

Corrections and Additions to “Microwave Spectra and Theoretical Calculations for Two Structural Isomers of Methylmanganese Pentacarbonyl”

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Inorg. Chem. 2020, 59 (9), 6432–6438. DOI: 10.1021/acs.inorgchem.0c00524

Cite This: *Inorg. Chem.* 2021, 60, 1274–1275

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In the original paper on methylmanganese pentacarbonyl,¹ good agreement was obtained between the experimental rotational constants and the calculated values for dihapto acyl- $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4$, but agreement between experimental and calculated quadrupole parameters was poor. Calculated χ_{aa} were negative whereas the previous experimental values were positive. This note provides corrections and some additions to the earlier paper.¹ Subsequent to the initial study, many calculations were carried out using different methods and basis sets and the calculated quadrupole coupling parameters between these different calculations were reasonably consistent. In particular, the calculations consistently gave negative values for the ^{55}Mn quadrupole parameters, whereas the reported experimental values were positive. However, alternative assignments of the quantum numbers to measured transitions could be found that yielded negative quadrupole parameters and a better fit to the spectrum. More details of the new analysis and computation are given in a recent paper.²

The new fit analysis included the rotational constants A , B , and C , centrifugal distortion constants D_J and D_{JK} , and the quadrupolar parameters $1.5\chi_{aa}$ and $0.25(\chi_{bb} - \chi_{cc})$. Results of the new spectral analysis are reproduced in Table 1 below. The best agreements between experimental and calculated values were obtained for B3LYP and M11 DFT with def2 basis sets, as shown in Table 1. Experimental molecular parameters from the new analysis are $A = 840.084(5)$, $B = 774.286(2)$, $C = 625.653(1)$, $D_J = 0.00021(2)$, $D_{JK} = 0.0049(2)$, $1.5\chi_{aa} = -47.0(1)$, and $0.25(\chi_{bb} - \chi_{cc}) = -13.44(3)$ MHz. These experimental parameters agree best with calculations for the dihapto isomer, rather than the agostic form of this complex. Excellent agreement is obtained for the rotational constants, and now a much better agreement for the quadrupole coupling parameters. The present and previous molecular parameters are given in Table 2.

The three lowest energy structures for methylmanganese pentacarbonyl are shown in Figure 1. The symmetric isomer (c) and the two distinct acyl-Mn isomers and the agostic form (b) and the dihapto form (a) are shown.

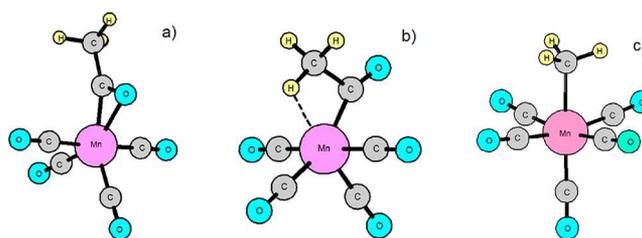


Figure 1. Three structural isomers of methyl manganese pentacarbonyl complex: (a) dihapto form; (b) agostic form; (c) symmetric top, which is the lowest energy structural isomer.

With the newer assignments, the 1σ standard deviation of the experimental fit to 40 transitions, dropped from 41 to 18 kHz. Importantly, the new fit yielded the nuclear quadrupole coupling constants that are consistent with the theory. As displayed in Table 1, rotational constants between different DFT methods for the same structure are in good agreement with the experimental value. The experimental $1.5\chi_{aa}$ values agree better with the calculated value for the dihapto form. In contrast, the calculated quadrupole parameters for the agostic isomer are much different from experimental values. We concluded that the observed asymmetric form of methyl manganese pentacarbonyl is the dihapto form on the basis of these results. For the B3LYP calculations (columns 3 and 7 of Table 1), the dihapto form is 3350 cm^{-1} lower in energy than the agostic form. The calculated energy for the dihapto is -1757.937 hartree, compared with -1757.921 hartree for the agostic form.

ACKNOWLEDGMENTS

We are extremely grateful to Carlos Jiménez Hoyos, Wesleyan University for providing some of the newer calculations for this

Published: January 7, 2021

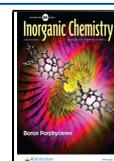


Table 1. Experimental and Calculated Molecular Parameters for Dihapto and Agostic Isomers of $\text{CH}_3\text{Mn}(\text{CO})_5$ in MHz^a

parameter	(1) experimental	(2) M11-dihapto	(3) B3LYP-dihapto	(4) MP2-dihapto	(5) CCSD-dihapto	(6) TPSSH-Agostic	(7) B3LYP-Agostic	(8) PBE1PBE-Agostic
A	840.084(5)	831.458	825.589	938.300	833.095	828.042	819.810	840.899
B	774.286(2)	778.362	770.664	838.050	777.454	797.837	788.101	807.776
C	625.653(1)	637.850	635.694	706.278	641.665	661.694	654.867	669.182
$1.5\chi_{aa}$	-46.96(11)	-45.50	-46.5	-47.3	-40.65	-89.3	-97.1	-94.6
$0.25(\chi_{bb} - \chi_{cc})$	-13.44(3)	-6.667	-7.2	-11.9	-7.697	-18.2	-12.9	-13.2
μ_a		2.14	2.65	5.39	2.125	0.30	-1.01	-0.98
μ_c		0.87	-0.62	0.68	0.590	-3.12	-2.93	-2.97
χ_{aa}	-31.31	-30.33	-31.0	-31.5	-27.1	-59.6	-64.7	-63.1
χ_{bb}	-11.23	1.83	1.1	-8.0	-1.85	-6.6	6.6	5.1
χ_{cc}	42.54	28.5	29.9	39.5	28.94	66.2	58.1	57.9
method/basis set		M11/def2TZVpp	B3LYP/Def2TZVPP	MP2/Def2TZVPP	CCSD/cc-pvQZ	TPSSH/Def2TZVPP	B3LYP/Def2TZVPP	PB1PBE/Def2TZVPP

^aBasis sets for the calculations are shown in this table, line 12. The experimental diagonal elements of the quadrupole coupling tensor (χ_{aa} , χ_{bb} , χ_{cc}) are directly obtained from the fit parameters $1.5\chi_{aa}$ and $0.25(\chi_{bb} - \chi_{cc})$; μ_a and μ_c are the computed dipole moments along the inertial axes of rotation, in Debye.

Table 2. Rotational Constants, Centrifugal Distortion Constants, and the Nuclear Quadrupole Hyperfine Coupling Constants Obtained from the Best Least-Squares Fit^a

measured constant	new fit	previous fit
A	840.0843(52)	839.955(42)
B	774.2861(17)	774.203(67)
C	625.6528(13)	625.628(14)
D_J	0.000212(21)	
D_{JK}	0.00488(18)	
$1.5\chi_{aa}$	-46.96(11)	44.9(47)
$0.25(\chi_{bb} - \chi_{cc})$	-13.44(3)	11.9(12)
no. of lines	40	31
RMS, kHz	16	39
1σ , kHz	18	41

^aSpectroscopic constants are in MHz. 1σ standard error = $\text{RMS} \times [\text{number of lines} / (\text{number of lines} - \text{number of fit constants})]^{1/2}$.

revised work and for discussions about the project. This material is based upon work supported by the National Science Foundation under Grant No. CHE-1057796 and CHE-1952289 at the University of Arizona. We are very grateful to UITS-HPC computing facilities for the computing time provided on the Ocelote system. This material is based, in part, upon High Performance Computing (HPC) resources supported by the University of Arizona TRIF, UITS, and Research, Innovation, and Impact (RII) and maintained by the UArizona Research Technologies department. We thank Jimmy Ferng for assistance with the calculations, which was made possible through University of Arizona Research Technologies Collaborative Support program.

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