Studies in Mössbauer Spectroscopy. Part 8.[1] Iron-57 Spectra of some Substituted Tricarbonylnitrosyliron Derivatives†

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Iron-57 Mössbauer spectra have been obtained for several compounds in which $Fe(CO)_2(NO)L$ groups (L = CO, tertiary phosphine or arsine) are bonded to mercury, lead, or gold. Trends in the data are discussed in terms of the bonding characteristics of the ligands, and σ-bonding effects are found to predominate.

DERIVATIVES of iron pentacarbonyl have been widely studied by Mössbauer spectroscopy but the corresponding nitrosyls have been neglected. We report now the ^{57}Fe Mössbauer spectra of some tricarbonylnitrosyliron derivatives. The only previous measurements on this type of compound are [2,3] for salts of the anion $[Fe(CO)_3(NO)]^-$ and two mercury compounds, $Hg[Fe(CO)_2(NO)L]_2$ (L = CO or PPh_3). Relevant data are presented in the Table.

Iron-57 Mössbauer data for $Fe(CO)_2(NO)L$ derivatives (mm s^{-1}, at 77 K)

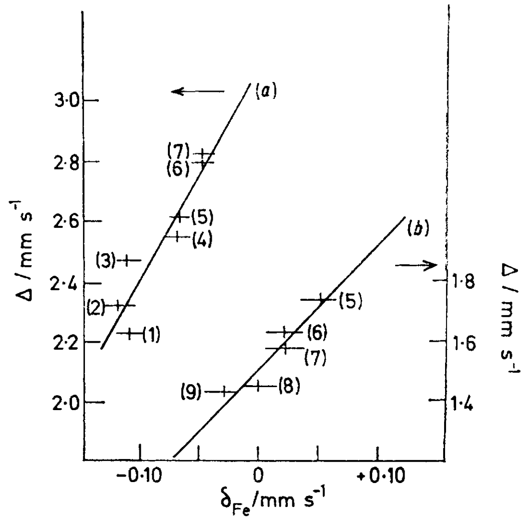
Compound	δ_{Fe} [a,b]	Δ [a]	Ref.
(1) $[PPh_2(C_6H_{11})_2][Fe(CO)_3(NO)]$	−0.04	0.54	*c*
(2) $Na[Fe(CO)_3(NO)]$	−0.08	0.36	2
(3) $K[Fe(CO)_3(NO)]$	−0.08	0.36	2
(4) $Hg[Fe(CO)_3(NO)]_2$	−0.02	1.26	3
	+0.02	1.32	2
(5) $Hg[Fe(AsPh_3)(CO)_2(NO)]_2$	+0.05	1.74	*c*
(6) $Hg[Fe(AsEt_2Ph)(CO)_2(NO)]_2$	+0.02	1.63	*c*
(7) $Hg[Fe(AsEt_3)(CO)_2(NO)]_2$	+0.02	1.58	*c*
(8) $Hg[Fe(CO)_2(NO)(PPh_3)]_2$	0.00	1.45	*c*
	−0.02	1.42	3
(9) $Hg[Fe(CO)_2(NO)(PMePh_2]_2$	−0.03	1.43	*c*
(10) $PbPh_2[Fe(AsEt_2Ph)(CO)_2(NO)]_2$	+0.01	1.75	*c*
(11) $PbPh_3[Fe(CO)_3(NO)]$	0.00	1.23	*c*
(12) $AuPh_3[Fe(AsEt_2Ph)(CO)_2(NO)]$	−0.01	1.15	*c*

[a] ±0.02 mm s^{-1}. [b] Relative to iron metal. [c] This work.

RESULTS AND DISCUSSION

In the anion $[Fe(CO)_3(NO)]^-$ the iron atom has a formal d^{10} configuration and tetrahedral stereochemistry. The small quadrupole splitting, 0.36—0.54 mm s^{-1}, arises from the inequivalence of the nitrosyl and carbonyl ligands. For the potassium salt, V_{zz} has been shown to be positive [2] consistent with the greater π-acceptor strength (and/or lower σ-donor strength) expected for the formal $[NO]^+$ group compared to the neutral CO ligand. The splitting is slightly greater for the large quaternary cation, suggesting that in the alkali-metal salts there may be some ion association resulting in geometric distortion or polarisation. The cation would be expected to interact more with the carbonyl than the nitrosyl ligands, and such interaction would enhance the π-acidity (and diminish the σ-basicity) of the CO group, thus reducing the electric-field gradient at the iron atom. Alternatively, the packing of the bulky cation, $[PPh_2(C_6H_{11})_2]^+$ may cause some distortion of the anion.

From their i.r. spectra, the mercury compounds $Hg[Fe(CO)_2(NO)L]_2$ (L = CO, tertiary phosphine or arsine) are thought to have linear L–Fe–Hg–Fe–L systems with two carbonyl groups and a nitrosyl group completing a trigonal bipyramid about each iron atom.[4] The Mössbauer spectra are consistent with such a structure, since all the compounds showed substantial quadrupole splitting, as expected from the formal d^8 configuration. The splitting changed systematically with variation in the ligand, decreasing in the order L = $AsPh_3$ > $AsEt_2Ph$ > $AsEt_3$ > PPh_3 ~ $PMePh_2$ > CO. Although the range of values and the differences between them are small, there is a systematic trend to decreasing isomer shift in the same series. These trends are very similar to those found for the compounds $[Fe(CO)_4L]$ (see Figure).[5]



Plots of quadrupole splitting against isomer shift for (*a*) $[Fe(CO)_4L]$ and (*b*) $Hg[Fe(CO)_2(NO)L]_2$. The points on line (*b*) correspond to the compound numbers in the Table. The ligands corresponding to the points on line (*a*) are: (1), $P(NMe_2)_3$; (2), $P(OEt)_3$; (3), $\frac{1}{2}Ph_2PCH{:}CHPPh_2$; (4), PPh_3; (5), 1,2-bis(diphenylphosphino)-3,3,4,4-tetrafluorocyclobutene, (6), 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene (ffars), (7), $\frac{1}{2}$ ffars

The small quadrupole splittings of $[Fe(CO)_3(NO)]^-$ and $[Fe(CO)_2(NO)_2]$[2] suggest that there is no great difference between the bonding characteristics of CO and $[NO]^+$ so

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† No reprints available.

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that the local symmetry of the iron atoms in the mercury compounds may be taken as C_{3v} to a first approximation. The major component of the electric-field gradient may then be assumed to lie along or close to the Hg-Fe-L axis in these compounds and along the trigonal axis in $[Fe(CO)_4L]$, and to be positive as found for $[Fe(CO)_5]$ and $[Fe(CO)_4(PPh_3)]$.[6] The quadrupole splitting is then expected to increase with increasing π-acidity or decreasing σ-basicity of the substituent, whereas the isomer shift should decrease with increase in either property of the ligand. The observed trends therefore suggest that σ-bonding effects are more important than π-bonding effects. This is also shown by the uniformly lower quadrupole-splitting values of the mercury compounds, the mercury atom presumably being a poor π-acceptor but a good σ-donor. However, the unsubstituted compounds, $Hg[Fe(CO)_3(NO)]_2$ and $[Fe(CO)_5]$, show different behaviour in that $[Fe(CO)_5]$ lies within the range spanned by $[Fe(CO)_4L]$ whereas the mercury compound has the lowest value of both parameters, suggesting that in this compound the σ-donor character of CO is enhanced synergistically. A similar decrease in isomer shift and quadrupole splitting is seen between $PbPh_2[Fe(AsEt_2Ph)(CO)_2(NO)]_2$ and $PbPh_3[Fe(CO)_3(NO)]$.

EXPERIMENTAL

Samples of the compounds were kindly donated by Dr. A. R. Manning and their purity checked by i.r. spectroscopy. Mössbauer spectra were recorded on the dry powders at 77 K using a $^{57}Co/Rh$ source and a Harwell series 6000 spectrometer. The velocity scale and isomer-shift standard was a natural iron foil.

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