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NOTE

THE MÖSSBAUER SPECTRA OF SOME BIS(PENTAFLUOROPHENYL)-DICHALCOGENIDE-BRIDGED IRON CARBONYL COMPLEXES

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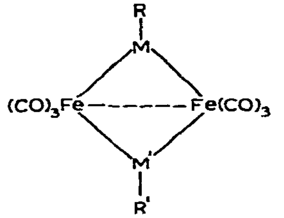
We report the Mössbauer parameters of a series of iron carbonyl complexes having bridging chalcogenide atoms of the type,



where M, M' = S and/or Se and R, R' = C_6H_5 and/or C_6F_5.

The iron-57 Mössbauer effect was measured with a Model NS-1 Mössbauer Spectrometer (Nuclear Science and Engineering Corp., Pittsburgh, Pennsylvania,

TABLE 1

MÖSSBAUER SPECTRAL DATA FOR CHALCOGEN-BRIDGED IRON CARBONYL COMPLEXES[a]

Compound		Isomer shift (δ)[b]	Quadrupole splitting (Δ)
(I)	$[C_6H_5SFe(CO)_3]_2$	+0.316	1.065
(II)	$C_6H_5SFe_2(CO)_6SC_6F_5$	0.319	1.144
(III)	$[C_6F_5SFe(CO)_3]_2$	0.322	1.354
(IV)	$[C_6H_5SeFe(CO)_3]_2$	0.299	1.037
(V)	$C_6H_5SeFe_2(CO)_6SeC_6F_5$	0.335	1.161
(VI)	$[C_6F_5SeFe(CO)_3]_2$	0.352	1.351
(VII)	$C_6H_5SFe_2(CO)_6SeC_6H_5$	0.335	1.032
(VIII)	$C_6F_5SFe_2(CO)_6SeC_6H_5$	0.359	1.144
(IX)	$C_6H_5SFe_2(CO)_6SeC_6F_5$	0.310	1.210
(X)	$C_6F_5SFe_2(CO)_6SeC_6F_5$	0.335	1.342

[a] All values are in mm/sec with an error of ±0.008 mm/sec. [b] Relative to sodium nitroprusside

U.S.A.) operating in the constant acceleration mode. The 14.4 keV gamma radiation from a source of cobalt-57 diffused into palladium was detected with a gas proportional counter and collected with a 400 channel analyzer operating in time sequence scaling mode. The source and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material No. 725). All isomer shifts are reported with respect to the zero position of this standard.

The details of the preparation of these compounds have been reported in a recent paper[1] along with preliminary room temperature Mössbauer data.

Table 1 presents the isomer shift (δ) and quadrupole plitting (Δ) at 80°K for each of the ten complexes under study. All values are in mm/sec and have an error of ± 0.008 mm/sec. Typical linewidths (Γ) were 0.35–0.45 mm/sec. As a comparison, the Mössbauer parameters for compound (I) have been measured by Gibb *et al.*[2], who reported values of $+0.318$ and 1.067 mm/sec for the isomer shift and quadrupole splitting, respectively, in excellent agreement with our measured values.

The following trends in these data (Table 1) are evident:

(1) In the series (I)–(III) (stepwise replacement of C_6H_5 by C_6F_5 with $M = M' = S$) there is an increase in both δ and Δ, indicating a decrease in the electric field gradient about the iron atom.

(2) A similar trend is present in the series (IV)–(VI) (similar replacement with $M = M' = Se$).

(3) In the series (VII)–(X) ($M \neq M'$, replacing C_6H_5 with C_6F_5) the magnitude of Δ increases while there is no obvious trend in δ.

(4) For each of the compounds (I)–(X) the values of δ and Δ lie in the region outlined by Gibb *et al.*[2] for octahedral coordination in bridged binuclear carbonyl compounds with a "bent" iron–iron bond occupying one coordination position.

At first sight, the trends in increasing quadrupole splittings Δ could be explained by a relatively larger steric interaction of the pentafluorophenyl group as compared to the phenyl group. This would be evident in the series (I)–(III), (IV)–(VI), and (I), (IV), (VII)–(X). However, indications are that the steric requirements for the C_6H_5 and C_6F_5 moieties are very nearly the same[3]. Notice that the substitution of a selenium bridging atom for a sulphur atom does not have the effect of increasing the "distortion" about the iron atoms.

An increase in isomer shift δ, corresponding to a decrease in *s*-electron density at the iron nucleus, is most likely due to an increase in the electron-withdrawing properties of the fluorinated benzene ring as compared to an unsubstituted benzene ring, which would reduce the sulphur-(or selenium)-to-metal σ-donation. However,

TABLE 2

INFRARED SPECTRA IN THE C≡O STRETCHING REGION FOR THE CHALCOGEN-BRIDGED IRON TRICARBONYLS (in cm^{-1}; samples in CS_2)

Compound[a]	ν_1	ν_2	ν_3 (or ν_4)	ν_4 (or ν_3)
(VII) $C_6H_5SFe_2(CO)_6SeC_6H_5$	2069.5	2032.5	1996.0	1990.5
(VIII) $C_6F_5SFe_2(CO)_6SeC_6H_5$	2075.0	2041.5	2004.0	2002.0
(X) $C_6F_5SeFe_2(CO)_6SeC_6F_5$	2082.5	2055.0	2019.0	2008.0

[a] For the C≡O frequencies of the other compounds listed in Table 1 see ref. 1.

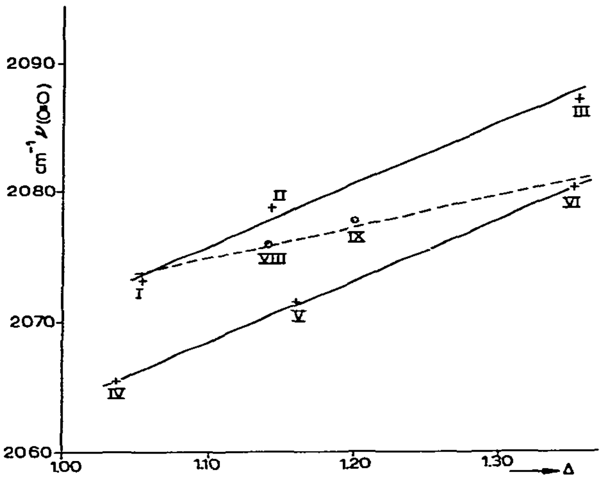
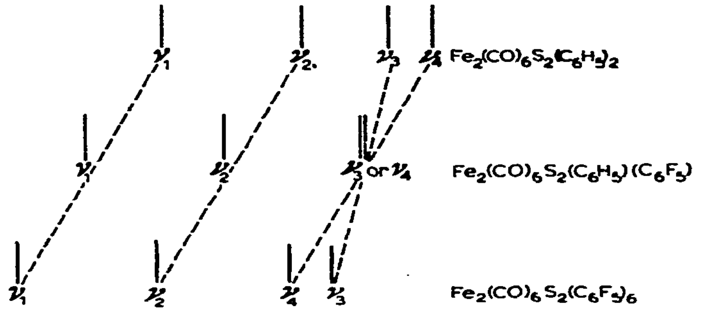


Fig. 1. Correlation of the highest carbonyl stretching frequency in the infrared spectra with the quadruple coupling constant, Δ, in the Mössbauer spectrum of chalcogen bridged iron carbonyl complexes. The three other carbonyl stretching frequencies of these complexes also give similar straight-line correlations when plotted against Δ (see text).

comparison of the compounds (VII) and (IX) indicates that the bridging moiety $-SeC_6H_5$ seems to be more effective than $-SeC_6F_5$ in reducing the *s*-electron density about the iron nucleus.

An interesting relation is found between the quadrupole splittings and the characteristic IR carbonyl stretching frequencies (Table 2) for this series of compounds. Each of the complexes has an IR spectrum in the carbonyl region which consists of four bands (here labelled ν_1–ν_4 with increasing wavelength). Graphs (see Fig. 1) of Δ *vs.* CO stretching frequency for ν_1 and ν_2 are linear for the three sulphur complexes [(I)–(III)], the three selenium complexes [(IV)–(VI)] giving lines parallel to the sulphur complexes; ν_3 and ν_4 do not give a straight correlation with Δ. However, in a previous paper[1], it was postulated that ν_3 would stay relatively constant while ν_4 would shift in frequency on substitution of C_6F_5 for C_6H_5; *e.g.*:



If this is taken into account a straight line plot of ν(C≡O) *versus* Δ is obtained for both ν_3 and ν_4 using the S and Se complexes. Furthermore, those complexes having hetero-bridges (M = S, M′ = Se) give values of Δ falling on a straight line linking their respective "parent" compounds. We feel that the CO stretching frequencies are closely related to

π-effects in the Fe–CO bonds. Hence it would appear from these correlations that Δ in these complexes is a measure of the Fe–S or Fe–Se π-bonding.

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