

# A Study of the Metal Satellite Spectra of Tetracyclopropyltin, Tetracyclopropyllead, and Dicyclopropylmercury and Its Implication on General Nuclear Magnetic Resonance Coupling Constants

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**Abstract:** The complete analyses of the metal satellite nmr spectra of tetracyclopropyllead, tetracyclopropyltin, dicyclopropylmercury, diethylmercury, and tetraethyltin are reported. The coupling constants in the cyclopropyl compounds are compared with the metal-proton coupling of the corresponding ethyl and vinyl compounds. The data allow development of a simple equation of the form  $J_{XH} = AJ_{YH} + B$  which accurately relates various observed metal-proton coupling constants and permits prediction of others. Extended Hückel calculation of coupling constants for the lead and tin compounds are also reported.

The study of the nmr coupling constants in cyclopropane derivatives has considerable interest for several reasons. First, one may gain some insight as to the mode of bonding in small ring systems. Secondly, the cyclopropyl ring is a rigid system so that the angular dependence of the coupling constants can be determined without a complicated consideration of molecular configurations. Unfortunately the five-spin cyclopropyl system is complex so that most of the earlier nmr analyses of these compounds have had several substituents present to reduce the size and complexity of the spin system. The polysubstituted rings have the severe disadvantage that the steric interaction among groups on the ring may distort trends in the nmr parameters. More recently, however, proton-proton,<sup>1-10</sup> proton-carbon,<sup>8-11</sup> and carbon-carbon<sup>12</sup> coupling constants have been determined in some mono-substituted derivatives.

Theoretical calculations of the H-H coupling constants for these derivatives utilizing Pople-Santry<sup>13</sup> and the finite perturbation methods<sup>14</sup> have had limited success in qualitatively describing the observed trends. The latter type of calculations, however, are restricted to the elements of the first row and further suffer from the fact that the observed changes in coupling constants arise from a number of factors including the effect of the electronegativity of the substituents and interaction of unshared electron pairs or multiple bonds with the ring system. The relative magnitudes of these

factors are not known and make it impossible to apportion the changes to a given effect, and as yet, no calculations have been carried out which allow prediction of metal-proton coupling constants in these small ring systems.

The number of molecular orbital or valence bond calculations on heavy metal-proton coupling is quite limited. Klose<sup>15</sup> has published a series of valence bond calculations on substituted ethanes including tin, lead, and mercury and concluded that the Fermi contact term is the dominant factor which determines the magnitude and sign of the coupling constants.<sup>16</sup> This generally accepted conclusion has led to the premise that various coupling constants may be expressed as ratios of other coupling constants, magnetogyric ratios, average excitation energies, and the electron densities at the nucleus of the valence shell s orbital.

In this paper, we report a determination of the metal-proton coupling constants in diethylmercury, tetraethyltin, and the monosubstituted cyclopropanes of tin, lead, and mercury. Secondly, extended Hückel calculations of the contribution of the Fermi contact term to the coupling constant are presented. Finally, a totally empirical equation is developed which may be used to predict coupling constants. This equation suggests that simple multiplicative factors are not adequate to correlate various coupling constants.

## Experimental Section

The preparation of dicyclopropylmercury,<sup>17</sup> tetracyclopropyltin,<sup>18</sup> and tetracyclopropyllead<sup>19</sup> was done according to methods reported in the literature. Tetraethyltin and diethylmercury were prepared by the reaction of ethylmagnesium bromide with tin tetrachloride and mercuric chloride, respectively. All compounds were purified using high-vacuum techniques.

The spectra of tetraethyltin and diethylmercury were recorded on a Jeol JNM-4H-100 spectrometer and were calibrated using a Hewlett-Packard 5245L frequency counter. Line positions were determined by triggering the count of multiple periods of the sweep frequency at the maxima of each line. Heteronuclear decoupling experiments were carried out using a Jeol/JNM-SD-HC spin decou-

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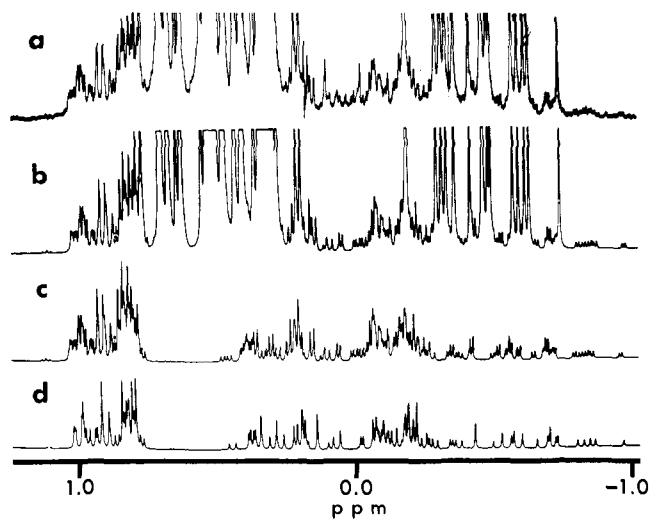


Figure 1. Spectra of tetracyclopropyltin: (a) experimental spectrum, 63 mol % in benzene; (b) calculated main spectrum and all satellite lines; (c)  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellite spectrum; (d)  $^{119}\text{Sn}$  satellite spectrum.

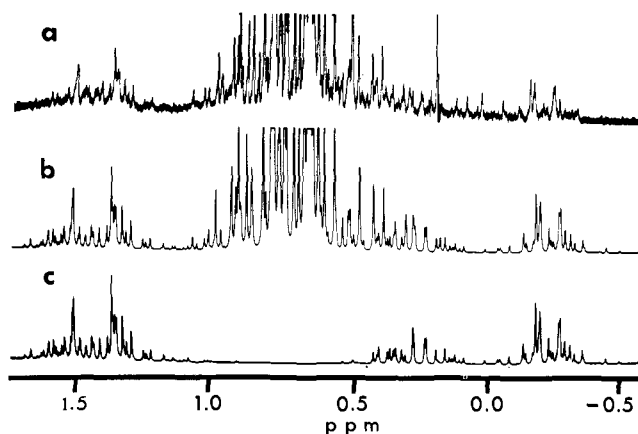


Figure 2. Spectra of tetracyclopropyllead: (a) experimental spectrum, 9 mol % in benzene; (b) calculated main spectrum and satellite lines; (c)  $^{207}\text{Pb}$  satellite spectrum.

pler. The spectra of the cyclopropyl compounds were obtained on a Varian DA-60-IL spectrometer. The spectra were calibrated by synchronizing the output of a Hewlett-Packard 211A square wave generator to the frequency difference between the locking and sweep frequency. Multiple period averages were counted on a modified Hewlett-Packard 523CR counter. The chemical shifts were measured relative to internal benzene and were reported relative to TMS using 7.203 ppm between benzene and TMS.

### Analysis of Spectra

The first stage in analyzing the satellite spectra of dicyclopropylmercury, tetracyclopropyllead, and tetracyclopropyltin is to determine the nmr parameters for the main spectrum. These results have been reported.<sup>1</sup> Next the satellite lines were assigned. The agreement between the theoretical and experimental line positions was optimized using LAOCOON3.<sup>20</sup> The agreement between the experimental and observed lines is within 0.1 Hz unless the line is part of a closely spaced group. The only parameters which were varied in the process were the heteronuclear coupling constants. As one can see from the experimental spectra in Figures 1-3,

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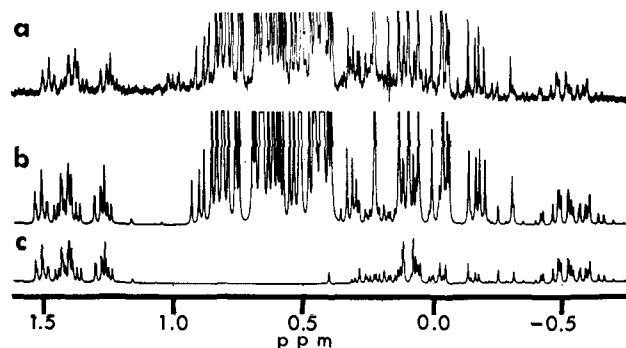


Figure 3. Spectra of dicyclopropylmercury: (a) experimental spectrum, 24 mol % in benzene; (b) calculated main spectrum and satellite lines; (c)  $^{119}\text{Hg}$  satellite spectrum.

these line assignments are not trivial. Many of the lines are buried under the main spectrum, and the splitting patterns are not those of simple first-order spectra.

In analyzing the tin compound, one can make use of the fact that tin has two spin  $1/2$  isotopes,  $^{119}\text{Sn}$  and  $^{117}\text{Sn}$ , in concentration of 8.58 and 7.61% abundance, respectively. The ratio of the magnetogyric ratios of  $^{119}\text{Sn}$  to  $^{117}\text{Sn}$  is 1.046. The satellite spectra, then, consist of two overlapping spectra with the coupling constants in the ratio 1:1.046. If one assumes that the isomer shift for the isotopes of tin is negligible and can identify a pair of corresponding lines in these two spectra such as the rightmost two lines in Figure 1c, one has a first approximation of the tin-proton coupling constant since the separation between the two lines is approximately equal to 2.3% of the  $^{117}\text{Sn}$ - $^1\text{H}$  coupling constant. As expected, the zero isomer shift approximation is quite valid since the determined shifts for all heavy metals were zero within experimental error. This technique can be a great aid in generating a preliminary spectrum for making line assignments.

The major difficulty in analyzing the mercury compound was to find and assign any of the satellite lines due to the geminal proton. To solve this problem, and simultaneously determine the relative signs of the metal proton coupling constants, the six-spin satellite spectrum was treated as two five-spin spectra, one with mercury in the  $\beta$  state,  $\text{Hg}_\beta$ , and the other with mercury in the  $\alpha$  state,  $\text{Hg}_\alpha$ . The effective chemical shift of a ring proton, P, in the  $\text{Hg}_\beta$  spectra is equal to  $\delta_P$ , the chemical shift of P in the main spectra minus one-half of  $J_{P-\text{Hg}}$ . In the  $\text{Hg}_\alpha$  spectra, this effective shift is given by  $\delta_P$  plus one-half of  $J_{P-\text{Hg}}$ . In the experimental spectra, the resonances to the left of the main spectrum are due to the vicinal protons in the  $\text{Hg}_\beta$  spectrum. These lines were analyzed assuming that the effective chemical shift of the geminal proton coincides with the chemical shift of this proton in the main spectrum. Since the second-order splitting pattern of the vicinal resonance is insensitive to the shift of the geminal proton, one must generate the  $\text{Hg}_\alpha$  spectrum, calculating the effective chemical shift of the vicinal protons from the  $\text{Hg}_\beta$  spectrum. The splitting pattern in resonances of these vicinal protons in the  $\text{Hg}_\alpha$  spectrum is sensitive to the effective chemical shift of the geminal proton. Therefore, the shift of the geminal proton is varied to reproduce the observed

pattern of the vicinal protons. It was then possible to assign all satellite lines.

The cyclopropyllead spectrum has no simple approach for analysis but must be treated by trial and error. If one divides the satellite resonances into those with lead in the  $\alpha$  and  $\beta$  states, the satellite line pattern downfield from the main spectrum is made up of overlapping resonances of all the protons with lead in the  $\beta$  state. The highest field satellite lines arise from the resonances of protons geminal and cis to the lead with lead in the  $\alpha$  state.

Since second-order splitting is very prominent in the spectra of the lead, tin, and mercury compounds, the calculated and experimental spectra can be brought into agreement only if all metal-proton coupling constants have the same relative sign. Using the data and arguments presented by Krebs and Dreeskamp,<sup>21</sup> one may safely assume that the absolute signs of all the metal-proton coupling constants are positive.

The values in the literature for the geminal and vicinal coupling for the tetraethyltin<sup>22,23</sup> and diethylmercury<sup>24-26</sup> covered ranges of 10-20 Hz. Therefore, we have reanalyzed the spectra of these compounds at 100 MHz. The analysis of the mercury compound presented no difficulties. The chemical shifts are 1.2886 ppm for the methyl and 1.0045 ppm for the methylene protons. The vicinal proton-proton coupling is 8.04 Hz and the mercury-proton coupling was in good agreement with the results of Hatton, *et al.*<sup>26</sup> The main spectrum of the tetraethyltin spectra has a vicinal coupling constant of 8.04 Hz. The chemical shifts are 1.2137 ppm for the methyl and 0.8298 ppm for the methylene protons. In the tin compound, the second-order splitting in the satellite spectra caused the proton resonances coupled to <sup>117</sup>Sn and <sup>119</sup>Sn to overlap. Also, the identification of some of the weak resonances as part of the satellite spectrum was far from being unequivocal. In this case, complete decoupling of the <sup>119</sup>Sn clearly identified the satellite lines. This simplified spectrum was also used to make line assignments in the uncoupled spectra. Although the values reported here for the tin compound do not correspond closely to other values in the literature, we have added confidence in our results in that the <sup>117</sup>Sn and <sup>119</sup>Sn coupling constants were in the theoretical ratio of 1 to 1.046.

### Correlation of Coupling Constants

According to the theory for nuclear spin-spin interactions developed by Ramsey,<sup>27</sup> the coupling constant is determined from the sum of three terms. The first term,  $J_{orb}$ , involves the interaction of the magnetic field of the nuclear dipole with the orbital magnetic moment of the electron. The second term,  $J_{dipole}$ , is the dipole coupling between the spin of the electron and the nuclear dipole. The third contribution,  $J_{contact}$ , is the Fermi contact term.

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The relative magnitudes of these three coupling mechanisms depend upon the molecular system under consideration. In the case of proton-proton coupling constants in the hydrogen molecule,<sup>28</sup> the approximate contributions of  $J_{contact}$ ,  $J_{dipole}$ , and  $J_{orb}$  are 200, 20, and 3 Hz, respectively. In a fluorine-proton system, up to 25% of the coupling may be attributed to  $J_{orb}$ .<sup>29</sup> Hatton<sup>26</sup> in a study of mercury-proton coupling concluded that  $J_{orb}$  is negligible,  $J_{dipole}$  may be important, and  $J_{contact}$  is the dominant coupling mechanism. Similarly, valence bond calculation on indirect spin-spin coupling between protons and heavy metals including tin, lead, and mercury brought Klose<sup>30</sup> to the conclusion that the Fermi contact contribution predominates. Therefore, the effects of  $J_{orb}$  and  $J_{dipole}$  are often ignored when predicting coupling constants.

If one considers only  $J_{contact}$ ,<sup>16</sup> the coupling constant would be given by

$$J_{NN'} = \frac{1}{h} \left( \frac{16}{3} \pi^2 \hbar \right)^2 \gamma_N \gamma_{N'} \Phi_N^2(0) \Phi_{N'}^2(0) \frac{C_{NN'}}{\Delta_{NN'}} \quad (1)$$

where  $\gamma_N$  is the magnetogyric ratio of nucleus N,  $\Phi_N^2(0)$  is the valence electron density at nucleus N,  $\Delta_{NN'}$  is the average excitation energy, and  $C_{NN'}$  is approximated by  $K$ , the coupling factor. For directly bonded nuclei,  $C_{NN'}$  is approximately equal to unity. Based on eq 3, Dreeskamp expressed the various direct bonded coupling constants as simple ratios such as

$$J_{XY} = \frac{J_{XH} J_{YH} \Delta_{XH} \Delta_{YH}}{J_{HH} \Delta_{HH} \Delta_{XY}} \quad (2)$$

Also, two and three bond couplings are related to direct bond coupling by the coupling factor defined<sup>16</sup> by the equations

$$K_{X-C-H} = J_{X-C-H} / J_{X-H} \quad (3)$$

$$K_{X-C-C-H} = J_{X-C-C-H} / J_{X-H} \quad (4)$$

Similarly, Maher and Evans<sup>31</sup> have related the Tl-H coupling constants in a series of  $R_2Tl^+$  cations to the corresponding H-H couplings. They found that the coupling constants involving thallium were equal to 60 times the corresponding H-H coupling constants. This relationship, however, did not hold in the case of geminal coupling. From our data, however, the utilization of these simple multiplicative factors to correlate coupling constants are grossly inadequate.

In Table I, we present the experimental values for a number of ethyl, cyclopropyl, and vinyl compounds. The first entries to note are the rows labeled 2-1 and 3-2. These rows denote the change which occurs in the geminal coupling constants when one goes from the ethyl to the cyclopropyl compound and from the cyclopropyl to the vinyl compound, respectively. The values of 2-1 and 3-2 are almost equal for all nuclei in the tables. More significant, however, is the fact that the ratio of these differences, that is, (3-2)/(2-1), is almost constant for each nucleus. This suggests that if one knew the differences (2-1)<sub>Pb</sub> and (3-2)<sub>Pb</sub> for lead and

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Table I. Experimental and Empirically Predicted Coupling Constants<sup>a</sup>

		Hg	Hg calcd from Pb	Pb	Pb calcd from Sn	Sn	Sn calcd from H	H	H calcd from F	F
1	Ethyl, gem	-96.10	-95.7	-41.0 <sup>e</sup>	-41.9	49.35	50.9	-12.4 <sup>e</sup>	-12.0	46.7
2-1		-114.07		127.85		-76.27		8.06		18.2
2	Cyclopropyl, gem	+17.97	17.2	86.85	88.8	-26.92	-30.3	-4.34	-5.0	64.9
3-2		111.5		126.4		-72.14		6.64		19.8
3	Vinyl, gem	128.3 <sup>b</sup>	128.8	213.3 <sup>d</sup>	212.3	-99.06 <sup>d</sup>	-97.2	2.30 <sup>f</sup>	2.6	84.7 <sup>i</sup>
4	Ethyl vicinal	126.57	128.6	125.0 <sup>e</sup>	123.9	-68.92	-58.6	8.0 <sup>f</sup>	10.5	25.2 <sup>h</sup>
5	Vinyl, cis	159.5 <sup>b</sup>	158.3	161.6 <sup>d</sup>	163.1	-90.34 <sup>d</sup>	-96.4	11.5 <sup>f</sup>	9.0	20.1 <sup>i</sup>
6	Vinyl, trans	296.4 <sup>b</sup>	296.9	331.8 <sup>d</sup>	331.8	-182.62 <sup>d</sup>	-186.6	19.1 <sup>f</sup>	18.8	52.4 <sup>i</sup>
7	Cyclopropyl, cis	120.38	111.4	103.86	101.2	-56.50	-69.1	8.97	9.2	21.02
8	Cyclopropyl, trans	71.51	78.5	63.44	65.6	-37.04	-32.5	5.58	5.8	9.87

<sup>a</sup> Absolute signs determined from data in F. A. L. Anet and J. L. Sudmier, *J. Magn. Resonance*, **1**, 124 (1969). <sup>b</sup> K. Hildenbrand and H. Dreeskamp, *Z. Phys. Chem. (Frankfurt am Main)*, **69**, 171 (1970). <sup>c</sup> Reference 23. <sup>d</sup> Reference 21. <sup>e</sup> Assuming same as methane, M. Karplus, D. H. Anderson, T. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957). <sup>f</sup> D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963). <sup>g</sup> R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962). <sup>h</sup> S. L. Stafford and J. D. Balde-schwiler, *J. Amer. Chem. Soc.*, **83**, 4473 (1961). <sup>i</sup> C. N. Banwell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **263**, 136 (1961).

also knew  $(2-1)_{\text{Hg}}$  for mercury, one would predict  $(3-2)_{\text{Hg}}$  from the formula

$$(3-2)_{\text{Hg}} = \frac{(3-2)_{\text{Pb}}(2-1)_{\text{Hg}}}{(2-1)_{\text{Pb}}} \quad (5)$$

A relationship of this form, however, cannot be used to directly relate the various geminal coupling constants for Pb-H coupling with those for Hg-H coupling. This is obvious when one observes that the signs of the geminal coupling in Table I are all positive for fluorine, one negative and two positive for mercury, and two negative and one positive for protons. Thus, a simple multiplicative factor cannot be used to relate these couplings. Since the ranges of the geminal couplings for different nuclei are shifted relative to one another, the coupling constants could be described by the empirical relationship

$$J_{\text{XH}} = AJ_{\text{YH}} + B \quad (6)$$

where  $J_{\text{XH}}$  is the coupling constant between a proton and atom X,  $J_{\text{YH}}$  is the corresponding coupling constant obtained when Y is substituted for X in the molecule, and  $A$  and  $B$  are empirical constants.

Using the experimental values in Table I,  $A$  and  $B$  have been determined for geminal and vicinal coupling constants using the method of least squares. These values and the correlation coefficients denoted by Corr are presented in Table II. The lowest values of the correlation coefficients, where X and Y are both heavy metals, are 0.99992 for geminal and 0.99644 for vicinal coupling, still quite close to the maximum value of 1.0. If one considers the entire table, the smallest correlation occurs between H-H and H-F coupling with coefficients of 0.99680 for geminal and 0.93772 for vicinal coupling. The decrease in correlation when one includes hydrogen and fluorine can be due to two effects. First, there is a drastic change in the electronic structure of a molecule upon exchanging tin for fluorine. Secondly, the values of H-H coupling are small; therefore, changes on the order of 0.5 Hz can affect the correlations. In general, however, the correlation coefficients are high and the use of the empirical equation should allow relatively accurate prediction of unknown coupling constants.

The first test of the empirical relationship was to predict the various  $J_{\text{HgH}}$  from the corresponding  $J_{\text{PbH}}$ . These results as well as other predictions are given in Table I. One will note the good agreement between the experimental and predicted value even in the worst case, the prediction of proton-proton coupling from fluorine-proton coupling.

A second test would be to use this relationship to predict coupling constants to a nucleus not considered previously in this paper. Let us assume that one wants to estimate  $J^{\text{vic}}_{\text{ethyl Tl}}$ , the vicinal coupling constant in diethylthallium perchlorate, knowing that  $J^{\text{cis}}_{\text{vinyl Tl}}$  and  $J^{\text{trans}}_{\text{vinyl Tl}}$ , the cis and trans coupling constants in divinylthallium perchlorate, are equal to 805 and 1618 Hz, respectively.<sup>32</sup> Let us base the calculation on the corresponding coupling constants in divinyl- and diethylmercury. Since a minimum amount of data is available, one does not use least-squares methods to obtain  $A$  and  $B$ . Instead  $A$  is given by the ratio of the differences in the vinyl vicinal coupling constants as given by

$$A = \frac{J^{\text{trans}}_{\text{vinyl Tl}} - J^{\text{cis}}_{\text{vinyl Tl}}}{J^{\text{trans}}_{\text{vinyl Hg}} - J^{\text{cis}}_{\text{vinyl Hg}}} = 5.982 \quad (7)$$

The value of  $B$  is the additive constant which would bring  $A$  times  $J^{\text{cis}}_{\text{vinyl Hg}}$  into agreement with  $J^{\text{cis}}_{\text{vinyl Tl}}$ , that is

$$B = J^{\text{cis}}_{\text{vinyl Tl}} - AJ^{\text{cis}}_{\text{vinyl Hg}} = 149.7 \quad (8)$$

Using these values for  $A$  and  $B$ , one predicts a vicinal coupling constant in the thallium compound of 607 Hz and observes a value of 623 Hz.<sup>33</sup>

Of course, the predictions are only valid when working with similar molecular systems. In the previous example, we predicted the Tl-H coupling in diethylthallium perchlorate from divinylthallium perchlorate. It would not have been valid to predict the vicinal Tl-H coupling in triethylthallium from divinylthallium perchlorate. Therefore, one will only obtain a good prediction when changes in hybridization, effective nuclear charge, and substituents are minimized.

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Table II. Empirical Parameters Relating Coupling Constants

$J_{X-H}$		$J_{Y-H}$				
		Hg	Pb	Sn	H	F
Hg geminal	A		1.322	-0.661	0.0654	0.1691
	B		67.37	-14.45	-5.91	62.59
	Corr		0.99998	-0.99998	0.99891	0.99944
Hg vicinal	A		1.223	-0.668	0.0608	0.1817
	B		-32.04	16.23	1.22	-2.40
	Corr		0.99761	-0.99644	0.99365	0.96621
Pb geminal	A	0.883		-0.584	0.0578	0.1494
	B	-59.51		24.88	-9.81	52.53
	Corr	0.99998		-0.99992	0.99862	0.99962
Pb vicinal	A	0.814		-0.547	0.0493	0.1479
	B	26.82		-0.18	2.88	2.47
	Corr	0.99761		-0.99982	0.98759	0.96387
Sn geminal	A	-1.513	-1.713		-0.0991	-0.2558
	B	-21.86	42.63		-7.34	58.90
	Corr	-0.99998	-0.99992		-0.99922	-0.99918
Sn vicinal	A	-1.487	-1.829		-0.0901	-0.2694
	B	25.23	-2.11		2.78	2.26
	Corr	-0.99644	-0.99983		-0.98677	-0.95968
H geminal	A	15.23	17.25	-10.07		2.57
	B	90.14	169.41	-74.03		77.82
	Corr	0.99891	0.99862	-0.99922		0.99680
H vicinal	A	16.23	19.78	-10.80		2.88
	B	-17.85	-53.09	27.76		-4.92
	Corr	0.93365	0.98759	-0.98676		0.93772
F geminal	A	5.91	6.68	-3.90	0.386	
	B	-369.64	-351.21	229.78	-30.08	
	Corr	0.99944	0.99962	-0.99918	0.99680	
F vicinal	A	5.14	6.28	-3.42	0.305	
	B	22.62	-4.38	0.84	2.78	
	Corr	0.96621	0.96387	-0.95968	0.93772	

### Calculation of Fermi Contact Term for Lead and Tin

A remaining question is whether the constant  $B$  represents, in some manner, relative contributions to the observed coupling constant from  $J_{orb}$  and  $J_{dipole}$  or if it is a natural property of the Fermi contact term. To investigate these possibilities, we have calculated the tin-proton and lead-proton coupling constants using extended Hückel (EH) molecular orbital calculations<sup>34, 35</sup> with iteration to charge self-consistency.

To simplify the calculation, the molecules used are the trimethylalkyltin and lead compounds where the alkyl group is ethyl, cyclopropyl, or vinyl. Standard bond angles and bond lengths were used for the C-C and C-H bonds. The Sn-C and Pb-C bond lengths are 2.14 and 2.29 Å, respectively. The atomic orbital wave functions for tin and lead were obtained by expressing the Herman-Skillman<sup>36</sup> wave functions for the atom in an  $s^2p^1$  configuration as least-squares combinations of Slater-type orbitals. The orbital energies for lead and tin in an  $s^2p^2$  configuration were used for the valence orbital ionization potentials. A more complete description of these orbitals is to be presented later.

The calculation of the coupling constants, which has been programmed by Henneike, uses the formula

$$J_{NN'} = -\frac{2}{3h} \left( \frac{16\pi\beta\hbar}{3} \right)^2 \gamma_N \gamma_{N'} \sum_I^{\text{occ}} \sum_J^{\text{unocc}} C_{I\lambda} C_{I\sigma} \times C_{J\nu} C_{J\mu} (E_J - E_I)^{-1} \quad (9)$$

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This treatment does not make the average energy approximation and does not limit the atomic orbitals used to only the s orbitals on nuclei N and N'. The results of these calculations, as shown in Table III,

Table III. Metal-Proton Coupling Constants Determined from Extended Hückel Methods

Alkyl group	Coupling	Tin-119	Lead
Ethyl	Gem	39.14	-26.71
Cyclopropyl	Gem	28.05	-8.49
Vinyl	Gem	-16.48	35.59
Ethyl	Vicinal	-23.08	30.33
Vinyl	Cis	-7.97	12.04
Vinyl	Trans	-61.20	80.98
Cyclopropyl	Cis	-12.52	15.37
Cyclopropyl	Trans	-23.68	35.56

mirror the gross trends in the experimental values. For example, the sign of the geminal coupling constant is opposite to the sign of the vicinal coupling in the ethyl compound, and these absolute signs agree with experiment. However, the results are not sufficiently precise to determine whether or not  $B$  arises from the Fermi contact term.

### Conclusions

We have demonstrated that a simple empirical equation of the form  $J_{XH} = AJ_{XH} + B$  can be used to predict and correlate coupling constants in monosubstituted ethanes, cyclopropanes, and ethylenes. It is not clear if  $B$  represents relative contributions of  $J_{orb}$

and  $J_{\text{dipole}}$ , or if  $B$  is a property of the Fermi contact term. The results suggest that the equation may be quite general for indirect coupling. For example, the work of Maher and Evans suggests that this relationship holds for aryl as well as alkyl and alkenyl systems.

One must be careful to keep the molecular systems very similar in order to obtain good predictions.

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## Thermodynamics and Kinetics of Complex Formation between Cobalt(II), Nickel(II), and Copper(II) with Glycyl-L-leucine and L-Leucylglycine

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**Abstract:** The thermodynamics of complex formation between cobalt(II), nickel(II), and copper(II) with glycyl-L-leucine and L-leucylglycine have been studied potentiometrically. Although the acidity constants of these two peptides and those of glycylglycine are nearly the same, the metal complexes of leucylglycine are considerably less stable than those of the glycyl dipeptides. The influence of the isobutyl group on the acidity constant for the deprotonation of the  $\text{CuL}^+$  complex is also very dependent on the place of attachment. The  $\text{CuL}^+$  complex of leucylglycine is far more acidic than those of the glycyl dipeptides. The kinetics of these reactions were studied using the temperature-jump technique. The forward rate constants for complexation show very little variation with the biggest effect appearing for the copper system. Even the rates of proton attack of the  $\text{Cu(L-1H)}$  species vary by less than a factor of 3 for the dipeptides. For the deprotonation effect, the rate constants correlate with the acidities of the  $\text{CuL}^+$  species leading to a variation of about 100. The thermodynamic and kinetic results are consistent with the Rabin model (coordination *via* the amino end group and the oxygen of the amide group) for bonding in metal-dipeptide complexes.

Investigations of the thermodynamics of complex formation between metal ions of the 3d transition series and dipeptides have demonstrated that the stability of complexes formed with glycyl dipeptides is mainly determined by the basicity of the amino end group.<sup>2,3</sup> Other studies, focused on the kinetics, showed that zwitterions of oligopeptides are extremely unreactive in complex formation. The reactive species are the anionic forms of the peptides, *i.e.*, species with an unprotonated amino end group.<sup>4-6</sup>

X-Ray studies of solid metal ion-peptide complexes disclosed that the metal ion is bound to the amino end group and the oxygen of the neighboring amide group in the pH region in which the amide NH is not deprotonated.<sup>7,8</sup> Evidence for the same binding mode in aqueous solution was given by studies of the thermodynamics<sup>2,9</sup> and kinetics.<sup>10</sup> In such peptide complexes,

especially with  $\text{Cu}^{2+}$  as the metal ion, the amide group may become deprotonated as the pH is increased and then the metal ion coordinates the amino end group and the nitrogen of the neighboring amide group.<sup>7-10</sup>

The aim of the present study is to learn how the rate of complex formation is influenced by the presence of a large alkyl group substituted at an  $\alpha$ -carbon, *i.e.*, to see if steric hindrance is important. We used as ligands, glycyl-L-leucine or L-leucylglycine, and as metal ions,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Cu}^{2+}$ . Even though several of the corresponding stability constants of the complexes are already known it seemed justified to determine them all under a uniform set of conditions.

### Experimental Section

**A. Thermodynamics Experiments. Materials and Measurements.** The metal perchlorates, glycyl-L-leucine, and L-leucylglycine were purchased from Fluka AG, Buchs, Switzerland. The measurements were performed by potentiometric titrations as previously described.<sup>11</sup>

**Acidity Constants of the Dipeptides.**<sup>12</sup> The values of  $K^{\text{H}}_{\text{H}_2\text{L}}$  of the dipeptides were determined by titrating 10 ml of aqueous  $4.4 \times 10^{-2} M$   $\text{HClO}_4$  and  $\text{NaClO}_4$  ( $\mu = 0.1$ ) in the presence and absence of the ligands ( $3 \times 10^{-2} M$ ) under  $\text{N}_2$  with  $0.5 M$   $\text{NaOH}$  and those of  $K^{\text{H}}_{\text{HL}}$  were determined by titrating 50 ml of aqueous  $10^{-4} M$   $\text{HClO}_4$

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(12) Abbreviations used: M, general metal ion; L, general ligand; the symbol HL represents the zwitterionic form of the dipeptide.