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EPR Investigations of Electronic Structure of Iron Nitrosyl Dithiophosphate Complexes

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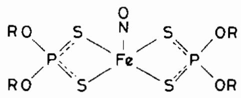
Nitrosyliron-bis-di-iso-propyl-dithiophosphate complex and nitrosyliron-bis-dicyclohexyl-dithiophosphate complex, FeNO(dtp)$_2$, were synthesized and studied by EPR. On the basis of frozen solution spectra ^{14}N, ^{31}P superhyperfine and ^{57}Fe hyperfine parameters were obtained. The postulated electron configuration $a_2(xy)^2 b_1(xz)^2 b_2(yz)^2 a_1(z^2)^1$ is suitable for interpretation of the all observed spin Hamiltonian parameters. The observed differences between parameters for the FeNO(dtp)$_2$ and FeNO(dtc)$_2$ (dtc = dithiocarbamate anion) were interpreted by the influence of the out-of-plane π-bonding with sulphur and increasing π(NO) character of b_1 and b_2 orbitals in the FeNO(dtp)$_2$ complexes.*

Dinitrosyl complexes with the same ligands were obtained and investigated by EPR; for the complexes, similarly to those of mononitrosyls, we found a characteristic positive sign of $A_p(^{57}Fe)$ values whereas $A_{iso}(^{57}Fe)$ is negative.

Introduction

Continuing our interest in the EPR studies of sulphur containing transition metal complexes, in the present paper we report the newly synthesized and investigated nitrosylironbis(O,O′-di-iso-propyl-dithiophosphato) complex and nitrosylironbis(O,O′-dicyclohexyl-dithiophosphato) complex with the formula:



(R = iso-propyl or cyclohexyl)

There is no information available in the literature about such complexes although many other nitrosyliron bis-chelate complexes have been investigated recently. The special interest for the complexes with FeNO(S$_4$) chromophore is particularly due to their importance in living organisms [1].

It is noteworthy that for both complexes of the FeNO(dtp)$_2$ type investigated we obtained identical spin Hamiltonian parameters within experimental limits of error.

Experimental

To an aqueous solution of ferrous sulphate (0.05 *M*) the dialkyldithiophosphate potassium salt in molar ratio 1:2.2 was added; then sodium nitrite and ascorbic acid in equal molar quantity were added in 4-fold excess in relation to Fe^{++}. The temperature of the reaction mixture was initially 280 °K and gradually increased to 305 °K. The mixture was extracted with toluene. By slow evaporation of the extract we obtained a very unstable, easily oxidable and NO-losing precipitate. The molar ratio metal: organic ligand obtained by usual chemical analysis of this precipitate is 1.00:2.00 ± 0.03.

The EPR spectra were recorded on a JES-ME-3X spectrometer in the temperature region 120–295 °K, at a microwave frequency of 9.16–9.18 GHz. It is worthwile to note that EPR spectra of toluene extracts and toluene solutions of the precipitate were identical.

The dinitrosyl complexes were obtained when the reaction mixture was brought to pH 11 and extracted with isoamyl alcohol. These extracts were studied by EPR technique.

The EPR spectra were simulated on a JEC-6 Spectrum Computer.

Results and Discussion

The EPR spectrum of the FeNO(dtp)$_2$ complexes in toluene was not visible at room temperature probably because of broadening of the lines. At 125

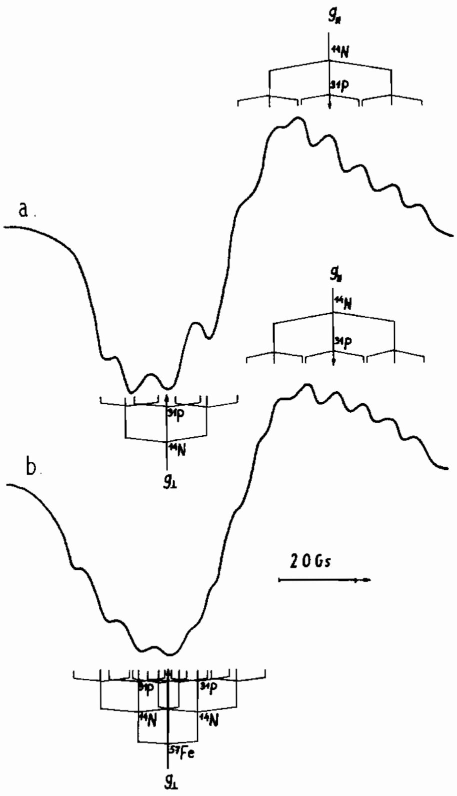


Figure 1. EPR spectrum of FeNO(dtp)$_2$ in toluene at 125 °K; ν = 9.174 GHz. a) normal abundance of iron isotopes; b) 85% of ^{57}Fe isotope.

°K the EPR spectrum showed resolved superhyperfine splitting (shfs) from one ^{14}N and two ^{31}P nuclei, and hyperfine splitting (hfs) from ^{57}Fe nucleus when the complex was enriched with this isotope (Fig. 1, a, b).

The EPR parameters calculated from these spectra are:

Orientation	g ±0.001	A(^{57}Fe)^a ±0.5	A(^{14}N)^a ±0.2	A(^{31}P)^a ±0.2
parallel	2.025	0	16.3	8.4
perpendicular	2.052	16.8	11.2	8.4

^{a} All data in gauss.

From the EPR spectra it follows that $A_{\parallel}(^{57}Fe) \approx 0$, and assuming that $A_{\perp}(^{57}Fe)$ and $A_{iso}(^{57}Fe)$ are negative, we obtain $A_{iso}(^{57}Fe) = -11.2$ Gs and $A_p(^{57}Fe) = +5.6$ Gs. The positive sign of $A_p(^{57}Fe)$ may indicate that the unpaired electron is located mainly on the d_{z^2} orbital. This result is in agreement with the results obtained for the other sulphur containing nitrosyliron complexes [2]. If $A_{\perp}(^{57}Fe)$ has an opposite sign, then $A_{\parallel}(^{57}Fe) = -22.4$ Gs is at variance with the observed spectra.

The unpaired electron in five coordinated $\{FeNO\}^7$ complexes occupies either $a_1(z^2)$ or $b_1(xz, \pi^*(NO))$ and $b_2(yz, \pi^*(NO))$ orbitals [3]. In view of this we assume that the electron configuration $a_2(xy)^2 b_1(xz)^2 b_2(yz)^2 a_1(z^2)^1$ is suitable for the interpretation of the observed spin Hamiltonian parameters.

In comparison with a series of nitrosylironbis(dithiocarbamato) complexes [2–5], in which $g_{\perp}$ is 2.040, $g_{\perp}$ in FeNO(dtp)$_2$ is increased to 2.052, whereas $g_{\parallel}$ is nearly constant, $A_{\perp}(^{14}N)$ is decreased from 12.8 to 11.2 Gs and $A_{\parallel}(^{14}N)$ is increased from 15.5 to 16.3 Gs. These changes are related to the sulphur out-of-plane π bonds since the symmetry of the orbitals b_1 and b_2 is suitable for interaction with it. When the unpaired electron is on the orbital $a_1(z^2)$, the destabilization of b_1 and b_2 levels gives rise to a positive shift in $g_{\perp}$, while $g_{\parallel}$ remains constant.

The calculated isotropic and anisotropic parts of the ^{14}N(NO) shf tensor – $A_{iso}(^{14}N) = +12.9$ Gs and $A_p(^{14}N) = +1.6$ Gs – were used for calculation of the unpaired electron density of the nitrogen 2s and 2p orbitals (the value of $A_p(^{14}N)$ was corrected with the dipolar contribution in a point-dipole approximation of 0.3 Gs). The calculated values were $c_{2s}^2 = 0.023$ and $c_{2p}^2 = 0.082$. The magnitude of c_{2p}^2 is different from the corresponding value of 0.04 for FeNO(dtc)$_2$ complexes [2] (dtc = dithiocarbamate anion), but c_{2s}^2 is approximately equal for both type complexes. The observed difference in the value of c_{2p}^2 is also due to the influence of the out-of-plane π bonding with sulphur. If for the dithiophosphate complexes the b_1 and b_2 orbitals are raised in energy, the $\pi^*(NO)$ character of these orbitals will increase and c_{2p}^2 therefore increases as well.

It is noteworthy that the ^{31}P shfs is isotropic. In this case using the theoretically calculated values for the hfs of ^{31}P (3636 or 4640 Gs [6]), we find that 0.18 to 0.23% of the total unpaired electron density is located on the phosphorus 3s orbital. However, at the moment it is difficult to explain the origin of the ^{31}P shfs in the studied FeNO(dtp)$_2$ complexes. One possible mechanism is the spin polarization of the $P \cdots S$ bonds inducing some unpaired s electron density on the phosphorus 3s orbital.

Another mechanism is the orbital hybridization because of which the unpaired electron occupies the following orbital:

$$\psi = a(z^2) + b(x^2 - y^2) + c(4s),$$

where a ≫ b, c and C_{4v} symmetry with a weak C_{2v} perturbation is assumed. The fact that $g_x = g_y = g_{\perp}$ and $A_x(^{57}Fe) = A_y(^{57}Fe) = A_{\perp}(^{57}Fe)$ shows that in FeNO(dtp)$_2$ complexes the symmetry is C_{4v}. However, the X-ray [9] and EPR data for analogous FeNO(dtc)$_2$ complexes [2, 5] show that the symmetry of the complex molecule is lowered and distinct rhombic distortion is observed. In view of

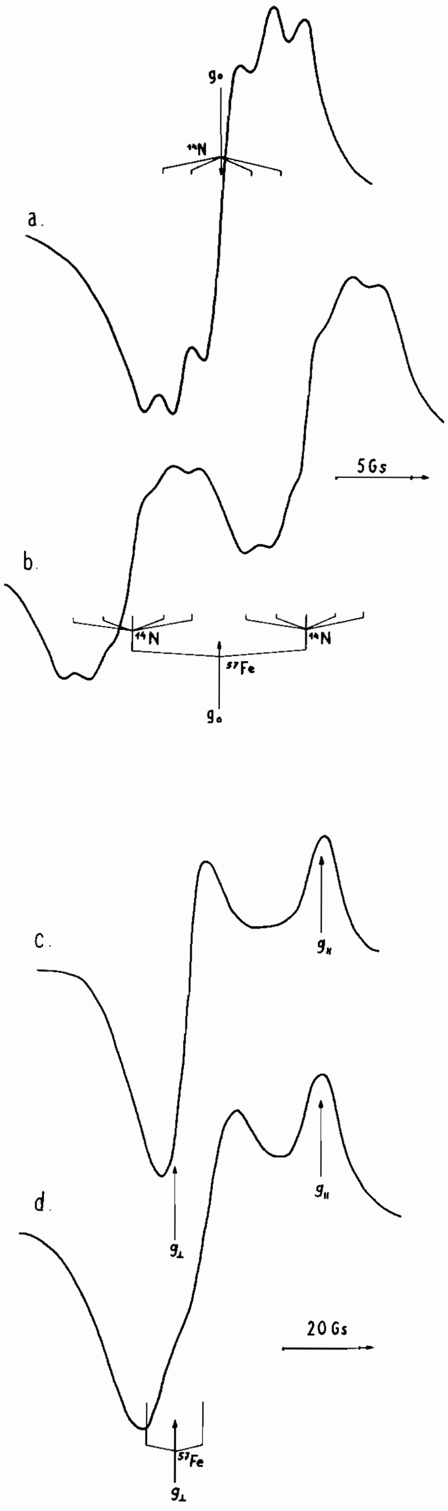


Figure 2. EPR spectrum of Fe(NO)$_2$dtp in isoamylalcohol. a) at 305 °K, normal abundance of iron isotopes, $\nu = 9.170$ GHz; b) at 305 °K, 85% of ^{57}Fe isotope; $\nu = 9.171$ GHz; c) at 120 °K, normal abundance of iron isotopes; $\nu = 9.168$ GHz; d) at 120 °K, 85% of ^{57}Fe isotope, $\nu = 9.168$ GHz.

this we assume that as a first approximation the symmetry of FeNO(dtp)$_2$ complex is C_{4v} with a very weak mixing of C_2 symmetry and therefore the ψ orbital is suitable for this complex. Recently, it was shown that similar orbital mixing takes place in some copper(II) [7] and oxovanadium(IV) [8] complexes but the unpaired electron in both complexes is located mainly on $(x^2 - y^2)$ orbital.

From the reaction mixture at pH 11 we obtained by extraction with isoamyl alcohol the other complex; its EPR spectrum of liquid solution exhibits a quintet with $g_{iso} = 2.031 \pm 0.001$, $A_{iso}(^{14}N) = 2.4 \pm 0.1$ Gs; the shfs arise from two equivalent ^{14}N nuclei of two nitrosyl groups (Fig. 2a). The axial spectrum with $g_\perp = 2.040 \pm 0.001$ and $g_\parallel = 2.013 \pm 0.001$ was observed at 150 K (Fig. 2c). The obtained EPR spectra are characteristic for many dinitrosyl complexes with sulphur ligands [5, 10, 11]. When the complex was enriched with the ^{57}Fe isotope the hfs in the solution spectrum (Fig. 2b) and broadening of the EPR line in the perpendicular region of the anisotropic spectrum (Fig. 2d) were observed.

The estimated hyperfine ^{57}Fe parameters for dinitrosyl complexes are: $A_{iso}(^{57}Fe) = -12.6 \pm 0.2$ Gs; $A_p(^{57}Fe) = +5 \pm 1$ Gs, assuming, as previously, the negative values for $A_\perp(^{57}Fe)$ and $A_{iso}(^{57}Fe)$. It is in good agreement with the observed lack of splitting in the parallel region of the spectrum (Fig. 2d).

It is characteristic that the ^{57}Fe hyperfine parameters and g parameters for the mono- and dinitrosyl complexes with dithiophosphate ligands are very much alike. We have postulated that the molecular orbital scheme described by Enemark and Feltham [3] for *cis*-square planar dinitrosyl complexes is in conformity with the experimental spin Hamiltonian parameters; this scheme is also valid when the complex was six coordinated with H_2O or OH^- as additional ligands. The similarities between mono- and dinitrosyl complexes indicate therefore that the unpaired electron in both cases has mainly (z^2) character.

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