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Studies on the Intermolecular Interactions of Metal Chelate Complexes. III. Studies on the Interactions of Ni(II) Chelates with NO_2

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The interaction of O, N, and S containing Ni(II) chelate complexes with NO_x ($x = 1$ or 2) is reported. It was found that no reaction takes place with NO. Free iminoxy radicals from the ligands are obtained during the interaction of Ni(II) bis-β-diketonates and bis-oxine complexes with NO_2. Ni(II) bis-dithiocarbamate and dithiocarbonate complexes give the corresponding Ni(III) chelates, characterized by their EPR spectra and identified by comparing with other Ni(III) chelates prepared by well-known methods. Further, Ni(III) chelates as well as Ni(II) bis-dithiophosphate, bis-dithiophosphinate and bis-thiooxine complexes react with NO_2 to give nitrogen-containing free radicals. The final reaction product in all cases was found to be $Ni(NO_3)_2$.

Introduction

Recently we have studied [1, 2] the interactions of several metal chelate complexes with NO_x (x = 1 or 2). The intermediate and final reaction products were found to depend on the metal ion and also on the ligand.

The present communication reports the results obtained on the interaction of Ni(II) β-diketonates, oxine, thiooxine, dithiocarbamates, dithiocarbonates, dithiophosphates and dithiophosphinates with NO_x. These studies are very important, not only from an academic point of view. For example, it is well known [3], that sulphur-containing Ni(II) chelates are not involved in the acceleration of the vulcanization process of rubbers and they act as one of the best stabilizers against oxidizing agents – O_2, NO_2, O_3 [4].

In the literature there are few communications about the interaction of Ni(II) bis-dithiocarbamate [5, 6] and Ni(II) bis-dithiocarbonate [5] complexes with NO in solution. The EPR spectrum obtained [5] is attributed to Ni(NO) $(dtc)_2$ and Ni(NO)$(xant)_2$ complexes respectively. An additional evidence reported from these authors [5] to the formation of such nitrosyl complexes, is the observed absorption in the IR region at 1750 cm^{-1} in the case of Ni(NO)$(xant)_2$ complex, which is assumed to be characteristic of the NO group. The other authors [6], on the basis of elemental analysis and IR spectra, have concluded that the $Ni(dtc)_2$ complex interacts with NO forming Ni(NO)(dtc)(H_2O) mixed-ligand complex. It is found also that the complex is paramagnetic – 1.7 BM. It is worthwhile noting that the above investigations were carried out passing NO through the sample solution for a long period of time (3–6 hours).

As will be shown throughout this paper there is no evidence for the formation of $Ni(NO)L_2$ (L = dtc or xant) and Ni(NO)(dtc)(H_2O) complexes, but most probably for the formation of $Ni(III)L_3$ paramagnetic species.

Experimental

Ni(II) bis-acetylacetonato [$Ni(acac)_2$], Ni(II) bis-dibenzoylmethane [Ni(dph-acac)$_2$], Ni(II) bis-tenoyltrifluoroacetylacetonato [Ni(ttf-acac)$_2$], Ni(II) bis-hexafluoroacetylacetonato [Ni(hf-acac)$_2$], Ni(II) bis-quinolinelato [$Ni(ox)_2$], Ni(II) bis-8-quinolinethiolato [$Ni(tox)_2$], Ni(II) bis-diisopropyl-dithiophosphato [$Ni(dtp)_2$], Ni(II) bis-diphenyl-dithiophosphinato [$Ni(dtph)_2$], Ni(II) bis-R-dithiocarbonato (R = Et, Bu) [$Ni(xant)_2$], Ni(II) bis-diethyl-dithiocarbamato [$Ni(dtc)_2$] complexes were synthesized by extraction of $NiCl_2$ and the corresponding ligands and recrystallized from chloroform.

Disulphides of dithiophosphate, dithiophosphinate, thiooxine, dithiocarbamate and dithiocarbonates were synthesized by oxidation of the corresponding alkyl salts of the ligands with H_2O_2 in aqueous solution. The precipitate was recrystallized from ethanol and heptane.

NO and NO_2 were obtained as described in [1, 2]. NO was purified additionally by passing through

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TABLE I. EPR Parameters of $Ni^{III}(dtc)_3$ and $Ni^{III}(xant)_3$ Complexes. Solvent toluene.

Starting Complex	g_1	g_2	g_3	g_o	Ref.
$Ni(Et_2\text{-}dtc)_3ClO_4$	2.037	2.126	2.146		9
$Ni(Et_2\text{-}dtc)_3PF_6$	2.037	2.130	2.146		9
$Ni(Cyclohex\text{-}dtc)_3ClO_4$	2.028	2.130	2.137		9
$Ni(Bu_2^n\text{-}dtc)_3$ + ds	2.033	2.129	2.146		9
$Ni(benz\text{-}dtc)_3ClO_4$	2.033	2.125	2.141		9
$Ni(Et_2\text{-}dtc)_2$ + NO?	2.034	2.129	2.140	2.103	5
$Ni(Et_2\text{-}xant)_2$ + NO?	2.034	2.129	2.140	2.103	5
$Ni(Et_2\text{-}dtc)_2$ + ds	2.033	2.133	2.144	2.100	8
$Ni(Et_2\text{-}dtc)_2$ + NO_2	2.033	2.130	2.140	2.099	a
$Ni(Et_2\text{-}dtc)_2$ + ds	2.033	2.130	2.140	2.099	a
$Ni(R\text{-}xant)_2{}^b$ + NO_2	2.033	2.128	2.137	2.096	a
$Ni(R\text{-}xant)_2{}^b$ + ds	2.033	2.128	2.137	2.096	a

[a] This work. [b] R = Et and But.

consecutively traps filled with a toluene solution of $Cu(dtc)_2$. NO and NO_2 were passed through the solutions of Ni(II) complexes with flow rates of ~0.5 l/h.

Deoxygenation of the sample solutions was performed with repeated freezing, pumping, refreezing and saturation with argon (99.999%).

The solvents chloroform, carbontetrachloride, toluene, have been purified and dried by standard methods.

The EPR spectra have been recorded on a 3BS-X spectrometer using 100 kHz modulation of the magnetic field. The magnetic field was calibrated with Mn^{2+} in MgO. The g-values have been obtained relatively to DPPH.

The IR spectra have been recorded on UR-20 spectrometer (Carl-Zeiss, Jena) in KBr pellets or in carbon tetrachloride solution.

The electronic spectra have been recorded on Specord UV-VIS spectrophotometer (Carl-Zeiss, Jena) in carbon tetrachloride solution.

Results

Passing NO gas (purified as described in the experimental section) through the oxygen-free solutions of $Ni(acac)_2$, $Ni(dph\text{-}acac)_2$, $Ni(ttf\text{-}acac)_2$, $Ni(hf\text{-}acac)_2$, $Ni(ox)_2$, $Ni(tox)_2$, $Ni(dtp)_2$, $Ni(dtph)_2$, $Ni(dtc)_2$ and $Ni(xant)_2$ complexes for 6–8 hours did not form any paramagnetic species and did not change their electronic absorption spectra.

Passing NO_2 through the solutions of Ni(II) bis-β-diketonates and Ni(II) bis-oxine complexes for a few minutes produced strong EPR spectra of iminoxy free radicals from the ligands, as previously described [1,2,7].

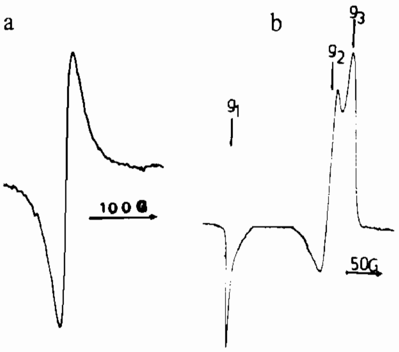


Fig. 1. Typical EPR spectra of $Ni^{III}L_3$ (L = dtc and xant). Solvent toluene. *a*. at 300 K, *b*. at 77 K.

Passing NO_2 through the solutions of $Ni^{II}(dtc)_2$ and $Ni^{II}(xant)_2$ complexes gave strong EPR spectra whose parameters are given in Table I. Typical EPR spectra at 300 and 77 K are shown in Fig. 1. Further passing NO_2 through these solutions was connected with the disappearance of these spectra, and new EPR spectra of nitrogen-containing free radicals were recorded. In the same experimental conditions $Ni^{II}(dtp)_2$, $Ni^{II}(dtph)_2$ and $Ni^{II}(tox)_2$ complexes were destroyed, yielding the free radicals already described [1,2].

The final reaction product precipitated from all the solutions has been found by elemental analysis to be $Ni(NO_3)_2$.

In order to identify the EPR spectra obtained in the reaction of $Ni^{II}(dtc)_2$ and $Ni^{II}(xant)_2$ with NO_2, we have recorded the spectra of $Ni^{III}(dtc)_3$, and

$Ni^{III}(xant)_3$ complexes, respectively, obtained by the reaction (1) [8]:

$$Ni^{II}L_2 + ds \rightleftharpoons Ni^{III}L_3 \qquad (1)$$

(where ds is the disulphide of the appropriate ligand). The EPR parameters of these spectra are given on Table I. Following reaction (1) we failed to obtain $Ni^{III}(dtp)_3$, $Ni^{III}(dtph)_3$ and $Ni^{III}(tox)_3$ complexes.

The IR spectra of $Ni^{III}(xant)_3$ formed by reaction (1), as well as by passing NO_2 and that of xanthate-disulphide itself (R = Et) have shown a weak absorption band at 1750 cm^{-1}, shifted at 1720 cm^{-1} in the $Ni^{II}(xant)_2$ complex.

Discussion

The above results have shown that Ni(II) chelate complexes do not interact with NO gas. Probably some impurities were present in the NO used by other authors [5,6].

In the reaction of Ni(II) bis-β-diketonates and oxine complexes with NO_2 the formation of free iminoxy radicals is in accordance with our previously proposed reaction scheme [1, 2], and therefore they will not be discussed here.

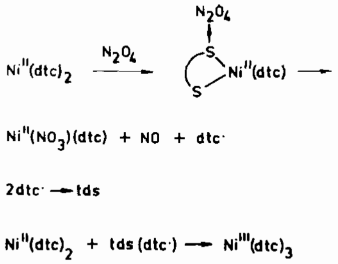
The most important part of the present studies are the results on sulphur containing Ni(II) chelates. The data shown in Table I strongly suggested the formation of $Ni^{III}(dtc)_3$ and $Ni^{III}(xant)_3$ complexes in the interaction of $Ni^{II}(dtc)_2$ and $Ni^{II}(xant)_2$ complexes with NO_2, rather than nickel nitrosyl complexes. The following arguments support this assumption:

(i) The present studies have shown that identical paramagnetic species are obtained in the reaction with NO_2 as well as following reaction (1). For comparison, the EPR parameters obtained from other authors [5, 8, 9] about $Ni^{III}(dtc)_3$ complexes are given in Table I. It is noteworthy that $Ni^{III}(xant)_2$ complex was unknown up to now.

(ii) Only $Ni^{II}(dtc)_2$ and $Ni^{II}(xant)_2$ complexes interacting with the corresponding disulphides give paramagnetic Ni^{III} species. As it has been shown $Ni^{II}(dtp)_2$, $Ni^{II}(dtph)_2$ and $Ni^{II}(tox)_2$ complexes do not interact with the corresponding disulphides and no EPR spectra have been recorded during the interactions with NO_2. These properties could be attributed to the structure of both the complex and the corresponding disulphide. It is noteworthy that metal chelate complexes from the first transition row forming the corresponding nitrosyl complexes with $Me(dtc)_n$ and $Me(xant)_n$, also give them with the $Me(dtp)_n$, $Me(dtph)_n$ and $Me(tox)_n$ complexes [1,2,10].

(iii) The appearance of the absorption band in the IR spectra at 1750 cm^{-1} of the paramagnetic species yielded in the reaction of $Ni(xant)_2$ with NO_2 could not be considered as evidence for the formation of nickel nitrosyl complex. The studies of the IR spectra of different $Me(xant)_n$ (R = Et) complexes have shown an absorption in the region 1700–1723 cm^{-1} [11]. On the other hand our IR studies on the $Ni^{III}(xant)_3$ complex and on xantate–disulphide (R = Et) have shown the appearance of the same absorption band at 1750 cm^{-1}.

In accordance with the above results and discussions, as well as with the previous papers from this series [1, 2] concerning the interaction of different metal chelate complexes with NO_2, the following reaction scheme (Scheme 1) could be proposed in the case when $Ni^{III}L_3$ chelates are formed: N_2O_4 molecule is coordinated at the S atoms from the chromophore of the complex and one electron transfer from $Ni(dtc)_2$ to N_2O_4 is realized. Furthermore, the complex $N_2O_4^{\cdot-}\cdots Ni(dtc)_2^{+}$ is destroyed with the formation of the complex $Ni^{II}(NO_3)(dtc)$, NO and dtc$^{\cdot}$ free radical. Two dtc$^{\cdot}$ molecules recombine forming thiuramedisulphide (tds). The tds molecule or dtc$^{\cdot}$ react with a second molecule of $Ni^{II}(dtc)_2$ thus forming $Ni^{III}(dtc)_3$. The same reaction scheme could be used for the formation of the $Ni^{III}(xant)_3$ complex, unknown until now.



Scheme 1

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