Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada

Manganese-55 Nuclear Magnetic Resonance Studies of Compounds Containing Mn-M (M = Si, Ge, Sn, Pb) Bonds and the Signs of e^2qQ in Manganese(I) Compounds

G. M. BANCROFT,* H. C. CLARK, R. G. KIDD, A. T. RAKE, and H. G. SPINNEY

Received September 15, 1972

^{55}Mn nmr spectra of 14 compounds of the type $L_3MMn(CO)_5$ (L = Cl, C_6F_5, Ph; M = Si, Ge, Sn, Pb) or $Ph_xX_{3-x}SnMn(CO)_5$ (X = Cl, C_6F_5) are reported. The large range of chemical shifts is attributed to increasing σ-donor ability of the ligands in the order $GeCl_3 < SnCl_3 < Ge(C_6F_5)_3 < SnCl_2Ph \sim SiCl_3 < Sn(C_6F_5)_3 < Si(C_6F_5)_3 < PbPh_3 < SnPh(C_6F_5)_2 < SnClPh_2 < GePh_3 < SnPh_2C_6F_5 < SiPh_3 < SnPh_3$. This order correlates well with Graham's σ parameter. There is a good correlation between $\sqrt{\Delta H}$ (ΔH = line width in gauss) and chemical shift for the series $Ph_x(C_6F_5)_{3-x}SnMn(CO)_5$. This and other correlations of $\sqrt{\Delta H}$ with chemical shift for other Mn^I compounds substantiate the above conclusion that the chemical shift is mainly sensitive to σ effects. The above correlation also indicates that the line widths are mainly sensitive to σ effects. Using partial quadrupole splittings (pqs) from Fe^{II} quadrupole splittings, we have deduced the sign of e^2qQ for $Mn(CO)_5X$ (X = Cl, Br, I, $SnCl_3$, H). For the first four compounds the signs are positive, and for the halides, the calculated magnitudes of e^2qQ (Cl, +16.2; Br, +17.5; I, +16.8) are in good semiquantitative agreement with those observed (Cl, 13.86; Br, 17.46; I, 19.85). The positive signs of e^2qQ are not in agreement with calculated signs from previous MO calculations. The correlations of $\sqrt{\Delta H}$ with chemical shift are consistent with the above signs of e^2qQ, and the expected relative line widths from the pqs calculations generally agree with the observed line widths.

Introduction

Because Mn is paramagnetic in a great deal of its chemistry, few ^{55}Mn nmr data have been reported. Mn^I compounds such as $Mn(CO)_5X$ (X = Cl, Br, I, etc.) are diamagnetic, and three recent papers[1-3] have indicated that useful bonding information can be obtained from both the chemical shifts and line widths. The chemical shifts have been interpreted using σ_p: an increase in σ-donor ability of X decreases σ_p and increases the chemical shift.[1-3] Correlations between the chemical shift and $\sqrt{\Delta H}$ (ΔH = line width) have been noted,[1,3] and Onaka, *et al.*, have shown a good correlation between chemical shift and Graham's σ parameter[4] for a series of $R_xX_{3-x}SnMn(CO)_5$ compounds (R = Ph, Me; X = Cl, Br).

Spiess and Sheline[5] have recently reported ^{55}Mn $|e^2qQ|$ values for $Mn(CO)_5X$ compounds (X = Cl, Br, I), but the signs of these coupling constants could not be obtained. Spiess, *et al.*, used orbital populations reported earlier[6] to calculate the ^{55}Mn and halogen e^2qQ values for these compounds. The signs of the ^{55}Mn e^2qQ values were negative (taking Q to be positive), and Spiess, *et al.*, noted that the orbital populations overestimate both the ^{55}Mn and halogen field gradients. Thus the MO calculations[6] apparently overestimate the σ-donor ability of the halogens.

In the present study of Mn-M (M = group IV metal) bonds, we have used previous ideas on the chemical shift outlined above to obtain a σ-donor ordering of ligands. Using partial quadrupole splittings (pqs),[7-10] we deduce the sign of e^2qQ for several of the Mn^I compounds and indicate the value of the calculated signs and magnitudes of e^2qQ to rationalize $\sqrt{\Delta H}$ *vs.* chemical shift correlations, line width variations, and bonding properties of ligands.

Experimental Section

Except for the compounds $Cl_3GeMn(CO)_5$ and $(C_6F_5)_3GeMn(CO)_5$, all compounds were prepared by previously published methods[11-15] and characterized by infrared, nmr, and mass spectra. The preparation of the above two compounds will be reported shortly.[16] The ^{55}Mn nmr spectra were obtained at 14.81 MHz using a Varian 4200B wide-line spectrometer with a V-4210A variable-frequency oscillator and a V-3400 9-in. magnet with Fieldial stabilization and sweep capacity. Resonance lines were recorded as derivatives of dispersion signals and calibration was effected by generation of audiofrequency side bands. Chemical shift values, designated by δ, are quoted in parts per million (ppm) relative to the MnO_4^- resonance in saturated aqueous solution. All spectra were measured at room temperature and positive shifts denote increased shielding. Quoted errors in δ values are standard deviations and result from calibration uncertainty.

Except for the $Ph_x(C_6F_5)_{3-x}SnMn(CO)_5$ series, just qualitative trends in line widths are given. Magnet inhomogeneity and small sample sizes made it unreasonable to quote actual numbers for most compounds.

To determine whether or not the metal-metal bond dissociates in solution, spectra of $Ph_3SnMn(CO)_5$ were obtained in various solvents of as widely differing polarity as possible (see footnote *b* of Table I). The similarity of both chemical shift and line width in all solvents indicates that no appreciable dissociation is occurring. It seems reasonable that extensive dissociation of the other compounds does not occur in solution.

Results and Discussion

^{55}Mn Chemical Shifts. ^{55}Mn chemical shifts for the 14 $L_3MMn(CO)_5$ and $Ph_xX_{3-x}SnMn(CO)_5$ compounds are given in Tables I and II. Chemical shift separations among the compounds $Ph_3SnMn(CO)_5$, $Ph_2ClSnMn(CO)_5$, $PhCl_2SnMn(CO)_5$, and $Cl_3SnMn(CO)_5$ are in good agreement with those given by Onaka, *et al.*,[3] but absolute values of the chemical shifts with respect to the external reference are 50-100 ppm lower than Onaka's values due to the different solvents and/

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Table I. ^{55}Mn Chemical Shifts for $L_3M\text{-}Mn(CO)_5$ Compounds

	Chemical shift[a]			
	M = Si	M = Ge	M = Sn	M = Pb
$Cl_3MMn(CO)_5$	2200 (15)	1870 (5)	1910 (9)	
$(C_6F_5)_3MMn(CO)_5$	2290 (6)	2140 (9)	2260 (11)	
$Ph_3MMn(CO)_5$	2470 (13)	2430 (12)	2510 (13)[b]	2350 (14)

[a] The chemical shifts are quoted in ppm in acetone solution upfield to aqueous $KMnO_4$. Errors are given in parentheses. [b] For $Ph_3SnMn(CO)_5$, the chemical shifts were recorded in other solutions: in benzene, 2510 (13); in dimethylformamide, ~2505; in tetrahydrofuran, 2530 (17).

Table II. ^{55}Mn Chemical Shifts and Line Widths for $Ph_{3-x}Y_xSnMn(CO)_5$ Species

Compound	Chemical shift[a]		Line width at half-height, Hz
	Our results	Ref 3	
$Ph_3SnMn(CO)_5$	2530 (15)	2610	3000 (300)
$Ph_2(C_6F_5)SnMn(CO)_5$	2470 (16)		2000 (200)
$Ph(C_6F_5)_2SnMn(CO)_5$	2380 (12)		1400 (140)
$(C_6F_5)_3SnMn(CO)_5$	2280 (15)		600 (60)
$Ph_2ClSnMn(CO)_5$	2424	2460	Medium
$PhCl_2SnMn(CO)_5$	2228	2278	Sharp
$Cl_3SnMn(CO)_5$	1967	2024	Very sharp

[a] Errors are given in parentheses. All spectra are taken in THF as solvent.

or calibration factors. The results show immediately that for the $L_3MMn(CO)_5$ compounds (Table I), the chemical shifts generally increase in the order $L = Cl < C_6F_5 < Ph$ and $M = Ge < Sn < Si$, although for L = Ph, the order is $M = Pb < Ge < Si < Sn$. It is also apparent from Table II that the chemical shift increases with substitution of C_6F_5 by Ph in $Ph_{3-x}Y_xSnMn(CO)_5$.

The interpretation of such trends has been discussed in two previous papers[1,3] using the results of Gray's MO diagram.[17] It is assumed that changes in the chemical shift are mostly due to changes in the paramagnetic term σ_p. σ_p can be written

$$\sigma_p = \frac{-4\beta^2}{3}\langle r^{-3}\rangle\left(\frac{8}{\Delta E_1} + \frac{4}{\Delta E_3} + \frac{12}{\Delta E_4}\right) \tag{1}$$

where the ΔE's refer to the following d-d transitions

$$\Delta E_1\text{:}\quad b_2[\pi; 3d_{xy}] \rightarrow b_1[\sigma^*; 3d_{x^2-y^2}]\ (^1A_1 \rightarrow {}^1A_1) \tag{2a}$$

$$\Delta E_3\text{:}\quad e[\pi; 3d_{yz}, 3d_{xz}] \rightarrow b_1[\sigma^*; 3d_{x^2-y^2}]\ (^1A_1 \rightarrow {}^1E_1) \tag{2b}$$

$$\Delta E_4\text{:}\quad e[\pi; 3d_{yz}, 3d_{xz}] \rightarrow a_1[\sigma^*; 3d_{z^2}]\ (^1A_1 \rightarrow {}^1E_1) \tag{2c}$$

Because of strong charge-transfer bands it is not possible to evaluate the ΔE's, but for an octahedral complex (in which $\Delta E_1 = \Delta E_3 = \Delta E_4$ = ligand field splitting Δ), Δ increases as the σ-donor plus π-acceptor ($\sigma + \pi$) ability of the ligand increases.[10,18] Generally, for the $LMn(CO)_5$ complexes of C_{4v} symmetry, the ΔE's will also increase as the $\sigma + \pi$ property of the ligand increases. An increase in ΔE causes a decrease in $|\sigma_p|$ (eq 1), which in turn gives an increase in the chemical shift as it is usually expressed. There are three pieces of evidence which indicate that the chemical shift is most sensitive to the σ-donor ability of the ligand L. First, as noted by Onaka, the correlation of ^{119}Sn Mossbauer center shift with the ^{55}Mn chemical shift is consistent with changes in σ properties of the SnX_3 group in $X_3SnMn(CO)_5$ compounds. Second, the correlations of $\sqrt{\Delta H}$ ($\propto e^2qQ_{Mn}$) with ^{55}Mn chemical shift indicates that σ effects are most important in determining both the chemical shift and the line width. This evidence will be discussed in detail in the next section of the paper. Third, except for $Ph_3PbMn(CO)_5$, there is an excellent linear correlation (Figure 1) between the ^{55}Mn nmr chemical shift and Graham's σ parameter. The least-squares straight line to these points gives the equation

$$\sigma = -1.3 \times 10^{-3}\delta + 2.8$$

while inclusion of chemical shifts for the $Mn(CO)_5X$ (X = Cl, Br, I) compounds[1] gives the line

$$\sigma = -1.2 \times 10^{-3}\delta + 2.5$$

[Different solvents were used for the $Mn(CO)_5X$ compounds and as noted earlier, solvent shifts of up to 100 ppm could be incurred. However, these shifts appear to be relatively small compared to errors in Graham's σ parameter.] A similar correlation was noted by Onaka, *et al.*[3,19] These correlations substantiate our rationalization of chemical shift being largely dependent on σ effects and/or lend more credibility to Graham's σ parameters.

The above evidence then indicates that the σ-donor ability of our ligands increases in the order $GeCl_3 < SnCl_3 < Ge(C_6F_5)_3 < SnCl_2Ph \sim SiCl_3 < Sn(C_6F_5)_3 < Si(C_6F_5)_3 < SnPh(C_6F_5)_2 < SnClPh_2 < Ph_3Pb < GePh_3 < SnPh_2(C_6F_5) < SiPh_3 < SnPh_3$, and generally this order should reflect increasing M-Mn bond strength, although π-bonding and steric effects for some of these ligands may alter relative bond strengths noticeably. In particular, it is interesting to note that the chemical shift order is generally $Ge < Sn < Si$. This order is incompatible with the measurement of metal-metal bond strengths in the series $Me_3MMn(CO)_5$ by mass spectrometry,[20] which shows if anything that the order of increasing metal-metal bond strength is $M = Sn < Si < Ge < Pb$. However, other bond dissociation data on compounds of the type $(\pi\text{-}C_5H_5)(CO)_3M^I\text{-}M^{II}Me_3$ (M^I = Cr, Mo, W; M^{II} = Ge, Sn)[21] indicate that the Ge compounds have substantially lower bond dissociation energies than their Sn analogs. Similar disagreement in group IV-transition metal bond strengths deduced from CO infrared data are found in the literature,[22,23] but a full force field analysis on the comparable system $Cl_3MCo(CO)_4$ (M = Si, Ge, Sn)[22] indicates that the value of the metal-metal stretching force constant k_{MM} increases in the order $Ge < Sn < Si$, as obtained above from the Mn chemical shift.

^{55}Mn Nmr Line Widths and the Sign of e^2qQ in Mn^I Compounds. It is generally recognized that the nmr line widths for nuclei having $I > 1/2$ are determined mainly by the quadrupole coupling constant e^2qQ.[24] For C_{4v} symmetry ($\eta \equiv 0$), we can express the line width ΔH by the expression[24]

$$\Delta H = C\left[\frac{e^2qQ}{h}\right]^2 \tau_c \tag{3}$$

where C is a constant and τ_c is the rotational correlation time which depends mostly on the size of the molecule, the type

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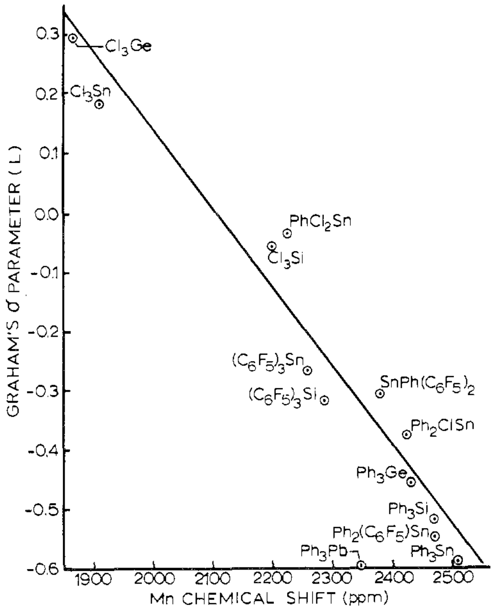

Figure 1. Plot of Graham's σ parameter *vs.* the ^{55}Mn chemical shift in ppm from $KMnO_4$. The line is a least-squares fit to all points except that for Ph_3Pb, and the value of σ for $(C_6F_5)_3Si$ was calculated from the values of the carbonyl stretching force constants given in ref 15. For all $R_3MMn(CO)_5$ compounds (R = Cl, C_6F_5, Ph; M = Si, Ge, Sn, Pb), the chemical shifts plotted on this graph were recorded in acetone; the chemical shifts for the four compounds $Ph_{3-n}X_nSnMn(CO)_5$ (X = Cl, C_6F_5; n = 1, 2) were recorded in THF. With the exception of $Cl_3SnMn(CO)_5$, the chemical shifts in the two solvents are within experimental error.

Table III. e^2qQ Values for Isoelectronic Fe^{II} and Mn^I Compounds

Compound	e^2qQ mm sec^{-1}	e^2qQ, MHz^a	
		Obsd	Calcd
$[Fe(CO)_5Cl]^+$	+1.00		+11.63
$[Fe(CO)_5Br]^+$	+1.08		+12.56
$[Fe(CO)_5I]^+$	+1.04		+12.10
$[Fe(CO)_5SnCl_3]^+$	+0.48		+5.58
$[Fe(CO)_5H]^+$	−1.96		−22.80
$Mn(CO)_5Cl$		13.86^b	+16.2
$Mn(CO)_5Br$		17.46^b	+17.5
$Mn(CO)_5I$		19.85^b	+16.8
$Mn(CO)_5SnCl_3$		73^c	+7.8
$Mn(CO)_5H$			−31.7

^{a} For ^{57}Fe, 1 mm sec^{-1} = 11.63 MHz. ^{b} Reference 4. ^{c} J. L. Slater, M. Pupp, and R. K. Sheline, *J. Chem. Phys.*, 57, 2105 (1972).

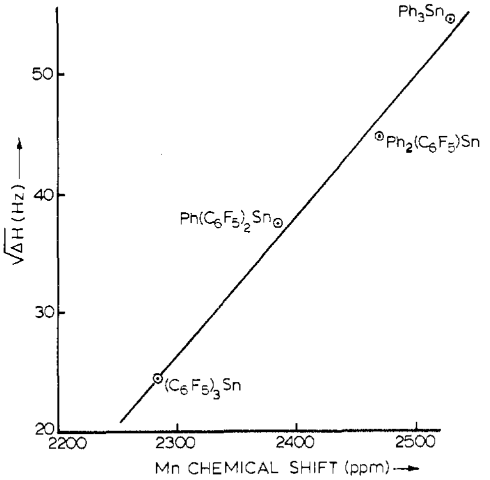

Figure 2. Plot of $\sqrt{\Delta H}$ in Hz for the compounds in the series $Ph_x(C_6F_5)_{3-x}SnMn(CO)_5$ (x = 0–3) *vs.* the ^{55}Mn chemical shift in ppm.

of solvent, and solvent-solute interactions. We have determined that dissociation of the metal-metal bond is probably not important for our compounds. It is possible that ligands such as the C_6F_5 group are not free to rotate about the M-Mn bond, but work on other systems[24] and on the $HMn(CO)_{5-x}(PF_3)_x$ suggests[2] that τ_c should remain reasonably constant, with quadrupole relaxation being the main mechanism of line broadening. Thus $\sqrt{\Delta H}$ should be proportional to e^2qQ.

Before discussing variations in line width and correlations of line width with chemical shift, it is important to know the sign of e^2qQ for some Mn^I compounds and to review previously outlined ideas[10] for interpreting magnitudes of e^2qQ. Using the method described in previous papers[9,10] we can predict ^{55}Mn quadrupole splittings for Mn^I species which are isoelectronic with Fe^{II} species. For the compounds $[Fe(CO)_5X]^+$ (X = Cl, Br, I, $SnCl_3$, H), we take the following partial quadrupole splittings (in mm sec^{-1}): Cl, −0.30; Br, −0.28; I, −0.29; $SnCl_3^-$, −0.43; H^-, −1.04;[10] CO, −0.55.[10,25,26] We then calculate the expected quadrupole splittings for these species in Table III. None of these quadrupole splittings have been measured at the present time, and because of the somewhat variable nature of the pqs value for strong π acceptors such as carbonyl,[26,27] the error in the e^2qQ values could be as large as 0.30 mm sec^{-1}, or about 30% of the values for the $Fe(CO)_5$ halide cations. Then, we take $\langle r^{-3}\rangle_{3d}$ for Mn^I as $3.13a_0^{-3}$, $\langle r^{-3}\rangle_{3d}$ for Fe^{II} as $4.49a_0^{-3}$,[28] $Q_{^{55}Mn} = 0.40b$,[29] and $Q_{^{57}Fe} = 0.20b$[9] and use the following formula to calculate the e^2qQ values for the isoelectronic Mn compounds

$$(e^2qQ)_{Mn} = \frac{(e^2qQ)_{Fe}\langle r^{-3}\rangle_{Mn}Q_{Mn}}{\langle r^{-3}\rangle_{Fe}Q_{Fe}} \tag{4}$$

The calculated values of $|e^2qQ|$ for the $Mn(CO)_5X$ (X = Cl, Br, I) (Table III) are in surprisingly good agreement with the observed considering the assumptions in the method[9,30] and the line width data discussed shortly indicate that relative $|e^2qQ|$ values are correct. In particular, we assume that the bonding in isoelectronic iron and manganese compounds is identical, whereas it is well known that CO in Mn^I compounds are worse σ donors but better π acceptors than in the isoelectronic Fe^{II} compounds.[31] However, because the partial quadrupole splittings are proportional to $\sigma - \pi$,[8,9] these two trends tend to cancel to give similar relative pqs values for Mn^I, Fe^{II}, and Co^{III}. Also, we assume that the L-Mn-L bond angles are 90° in these compounds, whereas structure data indicate that these angles deviate somewhat from 90° (90° ± 8°).[32] However, such deviations have been found to have only small effects on the predicted quadrupole splittings, and in general, predicted and observed e^2qQ are in very good agreement assuming the ideal bond angles.[7-10,27,33] However, we would not expect our calculated e^2qQ values in Table

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III for the Mn compounds to be accurate to better than about ±40% due to the above assumptions and errors in $\langle r^{-3} \rangle$ and Q values. Thus it is not at all surprising that the $(e^2qQ)_{\text{calcd}}$ values for $Mn(CO)_5X$ (X = Cl, Br, I) compounds do not give the same trend as $(e^2qQ)_{\text{obsd}}$ for these compounds. The signs of the e^2qQ values should definitely be correct and (e^2qQ) values should have semiquantitative significance.

Of particular interest are the positive signs of e^2qQ (taking Q positive) for $Mn(CO)_5X$ (X = Cl, Br, I, $SnCl_3$) and the negative sign for the hydride. The signs for the halides conflict with those calculated[5] using Fenske's orbital occupancy data.[6] This discrepancy in signs is almost certainly due to the overestimate of the σ-donor power of halides in the MO calculations, as noted by Spiess.[5] The field gradient q can be expressed as

$$q = K[-N_{d_{z^2}} + N_{d_{x^2-y^2}} + {}^1\!/_2 N_{d_{xy}} - {}^1\!/_2(N_{d_{xz}} + N_{d_{yz}})] \qquad (5)$$

and this can be rewritten for $Mn(CO)_5X$[7]

$$q \propto -\pi_{\text{CO}} + \pi_{\text{X}} + {}^4\!/_3\sigma_{\text{CO}} - {}^4\!/_3\sigma_{\text{X}} \qquad (6a)$$

or

$$q \propto \Delta\sigma - \Delta\pi \qquad (6b)$$

if we neglect crystal field contributions to the quadrupole splitting. The positive e^2qQ value for $Mn(CO)_5X$ compounds indicates that CO is a better σ donor and/or worse π acceptor than Cl. Since CO is certainly a better π acceptor than X from general chemistry and the photoelectron spectra of these compounds,[34] CO must be a much better σ donor than Cl.

It is apparent then that as the σ-donor strength of L in $Mn(CO)_5L$ compounds increases, the e^2qQ value becomes more negative; as the π acceptor ability of L increases, the e^2qQ value becomes more positive. Thus, we would expect compounds containing strong σ donors such as L = H^- to have relatively negative e^2qQ values, while if L is a comparatively weak σ donor (L = Cl, Br, I), the sign of e^2qQ should be positive. The signs in Table III reflect the above ideas.

The correlation of $\sqrt{\Delta H}$ *vs.* chemical shift and the magnitude of the line widths strongly support the above treatment. The previous correlations of $\sqrt{\Delta H}$ *vs.* chemical shift by Onaka, *et al.*,[3] suggested that there should be a change in sign of e^2qQ as predicted above and that the magnitude of e^2qQ should follow the order $Mn(CO)_5H > Mn(CO)_5X > Mn(CO)_5SnCl_3$ as predicted by the calculations in Table III. From the $\sqrt{\Delta H}$ *vs.* chemical shift correlation,[3] we suggest that all $Mn(CO)_5L$ compounds with chemical shifts below ~2150 ppm have positive e^2qQ values, while those compounds having chemical shifts above this value have negative e^2qQ values.

The positive correlations indicate strongly that both the chemical shift and e^2qQ are mainly sensitive to σ effects and it is interesting to note that the $\sqrt{\Delta H}$ ($\propto\sigma - \pi$) *vs.* chemical shift ($\propto\sigma + \pi$) plots are analogous to the quadrupole splitting ($\propto\sigma - \pi$)-center shift ($\propto\sigma + \pi$) plots noted earlier[26] for Fe^{II} low-spin compounds. In both cases, if π effects are dominant, a line of opposite slope to those observed should be obtained, while if π effects are important, no correlations should be observed. Strong π acceptors such as CO were found to lie off the line in the Fe^{II} series,[26] as expected from the above ideas.

Finally, there is good qualitative agreement between observed relative ΔH values and those expected from the calculated e^2qQ values in Table III. Thus the observed line widths for the $Mn(CO)_5X$ compounds are as follows (in gauss): $Mn(CO)_5SnCl_3$, 0.18; $Mn(CO)_5Cl$, 0.18; $Mn(CO)_5Br$, 0.378; $Mn(CO)_5I$, 0.557; $HMn(CO)_5H$, 2.39.[1,3] These values correlate reasonably well with $(e^2qQ)^2_{\text{calcd}}$, but more points are needed to establish a more quantitative correlation.

Registry No. $Cl_3SiMn(CO)_5$, 38194-30-8; $Cl_3GeMn(CO)_5$, 14768-39-9; $Cl_3SnMn(CO)_5$, 16165-09-6; $(C_6F_5)_3SiMn(CO)_5$, 25930-67-0; $(C_6F_5)_3GeMn(CO)_5$, 38135-65-8; $(C_6F_5)_3SnMn(CO)_5$, 38135-66-9; $Ph_3SiMn(CO)_5$, 38194-32-0; $Ph_3GeMn(CO)_5$, 38135-67-0; $Ph_3SnMn(CO)_5$, 34792-14-8; $Ph_3PbMn(CO)_5$, 38135-69-2; $Ph_2(C_6F_5)SnMn(CO)_5$, 38135-70-5; $Ph(C_6F_5)_2SnMn(CO)_5$, 37830-62-9; $Ph_2ClSnMn(CO)_5$, 38241-11-1; $PhCl_2SnMn(CO)_5$, 38135-72-7.

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Contribution from the William Rand Kenan Jr. and Francis Preston Venable Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Magnetization Studies of Bimetallic Copper(II) Complexes Which Have Triplet Ground States

KENNETH T. McGREGOR, DEREK J. HODGSON, and WILLIAM E. HATFIELD*

Received September 1, 1972

Magnetization studies have been carried out on the dimeric compounds $[Cu(pyO)_2(NO_3)_2]_2$, $[Cu(2,2'\text{-bipy})(OH)]_2SO_4 \cdot 5H_2O$, $[Cu(2,2'\text{-bipy})(OH)]_2(NO_3)_2$, and $[Cu(Et_2dtc)_2]_2$ (pyO is pyridine *N*-oxide, 2,2′-bipy is 2,2′-bipyridyl, and Et_2dtc is *N,N*-diethyldithiocarbamate). The experimental data were compared with theoretical values calculated from the expression $\langle \mu \rangle = gS'B_{S'}(X)$, where $B_{S'}(X)$ is the Brillouin function and S' is the effective spin. The data for each complex are consistent with a ferromagnetic intradimer interaction and an antiferromagnetic interdimer interaction and confirm the existence of a triplet ground state in each dimeric molecule.

Introduction

Only recently have there been reports[1-4] of copper(II) dimers which exhibit spin-spin coupling resulting in triplet ground states. Although the theory of exchange interactions

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