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Studies on the Intermolecular Interactions of Metal Chelate Complexes. I. Spectroscopic Study on the Interaction of Copper(II) Chelate Complexes with NO_x

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The interaction of $Cu(acac)_2$, $Cu(ox)_2$, $Cu(tox)_2$, $Cu(dtc)_2$ *and* $Cu(dtp)_2$ *with* NO_x $(x = 1$ *or* $2)$ *is studied by EPR and electronic spectroscopy. It is found that weak reversible adducts are formed between* $Cu(dtc)_2$, $Cu(dtp)_2$ *and* $Cu(tox)_2$ *and NO, while* NO_2 *oxidizes the ligands in all complexes. The reaction of* $Cu(dtc)_2$ *with* NO_2 *proceeds through mixed-ligand complexes with the participation of* NO_3^-. $Cu(NO_3)_2$ *and disulphides from the ligands are proved as final products from* $Cu(dtc)_2$, $Cu(dtp)_2$ *and* $Cu(tox)_2$. *Free radicals from the ligands of iminoxy type are detected in the reactions of* $Cu(ox)_2$ *and* $Cu(acac)_2$ *with* NO_2.

Introduction

Recently the interest in the interaction of NO_x, SO_x and CO_x with other molecules has increased in connection with air pollution and energetic problems. In the present paper we report the results obtained on the interaction of copper(II) acetylacetonate, oxine, thiooxine, dithiocarbamate, dithiophosphate complexes with NO_x (x = 1 or 2). Previous EPR studies on the reaction of $Cu(acac)_2$ with NO_2 [1, 2] have shown that free radicals·ON-acac are yielded with moderate stability. The only paper on Cu(II) dithiocarbamate reaction with NO [3] has proposed the formation of mixed-ligand complex of the type $Cu(dtc)NO(H_2O)$ in which NO is coordinated via the N atom to Cu(II).

Experimental

Bis(acetylacetonato)copper(II), [$Cu(acac)_2$], bis(8-hydroxiquinolinato)copper(II) [$Cu(ox)_2$], bis(8-mercaptoquinolinato)copper(II) [$Cu(tox)_2$], bis(dithiocarbamato)copper(II) [$Cu(dtc)_2$], bis(dithiophosphato)copper(II) [$Cu(dtp)_2$] were prepared by the methods described elsewhere [4] and were twice recrystallized from chloroform.

NO and NO_2 were obtained from Merck-Schuchardt. Exact amounts of NO_2 were obtained by thermal decomposition of weighed samples of $Pb(NO_3)_2$. Argon and nitrogen (99.999%) were used as inert gases.

All solvents were purified and dried by standard methods.

The EPR spectra were recorded on 3BS-X spectrometer using 100 kHz modulation of the magnetic field. The magnetic field was calibrated with Mn^{2+} doped in MgO, and g-values were obtained relatively to DPPH. The visible and UV absorption spectra were obtained on Specord UV–VIS (Carl Zeiss, Jena) spectrophotometer.

Results

Passing NO through oxygen-free solutions of $Cu(dtc)_2$ and $Cu(dtp)_2$ in toluene, and solutions of $Cu(tox)_2$ in chloroform, yielded broadening of the hyperfine lines in their EPR spectra while those of $Cu(acac)_2$ and $Cu(ox)_2$ remained unchanged under the same procedure. The EPR spectra recorded before (a) and after passing of NO (b) through the sample solution of $Cu(dtc)_2$ are shown in Fig. 1. When N_2 or Ar are passed after NO through the sample solutions the EPR spectra turn completely to the initial signals, indicating thus the removal of NO from the sample.

Passing of NO_2 for a few minutes through a 5×10^{-3} *M* solution of $Cu(dtc)_2$ in toluene yielded the EPR spectra of three copper(II) complexes, which were observed simultaneously with the initial EPR spectrum of $Cu(dtc)_2$ (Fig. 2). The EPR parameters of the spectra are:

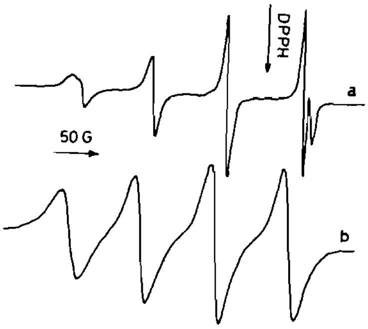


Fig. 1. EPR spectrum of Cu(dtc)$_2$ in toluene before (a) and after (b) passing of NO through the sample, T = 293 °K.

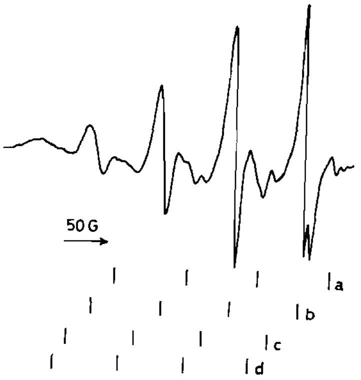


Fig. 2. EPR spectrum of Cu(dtc) in toluene after passing small amounts of NO$_2$ through the sample. T = 293 °K.

I. $g_0 = 2.046 \pm 0.001$; $A_0 = 78 \pm 2G$
II. $g_0 = 2.067 \pm 0.001$; $A_0 = 76 \pm 2G$
III. $g_0 = 2.085 \pm 0.001$; $A_0 = 75 \pm 2G$
IV. $g_0 = 2.102 \pm 0.001$; $A_0 = 80 \pm 2G$

The first of the above reported spectra corresponded to the initial Cu(dtc)$_2$ complex. The EPR spectra of other complexes were similar in shape and parameters to the spectra reported for the mixed-ligand complexes of the types CuX(dtc) (X = Cl, Br) and Cu(dtc)$^{+}\cdots$Y^{-} (Y = NO$_3$, ClO$_4$) [5]. When N$_2$ or Ar were passed through the sample solution containing all copper(II) complexes stated above (I–IV), only two of the signals remained in the spectrum: the initial EPR spectrum of Cu(dtc)$_2$—(I) and the spectrum with g_0 = 2.067 and A_0 = 76G—(II).

Attempts to record frozen solution EPR spectra (77 °K) have been unsuccessful—only a single broad line has been recorded.

When a large amount of NO$_2$ was passed through the solution the intense brown colour of Cu(dtc)$_2$ disappeared, together with the precipitation of an insoluble product. The elemental analysis of the precipitate has shown that it was Cu(NO$_3$)$_2$, yielded in the complete destruction of the copper(II) chelate.

The intense brown colour of Cu(dtc)$_2$ due to CT band at 437 nm (ϵ = 13 000) was used to study the stoichiometry of the reaction. It was found that after passing a gas sample containing 28 μg NO$_2$ through 2ml 1.5 X 10^{-4} *M* solution of Cu(dtc)$_2$ in toluene the band at 437 nm disappeared and a new absorption was noted at 400 nm. The flow rate of the gas sample was 0.1 l/min. A second portion of 28 μg NO$_2$ decolourized the Cu(II) solution. The ratio N$_2$O$_4$: Cu(dtc)$_2$ in both cases was 1:1 and 2:1 respectively. The stoichiometry of the reaction was checked by passing gas samples containing small portions of NO$_2$ in the range 10–20 μg NO$_2$ through two consecutive tubes, containing 2 ml 1.5 X 10^{-4} *M* solution of Cu(dtc)$_2$ in toluene. The absorbance of the solutions (A) was measured after every treatment with NO$_2$ and the molar parts of Cu(dtc)$_2$ evaluated by the decrease of A of the solution in the first tube were found to be 1:1 with respect to N$_2$O$_4$. In all experiments the absorbance of the solution in the second tube remained practically unchanged.

After passing NO$_2$ through 5 X 10^{-3} *M* solution of Cu(dtp)$_2$ in toluene the intensities of both the visible and EPR spectra were decreased. Gas samples containing 28 μg NO$_2$ decreased the initial absorption at 426 nm (ϵ = 13 000) of 2 ml 1.5 X 10^{-4} *M* solution from 0.390 to 0.195 (1 mm cells). The second portion of 28 μg NO$_2$ decolourized the solution. The molar parts of Cu(dtp)$_2$ evaluated by the decrease of A were 1:2 with respect to N$_2$O$_4$. The reaction proceeded without the formation of detectable amounts of mixed-ligand complexes.

Similar results were obtained about the reaction of Cu(tox)$_2$ with NO$_2$. Treating the sample with large amount of NO$_2$ yielded Cu(NO$_3$)$_2$, as in both previous reactions with Cu(dtc)$_2$ and Cu(dtp)$_2$. Disulphides (ds) from the ligand (dtc, dtp, tox) was the second reaction product in the reactions stated above. The formation of ds was proved by the addition of ascorbic acid to the final reaction solution, yielding the initial EPR spectrum of the corresponding copper(II) chelate [6].

After passing NO$_2$ for a few minutes through 5 X 10^{-4} *M* solution of Cu(ox)$_2$ in chloroform the intensity of the CT band of the complex at 410 nm was strongly increased (Fig. 3 - 2), the EPR spectrum remained practically unchanged. Further treatment with NO$_2$ yielded a new absorption series of six close bands at 315, 323, 333, 345, 357 and 371 nm and a shoulder at 390 nm (Fig. 3 - 3). A new triplet EPR spectrum appeared simultaneously with g_0 = 2.0069 ± 0.0005 and A^N = 15.7 ± 1G, probably due to the free iminoxy radical of the type 5-$^{\bullet}$ON-ox (Fig. 4).

The reaction of NO$_2$ with Cu(acac)$_2$ proceeded with the formation of the free radical 3-$^{\bullet}$ON-acac with EPR parameters equal to the published data [2]. The same absorption series as stated above appeared in the electronic absorption spectrum of the sample suggesting the same chromophore as in the free radical 5-$^{\bullet}$ON-ox.

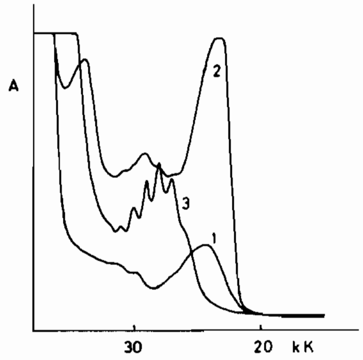


Fig. 3. Electronic absorption spectra of $Cu(ox)_2$ in chloroform before (1) and after passing small (2) and large (3) amounts of NO_2 through the sample. T = 293 °K.

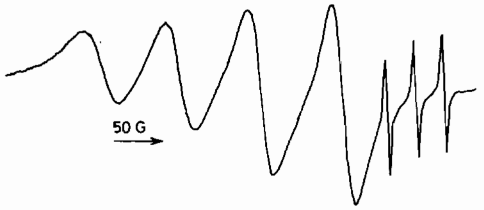
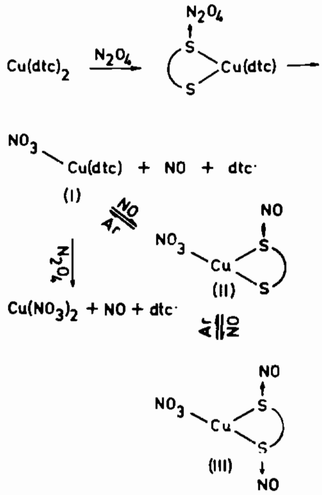


Fig. 4. EPR spectrum obtained after passing large amounts of NO_2 through a chloroform solution of $Cu(ox)_2$. T = 293 °K.

Discussion

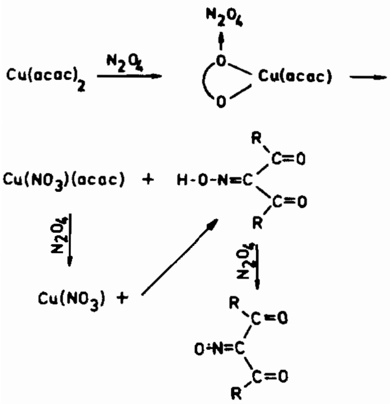
The coordination of NO to copper(II) chelates could proceed at the copper(II) ion or at the donor atom of the ligand, since NO exhibits both donor and acceptor properties. However the observed inactivity of NO towards $Cu(ox)_2$ and $Cu(acac)_2$ suggests the importance of the donor properties of the ligand atoms in the reaction. In view of this it seems that NO exhibits acceptor properties in the present reactions. The increased g-values of the new EPR spectra while the corresponding values of A^{Cu} were decreased (Fig. 1), in comparison with the initial spectra of Cu(II) complexes, confirms the assumption about adduct formation between the copper(II) complex and NO. The observed broadening of the hyperfine lines could be attributed to the fast exchange between coordinated and uncoordinated NO molecules. Therefore it can be concluded that NO forms weak reversible adducts with $Cu(dtc)_2$, $Cu(dtp)_2$ and $Cu(tox)_2$ because of its weak acceptor properties and the relatively strong donor properties of the S-atoms in the chromophore.

NO_2 exhibits strong acceptor properties ($E_a^{NO_2}$ = 1.8–3.1 eV) and forms D–A complexes with donor molecules [7]. In view of this NO_2 could be expected to attack the donor centers of the complex. The donor properties of the ligands in the metal complexes have been discussed in terms of S- (O-) atoms being the most powerful donors in them [8]. In view of this the formation of D–A complex with the participation of S- (O-) atoms is proposed as the first stage of the reaction.



The formation of D–A complex (Scheme I) between $Cu(dtc)_2$ and NO_2 (at room temperature N_2O_4) facilitates the homolytic cleavage of the Cu–S bond in this complex and the coordination of $NO_3^{\bullet}$ to copper(I). In this way a mixed-ligand complex (I in Scheme I) is formed. The EPR parameters of this complex fully coincide with those previously reported [5]. NO obtained in the reaction probably forms weak adducts (1:1 and 2:1) with the mixed-ligand complex $Cu(NO_3)(dtc)$—II and III in Scheme I, which correspond to the spectra III and IV reported in the results. The second chelate ring is opened in reaction with a second N_2O_4 molecule. The proposed reaction mechanism takes into account the stoichiometric factors of the reaction between N_2O_4 and $Cu(dtc)_2$, as well as the EPR behaviour of the system after passing NO_2 followed by N_2 or Ar. The product obtained at N_2O_4:$Cu(dtc)_2$ ratio 1:1 is the mixed-ligand complex $Cu(NO_3)(dtc)$ with light absorption at 400 nm and EPR parameters $g_0 = 2.067$ and A_0 = 76 G. Both this complex and the initial chelate $Cu(dtc)_2$ need further amounts of NO_2 to undergo the reaction. $Cu(NO_3)_2$ and ds are the main products of the reaction at a N_2O_4:$Cu(dtc)_2$ ratio 2:1.

The interaction of $Cu(acac)_2$ with N_2O_4 could be described with Scheme II. The first reaction product oximinoacetylacetone is further oxidized by N_2O_4 to give 3-·ON-acac free radical. By analogy we propose the formation of the corresponding 5-·ON-ox free radical in the oxidation of $Cu(ox)_2$ [9].



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