

MÖSSBAUER EFFECT IN NITROSYL IRON (II) BIS-DITHIOCARBAMATES*

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Abstract—Several iron (II) nitrosyl *bis*-dithiocarbamates have been studied by the Mössbauer and other spectroscopic methods. The Mössbauer effect has proved to be useful for studying slight changes in chemical bonding due to differences in the inductive effect of the ligands.

INTRODUCTION

IT HAS frequently been proposed that it would be of special interest to study a number of compounds using several spectroscopic techniques, including the Mössbauer effect. We present here the results of an investigation of some nitrosyl iron *bis*-dithiocarbamates using optical, i.r., electron spin resonance and Mössbauer spectroscopy.

Nitrosyl iron (II) *bis*-dithiocarbamates, $[(RRNCSS)_2Fe NO]$, are suitable for such studies for several reasons. Iron is an easy element to study by the Mössbauer effect. The presence of the nitrosyl group enables one to study the i.r. stretching frequency of the NO group and the ESR hyperfine spectrum arising from the interaction between the unpaired electron of the NO group and the nuclear spin of the nitrogen atom. Slight structural changes in the ligands can be effected by changing the substituent *R*. In this case *R* was methyl, ethyl, *iso*-propyl and phenyl.

Our aim was to compare the results from the different spectroscopic techniques to discover whether the Mössbauer effect is a useful tool in detecting minor chemical changes.

The X-ray structures of nitrosyl iron (II) *bis*-(NV-dimethyl dithiocarbamate)[1] and of nitrosyl iron (II) *bis*-(NN-diethyl dithiocarbamate)[2] have been studied. The four sulphur atoms lie on a plane with the iron atom slightly above this plane and the nitrosyl group above the iron completing a square pyramid. There is still some discrepancy as to whether the Fe—N—O bond is linear as in iron nitroprusside or bent as in nitrosyl cobalt (II) (NN—

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dimethyl dithiocarbamate)[3,4]. The Fe—N bond length of 1.7 Å indicates substantial π bond character.

RESULTS

Optical and u.v. spectroscopy. The first spectroscopic studies of these compounds were reported by Gray, Bernal and Billig[5] who explained the properties of the methyl derivative using an energy level diagram for compounds of the type ML_5NO . This description completely ignores π bonding in the plane and considers that all the π bonding is axial, that is between NO and the iron atom. Others[6] calculated an energy level diagram for the nitroprusside ion which shows a certain amount of in-plane π bonding. The symmetry of our complexes and the nitroprusside ion is formally the same and, therefore, the same energy level scheme may be used, at least in a qualitative manner.

The important features of this diagram are, (i) a very strong iron–nitrosyl bond, (ii) the order of the d levels in the metal is $z^2 > x^2 - y^2 > xy > xz, yz$ and (iii) an orbital of e symmetry, arising from a mixture of the d_{xz} and d_{yz} orbitals of the iron and the π antibonding orbital of NO, lies between the d_{xy} and the $d_{x^2-y^2}$ levels. From this scheme it appears that the ground state for the Fe(II) nitrosyl bis-dithiocarbamates is $e^4(d_{xz}, d_{yz})b^2(d_{xy})e^1(NO^*)$.

Details of the absorption spectrum (30,000–15,000 cm^{-1}) of the methyl derivative have been published by others [5]. No change was found in the positions and intensities of the bands for the four different derivatives studied during this work. Any possible differences were masked by broad charge transfer bands. The band in the near i.r. [5] (12,500 cm^{-1} , $\epsilon = 8.3$ in acetone) may be considered to be a true $d-d$ transition, and should be altered by slight variation in the strength of the ligand field. Again, however, the transition was hidden by charge transfer bands.

These complexes are paramagnetic as predicted by the energy level scheme of Manoharan and Gray [6].

Infrared spectroscopy. The very strong band around 1500 cm^{-1} in the spectra of all the dithiocarbamates, whether ionic or covalent, is assigned [7, 8] to the stretching mode of the polar CN bond with a partial double bond character. The transition around 1650–1700 cm^{-1} is due to stretching mode of the NO bond [9].

The NO and CN stretching frequencies found in this work are shown in Table I. The stretching frequencies change with substituent R , an effect similar to that observed [10] for the NO frequencies in derivatives of Schiff's base complexes, and for the CN stretching frequency for Cu(II) dialkyl dithiocarbamate [7]. In the present case the effect of the substituents is transmitted through a chain of five atoms. The significance of the trend in the values (Table 1) is questionable in view

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Table 1. Comparison of i.r., spin resonance and Mössbauer effect results in several Fe(II) nitrosyl bis-dithiocarbamates

Substituent in dithiocarbamate ligand	Infra-red stretching frequencies (cm ⁻¹)		ESR parameters		Mössbauer parameters (cm/sec)	
	CN	NO	Hyperfine splitting (gauss)	\bar{g}	Isomer* shift	Quadrupole interaction
methyl	1533 ± 10	1684 ± 10	12.41 ± 0.04	2.041 ± 0.004	0.037 ± 0.003	0.083 ± 0.003
ethyl	1501	1682	12.68	2.040	0.040	0.070
<i>isopropyl</i>	1484	1677	12.93	2.038	0.043	0.072
phenyl	1481	1693	12.35	2.042	0.048	0.064

*With respect to K₄Fe(CN)₆ standard absorber.

of the experimental error (± 10 cm⁻¹). The effect is less for the NO stretching mode, compared with the CN mode. This is expected as the inductive effect of substituents should weaken with an increase in the separation. The inductive effect increases in the series $R = \text{methyl} < \text{ethyl} < \textit{iso}$ -propyl. This is equivalent to postulating a decrease in electro-negativity in the series and is paralleled by an increase in electron-donation from the CN bond to the Fe atom, as will be seen later.

The frequency shifts of the CN and NO stretching modes are in accord with these postulates i.e. decreasing as R changes in the series $\text{Me} > \text{Et} > \textit{iPr}$. The decrease in frequency results from the increase in population of the π^* orbital of the NO bond as the contribution of electrons in the planar ligands increases.

The phenyl derivative constitutes a special case in which the mesomeric effect withdraws electron density from the CN bond. Consequently, as before, the frequency of the CN is diminished, but the NO mode increases because of the decrease in population of the π orbital.

Thus, in agreement with Ballhausen and Gray[11] who considered strong bonded complexes, in-plane bonding should not be neglected.

Electron spin resonance. The ESR spectra of the compounds show a triplet due to the hyperfine interaction between the unpaired electron and the nuclear spin of the nitrogen atom. The results are shown in Table 1. This interaction increases in the order $\text{Me} < \text{Et} < \textit{iPr}$, in agreement with the postulate of an increasing inductive effect. In the case of the phenyl derivative electron delocalisation by in-plane π bonding results in a relatively small hyperfine interaction.

The g values of the triplet are not easily explained on this basis as they reflect the changes in both ligand field and covalency. The observation of g_{\perp} and g_{\parallel} would have aided interpretation but this was not possible due to lack of success in isolating single crystals.

Mössbauer effect. The Mössbauer spectra consist of a doublet, caused by the quadrupole interaction. The intensity ratio of the doublet differs slightly from

unity. Goldanskii[12] explains this effect in terms of anisotropy of the f factor of Mössbauer transitions, which we would expect in compounds such as the ones being studied. The values for the isomer shift (IS) and quadrupole interaction in these compounds are shown in Table 1. The results for the methyl and ethyl derivatives agree with published values[13].

The increase in isomer shift from the methyl to phenyl derivatives shows two phenomena. An increase in electron-density on the sulphur atom in the sense $Me < iPr$ results in an increase in the population of the $3d$ orbitals, d_{xz} , d_{yz} and d_{xy} as may be seen from the energy level diagram. The screening due to these electrons increases in the same order, lowering the s electron density and raising the IS .

The values of the IS for the phenyl derivative is inconsistent with this postulate and with the i.r. results. The contribution of the s electron to bonding in this compound may well be different from that in the alkyl derivatives. This is qualitatively internally consistent. In a plot of CN and NO stretching frequencies versus isomer shift, it is found that a linear relation holds for the alkyl derivatives. The phenyl derivative is consistently anomalous. This is paralleled by a plot of ESR hyperfine interaction against IS . The anomalous behaviour is probably due to inplane π bonding and hyper-conjugative effects.

In general low spin Fe octahedral complexes exhibit only a small quadrupole splitting[14]. In the complexes studied here, the crystal field symmetry is much lower and we would predict, in agreement with the experimental findings, a large quadrupole splitting.

The electric field gradient created by a single d electron is given[15] by the expression

$$\Delta E_q = (1 - R)q\langle r^{-3} \rangle F\alpha^2 \quad (1)$$

where $(1 - R)$ is the Sternheimer factor which depends on the deformation of the inner core electrons by the outer d electrons, α^2 is the covalency factor, which is related with the nephelauxetic effect, q is the angular part of the field gradient calculated from the free ion and F is a function of the spin-orbit coupling, crystal field and temperature. To investigate the relation between structure and the quadrupole splitting we have used the method of Danon[13] in which the ratio of the quadrupole splittings of the nitrosyl *bis*-dithiocarbamates and the nitroprusside ion are compared with the theoretical ratio derived from the above equation. It is assumed that $(1 - R)$ and F are constant for both compounds as the energy level diagrams are qualitatively the same for each compound. Replacing the CN ligands by S atoms and eliminating the ligand trans to the NO group only acts as a perturbation of the levels without changing significantly F or $(1 - R)$.

Using published[6] values of α^2 we obtain, for the nitroprusside ion, $\Delta E_q = 0.8k$ where k includes $(1 - R)$, F and $\langle r^{-3} \rangle$. Similarly for the nitrosyl *bis*-dithiocarbamates $\Delta E_q = 0.3k$. The theoretical ratio, 2.66, is in acceptable agreement

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with the experimental ratio of 2.30 obtained using the mean value of ΔE_q , 0.075 cm/sec for the dithiocarbamates. The decrease in quadrupole splitting in the series methyl to *isopropyl* again is explained in terms of an increase in inductive effect; the population of Manoharan and Gray's $7e$ orbital is increased, decreasing the splitting. Again the value for the phenyl derivative is anomalous.

Thus Mössbauer spectroscopy may be used to study slight changes in chemical bonding in a series of homologous compounds. Mössbauer results can also be related to ESR data but optical methods are not as sensitive.

EXPERIMENTAL

The nitrosyl *bis*-dithiocarbamates were prepared by published methods[16]. Analytical results are in Table 2.

Infrared spectra were recorded for Nujol or halohydro-carbon mulls and using Beckman IR 5 and IR 9 spectrometers. The u.v. and visible spectra were recorded using a Perkin Elmer 137 UV and a Beckman DK 2, spectrometer. Chloroform, acetone and benzene were used as solvents.

Table 2. Analytical results

Substituent in-dithiocarbamate ligand	Required (%)					Found (%)				
	C	H	N	S	Fe	C	H	N	S	Fe
methyl	22.1	3.7	12.9	39.3	17.1	22.2	3.5	12.5	39.9	17.3
ethyl	31.4	5.3	10.9	33.6	14.6	31.2	5.1	10.6	34.0	14.9
<i>isopropyl</i>	38.3	6.4	9.6	29.2	12.7	38.1	6.0	9.3	29.6	12.9
phenyl	54.3	3.5	7.3	22.3	9.7	54.4	3.4	7.0	22.1	9.5

The ESR spectra were recorded on a Varian V 4500 spectrometer, using quartz tubes of 3 mm diameter. Chloroform was used as solvent and the usual concentrations were of 10^4 – 10^5 molecules of solvent per iron atom. DPPH was used[17] as a reference. A constant acceleration spectrometer for the Mössbauer spectra was used with a Co^{57} :Cr source[18].

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