

Studies on the Intermolecular Interactions of Metal Chelate Complexes.

IV. EPR Study of the Interaction between the Adducts of Copper(II) Chelate Complexes and Halogen Containing Hydrocarbons

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Received November 30, 1981

The interaction between the adducts of copper(II) chelate complexes with (O_4), (O_2N_2), (N_2S_2) and (S_4) chromophores and halogen containing hydrocarbons is studied. It was found that the complexes with (N_2S_2) and (S_4) chromophores interact with halogen containing hydrocarbons only in the presence of weak Lewis bases. The mixed-ligand complex $Cu(X)(dtc)$ ($X = Cl$ or Br) was detected by the EPR method in the reaction of copper(II) bis-dithiocarbamates. In all other cases a decrease of the intensity of the typical EPR and electronic absorption spectra of the complexes was observed. CuX_2 was found to precipitate as the final reaction product. Copper(II) complexes with (O_4) and (O_2N_2) chromophores do not react with halogen-containing hydrocarbons under the above conditions – only their adducts with the Lewis bases have been detected.

Introduction

Recently we have found that the EPR spectra obtained during the reaction of copper(II) dithiocarbamates ($Cu(dtc)_2$), with strong Lewis acids like $SnCl_4$, $SbBr_3$ [1] or CuX_2 ($X = Cl, Br$) [2], show additional superhyperfine splitting (shfs) due to the interaction of the copper(II) unpaired electron with one Cl or Br nucleus. The appearance of shfs in the observed EPR spectra indicated that one Cl or Br atom was coordinated in the plane xy of the chelate and that the mixed-ligand complex $Cu(X)(dtc)$ was formed [1, 2]. On the other hand, the reaction of copper(II) dithiophosphates ($Cu(dtp)_2$) and copper(II) thiooxine ($Cu(tox)_2$) complexes with $SnCl_4$ and $SbBr_3$ was accompanied by electron transfer and the formation of disulphides from the ligands [1].

In the present paper the reaction of copper(II) chelates with weak Lewis acids like halogen-containing hydrocarbons and the influence of the Lewis bases, increasing the donor properties of copper(II) chelates is studied.

Experimental

The copper(II) chelates used in the present studies were copper(II) bis-dialkyldithiocarbamates, copper(II) bis-dialkyldithiophosphates, copper(II) bis-thiooxine, copper(II) bis-oxine ($Cu(Ox)_2$), and copper(II) bis-acetylacetonate ($Cu(acac)_2$). They were prepared and purified by the methods described previously [3].

All solvents used in the experiments (CCl_4 , $CHCl_3$, $CHBr_3$, $C_2H_4Cl_2$, $C_2H_4Br_2$, $C_2H_2Cl_4$, $n-C_4H_9Br$, benzene, toluene, hexane, etc.) were purified and dried by standard methods.

The EPR spectra were recorded on a 3BS-X spectrometer using 100 kHz magnetic field modulation. The magnetic field was calibrated with Mn^{2+} doped in MgO. The g-values were determined relative to DPPH.

The electronic absorption spectra were recorded on Specord UV-VIS spectrophotometer (Carl-Zeiss, Jena).

Results and Discussion

The EPR spectra of copper(II) chelates dissolved in halogen-containing solvents were identical to the spectra of the corresponding complexes in non-halogen containing solvents (Table I) and there were no changes with time. These results show that, in contrast to the strong Lewis acids like $SnCl_4$ and $SbBr_3$, the interaction between copper(II) chelates and halogen containing hydrocarbons must be extremely weak (if present).

Since our previous studies [4] have shown that weak Lewis bases like pyridine, quinoline, etc. form adducts along the z axis of the copper complex, thus increasing the donor properties of the equatorial ligands, we have studied the influence of the same bases on the reaction of the complexes with halogen-containing hydrocarbons.

TABLE I. EPR Parameters of Copper(II) Chelate Complexes and their Adducts (in Different Solvents) and of Mixed-Ligand Complexes Obtained during the Interaction of the Adducts with Halogen Containing Hydrocarbons.

Complex	Solvent ^a	$g_o + 0.002$	A_o^{Cu} (G)	$A_o^{shf} \pm 1G$
Cu(dtc) ₂	A, B, C	2.046	78	
	A + base	2.052	69	
	B + base	2.052	69	
		2.081	70	9.1 ^b
	C + base	2.052	69	33.0 ^c
		2.081	64	
Cu(dtp) ₂	A, B, C	2.045	74	9.5 ^d
	A, B, C + base	2.054	56	
Cu(tox) ₂	A, B, C	2.075	67	15.0 ^e
	A, B, C + base	2.080	62	
Cu(ox) ₂	A, B, C	2.107	85	11.5 ^e
	A, B, C + base	2.121	71	
Cu(acac) ₂	A, B, C	2.120	78	
	A, B, C + base	2.142	62	

^aA: hexane, heptane, octane, benzene, toluene, *etc.*; B: CCl₄, CHCl₃, C₂H₂Cl₄, C₂H₄Cl₂; C: CHBr₃, C₂H₄Br₂, C₂H₂Br₄, n-C₄H₉Br. ^bshfs from one ^{35,37}Cl nucleus. ^cshfs from one ^{79,81}Br nucleus. ^dshfs from ³¹P nuclei of dithiophosphate. ^eshfs from ¹⁴N nuclei of thiooxine or oxine.

The initial EPR spectra of Cu(dtc)₂ in C₂H₂Cl₄ and C₂H₂Br₄ in the presence of *ca.* 10⁻² M pyridine are shown on Figs. 1-b, c. (For comparison Fig. 1-a shows the EPR spectrum of Cu(dtc)₂ dissolved in C₂H₂Cl₄). It can be seen from Figs. 1-b, c that an additional shfs is observed, arising as a result of the interaction of the copper(II) unpaired electron with one Cl (Fig. 1b) or Br (Fig. 1c) nucleus. Since the unpaired electron in copper(II) chelates is located mainly on the d_{x²-y²} orbital, the observed shfs could be explained only with the coordination of one Cl or Br atom in the plane *xy* of the complex. The shape and the parameters of the EPR spectra of Fig. 1b, c and Table I are identical with those of the corresponding mixed-ligand Cu(X)(dtc) complexes reported in the previous papers [1, 2]. The appearance of shfs from halogen atoms is evidence of the reaction between Cu(dtc)₂ adduct and halogen containing hydrocarbons. The frozen solution EPR spectra contained a broad unresolved line.

When Cu(dtp)₂ and Cu(tox)₂ complexes were dissolved in halogen-containing hydrocarbons and *ca.* 10⁻² M pyridine, the intensity of their EPR and electronic absorption spectra gradually decreased without formation of any mixed-ligand complexes. The same results have been obtained about the interaction of these complexes with strong Lewis acids [1].

Cu(acac)₂ and Cu(ox)₂ complexes did not react with halogen-containing hydrocarbons and the only products were their adducts with the bases.

In all solutions of Cu(dtc)₂, Cu(dtp)₂ and Cu(tox)₂ complexes in halogen-containing hydrocarbons, and in the presence of the bases, a new

singlet EPR spectrum ($g \cong 2.15$ and $\Delta H_{pp} = 80-100$ G) appeared with time, due to one of the final reaction products which was precipitated. The elemental analysis of the precipitate was consistent with the formation of CuX₂-base complex in which the X-atom is of halogenated-hydrocarbon origin.

The other reaction product was a diamagnetic substance, soluble in nonpolar solvents but which turned resin-like very quickly, and which was thus not suitable for elemental analysis. Evidence about the formation of unstable halogen-alkyl-thioesters of the appropriate ligands arose since the chelate ring was opened in the formation of the mixed-ligand complex, [1, 2, 4], and the chelate ligand was further removed from the complex. As we have found previously [5], the disulphides from the dithiophosphates and thiooxine react with copper(I) complexes yielding the corresponding copper(II) bis-chelates Cu(dtp)₂ or Cu(tox)₂. The same reaction takes place with the thioesters from some ligands [6]. In view of this, ascorbic acid in ethanol was added to the final reaction solution in order to produce Cu(I). The reappearance of the initial EPR spectra of the reactants after the addition of ascorbic acid was a proof for the presence of disulphides or thioesters from the ligands. Furthermore, since Ni^{II}(dtc)₂ reacts with the disulphides but not with thioesters yielding the corresponding Ni^{III}(dtc)₃ [7], Ni^{II}(dtc)₂ was added to the solution after removing the precipitate. Since no Ni^{III}(dtc)₃ complex was detected by EPR, proof was obtained about the formation of thioesters from the ligands as a second reaction product.

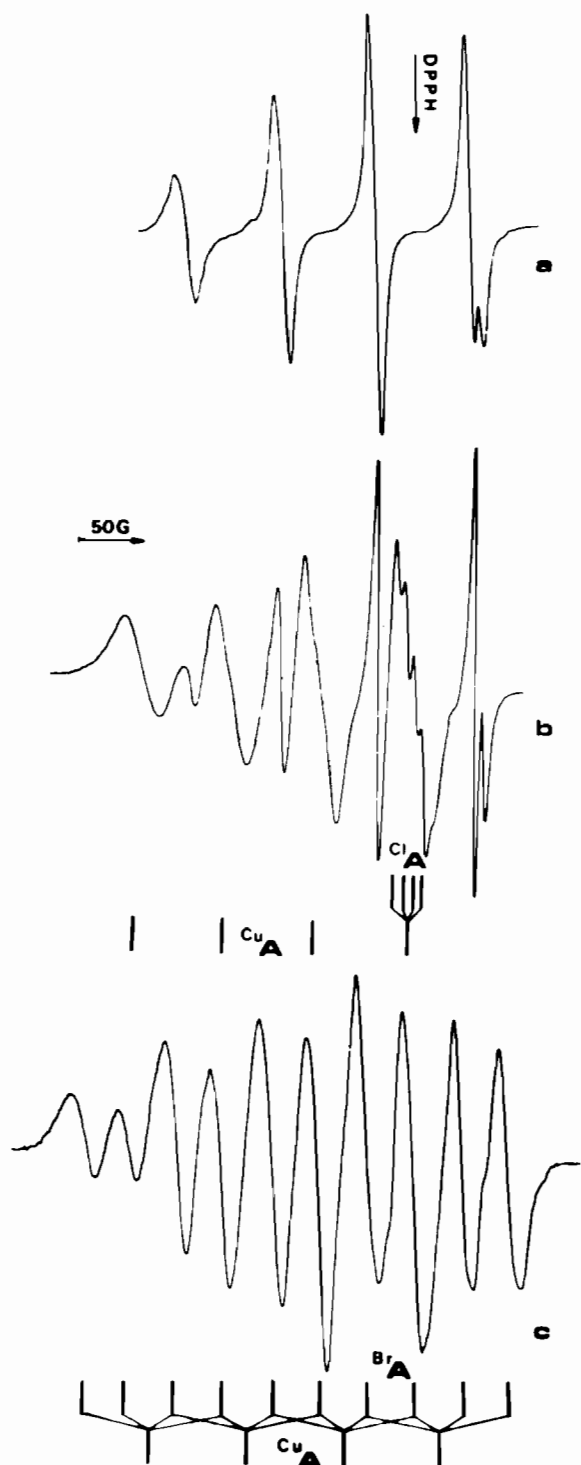
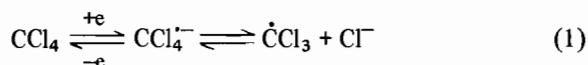


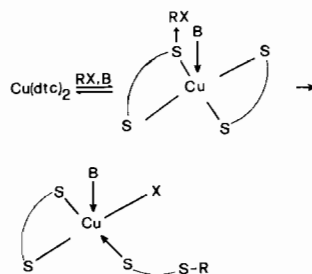
Fig. 1. Typical EPR spectra of $\text{Cu}(\text{dte})_2$ complex dissolved in: a. $\text{C}_2\text{H}_2\text{Cl}_4$, b. $\text{C}_2\text{H}_2\text{Cl}_4$ + base; c. $\text{C}_2\text{H}_2\text{Br}_4$ + base. $T = 300 \text{ K}$.

Halogen-containing hydrocarbons are weak acceptors [8], and as a result of donor-acceptor interactions they could be destroyed according to eqn. (1):



Evidence for the above reaction (eqn. 1) was found [8, 9] during the formation of CT complexes [8], and in the interaction with some metal complexes [8c, d, f, 9b].

In order to verify the present mechanism the reaction was carried out in methylmethacrylate, *p*-nitroso-aniline, 1,1-diphenyl-2-picrilhydrazine. It is known that the destruction of halogen-paraffins by metal complexes is accompanied by the polymerization of methylmethacrylate [9]. The formation of stable free radicals could be expected in both the other cases. A secondary evidence for radical reaction is the formation of halogen-paraffins with less than the initial X/C ratio [7b, 10]. However, neither the gas-chromatographic measurements succeeded in detecting such halogen-paraffins, nor did the other experiments confirm the free radical formation. In view of this the conclusion was made that the reaction proceeded *via* intramolecular electron transfer in the complex among the Lewis acid-CuL₂-Lewis base. (The ionic mechanism was rejected because of the low polarity of the reaction medium.) Therefore, the first step of the intramolecular interaction of Lewis acids and bases with copper(II) chelate complex can be represented according to scheme 1:



The above reaction is possible since the axial coordination of bases decreases the covalency of the L-M bonds, thus expanding and causing a distortion of the complex in the equatorial plane of CuL₂ molecule. The donor properties of S atom in the chelate ligands are increased as a result of this effect.

For $\text{Cu}(\text{acac})_2$ complexes however, the most powerful donor point is located at the γ -carbon atom of the ligand [11], and for $\text{Cu}(\text{ox})_2$ at the 5-C atom of the aromatic system [12]. Thus, in both complexes the distance between the donor and acceptor centers is larger than in $\text{Cu}(\text{dte})_2$, $\text{Cu}(\text{dtp})_2$, $\text{Cu}(\text{tox})_2$ complexes, and the effect of adduct formation could not change considerably the electron density at these atoms.

A possible alternative explanation is that halogen containing hydrocarbons may form weak molecular

complexes with some bases, e.g. pyridine [8c]. The formations of the complex facilitate the orientation of the donor and acceptor molecules in such a way as to allow the redox reaction to proceed.

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