Studies of the Intermolecular Interactions of Metal Chelate Complexes. II. EPR Study on the Interactions of Metal Chelate Complexes with NO_x (x = 1 or 2)

N. D. YORDANOV*, V. ILIEV, D. SHOPOV
Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

A. JEZIERSKI and B. JEŻOWSKA-TRZEBIATOWSKA
Institute of Chemistry, University of Wrocław, Wrocław, Poland

Received November 30, 1981

The interaction of NO_x (x = 1 or 2) with Fe(III) β-diketonates, oxine, thiooxine, dithiocarbamates, dithiocarbonates, dithiophosphates, dithiophosphinates, as well as some Mn(II) and Mn(III), Cr(III), Zn(II), VO(II) complexes, are studied. The reaction of β-diketonates and oxine complexes with NO_2 yields free iminoxy radicals, the corresponding complexes with fluoro substituted ligands being inactive towards NO_2. Fe(III) complexes containing S atoms in the chromophores form mono-nitrosyl complexes, whereas Fe(III) dithiophosphinates give rise to mono- and di-nitrosyl complexes. Free radicals due to the reaction of NO_2 with the ligands or their products are detected by EPR. Reaction between NO and Fe(III) and Mn(III) dithiocarbamates, dithiocarbonates, thiooxine complexes in non-polar solvents yields nitrosyl complexes. The corresponding β-diketonate complexes did not interact with NO.

Introduction

In the last decade the interactions of metal chelate complexes with NO_x (x = 1 or 2) have been the subject of various investigations [1–6]. The results available in the literature have shown that different intermediates and final reaction products have been found depending on the metal ion and ligands. Free radicals are formed in the reaction of Cu(II), Co(III), VO(II), Fe(III) acetylacetonates [1, 2], and Cu(II) oxine [2] complexes with NO_2. The formation of three mixed-ligand complexes in the reaction of copper(II) dithiocarbamates with NO_2 can be detected by EPR [2]. Neither mixed-ligand complexes nor free radicals have been observed with Cu(II) dithiophosphates and Cu(II) thiooxine, independent of the fact that the redox reaction with NO_2 proceeds. The final reaction product in all cases is $Cu(NO_3)_2$. On the other hand the results available in the literature have shown that relatively weak adducts can be detected by EPR [2] during the interaction between NO and copper(II) dithiocarbamates, dithiophosphates and thiooxine complexes, the adduct formation being a reversible process. The formation of stable nitrosyl-iron complexes $\{Fe(NO)(dtc)_2\}$ was found in the reaction of $Fe^{II}(dtc)_2$ with NO, and has been characterized by its typical EPR spectrum [6].

In the present paper the results found by EPR during the interactions of NO and NO_2 with Fe(III) β-diketonates, oxine, thiooxine, dithiocarbamates, dithiocarbonates, dithiophosphates, dithiophosphinates as well as some of the corresponding Mn(II), Mn(III), Cr(III), Zn(II) and VO(II) complexes are reported.

Experimental

Tris[(2-phenylbutandionato(1,3)] Iron(III), $\{Fe(ph\text{-}acac)_3\}$, tris[(dibenzoylmethan)] Iron(III), $\{Fe(dph\text{-}acac)_3\}$, tris[(1-naphtylbutandionato)] Iron(III), $\{Fe(napht\text{-}acac)_3\}$, tris[(tenoyltrifluoroacetylacetonato)] Iron(III), $\{Fe(ttf\text{-}acac)_3\}$, tris[(hexafluoroacetylacetonato)] Iron(III), $\{Fe(hf\text{-}acac)_3\}$, and $Mn(dph\text{-}acac)_2$ have been synthesised by extraction with $CHCl_3$ from aqueous solutions of $FeCl_3$ and $MnCl_2$ respectively and have been purified by recrystallization from an equimolar mixture of ethanol and toluene.

Fluka $Fe(acac)_3$, $Mn(acac)_3$ and $Cr(acac)_3$ were used without further purification.

Tris(diethyldithiocarbamato)Iron(III), $\{Fe(Et_2\text{-}dtc)_3\}$, tris(ethyldithiocarbonato) Iron(III), $\{Fe(Et\text{-}xant)_3\}$, tris(n-butyldithiocarbonato) Iron(III), $\{Fe(Bu\text{-}xant)_3\}$, tris(8-quinolinolato) Iron(III),

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

TABLE I. EPR Parameters of the Imioxy Free Radicals Recorded during the Interaction of Different Substituted Acetylacetonate Complexes with NO_2.

Complex	g_{iso} [a]	A_{iso}^{14N} [b] (G)	$g_{\parallel}$ [a]	$g_{\perp}$ [a]	$A_{\parallel}^{14N}$ [b] (G)	$A_{\perp}^{14N}$ [b] (G)
$Fe(acac)_3$	2.0045	28.0	2.0031	2.0055	41.5	21.7
$Fe(ph\text{-}acac)_2$	2.0045	29.3	2.0030	2.0056	42.8	22.2
$Fe(naphth\text{-}acac)_3$	2.0044	29.6	2.0032	2.0055	43.3	22.4
$Fe(dph\text{-}acac)_3$	2.0045	30.8	2.0030	2.0056	44.4	23.4
$Mn(acac)_3$	2.0046	27.9				
$Mn(dph\text{-}acac)_2$	2.0045	30.6				
$Cr(acac)_3$	2.0045	28.0				

[a] ±0.0003. [b] ±0.5 G.

{Fe(ox)$_3$}, tris(8-quinolinethiolato) Iron(III), {Fe(tox)$_3$}, tris(di-alkyl-dithiophosphato) Iron(IIII), {Fe(dtp)$_3$}, tris(di-alkyl-dithiophosphinato) Iron(III), {Fe(dtph)$_2$}, $Mn(Et_2\text{-}dtc)_3$, $VO(Et_2\text{-}dtc)_2$, Zn(dbenz-dtc)$_2$ were obtained by extraction with $CHCl_3$ from aqueous solutions of the corresponding metal salts and the ligands. $Fe(Et_2\text{-}dtc)_3$ and $Mn(Et_2\text{-}dtc)_3$ were purified by recrystallization from an equivolume mixture of ethanol and toluene; the other complexes were used immediately after extraction.

The disulphides of the appropriate sulphur-containing ligands were prepared by reaction of the ligand alkaline salts with I_2 in a water–alcohol mixture.

NO_2 was obtained by the reaction of elemental copper and conc. HNO_3, and purified and dried by the methods described in the literature [1].

NO gas was obtained from Merck-Schuchardt.

Fluka $C(NO_2)_4$ was used in all experiments in toluene solution.

All experiments were carried out in an inert (argon) atmosphere (99.999%).

The EPR spectra were recorded at 300 and 77 K on an Me-X and 3BS-X spectrometer using 100 kHz modulation of the magnetic field. The magnetic field was calibrated with gaussmeter (at Me-X) and with Mn^{2+} in MgO (at 3BS-X spectrometer). The g-values were calculated relatively to DPPH.

Results

Interactions with NO_2

After passing NO_2 for a few minutes through the toluene solutions of $Fe(acac)_3$, $Fe(ph\text{-}acac)_3$, $Fe(dph\text{-}acac)_3$, $Fe(napht\text{-}acac)_3$, $Mn(acac)_3$, $Mn(dph\text{-}acac)_2$, $Cr(acac)_3$ complexes triplete EPR spectra were recorded, and parameters at 300 and 77 K are shown in Table I. The increased time for passing NO_2 through these solutions (resp. increased quantity of NO_2) was noted to correlate with precipitation of an insoluble product. The elemental analysis of the precipitate has shown that it was $Fe(NO_3)_3$, thus suggesting complete destruction of the chelate complexes.

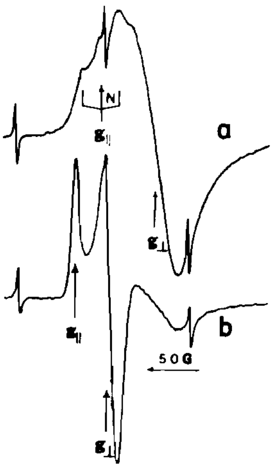


Fig. 1. EPR spectra of the intermediate products of the reaction between NO_2 and $Fe(Et_2\text{-}dtph)_3$ recorded after freezing the sample at 77 K. Three lines of Mn^{2+} in MgO are also recorded. a. Mononitrosyliron complex. b. Dinitrosyliron complex with small amounts of mononitrosyliron.

No changes in the solution appeared and no EPR spectra were recorded under the same experimental conditions upon passing NO_2 through solutions of fluoro-containing acetylacetonate complexes of Fe(III).

The complexes $Fe(dtc)_3$, $Fe(tox)_3$, and $Fe(xant)_3$ dissolved in toluene or chloroform did not show EPR spectra in the temperature range 77–300 K, because of very short relaxation times and therefore extremely broad EPR lines [7].

Passing NO_2 through toluene solutions of $Fe(Et_2\text{-}dtc)_3$, $Fe(dtp)_3$, $Fe(tox)_3$, $Fe(xant)_3$, $Fe(dtph)_3$

TABLE II. EPR Parameters of the Nitrosyliron Complexes Recorded during the Interaction of the Corresponding Fe(III) tris-Chelates with NO_2.

Complex	g_{iso}^a	A_{iso}^b (G)	$g_\parallel^a$	$g_\perp^a$	$A_\parallel^{^{14}N\ b}$ (G)	$A_\parallel^{Pb}$ (G)	$A_\perp^{^{14}N\ b}$ (G)	$A_\perp^{Pb}$ (G)
$Fe(NO)(tox)_2$	2.035	13.2	2.025	2.044^c 2.041^d	14.0		14.3^e 14.0^f	
$Fe(NO)(Et_2\text{-dtc})_2$	2.040	12.9	2.026	2.045^c 2.041^d	15.6		13.2^e 12.9^f	
$Fe(NO)(Et\text{-xant})_2$	2.044	12.4						
$Fe(NO)(Bu\text{-xant})_2$	2.042	11.8	2.022	2.045^c 2.043^d	14.3		12.4^e 12.1^f	
$Fe(NO)(Pr^i_2\text{-dtp})_2$			2.026	2.055	16.2	8.3	11.3	8.3
$Fe(NO)(Et_2\text{-dtph})_2$	2.048		2.029	2.061	18.2			
$Fe(NO)_2(Et_2\text{-dtph})_2$	2.033	2.4	2.015	2.036				

[a]±0.002. [b]±0.5 G. [c]g_1. [d]g_2. [e]A_1. [f]A_2.

TABLE III. EPR Parameters of the Free Radicals Recorded during the Interaction of NO_2 and $C(NO_2)_4$ with Different Nitrosyl and Other Complexes, as well as with some Disulphides from the Ligands.

Complex	Acceptor	g_{iso}^a	$A_{iso}^{N\ b}$ (G)	$g_\parallel^a$	$g_\perp^a$	$A_\parallel^{N\ b}$ (G)
$Fe(Et_2\text{-dtc})_3$	NO_2	2.0060	15.0	2.0030	2.0057	33.5
		2.0068	10.0			
$Fe(Pr^i_2\text{-dtp})_3$	NO_2	2.0067	14.9	2.0032	2.0056	33.2
$Fe(Et_2\text{-dtph})_3$	NO_2	2.0068	15.0			
$Fe(Bu\text{-xant})_3$	NO_2	2.0069	15.0			
		2.0069	9.9			
$Fe(ox)_3$	NO_2	2.0066	14.8			
$Fe(tox)_3$	NO_2	2.0050	12.0			
		2.0074	12.0			
		2.0066	14.9			
$VO(Et_2\text{-dtc})_2$	NO_2	2.0069	15.0			
		2.0069	10.0			
$Mn(Et_2\text{-dtc})_3$	NO_2	2.0070	15.1			
$Zn(dbenz\text{-dtc})_2$	NO_2	2.0070	15.0			
		2.0070	10.0			
Et_2-dtc-ds	NO_2	2.0068	10.0			
Et_2-dtph-ds	NO_2	2.0069	15.0			
Bu-xant-ds	NO_2	2.0069	15.0			
$Fe(Et_2\text{-dtc})_3$	$C(NO_2)_4$	2.0068	15.0			
$Fe(Bu\text{-xant})_3$	$C(NO_2)_4$	2.0068	14.9			
		2.0068	8.0			
		2.0078	8.0			

[a]±0.0003. [b]±0.5 G.

(Fig. 1) leads to the appearance of intensive EPR spectra (Table II). Further passing of NO_2 is connected with some color changes in the solutions, decreasing of the intensity of the recorded spectra and appearance of new EPR spectra (Table III, Fig. 2). In the case of $VO(Et_2\text{-dtc})_2$, $Mn(Et_2\text{-dtc})_3$ and $Zn(dbenz\text{-dtc})_2$ the parameters of all recorded spectra are shown in Table III. (The same EPR spectra have been recorded by passing NO_2 through solutions of the corresponding disulphides of the ligands, Table III). Further passing NO_2 through the solutions of the complexes is connected with the disappearance of the

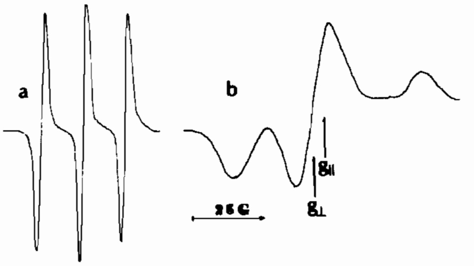


Fig. 2. EPR spectra of free radicals recorded during the reaction of nitrosyliron complexes with NO_2. $Fe(NO)(dtc)_2$ in the present figure. a at 300 K, b at 77 K.

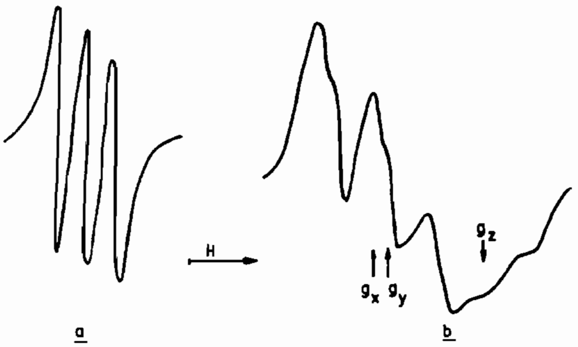


Fig. 3. EPR spectra of $Fe(NO)(tox)_2$ complex obtained in the reaction of NO with $Fe(tox)_3$. Solvent toluene. a at 300 K, b at 125 K.

spectra. In all cases precipitation of $Fe(NO_3)_3$, $Mn(NO_3)_3$, $Cr(NO_3)_3$ respectively takes place.

Interactions with NO

After passing NO for a few minutes through the $Fe(dtc)_3$, $Fe(tox)_3$, $Fe(xant)_3$ solutions, followed by argon, the appearance of stable triplete EPR spectra was observed (Fig. 3). The obtained EPR iso- and anisotropic parameters are given in Table IV.

It is noteworthy that the same reaction products were obtained upon passing NO_2 through toluene solutions of the chelates.

TABLE IV. EPR Parameters of $Fe(NO)(chel)_2$ Complexes Recorded during the Interaction of the Corresponding $Fe^{III}(chel)_3$ Complexes with NO (solvent toluene).

T (K)	Parameters	chel		
		xant	dtc	tox
300	$g_o \pm 0.002$	2.043	2.039	2.039
	$A_o(^{14}N) \pm 0.5$ G	11.7	13.0	13.1
	$A_o(^{57}Fe) \pm 0.5$ G	9.1	9.6	10.2
125	$g_x \pm 0.002$	2.045	2.045	2.044
	$g_y \pm 0.002$	2.043	2.045	2.041
	$g_z \pm 0.002$	2.022	2.026	2.025
	$A_x(^{14}N) \pm 0.5$ G	12.4	13.2	14.3
	$A_y(^{14}N) \pm 0.5$ G	12.1	12.9	14.0
	$A_z(^{14}N) \pm 0.5$ G	14.3	15.6	14.0
	$A_{xy}(^{57}Fe) \pm 0.5$ G	13.9	15.5	16.1

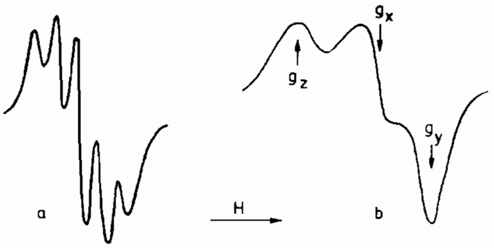


Fig. 4. EPR spectra of Fe(NO)(xant)(pip) complex obtained in the reaction of NO with $Fe(xant)_3$ in the presence of piperidine. Solvent iso-amyl alchol. a at 310 K, b at 125 K.

In the presence of strong bases in the reaction mixture (amines, imidazole, *etc.*) the dinitrosyl complexes are formed (Fig. 4).

NO reacts also with $Mn(dtc)_3$, $Mn(tox)_3$, and $Mn(xant)_3$. The reaction yields $Mn(NO)(chel)_2$ complexes, where chel = dtc, tox, xant. The EPR parameters obtained for the complexes are given in Table V.

TABLE V. EPR Parameters of $Mn(NO)(chel)_2$ Complexes Recorded during the Interaction of the Corresponding $Mn^{III}(chel)_3$ Complexes with NO (solvent toluene).

chel/parameter	235 K		125 K			
	$g_o \pm 0.002$	A_o (^{55}Mn) $\times 10^4$ cm^{-1}	$g_\parallel$ ± 0.002	$g_\perp$ ± 0.002	$A_\parallel$ (^{55}Mn) $\times 10^4$ cm^{-1}	$A_\perp$ (^{55}Mn) $\times 10^4$ cm^{-1}
xant	2.013	79.1	1.992	2.023	150.7	43.3
Bu^i_2-dtc	2.013	79.4	1.992	2.023	152.1	43.1
pyrl-dtc	2.011	80.9	1.993	2.021	154.5	44.1
tox	2.012	81.2	1.993	2.022	155.2	44.0

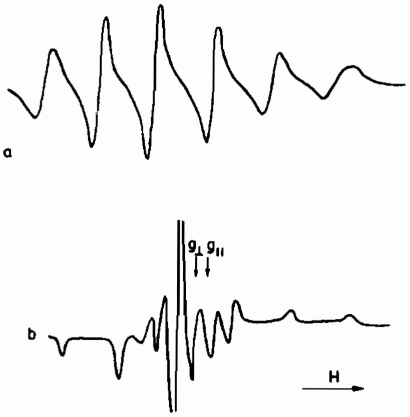


Fig. 5. EPR spectra of Mn(NO)(tox)$_2$ complex obtained in the reaction of NO with Mn(tox)$_3$. Solvent toluene. a at 235 K, b at 125 K.

Typical EPR spectra for the nitrosylmanganese complexes are given in Fig. 5.

Passing NO under the above experimental conditins, and even using five-ten times larger quantity through the solutions of differently substituted Fe-(III) and Mn(II) acetylacetonates (as well as Fe(III) oxine complexes) did not cause any detectable changes in their EPR spectra.

Discussion

Interactions with NO_2

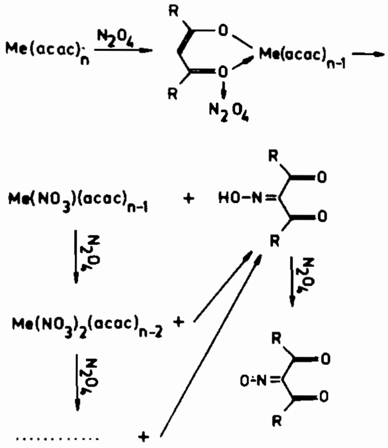
In order to explain the above results we have assumed that in the first stage of the observed interactions the most important feature is the role of the donor-acceptor properties of the reactants (NO_2 and the chelate complexes). Since NO_2 shows strong acceptor properties ($E_a^{NO_2}$ = 1.8–3.1 eV) and forms D–A complexes [8] it could be expected to attack the donor centre of the ligands. The donor properties of the ligands in the metal complexes have been investigated with respect to the formation of CT complexes [9], as well as in the interactions with some acceptor molecules [10]. Therefore, the formation of D–A complex between NO_2 and the donor centers of the ligands could be proposed to be the first step of the reaction.

The parameters of the EPR spectra obtained during the interaction between acetylacetonate complexes and NO_2 (Table I) are very close to those previously found [1, 2] and attributed to iminoxy free radicals. The data of Table I show the increasing magnitude of the nitrogen hyperfine splitting in the following order of substituents:

$$CH_3, CH_3 < CH_3, C_6H_5 < CH_3, C_{10}H_{16} < C_6H_5, C_6H_5$$

which could be associated with the mesomeric effec t of the aromatic ring. The fact that the EPR parameters of the free radicals are not influenced by the metal ion and the same radicals are obtained during the interaction of the corresponding free ligands with NO_2 indicate that the radicals are formed after destruction of the chelate complex.

The formation of D–A complex (Scheme 1) between Me(acac)$_n$ and NO_2 (at room temperature most probably N_2O_4) facilitates the electron transfer to N_2O_4. The $N_2O_4^{\cdot -}$ is decomposed in the frame of the D–A complex, and mixed-ligand Me(NO_3)-(acac)$_{n-1}$ complex and oximinoacetylacetone are the first reaction products. Further oximinoacetylacetonate is oxidized by a second molecule of N_2O_4 to give 3-$\dot{O}$N-acac iminoxy free radical, as shown in [1, 2]. Me(NO_3)(acac)$_{n-1}$ can further interact in a similar way with other N_2O_4 molecules.



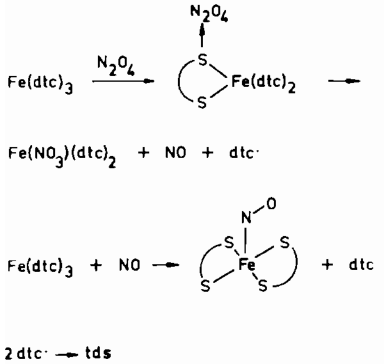
Scheme 1

It could be suggested in the frame of the above proposed mechanism, that because of the strong electron-acceptor influence of fluoro-substituted acetylacetonates, the electron density on the ligand oxygen atom is strongly decreased and therefore they are much weaker electron-donors when compared with the other acetylacetonate complexes studied. The nature of the metal ion is also important for the reaction since the corresponding fluoro-substituted copper(II) complexes interact with NO_2 [1].

The EPR parameters of the spectra recorded after passing a small amount of NO_2 through the solutions of Fe(Et$_2$-dtc)$_3$, Fe(xant)$_3$, Fe(dtp)$_3$, Fe(tox)$_3$ correspond to the mono-nitrosyliron complexes [6, 11–14]. Under the same experimental conditions, in the case of Fe(dtph)$_3$ complex two EPR spectra have been simultaneously recorded due to mono- and di-nitrosyliron complexes. It is noteworthy that no method of formation of nitrosyliron complex from iron tris-chelates and NO_2 is reported in the literature. The nitrosyl complexes of the other complexes Fe(ox)$_3$, Mn(Et$_2$-dtc)$_3$, VO(Et$_2$-dtc)$_2$ and

$Zn(dbenz\text{-}dtc)_2$ were not obtained, probably because they are unstable at room temperature.

It could be suggested (Scheme 2) that the first step of the reaction is the formation of the D–A complex



Scheme 2

with the participation of the S atoms from the chelate ligands [2, 10]. In the frame of this complex, electron transfer from the S atom to N_2O_4 takes place and as a result $Fe(NO_3)(dtc)_2$, NO and dtc$^{\cdot}$ free radical are formed. A NO molecule interacts with a second molecule of $Fe(dtc)_3$ to give $Fe(NO)(dtc)_2$ complex and dtc$^{\cdot}$ free radical.

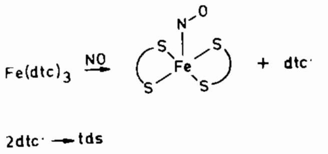
If NO_2 gas is passed through the solution after the formation of mono-nitrosyl complexes, the EPR spectra disappear which could be attributed to the formation of six-coordinated diamagnetic complex, $Fe(NO)(NO_2)(R_1,R_2\text{-}dtc)$ [15]. The presence of disulphides from the ligands have been proved by adding $Ni^{II}(dtc)_2$ complex to the solution, after removing the excess of NO_2 and filtration of the precipitate. The formation of $Ni^{III}(dtc)_3$ (known to be formed when $Ni^{II}(dtc)_2$ interacts with tiuramedisulphide [16]) was found by EPR. After the complete disappearance of nitrosyl complexes upon passing NO_2 through the solutions in all cases of Fe(III), Mn(III), VO(II) and Zn(II), complexes with (S, S), (S, N) and (N, O) chromophores yield new triplete EPR spectra of free radicals (Table III). One of the radicals with $g_o \cong 2.007$ and $a_o = 15$ G appears in all EPR spectra. The formation of more than one free radical could be attributed to the specific properties of the ligand molecules. The triple hyperfine splitting is assigned to the interaction of the unpaired electron with an N atom. Since some of the chelate ligands (dithiophosphates, dithiophosphinates, dithiocarbonates) do not contain nitrogen, it may be suggested that the nitrogen originated from NO_2. The same EPR spectra have been recorded during the interaction of the appropriate disulphides and NO_2, but the free radicals yielded in the system are less stable. Therefore, a stabilizing effect of the ligand (or part of the ligand molecule) on the recorded free radicals is observed. We propose that the EPR signal with $g_o \cong 2.007$ and $a_o = 15$ G, which is common for all spectra, is due to the ion-radical of $NO_2^{\cdot -}$ stabilized by a counter ion from the ligand. This assumption is made on the ground of the results obtained in [17], the EPR parameters being very close to those shown in Table III. The EPR spectra obtained in the interaction of some of the studied complexes with $C(NO_2)_4$ confirm this assumption (Table III). It is known that in donor-acceptor interactions $C(NO_2)_4$ forms anion-radicals [18], which are disproportionate according to the eqn. (1):

$$C(NO_2)_4 \xrightarrow{+e} C(NO_2)_4^{\cdot -} \rightarrow C(NO_2)_3^{\cdot} + NO_2^- \qquad (1)$$

Interactions with NO

It is well known that NO molecules can function as electron donors or electron acceptors [19]. Assuming that NO acts as an electron donor, it could be proposed that in the methods for preparation of the iron mononitrosyls from $Fe(dtc)_2$ and NO [6], one electron is transferred in the frame of the axial adduct between $Fe(dtc)_2$ and NO and the complex $Fe(NO)(dtc)_2$ is formed.

It is noteworthy that the method for preparation of nitrosyliron complexes with Fe(III) chelates is not known. In the case of the reaction of tris-chelate complexes a direct attack on iron could be proposed in the chelate by a small NO molecule (Scheme 3).



Scheme 3

Therefore, following the opening of the chelate ring the direct attack of NO to the metal will take place.

As it has been pointed out, Fe(III) and Mn(III) acetylacetonates and oxine complexes do not cause any detectable changes in their EPR spectra when NO has been passed through their solutions. This fact has been attributed to the high spin complexes [20].

On the Structure of the Nitrosyl Complexes formed

The studied mononitrosyliron complexes have low-spin (S = ½) ground state and $FeNO^{2+}$ molecular moiety; this moiety is the ($d_{metal} + \pi^*(NO)$) seven-electron case [6, 10–14, 21]. On the basis of the general theory [22], the M–NO group must be bent; electron population of the molecular orbitals strongly depends on the additional ligands present in the molecule. EPR parameters are listed in Table IV. The typical EPR spectra (Fig. 1) show the rhombic symmetry, but the difference between g_x and g_y is very small. If for the complexes A_{iso}^{14N} is positive, $T_{zz} = A_{\parallel} - A_{iso}$ is also positive which corresponds to positive spin density on nitrogen *p* orbital. The T_{zz} value, which is a measure of *p* electron density on nitrogen, is smallest for $Fe(NO)(tox)_2$ complex; the A_{iso} value, which is a measure of *s* electron density on nitrogen, is largest in the case of $Fe(NO)(tox)_2$ complex. These changes are related to the influence of out-of-plane π-bonding with sulphur or nitrogen. The difference between dithiocarbamate and dithiocarbonate nitrosyls is connected with the donor-acceptor properties of the ligands [10].

The A_{iso}^{57Fe} parameter increases in the order: dithiocarbonate → dithiocarbamate → thiooxine complexes. On the basis of the general properties of the isotropic contact term [22], and the studies on the parameter in the case of nitrosyl complexes [23], we can suppose that the above order is connected with decreases of the π-acceptor properties of the ligands in the same direction. The five-line isotropic spectrum shown in Fig. 4 is characteristic for iron dinitrosyls with various ligands [13, 14, 24, 25], but anisotropic parameters of the dinitrosyl complex obtained in Fe-dithiocarbonate-piperidine system are characteristic for $Fe(NO)_2$(nitrogen coordinating ligand)$_x$. In this case the complex $Fe(NO)_2(pip)_2$ may be present in the reaction mixture. The $g_z = 2.044$, $g_x = 2.013$, $g_y = 2.026$, $A_{iso}^{14N} = 2.0$ G and $|A_{iso}^{57Fe}| = 13.1$ G, $T_{zz}^{57Fe} = -14.2$ G values, especially the negative value of T_{zz}^{57Fe}, are suitable for electron configuration with unpaired electron on $d_{x^2-y^2}$ orbital [24, 25]. Dinitrosyliron complexes of this type must be six-coordinated [24, 25], and therefore the existence of $Fe(NO)_2(xant)(pip)_2$ complex is possible; the EPR parameters differ from $Fe(NO)_2(amine)_4$ complexes [25]. The substitution of the chelate ligand by NO could be proposed when the dinitrosyls are formed.

The $MnNO^{2+}$ moiety is the $(d_{metal} + \pi^*(NO))$ five-electron case and the M–NO group is linearly coordinated. The EPR spectra have axial symmetry. Similar to the investigated nitrosyliron complexes the $|A_{iso}^{55Mn}|$ parameter is the biggest in the case of thiooxine complex and the smallest for the dithiocarbonate complex. It is worthwhile noting that the unpaired electron occupies $b_2(xy)$ orbital for all the types of paramagnetic nitrosylmanganse complexes, which is confirmed by the EPR data.

References

1 W. H. Wolodarsky, J. Faniran and J. K. S. Wan, *Canad. Chem., 51,* 4072 (1973).

2 N. D. Yordanov, B. G. Zheliaskowa and V. Terziev, part I of this series, *Inorg. Chim. Acta, 00,* 000 (1982);
N. D. Yordanov, V. Terziev and D. Shopov, *Proc. XIX I.C.C.C.,* Prague, vol. II, p. 133, report A.

3 R. N Dash and D. V. R. Rao, *Ind. Chem. Soc., 52,* 1009 (1975).

4 V. Balsubramanian, N. D. Dixit and C. C. Patel, *J. Inorg. Nucl. Chem., 41,* 1221 (1979).

5 1. Mochida, K. Takeyoshi, H. Fujisu and K. Takashita, *J. Mol. Catalysis, 3,* 417 (1978).

6 N. S. Garifyanov and S. L. Luchkina, *Dokl. Akad. Nauk SSSR, 189,* 774 (1969).

7 N. S. Garifyanov, S. L. Kamenev, B. M. Kozirev and I. V. Ovchinnikov, *Dokl. Akad. Nauk SSSR, 177,* 880 (1967).

8 L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry', Holden-Bay, San Francisco, 1964.

9 A. S. Bailey, R. L. P. Williams and J. D. Wright, *J. Chem. Soc.,* 2579 (1965).

10 N. D. Yordanov, to be published.

11 B. A. Goodman, J. B. Raynor and M. C. R. Symons, *J. Chem. Soc. (A),* 2572 (1969).

12 B. Jeżowska-Trzebiatowska and A. Jezierski, *J. Mol. Struct., 46,* 197 (1978).

13 B. Jeżowska-Trzebiatowska, N. D. Yordanov, A. Jezierski and H. Kozłowski, *Inorg. Chim. Acta, 31,* 31 (1978).

14 B. Jeżowska-Trzebiatowska, A. Jezierski and H. Kozłowski, *Bull. Acad. Sci. Pol., Ser. Sci. Chem., 22,* 11 (1974).

15 D. A. Ileperuma and R. D. Feltham, *Inorg. Chem., 16,* 1876 (1977).

16 P. M. Solojenkin and N. Kopitsja, *Dokl. Akad. Nauk Tadzh. SSR, 12,* 30 (1969).

17 P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals', Elsevier, London, 1967.

18 A. Henglein and J. Jaspert, *Z. Phys. Chem., 12,* 224 (1957).

19 J. A. McCleverty, *Chem. Rev., 79,* 53 (1979).

20 N. S. Garifyanov and S. A. Luchkina, 'Stroenie Molekul i Kvantovaya Khimia', Naukova Dumka, Kiev, p. 62, 1970.

21 J. Enemark and R. D. Feltham, *Coord. Chem. Rev., 13,* 339 (1974).

22 B. R. McGarvey, *J. Phys. Chem., 71,* 51 (1967).

23 A. Jezierski, to be published.

24 A. Jezierski and B. Jeżowska-Trzebiatovska, *Nouv. J. Chem.,* in press.

25 C. C. McDonald, W. D. Phillips and H. F. Mower, *J. Am. Chem. Soc., 87,* 3319 (1965).