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Mössbauer Investigation of Dinitrosyl Iron Compounds

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In continuation of earlier work with mononitrosyl iron compounds,[1] we have investigated several dinitrosyl compounds $Fe(NO)_2LL'$, which can all be derived from $Fe(NO)_2(CO)_2$. It is found that the quadrupole splitting increases as the N – O stretch constant decreases. This dependence can be explained qualitatively by the strong π-bonding in the complexes, but in order to arrive at a quantitative conformity it is apparently necessary to suppose that in the compounds $Fe(NO)_2LL'$ the (ON) – Fe – (NO) bond angle depends on the ligands present.

All the investigated compounds (symbolized: $Fe(NO)_2LL'$ where L(L') is a Lewis base) can be theoretically derived and conveniently made from $Fe(NO)_2(CO)_2$. For this latter compound there exists an early determination of the molecular structure [2] (by means of electron diffraction in the gas phase) which shows that the iron atom is surrounded by the 4 ligands in an approximately tetrahedral way, making the overall symmetry of the compound C_{2v}. This structure will be assumed to be valid also for the substituted complexes.

The scope of this work was to investigate the bonding in such dinitrosyl complexes by using the Mössbauer effect, a technique which has already given valuable results with nitrosyl complexes.[1,3,4] As with the mononitrosyl iron compounds, there have been discussions regarding the bonding in the dinitrosyl complexes, but in one respect these discussions have differed from those regarding the mononitrosyl complexes. It has never really been challenged that for these complexes the only reasonable structures involve coordination of the nitrosyl group as NO^+; more or less connected with this view is the fact that the linearity of Fe – N – O has never been questioned.

The only application of a formal oxidation number will be to lead to a d^{10} electronic configuration as the starting point of the discussion.

The assumption of a d^{10} configuration agrees with the diamagnetic properties [5] of the complexes and their inclusion in the isoelectronic series: $Fe(CO)_4^{2-}$, $Fe(CO)_3NO^-$, $Fe(CO)_2(NO)_2$, $Co(CO)_4^-$, $Co(CO)_3NO$, $Ni(CO)_4$.

EXPERIMENTAL

The Mössbauer spectra were obtained with the instrument previously described.[6] ^{57}Co in Pd-matrix was used as a source of approximately 2 mCi strength. Except in the case of $Fe(NO)_2(CO)_2$ for which the spectrum was taken in frozen benzene, the spectra were taken on the solids wafered between aluminium foils and polyethylene. The temperature of the absorbers was *ca.* 100 K (metallic contact with liquid N_2). All the parameters mentioned are given relative to sodium nitroprusside and were obtained by a least squares fitting with Lorentzian curves. The force constants used in this paper were obtained using the Cotton-Kraihanzel method [7] except those in Table 2, where literature values are used.

Preparations and identifications of the compounds were as follows: $Fe(NO)_2(CO)_2$,[28] m.p. 18°C,[28] found: 15°C; νNO 1808, 1760 cm^{-1}, νCO 2084, 2037 cm^{-1};[29] found: νNO 1810, 1760 cm^{-1}, νCO 2084, 2038 cm^{-1}. $Fe(NO)_2(P(OC_6H_5)_3)_2$,[30] Fe: calc. 7.6 %, found 7.5 %; νNO: 1770, 1719 cm^{-1},[29] found 1775, 1715 cm^{-1}. $Fe(NO)_2(CO)P(C_6H_5)_3$,[30] Fe: calc: 13.8 %, found 14.2 %; m.p. 138 – 140°C,[30] found 138°C; νNO 1766, 1721 cm^{-1}, νCO 2010 cm^{-1},[30] found νNO 1763, 1722 cm^{-1}, νCO 2010 cm^{-1}. $[Fe(NO)_2CO]_2P(C_6H_5)_2C_2H_4P(C_6H_5)_2$,[31] Fe: calc. 16.3 %, found 16.2 %, N: calc. 8.1 % found 8.2 %; νNO 1760, 1713 cm^{-1}, νCO 2010 cm^{-1},[31] found νNO 1715, 1753 cm^{-1}, νCO 2013 cm^{-1}. $Fe(NO)_2(P(C_6H_5)_3)_2$,[14] Fe: calc. 8.8 %, found 8.6 %, N: calc. 4.4 %, found 4.3 %, m.p. 194°C,[30]

found 190°C; νNO 1723, 1679 cm^{-1},[29] found νNO 1722, 1680 cm^{-1}. $Fe(NO)_2(C_6H_5NC)_2$,[32] Fe: calc. 17.4 %, found 16.6 %. N: calc. 17.4 %, found 17.6 %; m.p. 143°C,[32] found 143°C. $Fe(NO)_2(C_2H_5NC)_2$,[33] Fe: calc. 24.6 %, found 23.6 %; m.p. 97°C,[33] found 95°C. $Fe(NO)_2$ phenanthroline,[34] Fe: calc. 28.1 %, found 27.2 %, N: calc. 28.1 %, found 27.2 %.

DISCUSSION

When considering the electronic structure of d^{10} complexes it is a great simplification that there is no need to take the σ-bonds into consideration; this is possible because the bonding and antibinding σ-orbitals are both filled (using the electronic structure of tetrahedral complexes as a guide). Consequently, these σ-orbitals will have an approximately spherical appearance and will only give minor contributions to the changes observed in the Mössbauer parameters. These minor changes will be due only to differences in overlaps which are considered small. This lack of σ-contribution should be especially pronounced since MO calculations for isoelectronic and isostructural nitrosyl cyanide compounds of first row transition metals indicate that there is a constancy in the strength of σ-(NO) bonds.[8]

In what follows the charge transferred to NO and CO will frequently be considered. It is calculated here as charge transferred to the π^* (NO, CO) orbitals only, a procedure which we find justified by the above mentioned constancy of σ-(NO) bond strength and the smoothing effect of the completely filled bonding and antibonding σ-orbitals on any differences. However, we are aware of the fact that the antibonding character of the σ-(NO, CO) orbital with regard to the NO (CO) bond makes calculations sensitive to large variations in σ-bonding to the central atom.

The isomer shift. All the Mössbauer parameters of the investigated compounds appear in Table 1 together with IR-data. It is obvious that within reasonable limits there is a constancy in the isomer shift and consequently also in the s-electron density at the iron nucleus, disregarding in the first instance the compounds with nitrogen bonded L-ligands.

There has been much controversy regarding the most important influence on the total s-electron density in iron-compounds but up till now it has apparently not been possible to produce any general theory concerning this phenomenon.[9] In this paper it will be assumed that only changes in $3d$-electron density have an influence on the s-electron density at the iron nucleus in the investigated series. This rather coarse approximation can be partly justified by the following 2 points:

1. The above mentioned constancy of the σ(NO)-bonding in isoelectronic compounds.

2. It is possible to account for the changes in isomer shift (Table 2) qualitatively and also semi-quantitatively (considering the accumulated correlations between electron configurations and isomer shifts [9]) simply by considering the changes in charge transferred from the iron $3d$ orbitals to the π^* (XO) orbitals (X=N,C); These changes are calculated from the X−O stretch constants and the magnitude of $\Delta k_{XO}/\Delta N$ (N = bond order).

The constancy of the isomer shift in Table 1 must imply the same $3d$ electron density in the listed compounds. As it can be inferred from k_{NO} that the charge transferred to the π^*-orbitals of NO is a variable it follows that the charge transferred by π-bonding to the other ligands must change in the opposite way. Using IR-data it is found that the sequence

Table 1. Mössbauer and infrared data of dinitrosyl iron compounds. σ, (isomershift) and ΔE_Q, (quadrupole splitting) are in mm/s and are given relative to sodium nitroprusside. The temperature of the absorbers was approximately 100 K.

2 L	σ	ΔE_Q	k_{NO} mdyn/Å
2 CO	0.34	0.34	14.1
2 $P(OC_6H_5)_3$	0.28	0.48	13.4
$P(C_6H_5)_3$,CO	0.29	0.53	13.2
CO,½$[(C_6H_5)_2PC_2H_4]_2$	0.30	0.54	13.2
2$P(C_6H_5)_3$	0.33	0.67	12.7
2 C_6H_5NC	0.31	0.76	12.6
2 C_2H_5NC	0.34	0.80	12.6
2$[(CH_3)_2N]_3P$ [a]	0.31	0.87	12.4
o-phenanthroline	0.54	0.71	12.3
o-phenanthroline[b]	0.56	0.74	12.3
α,α′-bipyridine[b]	0.52	0.72	12.5
2 CO [c]	0.29	0.32	14.1
2 $P(C_6H_5)_3$ [c]	0.33	0.69	12.7
CO, $P(C_6H_5)_3$ [c]	0.29	0.55	13.2

[a] From Ref. 5. [b] From Ref. 12. [c] From Ref. 14.

Table 2. Force constants for d^{10} iron compounds.

$\Delta k_{NO}/\Delta N_{NO} = 9.1$ mdyn/Å [25]
$\Delta k_{NO}/\Delta N_{CO} = 7.8$ mdyn/Å [25]
ΔN = change in bond order
Δe_M = electrons transferred to π-orbitals of M

Compound	k_{NO}	k_{CO}	Δe_{NO} (electrons)	Δe_{CO} (electrons)	$\sum \Delta e$ (electrons)	σ^a mm/S	Ref.
$Fe(CO)_4^{2-}$	–	11.4	–	1.90	7.6	0.08	23, 26
$Fe(CO)_3NO^-$	10.0	13.8	2.9	1.25	6.65	0.20	25, 14
$Fe(CO)_2(NO)_2$	13.02	16.92	2.2	0.40	5.20	0.33	24,

[a] σ relative to sodium nitroprusside.

of the π-bond strengths is very close to "the spectrochemical row for π-bonding ligands" as found by Horrocks and Taylor.[10] Only the isocyanide compounds are a little out of place. Returning to the complexes with N-bonded ligands it is obvious that the above mentioned explanations cannot be applicable because the constancy of the isomer shift is not extended to such compounds. It is now well known that such ligands in contrast to the other ligands in Table 1 are quite good σ-donors and rather poor π-acceptors.[11] Even though one should expect a gradual transition from good acceptors to poor acceptors, it may be that these complexes have a quite different electronic structure (*i.e*, not d^{10}) and they will therefore not be included in the following discussion. One of the reasons for proposing a different structure for the complexes with N-bonded ligands is their anomalous behaviour after oxidation, when the compounds display an increase in isomer shift corresponding to either an increase in $3d$ electron density or decrease in $4s$ electron density.[12] None of these explanations seems to be in accordance with bonding to a rather good σ-donor. The reason for rejecting the latter interpretation of the change in isomer shift is that the half-filled orbital in the oxidized species is supposed to be of a symmetry corresponding to d_{xz}, d_{xy} or d_{yz}. In the case of C_{2v} symmetry, these orbitals cannot mix with the $4s$ orbital of iron.

Only unsymmetric π-bonding can give rise to quadrupole splitting in these d^{10} complexes and all d-orbitals participate in the π-bonding due to the low symmetry (C_{2v} and C_s). Hence, the magnitude of the π-overlap (S_π) was selected as the measure of the π-bond strength between ligands and central-ion d-orbitals. S_π^2, which is then proportional to the charge transferred *via* relevant molecular orbitals (Table 3), was calculated by wellknown methods.[18,19]

Table 3. Group overlap of molecular orbitals. The group overlap is given relative to the atomic overlap integral, $S(d_{\pi M}, p_{\pi L})$. Only the angular dependence is considered.

Representation	Metal orbital	Ligand combination	Group overlap (S_π)
a_1	d_{z^2}	$(1/\sqrt{2})(\pi_{y_1} + \pi_{y_2})_{NO}$	$\frac{1}{2}\sqrt{6} \sin 2\theta$
a_1	$d_{x^2-y^2}$	$(1/\sqrt{2})(\pi_{y_1} + \pi_{y_2})_{NO}$	$\frac{1}{2}\sqrt{2} \sin 2\theta$
a_2	d_{xy}	$(1/\sqrt{2})(\pi_{x_1} + \pi_{x_2})_{NO}$	$\sqrt{2} \sin \theta$
b_1	d_{xz}	$(1/\sqrt{2})(\pi_{y_1} - \pi_{y_2})_{NO}$	$\sqrt{2} \cos 2\theta$
b_2	d_{yz}	$(1/\sqrt{2})(\pi_{x_1} - \pi_{x_2})_{NO}$	$\sqrt{2} \cos \theta$
a_1	d_{z^2}	$(1/\sqrt{2})(\pi_{y_1} + \pi_{y_2})_L$	$\frac{1}{2}\sqrt{6} \sin 2\theta$
a_1	$d_{x^2-y^2}$	$(1/\sqrt{2})(\pi_{y_1} + \pi_{y_2})_L$	$\frac{1}{2}\sqrt{2} \sin 2\theta$
a_2	d_{xy}	$(1/\sqrt{2})(\pi_{x_1} + \pi_{x_2})_L$	$\sqrt{2} \sin\theta$
b_1	d_{xz}	$(1/\sqrt{2})(\pi_{x_1} - \pi_{x_2})_L$	$\sqrt{2} \cos \theta$
b_2	d_{yz}	$(1/\sqrt{2})(\pi_{y_1} - \pi_{y_2})_L$	$\sqrt{2} \cos 2\theta$

Table 4. EFG elements of ON–Fe–NO molecule.

θ	V_{xx}	V_{yy}	ΔV_{zz}	ΔE_Q	η
50	−1.39	0.90	0.71	−1.41	0.31
52	−1.10	0.82	0.28	−1.14	0.50
54	−0.67	0.67	0.00	±0.77	1.00
56	−0.45	0.57	−0.12	−0.61	0.57
58	−0.11	0.42	−0.31	+0.44	0.49
59	0.06	0.34	−0.40	−0.47	0.58
60	0.25	0.25	−0.50	−0.50	0.0
61	0.43	0.16	−0.59	−0.61	0.46
62	0.62	0.06	−0.68	−0.75	0.81
63	0.80	−0.02	−0.76	+0.91	0.91
64	0.98	−0.14	−0.84	+1.06	0.72
65	1.17	−0.24	−0.93	+1.23	0.59

Values for the elements of the EFG tensor calculated in this way are shown in Table 4. It is seen that for fixed θ [$2\theta = \angle(\mathrm{ON})-\mathrm{Fe}-(\mathrm{NO})$ and $\theta < 60°$] and in agreement with our experimental data, ΔE_Q increases with increasing difference in the transferred charge. On the other hand, IR-data and the nearly constant isomer shift point to other causes for the sizeable ΔE_Q-differences rather than the relatively small transferred charges. Table 4 indicates that variation in θ could be responsible.

To obtain a reasonable conformity between calculated and experimental values the (ON)–Fe–(NO)-bond angle in $Fe(NO)_2(CO)_2$ should be *ca.* 58°. The angle should be larger in the complexes with ligands of smaller π-bond strength than CO. Table 5 gives the results of a detailed calculation of the quadrupole splitting. The magnitude of θ used in the table differs significantly from earlier estimates, but is in reasonable agreement with the value indicated by the X-ray structure of $(NO)_2Fe P\phi_2C_5F_6P\phi_2$ and with the structures of Co(NO)-$(CO)_2P\phi_3$ and $Co(NO(CO)(P\phi_3)_2$.

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Table 5. Calculation of quadrupole splitting for 2 $Fe(NO)_2L_2$ compounds.

	$Fe(NO)_2(CO)_2$	$Fe(NO)_2[P(C_6H_5)_3]_2$
θ_N	60°	62°
θ_L	52°	54°
$\sum \Delta e(L)$ [a]	0.8 elec.	0.2 elec.
$\sum \Delta e(NO)$ [a]	4.0 elec.	4.6 elec.
$\sum S_\pi^2$	4.0	4.0
$V_{xx}(L)\frac{\sum \Delta e(L)}{\sum S_\pi^2} + V_{xx}(NO)\frac{\sum \Delta e(NO)}{\sum S_\pi^2}$	0.41	0.74
$V_{yy}(L)\frac{\sum \Delta e(L)}{\sum S_\pi^2} + V_{yy}(NO)\frac{\sum \Delta e(NO)}{\sum S_\pi^2}$	0.03	0.04
$V_{zz}(L)\frac{\sum \Delta e(L)}{\sum S_\pi^2} + V_{zz}(NO)\frac{\sum \Delta e(NO)}{\sum S_\pi^2}$	−0.44	−0.78
η	0.84	0.74
ΔE_Q, calc.	−0.48	−0.85
ΔE_Q for 1 electron	4.0	4.0
Quadrupole splitting for 1 elec.	3.60 mm/S	3.60 mm/S
ΔE_Q	−0.43 mm/S	−0.77 mm/S
ΔE_Q experimental [b]	−0.34 mm/S	−0.67 mm/S
η experimental [b]	0.85	0.76

[a] See Table 3. [b] Ref. 14.

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