

Mössbauer Parameters in Five-Coordinate Tetracarbonylferrate Complexes

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Formal d^8 -[Fe(CO)₄L] complexes show two distinct Mössbauer trends depending on the site of substitution. TBP equatorial substitution shows a direct dependence of both ΔE_Q and δ on σ donation. TBP axial substitution displays a synergistic dependence of Δ upon δ . Deviation from these two modes of behavior occurs because of a change in electronic occupancy. As d^{10} -[Fe(CO)₄²⁻L²⁺] is approached, two types of behavior are noted. Strong σ -donor species (presumed axial TBP) retain a negative e^2qQ and do not substantially change η . Distortion of the Fe(CO)₄²⁻ moiety toward tetrahedral reduces ΔE_Q substantially. Poor σ -donor ligands (presumed equatorial) give rise to a change in the sign of e^2qQ (to positive). Moderate ΔE_Q values are retained in this case while δ values remain higher than expected. While poor σ donors show ionicity in a structural and electronic sense (about iron), this effect is not transmitted at the nucleus.

Introduction

Mössbauer spectroscopy¹ has been a powerful method for the characterization of the organometallic chemistry of iron.² We are studying a series of mixed-metal bimetallic five-coordinate tetracarbonylferrates³⁻⁷ and using ⁵⁷Fe Mössbauer spectroscopy in their characterization; their spectra are reported within. More generally, this work has aroused our interest in the Mössbauer parameters of five-coordinate [Fe(CO)₄L] complexes.

It might appear upon cursory inspection that the σ - and π -donor/acceptor capabilities of a ligand would be estimable from the parameters of the Mössbauer experiment, namely, isomer shift (δ) and quadrupole splitting (ΔE_Q (or Δ)). Such is indeed the case in the octahedral field of six-coordination, where each ligand's contribution to δ and Δ can be analyzed for a chemical series in terms of partial isomer shifts and partial quadrupole splittings, which contribute additively to each parameter.⁸ Five-coordination represents a more complex problem because of the distortion of the crystal field from cubic (or octahedral) geometry so that a ligand's position becomes crucial in setting the values of its δ and Δ parameters.^{9,10}

An initial series of compounds [Fe(CO)₄L] (L = CO, phosphines, phosphites, allyls(1+), and alkenes (compounds 1, 3-5, 23-25, 29-31, and 45)), reported¹¹ in 1962 by Collins and Pettit (C-P) shortly after Mössbauer spectroscopy was developed, established the linear dependence of Δ vs. δ with a negative slope as in Figure 1. This represents an inverse correlation to that anticipated assuming σ donation is offset by π acceptance (for L) as one might expect in the d^8 - D_{3h} case. C-P behavior implies the dominance of σ effects in both pa-

rameters. The apparent insensitivity to the site of substitution (3-5 are axially substituted D_{3h} ; 23-25 are equatorially substituted D_{3h} eq; 29-31 and 46 are C_{2v}) was also noted at that time. Subsequent work by Carrol, Deeney, and Lalor on a more closely related series of axially substituted D_{3h} [Fe(CO)₄L] (L = CO, phosphines, phosphates, arsines, and stibines (compounds 3, 6, and 8-12)) and disubstituted C_{3v} [Fe(CO)₃L₂] complexes established¹² that these complexes follow the line in Figure 2 with the expected positive slope implying σ donation is offset by π acceptance for these ligands and geometries.

Our attention was drawn to this dichotomy in the Mössbauer parameters by the observation that some five-coordinate mixed-metal bimetallic [M'Fe(CO)₄] (M' is a main-group metal) complexes do not obey either of the two relationships just previously described.^{3-7,13-15} In this paper we will describe the factors that affect Mössbauer parameters. From this information we hope to assess the bonding capabilities of mixed metals as ligands and the nature of the L-Fe and M'-Fe bonds. In Table I we present a complete and self-consistent listing of Mössbauer parameters for monosubstituted five- and pseudo-five-coordinate [Fe(CO)₄L] complexes.

Experimental Section

The Mössbauer spectra were recorded at Rice on a spectrometer described previously in the literature.¹⁶ Subsequent to this description an Elron Model MGF-2 variable-velocity function generator and a Northern NS-560 multichannel analyzer were added to aid in data acquisition. Spectra were analyzed by using a computer program that has appeared elsewhere.¹⁷ The samples were loaded in a Vacuum Atmospheres glovebox and prepared in the form indicated. The temperature was measured by a copper-constantan thermocouple imbedded in the sample. Samples were run referenced to sodium nitroprusside and converted to an iron metal reference by addition of 0.26 mm s⁻¹. All values quoted are relative to iron metal.

All pertinent Mössbauer data from this study and elsewhere are listed in Table I, along with the temperature at which the spectrum was recorded, ΔE_Q , a corrected δ , and a compound number. Since the comparison between Mössbauer parameters of spectra run on different instruments involves some uncertainty (mostly in δ), we have endeavored to generate a self-consistent set of data by the following procedure. After being referenced to Fe metal, data from ref 11, 14,

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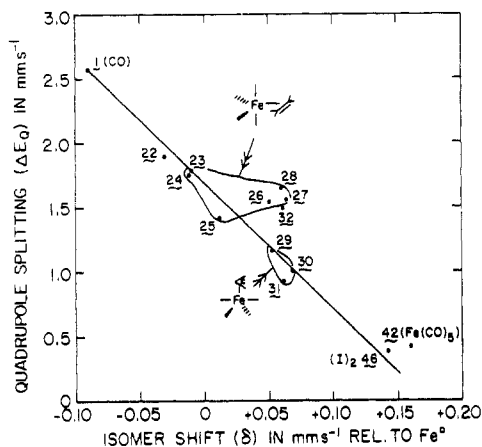


Figure 1. Mössbauer parameters for a series of equatorially substituted D_{3h} $[\text{Fe}(\text{CO})_4\text{L}]$ and pseudo-five-coordinate tetracarbonylferrates.

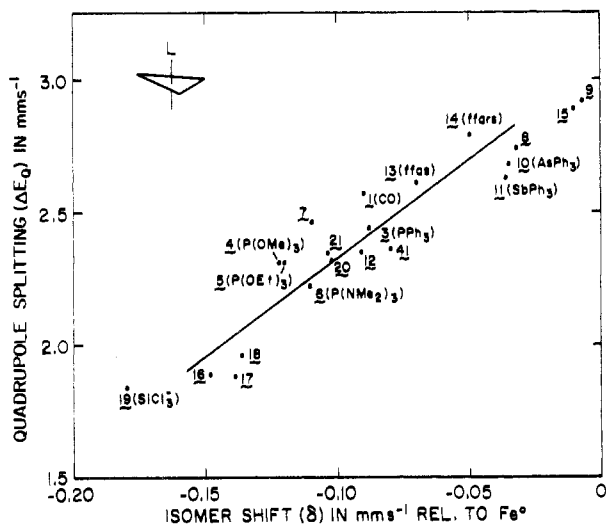


Figure 2. Mössbauer parameters for a series of axially substituted D_{3h} $[\text{Fe}(\text{CO})_4\text{L}]$.

and 18–21 and our data appeared consistent. Reference 12 contains a common spectrum (3), and so a correction of -0.122 mm s^{-1} was made to all spectra from this study. Reference 22 also contained a common spectrum (25 as well as 1), and a correction of $+0.06$ was made to this study. There is some uncertainty associated with blanketly making this type of a correction since second-order Doppler terms, which are due to intrinsic lattice vibrations, are not the same in all compounds or preparations. The order of the uncertainty is roughly $\pm 0.2 \text{ mm s}^{-1}$, which may largely account for the spread of the compounds around each line. We specifically use low-temperature spectra in order to minimize the second-order Doppler effect. At 78 K this is not a large (ca. $\pm 0.1 \text{ mm s}^{-1}$) effect, as can be seen in Table I for several of the compounds.

Results and Discussion

Relationship of Mössbauer Parameters to the Electronic and Geometrical Configuration in Five-Coordination. Isomer shift is commonly expressed as

$$\delta = \frac{1}{2} \epsilon_0 (Ze^2 R^2) (\Delta R / R) (|\psi_s(0)_{\text{absorber}}|^2 - |\psi_s(0)_{\text{source}}|^2) \quad (1)$$

(δ = isomer shift; ϵ_0 = permittivity of a vacuum; Ze = nuclear charge; $-e$ = electron charge; ΔR = change in nuclear radius; $|\psi_s(0)|^2$ = s-electron density at the nucleus) and simplified to (2), a product of a nuclear and a chemical term, the former

$$\delta = \text{constant} \times (|\psi_s(0)_A|^2 - |\psi_s(0)_B|^2) \quad (2)$$

being normally treated as a constant for a given transition.¹ Sometimes equations similar to (1) are given expression R as a mean-square value to indicate deviation of the nucleus from spherical geometry. For ^{57}Fe $\Delta R/R$ is a negative, the nucleus shrinks on excitation, and consequently enhanced $|\psi_s(0)|^2$ leads to a negative isomer shift.¹

Although it is convenient to begin our analysis of Mössbauer parameters with δ , $|\psi_s(0)|^2$ includes not only contributions from all s-electron levels but interpenetration shielding for valence p, d, and f electrons so that δ should depend obliquely on factors that contribute to quadrupole splitting ΔE_Q . ΔE_Q is the deviation from cubic symmetry arising from the electric quadrupole interaction between the nuclear quadrupole moment and the local electric field gradient tensor at the nucleus. In attempting to establish an isomer shift scale for compounds measured in various studies, we tried to reduce the second-order Doppler shift by using low-temperature measurements whenever possible. Correction procedures yielding a self-consistent set of δ data are discussed in the Experimental Section.

Quadrupole splitting (ΔE_Q) for ^{57}Fe is commonly represented by (3)¹ (eQ = nuclear quadrupole moment; e = charge

$$\Delta = \frac{1}{2} e^2 q Q (1 + \eta^2/3)^{1/2} \quad (3)$$

of a proton; eq = principal component of the electric field gradient; η = asymmetry parameter measuring departure from axial symmetry ($\eta = V_{xx} - V_{yy} / V_{zz}$, z is the principal axis)). For the $I_g = 1/2 \rightarrow I_g = 3/2$ a transition takes place according to the selection rule $\Delta M_z = 0, \pm 1$ ($M1$ dipolar radiation), giving rise to a symmetrical doublet with $2\Delta E_Q$ separation. When $\eta = 0$ (axial symmetry), $\Delta = e^2 q Q / 2$ or the quadrupole coupling constant is half the peak separation as defined in nuclear quadrupole resonance spectroscopy. It is not possible to measure η or $e^2 q Q$ directly from a powder Mössbauer spectrum. Single-crystal measurements of the angular dependency of line intensities or the dependence of the Mössbauer spectrum upon large external magnetic fields can, however, establish these parameters.

Two papers have appeared describing the experimentally derived and theoretically calculated electric field gradient in isoelectronic pentacoordinate $[\text{M}(\text{CO})_{5-x}(\text{phosphine})_x]^n$ ($\text{M} = \text{Fe}^{10,16}, \text{Mn}^{10}, \text{and Co}^{10}$) complexes. The predominant contribution to this is normally considered to be the deviation of the valence shell from cubic symmetry. Charges beyond the iron nucleus are also measured to have an effect, but because the field gradient varies as the inverse cube of the distance, their effect drops off rapidly. In $[\text{Fe}(\text{CO})_5]$ it has been shown²⁴ that the quadrupole coupling constant $e^2 q Q$ is positive. The two studies on the effect of phosphine substitution in $[\text{Fe}(\text{CO})_4\text{L}]$ complexes upon the electric field gradient established^{10,15} that for axial substitution ($\eta = 0$) there is little effect on either the magnitude or the sign of the electric field gradient. However, both η and the sign of the quadrupole splitting are very sensitive to breaking the threefold symmetry by substitution whereas the overall magnitude $|\Delta E_Q|$ is not.

For five-coordination²⁵ the following geometries will be favored: d^0-d^2 , C_{4v} ; d^3-d^4 , D_{3h} ; d^5-d^7 , C_{4v} ; d^8-d^{10} , D_{3h} . The major effect on the electric field gradient in D_{3h} is the vacancy of the LUMO d_{z^2} orbital. For d^8-D_{3h} the stronger σ donors

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Table I. ⁵⁷Fe Mössbauer Parameters

ligand L ([Fe(CO) ₄ L])	no.	δ (Fe ⁰), mm s ⁻¹	ΔE _Q , mm s ⁻¹	temp, K	ref
Axially Substituted Trigonal Bipyramids					
CO	1	-0.09	2.57	80	14
[Fe(CO) ₄] ²⁻ (Et ₄ N) ⁺ ₂	2	-0.08	2.22	80	14
PPh ₃	3	-0.088	2.44; 2.54	278; 78	11; 12
P(OMe) ₃	4	-0.122	2.31	78	11
P(OEt) ₃	5	-0.12	2.31	78	11
P(NMe ₂) ₃	6	-0.11	2.22	80	18
[(μ-PPH ₂ (CH=CH)PPh ₂)Fe(CO) ₄]	7	-0.11	2.46	80	19
P(<i>o</i> -MeC ₆ H ₄) ₃	8	-0.032	2.74	293	12
As(<i>o</i> -MeC ₆ H ₄) ₃	9	-0.007	2.93	293	12
AsPh ₃	10	-0.035	2.68	293	12
SbPh ₃	11	-0.036	2.63	293	12
MTPB (4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)	12	-0.091	2.35	293	12
ffos (Ph ₂ PC=C(PPh ₂)CF ₂ CF ₂)	13	-0.07	2.61	80	19
ffars (Me ₂ AsC=C(AsMe ₂)CF ₂ CF ₂)	14	-0.05	2.79	80	19
[ffarsFe(CO) ₄]	15	-0.01	2.89	80	19
C(NMe ₂)(OAl(NMe ₂) ₂)	16	-0.148	1.89	78	20
C(NMe ₂)(OTi(NMe ₂) ₃)	17	-0.139	1.88	78	20
C(NMe ₂)(OLi(THF) ₂)	18	-0.134	1.96	78	20
(SiCl ₃) ⁻ (Et ₄ N) ⁺	19	-0.18	1.84	80	21
(P(Fe(C ₅ H ₅) ₂) ₂ Cl)	20	-0.103	2.322	60	10
(P(Fe(C ₅ H ₅) ₂) ₂ Cl) ⁺ (AlCl ₄) ⁻	21	-0.103	2.322	60	10
Equatorially (and Pseudoequatorially) Substituted Trigonal Bipyramids					
(P(NMe ₂) ₂) ⁺ (AlCl ₄) ⁻	22	-0.031	1.896	60	10
acenaphthalene (C ₁₀ H ₆ (CH ₂) ₂)	23	-0.010	1.78	78	11
<i>trans</i> -cinnamaldehyde (C ₆ H ₅ CH=CHCHO)	24	-0.012	1.75	78	11
maleic anhydride (HC=CHC(O)OC(O))	25	0.012	1.41	78	11; 22
<i>N</i> -phenylmaleimide (NPhC(O)CH=CHC(O))	26	0.05	1.54	78	22
dimethyl fumarate (<i>trans</i> -MeO ₂ CCH=CHCO ₂ Me)	27	0.063	1.56	78	22
<i>N,N</i> -dimethylacrylamide (NMe ₂ C(O)CH=CH ₂)	28	0.06	1.65	78	22
(<i>syn-syn</i> -1,3-Me ₂ -η ³ -C ₃ H ₅) ⁺ (BF ₄) ⁻	29	0.052	1.16	78	11
(<i>syn</i> -1-Me-η ³ -C ₃ H ₅) ⁺ (BF ₄) ⁻	30	0.068	1.01	78	11
(η ³ -C ₃ H ₅) ⁺ (BF ₄) ⁻	31	0.061	0.093	78	11
Mixed-Metal Tetracarbonylferrates					
(SnMe ₂ ⁻)(Na(THF) ₂) ⁺	32	0.061	1.498	78	3
(SnMe ₂ ⁻)(Na(4-MeC ₅ H ₄ NO) _{0.7}) ⁺	33	0.169	1.498	78	3
[ZnFe(CO) ₄] ²⁻ (Na(THF) ₂) ⁺ ₂	34	0.156	1.429	78	5
(P(CH(SiMe ₃) ₂) ₂) ⁻	35	-0.03	0.52	60	13
(Zn(NH ₃) ₃)	36	-0.18	0.80	80	18
[CdFe(CO) ₄] ²⁻ (Na(THF) ₂) ⁺ ₂	37	-0.64, 0.105, 0.186	<i>a</i>	78	this work
(Sn(C ₅ H ₄ Me)(C ₅ H ₅ N))	38	-0.08	2.36	78	24
(SnPh ₂ ⁻)(Na(THF) ₂) ⁺	39	0.154	1.457	78	this work
(SnMe ₂ (CH ₂ C ₆ H ₄) ₂) ⁻ (Na) ⁺	40	-0.20	1.80	78	this work
(SnMe ₂ (C ₅ H ₅ N))	41	0.97	br	78	this work
Miscellaneous Tetracarbonylferrates					
Fe(CO) ₅ (Fe ₂ (CO) ₉)	42	0.16	0.42	80	14
(H) ⁻ (Et ₄ N) ⁺	43	-0.048; -0.08	1.36	273; 80	14
(HFe(CO) ₄) ⁻ (Et ₄ N) ⁺	44	-0.07	0.50	80	14
(I) ₂	45	0.012	0.38	78	11
(2 e ⁻)(Fe(CO) ₄) ²⁻	46	-0.18	0	78	1a

^a [Cd(Fe(CO)₄)₂]²⁻ appears as an asymmetric triplet. The data may be assigned as follows: three singlets (-0.58, 0.528, and 1.336 mm s⁻¹), two doublets (δ = -0.03 mm s⁻¹, Δ = 1.112 mm s⁻¹; δ = 0.932, Δ = 0.808 mm s⁻¹), and a doublet and a singlet (δ = 0.788 mm s⁻¹; δ = 0.376 mm s⁻¹, Δ = 1.921 mm s⁻¹).

substitute axially; the weaker σ donors, equatorially. In d⁰-d⁴ and d¹⁰-D_{3h} the situation is reversed. Thus, for compounds obeying the C-P relationship (Figure 1), all are equatorially or pseudoequatorially substituted. Compounds in Figure 2 are axially substituted.

Compounds obeying the relationship shown in Figure 1 such as an alkene (which should bond parallel to the equatorial plane) show that σ donation dominates both the δ and ΔE_Q parameters. This may be attributed to the inability of the alkene to accept charge from the d_{xz} orbital (a factor that should also lead to smaller values of ΔE_Q and larger values of δ). σ donation dominates bonding in the xy plane, and any π bonding enhances its effect. Extrapolating this behavior out to the maximum σ-donating ability is when L becomes nearly

as good a σ donor as CO and symmetrical ("axial") substitution occurs.

Complexes obeying the relationship shown in Figure 2 lie on either side of [Fe(CO)₅], and it appears that π-acceptor capability becomes important in offsetting the σ-donation effect. Thus both values increase as the σ-donor power decreases and the π acceptance increases due to deshielding effects. Decreased donation into the d_z² orbital would increase the positive field gradient as would the back-donation from d_{xz} and d_{yz} orbitals. The major difference separating both types of behavior is that in axially substituted systems σ donation leads to a "formally" spherically symmetrical d shell and in equatorial substitution σ donation leads always to asymmetry of the d shell and a deficit of electron density about the z axis.

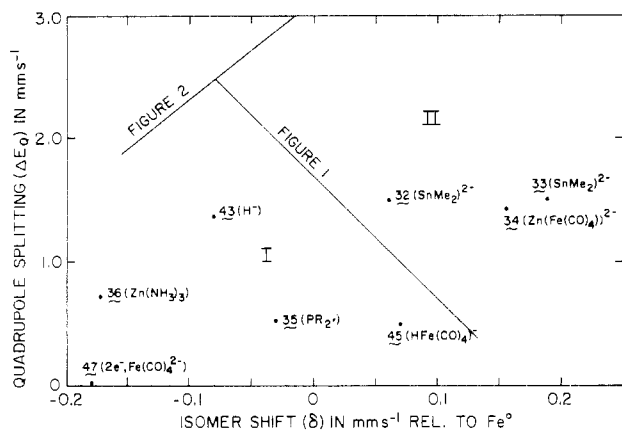


Figure 3. Mössbauer parameters for mixed-metal tetracarbonylferrates.

π -Orbital penetration of nuclear *s*-electron density will be much greater in the former case than in the latter.

The relationship described in Figure 1 is relatively insensitive to the geometry of the fifth ligand (η^2 , monodentate (e.g., alkenes); η^3 , mono- or bidentate (e.g., allyls); or even $2\eta^2$, monodentate (e.g., $2I^-$)). When σ effects are dominant for both δ and ΔE_Q , the relationship will decrease δ and Δ in the order $[Fe^0(CO)_4L^0] > [Fe^+(CO)_4L^-] > [Fe^{2+}(CO)_4L^{2-}]$. Distortions such as having two *cis* I^- ligands do not deviate enough from five-coordination to make a difference in this case. It is worthwhile noting that analyses of the trends in δ and ΔE_Q are based on the interaction of L and assume fixed bond distances for the Fe–C bonds in the $Fe(CO)_4$ fragment. We believe that changes in the bond length are small enough (ca. to 0.2 Å) not to affect the arguments. The geometries of the complexes are supported by data from ref 25 and 26.

Nature of the L–Fe and M'–Fe Bonds in Tetracarbonylferrates. There is no problem describing the nature of the covalent L–Fe or M'–Fe bond that follows the relationship described previously in Figure 2. It is synergistic *at the nucleus* and well-behaved in five-coordination. Similarly, compounds obeying the relationship in Figure 1 show that the synergistic behavior of the species that obey this relationship is destroyed *at the nucleus* by the inability of the π -acceptor orbitals to penetrate the unsymmetrical d shell. When nonsynergistic effects are felt at the nucleus, the Mössbauer parameters are less sensitive to geometry and these complexes behave as if they are still five-coordinate. In Figure 3 we have plotted a variety of mixed-metal and non-metal and five- and pseudo-five-coordinate tetracarbonylferrates that deviate from both relationships, and here we examine the factors that lead to their deviance.

The major cause of deviance relates to the d^n configuration of the tetracarbonylferrate moiety, and this problem can be analyzed by a metal carbonyl fragment analysis.²⁶ For d^8 - and d^9 - $Fe(CO)_4$ the lowest energy form is D_{2d} . At d^{10} - $Fe(CO)_4$, which prefers a T_d geometry, completion of the d shell leads to ligand–ligand repulsions becoming dominant in setting geometry. Very strong σ donors with no π -acceptor orbitals like H^- (43), $Zn(NH_3)_3$ (36), or $(2e^-)(Fe(CO)_4)^{2-}$ (46), drive the $Fe(CO)_4$ moiety toward d^{10} - Fe^{2-} tetrahedral array, thereby reducing the quadrupole splitting values. The distortion of the $Fe(CO)_4$ moiety in complexes like $[Fe(CO)_4H]^-$ (43)²⁷ and $[Fe_2H(CO)_8]^-$ (45)²⁷ toward the low ΔE_Q (quadrant I in Figure 3) is undoubtedly due to the distortion of these complexes toward tetrahedral d^{10} - Fe^{2-} case of $[Fe(CO)_4]^{2-}$ (46).²⁸

Two complexes, $[Fe(CO)_4(P(CH(SiMe_3)_2)_2)]^-$ (35) and a mixed-metal species $[Fe(CO)_4(Zn(NH_3)_3)]$ (36), lie in quadrant I. Unfortunately, neither has been structurally characterized as yet, but it is difficult to imagine that either of these species could distort as substantially toward a T_d geometry as, e.g., 43. For 36 axial substitution is predicted, $Zn(NH_3)_3$ must be a very good σ donor and extremely poor π acceptor. A certain amount of umbrella distortion^{25,26} of equatorial carbonyl ligands toward zinc is to be expected in 36 as well because of the ionicity of the bond. For comparison $[Fe(CO)_4(SiCl_3)]^-$ (19) obeys the synergistic relationship described by Figure 2. The $(SiCl_3)^-$ ligand, which curiously is found at the same δ value as 36, is also a good σ donor and poor π acceptor. Evidently $(SiCl_3)^-$ is not a sufficiently strong enough σ donor to dramatically change the iron electric field gradient at the nucleus as must be occurring in 36. It is difficult to imagine that $(SiCl_3)^-$ has any real π -acceptor capability unless d-orbital participation is invoked.

The observation that $[Fe(CO)_4(P(CH(SiMe_3)_2)_2)]^-$ (35) substantially deviates from previously observed Mössbauer relationships is quite curious. The PR_2 ligand derived from a tertiary phosphine by alkyl radical abstraction should be of similar σ -donor ability. The greatly diminished ΔE_Q value of 35 suggests that the unpaired electron acts as if it resides predominantly on iron as has been postulated previously,^{4,29} and this is in accord²⁹ with its NMR and ESR properties. We have suggested⁴ possible $P_{p\pi} \rightarrow eq CO_{\pi^*} \rightarrow eq CO_{\pi^*}$ bonding in 35 by analogy to $[Fe(CO)_4SnH_2]^{2-}$ for which an extended Hückel calculation predicts $Sn_{p\pi} \rightarrow eq CO_{\pi^*}$ overlap. Apparently, however, 3d-orbital mixing of the unpaired electron density is occurring, raising the 3d-occupancy level and thus lowering the iron electric field gradient.

Deviation of compounds found in quadrant II (Figure 3) occurs for $[Fe(CO)_4(SnMe_2)]^-$ (32 and 33), $[Zn(Fe(CO)_4)_2]^{2-}$ (34), and $[Fe(CO)_4(SnPh_2)]^-$ (39). It is somewhat surprising that 32 and 33 retain nearly identical ΔE_Q values but have δ values that differ by 0.11 $mm s^{-1}$ considering 32 and 33 only differ by counterions ($Na(THF)_{1,4}^+$ and $Na(4-MeC_6H_4NO)_{1,4}^+$, respectively).³⁰ Tight ion pairing is an important interaction in this system, but the difference could be accounted for by the second-order Doppler shift. We ascribe the occurrence of 32, 33, and 39 in quadrant II to population of *eq* CO_{π^*} orbitals by analogy to $[Fe(CO)_4SnH_2]^{2-}$, which should enhance the positive field gradient along the z axis.

For the series of compounds^{5–7} $[M'(Fe(CO)_4)_2]^{2-}$ ($M' = Zn$ (34), Cd (37), and Hg) we have structural characterization. The Hg compound may best be described as a normal face-capped $Fe(CO)_4^{2-}$ tetrahedron with a slight umbrella distortion of the equatorial carbonyls toward mercury. The geometry about iron is best described as nearby D_{3h} , suggestive of a d^8 - Fe^0 electronic description. Unfortunately, the mercury compound fails to give a Mössbauer spectrum, most probably because of some sort of lattice relaxation process. We have had this problem with other organometallic species where one member of an isoelectronic series behaves badly. An alternate explanation that mercury isotopes interfere does not appear to be the case as mercury has a high nonresonance scattering cross section. Calculations suggest that a much thinner sample absorber should alleviate the problem, but we are unable to obtain a spectrum at 78 K (14.4 keV) using a sample of 30 mg/cm^2 , which should be optimal. The cadmium structure

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(30) Crystals of a purported analogue of 32 and 33 have been made from the reduction of $[Fe(CO)_4(SnPh_2)]_2$. This species shows an unpaired spin of 1 by the Evans method. Recent sodium analyses show one sodium per iron so it appears that 32 and 33 are best formulated as radical anions.

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is very similar to the mercury case. Progressing from Cd to Zn, the group 2B metal slips from capping a face to a situation nearer edge capping. In **34** four carbonyls closely approach the zinc atom in a square-planar array with a nearly D_{2d} array about iron. Variation in the electronegativity of M' ($Zn \rightarrow Hg$) is enough to shift the bonding description from nearly ionic to covalent, respectively. This has the effect of changing electronic occupancy but also probably changes the electric field gradient and the asymmetry parameter substantially. The V_{zz} term which is the principal component of the electric field gradient, is most likely changed in sign or direction leading to **37** occurring in quadrant II of Figure 3. The M' metal in these cases must be a poor enough σ donor to effect this change in e^2qQ and η . With $Zn(NH_3)$ σ donation is strong and it is found in quadrant I.

In $[Cd(Fe(CO)_4)_2]^{2-}$ (**37**) we observe a resolved "triplet" Mössbauer spectrum with the two peaks at low δ being broad and the higher δ peak being sharp. This spectrum may be fit by the following solutions: as three singlets ($\delta = -0.064, 0.105$, and 0.186 mm s^{-1}), as two doublets ($\delta = 0.049$ and 0.145 mm s^{-1} ; $\Delta = 1.112$ and 0.808 mm s^{-1} , respectively), and as a doublet around a singlet ($\delta = 0.105$ (Δ small) and 0.090 ($\Delta = 1.921$) mm s^{-1}). The empirical formula argues against a three-singlet description as well as the asymmetry in the middle peak and the unusual positions of two of the singlets above the d^8 - d^{10} Fe range. The location and symmetry of the peaks also argue against a doublet around a singlet description. A two-doublet solution for the Mössbauer spectrum of **37** is

suggestive of magnetically inequivalent iron atoms. In **37** the one iron atom found in quadrant I may have an electronic description near d^{10} -Fe while there is one iron atom obeying the C-P (Figure 1) relationship, which works best for a d^8 -Fe electronic description. The structure of **37** is nearly identical with its analogue.^{6,7} In the electronic crossover d^8 -Fe \rightarrow d^{10} -Fe one iron atom changes in **37** at a time. In **34** both iron atoms have changed toward d^{10} -Fe but are found in quadrant II because of a change in the nuclear description.

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Clay Column Chromatography for Optical Resolution: Initial Resolutions of Bis(acetylacetonato)(glycinato)cobalt(III) and (Acetylacetonato)bis(glycinato)cobalt(III) on a Δ -Tris(1,10-phenanthroline)nickel(II)-Montmorillonite Column

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Liquid column chromatography was performed on a Δ -tris(1,10-phenanthroline)nickel(II)-montmorillonite column of 1-cm length by 3-cm o.d. at 2 °C for the purpose of resolving racemic neutral cobalt(III) chelates. The investigated chelates were of the type $Co(acac)_n(gly)_{3-n}$ ($n = 3, 2, 1$, and 0), where $acac =$ acetylacetonato and $gly =$ glycinato. With water as an eluting solvent, $Co(acac)_3$, $Co(acac)_2(gly)$, and $Co(acac)(gly)_2$ were partially resolved, resulting in molecular rotations of -2.6×10^4 (at 500 nm), $+4.6 \times 10^3$ (at 450 nm), and $+1.3 \times 10^3$ (at 450 nm) for the initially collected fractions, respectively. The column showed no affinity toward mer - $Co(gly)_3$ and did not resolve it to any measurable extent.

Introduction

A clay adsorbs a metal ion or a metal complex cation at its cation-exchange sites. Recently we investigated the adsorption behavior of tris(1,10-phenanthroline)iron(II) ($Fe(phen)_3^{2+}$) on a colloidal surface of montmorillonite.¹ Each configurational isomer of $Fe(phen)_3^{2+}$ was found to be adsorbed with identical strength. Thus the cation-exchange sites of a clay did not recognize the absolute configuration of a trischelated complex. Notably, however, the adsorption amount of $Fe(phen)_3^{2+}$ was doubled, when the chelate was added as a racemic mixture. The results imply that the sites fully occupied by the one enantiomer (e.g., Δ - $Fe(phen)_3^{2+}$) are still capable of accepting the binding of the other enantiomer (or Δ - $Fe(phen)_3^{2+}$).

The above finding prompted us to investigate the possibility that the clay modified by an optically active metal complex would be able to discriminate the chirality of an approaching molecule. This expectation was supported by the kinetic experiments, in which an adsorption rate of Δ - $Fe(phen)_3^{2+}$ on Δ - $Ni(phen)_3^{2+}$ -montmorillonite was compared with that on its counterpart.² It was found that Δ - $Fe(phen)_3^{2+}$ was adsorbed on Δ - $Ni(phen)_3^{2+}$ -montmorillonite about 4 times faster than on Δ - $Ni(phen)_3^{2+}$ -montmorillonite. The difference pointedly illustrates the preference of Δ - $Fe(phen)_3^{2+}$ for Δ - $Ni(phen)_3^{2+}$ to Δ - $Ni(phen)_3^{2+}$ as a stacking partner on the clay surface.

On the basis of the above principles, the liquid column chromatography was performed on a Δ - $Ni(phen)_3^{2+}$ -montmorillonite column in order to resolve racemic metal chelates.^{3,4}

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