

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON**Mössbauer Spectra of Iron in $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and $\text{Na}[\text{Fe}_3(\text{CO})_{11}\text{H}]$ and Comments Regarding the Structure of $\text{Fe}_3(\text{CO})_{12}$ ¹**

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The chemical-isomeric shift of iron in the compound $\text{Na}_2[\text{Fe}(\text{CO})_4]$, in which iron is formally in a -2 oxidation state, is large and negative. A negative shift is associated with an increased electron density in the nucleus and in this case is probably due to decreased shielding of the $3s$ electrons in the iron atom as the d electrons delocalize by π bonding. The Mössbauer patterns for both $\text{Na}[\text{Fe}_3(\text{CO})_{11}\text{H}]$ and $\text{Fe}_3(\text{CO})_{12}$ show that in both compounds two of the iron atoms are equivalent while the third is different. The X-ray data and the Mössbauer data considered together indicate that both of these compounds have similar nonsymmetrical, bridged triangular structures.

Mössbauer spectra have been reported for iron in a variety of (formal) oxidation states.² It has been found that the electron density in the nucleus, $|\Psi(0)|^2$, is dependent on both the degree of covalency of the bonding and the formal oxidation state of the iron. Thus, in ionic (high-spin) iron compounds, chemical isomeric (CI) shifts,³ δ , in the Mössbauer spectra become more negative in the order Fe^{+2} , Fe^{+3} , Fe^{+4} , and Fe^{+6} . (In Fe^{57} , increasing negative values of δ correspond to increased values of $|\Psi(0)|^2$.) The increase in $|\Psi(0)|^2$ with increasing positive oxidation state is due to a decrease in electronic shielding of (primarily) the $3s$ electrons as $3d$ electrons are lost by ionization.⁴

Covalent (low-spin) compounds show the same general behavior. Thus, ferricyanide ion shows a more negative shift than does ferrocyanide, although the shifts of both of these ions are more negative than those found for ionic ferric compounds. The relatively large negative shifts associated with covalent compounds are thought to be due to extensive d electron delocalization due to π bonding.^{2,5,6} An alternative view^{7,8} which appears to maintain that the σ bond network dominates the shifts observed in iron compounds, presumably *via* forward donation of $4s$ electrons, is,

we believe, inconsistent with Mössbauer data. This question will be discussed further in a future report.

Compounds in the zero oxidation state show a range of shifts which roughly bracket the values covered by the covalent ferrous and ferric compounds.^{2,9} Although the metal atom in these compounds has a $3d^8$ electronic configuration, *i.e.*, it has more $3d$ electrons than in ferrous and ferric complexes, the lack of formal charge probably permits these electrons to delocalize to a greater extent than in the charged species. They may also undergo more extensive $4s$ hybridization. The over-all effect is that $|\Psi(0)|^2$ is roughly the same for strongly covalent Fe^0 , Fe^{+2} , and Fe^{+3} complexes.

The question of what shift one would expect for iron in a negative oxidation state has apparently not previously been answered. At first sight it might be expected that the shift should be more positive than for the positively charged or neutral species since in the $[\text{Fe}(\text{CO})_4]^{-2}$ ion, for example, the electronic configuration of iron is described as being $3d^{10}$.¹⁰ On the other hand, the (formal) negative charge on the metal will allow the d electrons to strongly delocalize *via* π bonding. Extensive delocalization has, in fact, been proposed to account for the low CO stretch frequency in this ion.¹¹ It is conceivable that the negative charge could actually permit sufficient π bonding so that the CI shift might be more negative than in positively charged species. There is also the possibility, of course, that the negative charge might give rise to considerable $4s$ character in the bonds which could drive the shift negative.

Experimental

Mössbauer spectra of $\text{Na}_2\text{Fe}(\text{CO})_4$ and $\text{Na}[\text{Fe}_3(\text{CO})_{11}\text{H}]$ were obtained with a spectrometer of conventional design. Motion of the source (Co^{57} diffused into platinum foil) relative to the stationary compound under investigation, which acted as the absorber, was produced and measured by the coupled-loudspeakers technique. The intensity of γ rays which passed through the absorber was measured in a thin NaI crystal coupled to a single

(1) Taken in part from a thesis submitted by Nils E. Erickson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, at the University of Washington, Nov. 1964.

(2) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

(3) Also known as "chemical shift," "isomer shift," and "isomeric shift." For this shift to be seen in Mössbauer spectroscopy, there must be a change in both the excited and ground state nuclear charge radii and a difference in $|\Psi(0)|^2$ between source and absorber nuclei. The change in nuclear charge radii is a fixed quantity for each particular isomeric transition and it is only because there is a difference in $|\Psi(0)|^2$ due to chemical bonding (neglecting small temperature dependent shifts) that one observes an effect due to the difference in nuclear charge radius. It seems inappropriate therefore to refer to this shift solely as the "isomer" or "isomeric" shift. The term "chemical shift" would be more appropriate but might lead one to erroneously conclude that its interpretation was the same as that for chemical shifts in n.m.r. spectroscopy. The primary difference is that paired and unpaired electron density contributes inordinately strongly to n.m.r. shifts. We therefore propose that Mössbauer shifts due to differences in bonding be denoted as chemical isomeric shifts reflecting their dependence on changes in both nuclear and chemical properties.

(4) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters*, **6**, 98 (1961).

(5) J. Danon, *J. Chem. Phys.*, **39**, 236 (1963).

(6) N. E. Erickson, Ph.D. Thesis, University of Washington, 1964 (unpublished).

(7) R. L. Collins and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2332 (1963).

(8) R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).

(9) V. I. Goldanskii, "Proceedings of the Dubna Conference on the Mössbauer Effect," English translation by Consultants Bureau Enterprises, Inc., New York, N. Y., 1963.

(10) C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p. 149.

(11) See, for example, E. W. Abel, *Quart. Rev. (London)*, **17**, 133 (1963).

channel analyzer centered on the 14.4-keV γ ray of Fe^{57} . The output of the single channel analyzer was used to gate a multi-channel analyzer which analyzed the velocity-dependent signal from the loudspeaker system.

The chemical isomer (CI) shifts, δ , are measured relative to the midpoint of the spectrum of an absorber of natural iron foil at 25°. Following convention, the sign of δ is taken to be positive when the source is moved toward the absorber, and velocity units are used. In addition to measurement of δ the spectrum can be analyzed for splitting of the excited state of Fe^{57} in the electric quadrupole crystal field of the absorber lattice. The magnitude of the splitting (ΔE) is conventionally measured in velocity units also.

Results and Discussion

The Mössbauer data for $\text{Na}_2[\text{Fe}(\text{CO})_4]$ at 25° are given in Table I. The spectrum shows only a single line which is consistent with tetrahedral symmetry around the iron. The value of δ is one of the most negative shifts so far reported for an iron compound. Only nitroprusside ion, which contains the extremely strongly π bonding NO^+ group, and Fe^{+6} in the $[\text{FeO}_4]^{-2}$ ion seem to have shifts more negative than the $[\text{Fe}(\text{CO})_4]^{-2}$ ion. It is interesting that both extremes of formal oxidation state yield shifts that are quite negative while intermediate oxidation states have shifts that are more positive. The explanation for the negative shifts with extremes of oxidation number is the same in both cases, however: loss of d electron density and resultant increase of (3s) electron density at the nucleus. In one case it is loss of d electrons by oxidation while in the second it is loss by delocalization with perhaps an assist from 4s hybridization.

TABLE I

MÖSSBAUER DATA FOR SOME IRON CARBONYL COMPLEXES

Compound	δ , mm./sec. (Fe = 0)	ΔE , mm./sec.	T, °K.	Ref.
$\text{Na}_2\text{Fe}(\text{CO})_4$	-0.251	~0	298	This work
$\text{Na}[\text{Fe}_3(\text{CO})_{11}\text{H}]$	I -0.08	~0	298	This work
	II -0.10	1.32	298	This work
$\text{Fe}_3(\text{CO})_{12}$	I ~+0.02 ^a	~0	188	2
	II ~+0.07 ^a	1.05	188	2
$\text{Fe}_3(\text{CO})_{12}$	I -0.043 ^{a,b}	~0 ^b	298	2
	II -0.016 ^{a,b}	~0.94 ^b	298	2

^a Value adjusted to an iron absorber shift of 0. On this velocity scale, sodium nitroprusside has a shift of -0.361 mm./sec. at 298°K. ^b Linearly extrapolated value to $T = 298^\circ\text{K}$. using data in ref. 2.

This duality in shift with oxidation state indicates that one has to exercise considerable care in deducing the relative sizes of isomeric and ground-state charge radii from CI shifts.¹² It is possible that one could get the wrong sign by using compounds of different oxidation states if the ligands differed greatly in their covalency.

Some other ions which contain iron in a negative oxidation state are $[\text{Fe}_2(\text{CO})_8]^{-2}$, $[\text{Fe}_3(\text{CO})_{11}]^{-2}$, and, possibly, depending upon its structure, $[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$. The first contains Fe^- . The formal charge one assigns to any individual iron atom in the other compounds would depend on the structures of the complexes.

We have run Mössbauer spectra on two separate preparations of an ether-soluble, anionic, trinuclear iron species with a Na/Fe ratio of 1:3 isolated from a strongly basic, aged solution of iron pentacarbonyl which we believe to be $\text{Na}[\text{Fe}_3(\text{CO})_{11}\text{H}]$. The Mössbauer data are reported in Table I. The spectra of both preparations were identical and are quite similar to that reported^{2,13,14} for $\text{Fe}_3(\text{CO})_{12}$ in that they consist of three lines of approximately equal intensity (which, from arguments given in ref. 2, 11, and 12, establishes the compound as a trinuclear species), although the shifts are not the same and the quadrupole splitting is rather larger than in $\text{Fe}_3(\text{CO})_{12}$. The similarity in the spectra indicates that the structures of both compounds are nearly the same and that the ion is derived from the neutral species by abstraction of a carbonyl group without rearrangement of the basic structure.

The structures of the trinuclear iron species have been a matter of speculation for a number of years. The infrared spectrum of $\text{Fe}_3(\text{CO})_{12}$ has been said to be consistent with both a triangular as well as several linear structures.^{15,16} Dahl and Rundle¹⁷ concluded from X-ray studies that the molecule was triangular, although they were not able to do a complete structure determination due to disorder in the crystal. They suggested that a symmetrical structure with zero, three, or six bridging carbonyl groups was the most probable structure, but they did not completely rule out an asymmetrical structure. The general consensus of opinion appeared finally to settle on a triangular structure.¹⁸

When Mössbauer measurements on this compound became available,^{2,13,14} this conclusion was challenged. The data show that two iron atoms have equivalent positions with rather large field gradients while the third iron atom is in a different site with no, or only a small, field gradient. This rules out any of the symmetrical triangular structures proposed by Dahl and Rundle, since all three irons are equivalent in these structures. A reasonable assumption to make on the basis of the Mössbauer data for that compound alone is that the molecule is linear. Fluck, *et al.*,² and Kalvius, *et al.*,¹³ have preferred a model in which the middle iron atom is tetrahedrally bonded to four bridging carbonyl groups leaving each of the terminal iron atoms with bonds to two bridging and four terminal carbonyls (Figure 1a). On the other hand, Herber, *et al.*,¹⁴ prefer a structure which has the center iron atom octahedrally bonded to six bridging carbonyl groups (Figure 1b). Either structure would be consistent with the Mössbauer data alone, although as Wertheim has pointed out,¹⁹ the Mössbauer data cannot *prove* what the struc-

(13) M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch.*, **17a**, 494 (1962).

(14) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

(15) R. K. Shelton, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

(16) F. A. Cotton and G. Wilkinson, *ibid.*, **79**, 752 (1957).

(17) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957); *ibid.*, **27**, 323 (1957).

(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962.

(19) G. K. Wertheim, "Mössbauer Effect: Principles and Applications," Academic Press, New York, N. Y., 1964.

(12) D. A. Shirley, *Rev. Mod. Phys.*, **36**, 339 (1964).

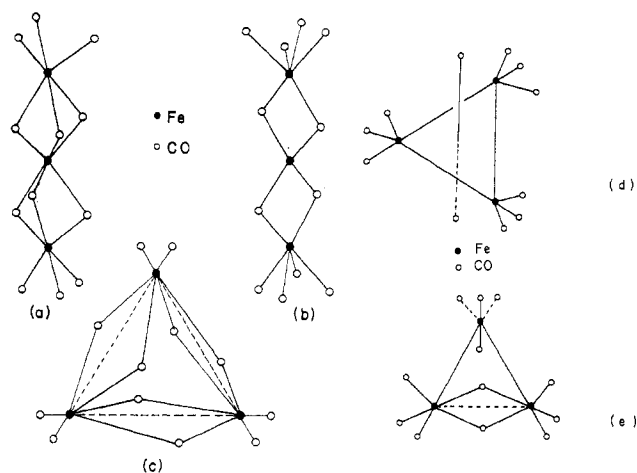


Figure 1.—Some proposed structures for $\text{Fe}_3(\text{CO})_{12}$ (a, b, c, e) and $\text{Fe}_3(\text{CO})_{11}^{-2}$ (d). Structures a, b, and c are patterned after drawings found in ref. 19. Consideration of X-ray evidence and Mössbauer data together leads to the conclusion that structure e is the correct one for $\text{Fe}_3(\text{CO})_{12}$.

ture is. One of the symmetrical structures proposed by Dahl and Rundle is shown in Figure 1c for comparison.

The inconsistency in the structure deduced from X-ray data and from Mössbauer data is quite puzzling. Even though the structure was not completely solved by X-ray analysis, there was little doubt that it was not linear.¹⁷ The X-ray data²⁰ for the $[\text{Fe}_3(\text{CO})_{11}]^{-2}$ ion are again of a preliminary nature but they too indicated a triangular structure. The proposed structure (Figure 1d) had two carbonyl groups in the center of the triangle, one above and one below the plane. This is a symmetrical structure and would leave all three iron atoms equivalent, which is inconsistent with the Mössbauer data for our trinuclear complex. This fact along with the Na/Fe ratio of 1:3 leads us to conclude we had the $[\text{Fe}_3(\text{CO})_{11}\text{H}]^{-}$ ion.²¹

The similarity of the Mössbauer spectra for $\text{Fe}_3(\text{CO})_{12}$ and our triiron species indicates that they have a similar structure and that the ion is derived from the neutral compound by simple abstraction of a CO group and replacement by a hydride ion. If this is the case, the parent molecule cannot be linear since removing a CO group from a linear structure would change the geometry around either one terminal iron atom or one terminal and the middle iron atom. Yet the Mössbauer data show that two iron atoms are still equivalent. The only way this seems possible is for the molecule to be triangular, but not any of the simple, symmetrical structures suggested by Dahl and Rundle. A triangular structure which is compatible with both the Mössbauer and X-ray data is shown in Figure 1e. The two bridging carbonyl groups would probably be above and below the plane of the molecule, although they need not be in a plane which includes the "terminal" iron atoms.

(20) O. S. Mills, A. A. Hock, and G. Robinson, quoted in ref. 11.

(21) We are indebted to Professor L. F. Dahl for bringing to our attention the fact that under the preparative conditions which we used, either anion may be formed.

The bent structure around the middle iron atom need not necessarily give rise to a field gradient at this atom. This structure is somewhat similar to a *cis* complex in which case the field gradient axis would be perpendicular to the plane of the molecule. In the present case, the field gradient could be canceled by suitable bonds from the middle iron atom to carbonyl groups above and below the plane of the triangle, although they probably would not be perpendicular to this plane. X-Ray data on the $[\text{Fe}_3(\text{CO})_{11}\text{H}]^{-}$ ion,²² which came to our attention after our original formulation⁶ of a structure for $\text{Fe}_3(\text{CO})_{12}$, show that the structure of the anion is triangular and that the "central" iron atom does have four carbonyl groups arranged as suggested. The similarity of the Mössbauer spectra for the two "terminal" iron atoms dictates that both atoms have the same geometry. This places the hydride ion in a bridging position replacing the CO group which has been lost. This is in agreement with conclusions derived from X-ray studies.²² If the hydride ion were instead on the "central" iron atom, the quadrupole splitting of the two "terminal" irons would then be expected to be virtually identical with that found for these atoms in the neutral compound which is contrary to experimental results.

Table I also gives the CI shifts and ΔE values for $\text{Fe}_3(\text{CO})_{12}$ at 188°K. and linearly extrapolated values for 298°K.² The shifts for the "central" iron atoms agree quite closely in both compounds considering the limited accuracy involved in the extrapolation. The peaks corresponding to the "terminal" atoms, however, have become relatively more negative in the anionic compound. This can be rationalized if one allows for a partial donation of iron σ d electrons toward the hydrogen, completing, in a sense, the formal charge assignment of -1 for the hydride ion. Both of these points are a further indication that it is the terminal iron atoms which have been affected by removal of a CO group and that the "central" atom has essentially the same geometry and electronic structure in both compounds.

The Mössbauer data presented offer strong evidence that $\text{Fe}_3(\text{CO})_{12}$ and $[\text{Fe}_3(\text{CO})_{11}\text{H}]^{-}$ are closely related structurally and that both have the same basic geometry, namely triangular. The only reasonable structure which leaves one atom unequivalent, but unchanged, and which permits both "terminal" atoms to be affected equally by removal of a carbonyl group is that shown in Figure 1e.

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(22) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).