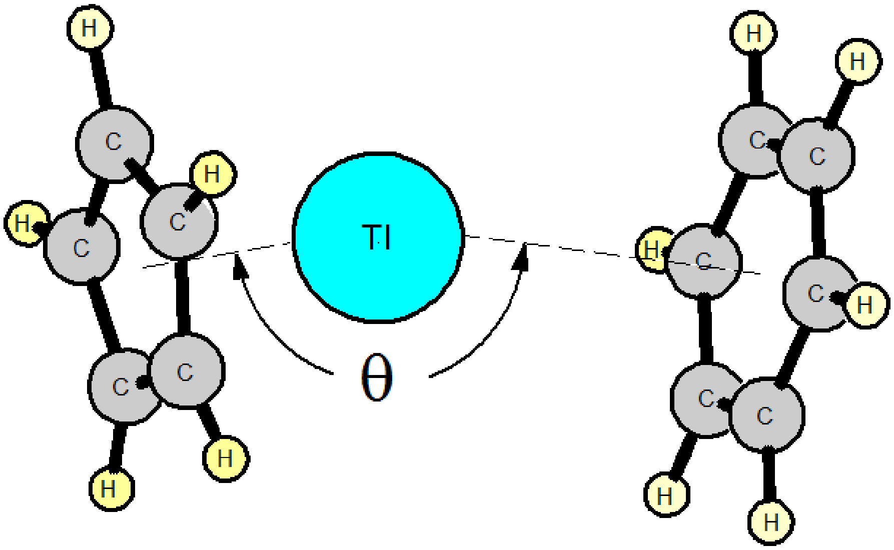

Figure 1. Structure of the cyclopentadienyl thallium – benzene complex as obtained from Spartan calculations. (B3LYP – 6-311-G*), The angle Θ is the angle between the c-axis for cyclopentadienyl and the c-axis of benzene.

2. CALCULATIONS

Structural parameters and rotational constants were calculated using Gaussian G-16 [8] on the University HPC system and using Spartan 18 on a PC computer.[9] The Gaussian calculations were done on the Ocelote HPC, 28 processor system using 268 Gb memory.[10] For the Gaussian-16 suites (G-16), the use of the keyword "output=pickett", provides microwave parameters, such as A, B and C. The calculated rotational constants from different methods and functionals are given in Tables 1 and 2. When starting with a symmetric top initial structure, the G-16 calculations converged to symmetric top structures. (Table 1, column 1 and Table 2. Rows 2, 4 and 6). When starting with an asymmetric top initial structure, G-16 calculations converged to asymmetric top structures with slightly lower energies than the symmetric top structures (see Table 1, column 3 and Table 2. rows 1, 3 and 5). The Spartan calculations[9] using similar methods and basis sets yielded near-symmetric top (slightly bent or bent) structures. For Table 1, column 7 the angle Θ was fixed to various values to better reproduce the experimental B-C value. We believe the B-C is the best experimental parameter to correlate with the bending angle theta. With the angle Θ constrained to 156.5° the rotational constant difference, B-C = 4.5 MHz, very close the best fit value of 3.3 MHz.

Most of the present calculations involved the use of ab-initio core potential basis sets (ECP), CRENBL from Ross, et al [11] , and LANL2DZ of Hay and Wadt, [12]. Carbon and hydrogen basis sets were either diffuse and augmented 6-311++G** [13] or triple zeta basis sets def2-TZPVpp [14]. Methods were chosen for their success in other gas phase complexes, M11 [15] and MP2 [16]. B3LYP[17] was used to compare with the cyclopentadienyl argon complex[7].

3. EXPERIMENTAL

Rotational transitions were measured for the cyclopentadienyl thallium-benzene dimer system in the 4.5-8.3 GHz range using the Flygare-Balle type pulsed-beam Fourier Transform microwave spectrometer that was previously described[18,19] at the University of Arizona. Cyclopentadienyl thallium (95%) was purchased from Strem Chemicals and used without any further purification. The cyclopentadienyl thallium sample was loaded into a glass cell that was heated to about 96 ^{o}C in order to produce sufficient vapor pressures for microwave measurements. One end of the glass cell was connected to the pulsed valve of the microwave spectrometer while the other end was connected to a different glass cell containing a few drops of distilled benzene. Due to its high vapor pressure, benzene was cooled to and maintained at around -15^{o}C using a Peltier cooler to reduce the vapor pressure. The other end of the glass cell containing benzene sample was connected to a gas passing system that uses neon as carrier gas. The whole gas passing system was maintained at around 0.8atm throughout the measurement while the pressure inside the spectrometer chamber was kept at 10^{-6} to 10^{-7} Torr powered by a diffusion pump system. Under these conditions, the molecules were pulsed into the chamber at 2 Hz through a General Valve pulsed valve.

To predict rotational transitions in the 4.5-8.3 GHz range, theoretical rotational constants from M - 11 with 6-311-G** basis set in Table 1, Column 2 were used in the SPCAT program in Pickett's program suite[20]. With about 250 pulsed beam cycles, a 5/1 signal to noise ratio signal could be observed for the a-type 8_{08}-7_{07} (quantum numbers J, K_a and K_c) transition at 6014.296 MHz.

4. EXPERIMENTAL RESULTS

Rotational transitions were observed and measured in the 4-10 GHz range with the pulsed-beam Fourier transform (PBFT) spectrometer. The groups of observed a-type transitions followed a near symmetric top pattern for J= 5→6, 6→7, 7→8, 8→9 and are listed in Table 3. Observed lines which were not included in the fit (Table 4) could be from internal motion or other molecules in the beam. A plot of measured (green) and calculated(red) transitions is shown in Figure 2.

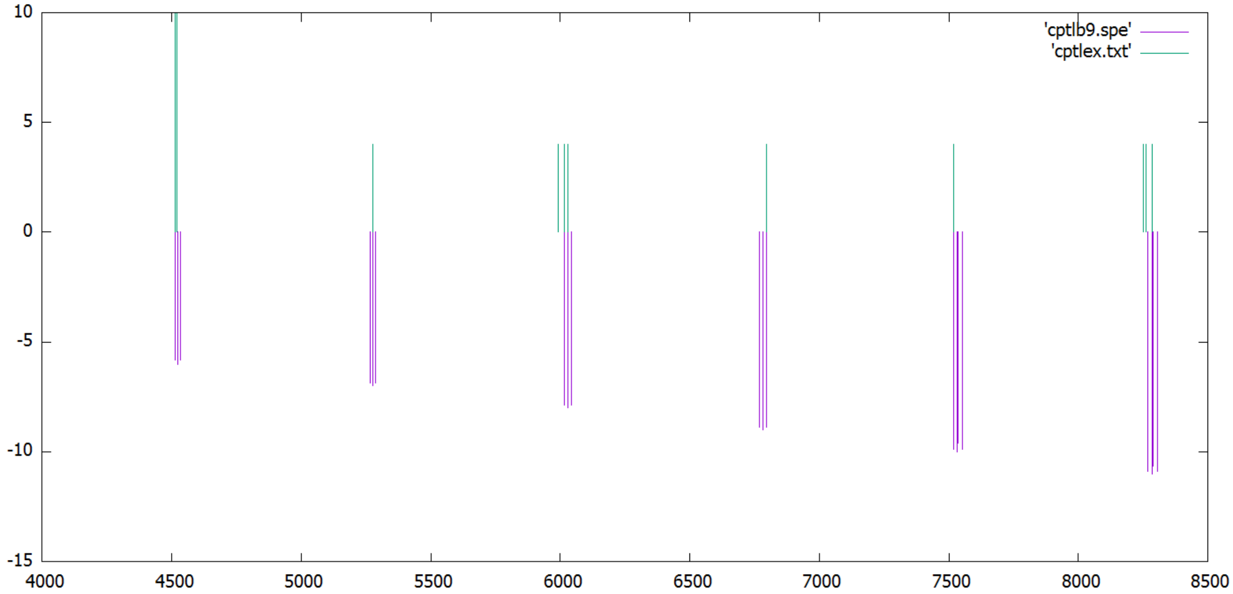

Figure 2. Experimental(green) and calculated(purple) stick plots of the microwave spectrum for cyc in the range 4000 to 8500 MHz. The calculated(purple) lines are for a-dipole transitions only

A total of seven groups of a-type transitions for cyclopentadienyl thallium-benzene dimer were found and measured during the experiment. The measured transitions are given in Table 3. The prediction of the b-dipole allowed transitions based on this fit and fixing the A rotational constant to the calculated value in Table 1, column 3 at 1522 MHz, helped in the assignment of two b-type transitions. The first transition 7_{07}-6_{16} was fit and a second prediction was made. The 8_{27}-7_{16} transition was predicted to be within 1 MHz of the measured value of 8263.066. The results of a least squares fit to 12 of the measured microwave transitions and the deviations from the calculated values are listed in Table 4. These 12 measured rotational transitions were used to fit the rotational constants A, B, C and D_J using the SPFIT program. The deviations between measured and best-fit calculated values (M-C) are also listed in Table 4. From the fit with 10 transitions, the standard deviation of 1.3 MHz was obtained. This standard deviation is larger than expected for a rigid molecule. This problem could be due to internal rotation or other internal motion of this complex. In all calculations, the b-dipole moment for bent geometries were predicted to be smaller than a-dipole values and may be the reason more transitions were not measured. In addition, several tests were performed with and without benzene and cyclopentadienyl thallium to confirm that measured signals originate from the mixture of these two substances.

5. DISCUSSION

It is clear from the observed transitions that this complex is not a simple symmetric top, as was predicted from some of the G-16 calculations. The G-16, B3LYP calculation (Table 1. Column 3) predicts a bent structure but B-C is larger than the experimental value. The Spartan calculation (Table 1, column 6), with the angle Θ constrained to 156.5°, yielded rotational constant difference, B-C = 4.5 MHz, close to the best fit value of 3.3 MHz. Interestingly, the Spartan calculations all predicted bent, slightly asymmetric structures. The B3LYP, G 16 calculation, Table 1., Column 2 gives results similar to the experimental spectrum, with angle $\Theta = 149°$. Using the G16 data for starting geometries in bent and linear orientations an estimate for the difference in energy can be obtained. Using the MP2 method with LANL - core potential on Thallium and 6-311++G** on C and H and using the density functional method M11 with CRENBL - core potential on Thallium and def2-TZVpp on C and H give a minimum energy for the bent structure, whereas the linear ($\theta = 180°$) structures are higher in energy by 497 cm^{-1} and 574 cm^{-1} respectively.

Structures similar to this complex were observed for zig-zag chain polymers of cyclopentadienyl thallium and characterized with x-ray diffraction.[21, 22]

6. CONCLUSIONS

Calculations to obtain the structure of the cyclopentadienyl thallium-benzene complex were done using DFT and MP2 methods and various basis sets (Tables 1. and 2.). Converged calculations could be obtained for both the bent ($\Theta < 180°$) and linear ($\Theta = 180°$). Energies for the bent structures were slightly lower for the same basis sets.

11 measured rotational transitions (Table 3.) were assigned to this complex based on gas tests. Both the cyclopentadienyl thallium and benzene were required to observe these transitions. These transitions form a general pattern expected for a slightly asymmetric top. The fit (Table 4) to a rigid asymmetric top Hamiltonian shows much larger deviations than expected relative to the measurement precision. One explanation for this is possible internal motion of the complex. For the linear structure the internal rotation barrier would be high multiplicity. For high multiplicity the barrier will be low. A calculated barrier height is 4.4 cm^{-1} which would mean internal rotation levels are likely excited. Calculate vibrational frequencies are also very low with 5 levels between 1 and 40 cm^{-1}, making vibrational satellites likely.

7. Acknowledgements

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Tables

Table 1. The experimental and calculated molecular parameters for cyclopentadienyl thallium -benzene. For the experimental results, 9 transitions were included with standard deviation of 1.3 MHz for the experimental fit. Frequencies in MHz. Energies in Hartrees (H)

Parameter	1. Experimental	2. B3LYP G 16	3. M11 SPARTAN	4. MP2-SPARTAN	5. B3LYP SPARTAN	6. B3LYP (constrained)
A	1137.00(64)	1522.859	1740.626	1728.377	1694.530	1608.44
B	378.56(10)	305.460	356.622	354.105	310.968	319.09
C	375.282(74)	297.818	356.412	353.965	309.794	314.62
B-C	3.28	7.64	0.21	0.14	1.17	4.47
Linear?	bent	bent	bent	bent	bent	bent
μ_a		3.283	4.385	3.12	2.73	2.70
ANGLE (Θ) Cp-Tl-Bz		148.5	175.36°	175.64°	166.6°	156.5° CONSTRAINED
ENERGY (H)		-598.565	-598.004	-428.965	-427.816	-427.816
Method		B3LYP	M11	MP2 SPARTAN	B3LYP-sk SPARTAN	B3LYP-sk SPARTAN
Basis set C,H / Tl		genECP cc-pvQZ	6-311+G** / SK	6-31G*	6-31G* / (LANL)	6-31G* / (LANL)

Table 2. Results of G-16 calculations for various basis sets and starting geometries*.

File	Method	A, B, C (MHz)	ENERGY(H)	ANGLE (Θ)	μ(D)**
1) CTB3kuk2	B3LYP/genECP cc-pVQZ	1522.9 305.45 297.81	-598.5650	148.5	3.280
2) CTB3kuk 5b	M11/genECP def2tzvpp	1750.4 359.99 359.99	-598.06101	179.6	4.478
3) CTB3kuk 3	M11/genECP def2tzvpp	1182.0 466.75 413.67	-598.06363	114.5	4.096
4) CTB3kuk 4	MP2/genECP 6-311++G**	1210.7 462.50 415.32	-596.21205	117.4	3.343
5) CTmp24a	MP2/def2tzvpp	1320.3 478.25 439.94	-596.86358	124.4	3.618
6) CTB3kuk 6	MP2/genECP 6-311++G**	1723.6 372.72 372.72	-596.20977	179.8	3.998
7) M11 - DM	def2QZ / genECP-crenbl	1752.440 361.237 361.235	-598.109	180.	4.463

*Calculations started in G16 with angle of Θ = 180° remained in the linear geometry.

** Dipole given as the total dipole contribution. Bent structures have non-zero b-dipole components.

Table 3. List of the measured lines in MHz. Uncertainty in frequency is 0.010 MHz.

Frequency	Strength
4512.207	Strong
4521.219	Strong
5276.051	Medium

5990.479	Medium
6014.294	Medium
6029.627	Medium
6796.540	medium
7518.868	medium
8249.616	Medium
8263.066	Medium
8284.105	Medium

Table 4. Results of least squares fit to determine A, B, and C rotational constants in cyclopentadienyl thallium benzene. (Values in MHz) Standard deviation for the fit is 1.3 MHz.

	Variable	Value (error)	
	A	1137.00(64)	
	B	378.56(10)	
	C	375.282(74)	
J_{KaKc}''	J_{KaKc}'	Measured	Deviation
5_{15}	6_{16}	4512.2065	-0.1377
5_{05}	6_{06}	4521.2188	-0.6848
6_{06}	7_{07}	5276.0508	0.9960
7_{17}	8_{18}	6014.2944	-1.2340
7_{07}	8_{08}	6029.627	1.6514
8_{17}	9_{18}	6796.54	0.1746
9_{19}	10_{110}	7518.8682	0.9511
6_{06}	7_{17}	5990.479	0.2585
7_{16}	8_{27}	8263.066	-0.0859
10_{010}	11_{011}	8284.1045	-0.9263

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