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Effect of alcohols on the photochemical reaction of bis(*N,N'*-diethyldithiocarbamato)copper(II) in $CHCl_3$

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Abstract

Bis(*N,N'*-diethyldithiocarbamato)copper(II) ($Cu(Et_2dtc)_2$) is initially photoreduced to Cu^I within its donor–acceptor (DA) complex with $CHCl_3$ and the quantum yields obtained are independent of the composition of the $CHCl_3$–EtOH solvent mixture. Two intermediate copper(II) complexes are subsequently formed in equilibrium, in a dark reaction of the primary photoproduct with $CHCl_3$, when $Cu(Et_2dtc)_2$ photolysis is carried out in $CHCl_3$–EtOH (150:1 to 50:1). These are the monomeric species $Cu^{II}(Et_2dtc)Cl$ and its chloride-bridged dimeric form $Cu_2(Et_2dtc)_2Cl_2$. The latter is the only intermediate Cu^{II} complex obtained in pure $CHCl_3$. A reaction mechanism is proposed and the role of alcohol is discussed from a combined analysis of spectrophotometric and electron paramagnetic resonance (EPR) data.

Keywords: Photochemical reaction; $Cu(dtc)_2$; $CHCl_3$

1. Introduction

This work is a continuation of our studies on the charge transfer photochemistry of Cu^{II} bis-chelates containing the CuS_4 chromophore. In a recent paper [1], we described the photochemical behaviour of bis(*N,N'*-diethyldithiocarbamato)copper(II) ($Cu(Et_2dtc)_2$) and bis(diisopropyldithiophosphato)copper(II) ($Cu(dtp)_2$) in aprotic solvents. In this study, we report the data obtained on irradiation of $Cu(Et_2dtc)_2$ in the presence of small amounts of alcohol in $CHCl_3$. The following areas are investigated: (a) the intermediates obtained during the photolysis of $Cu(Et_2dtc)_2$; (b) the changes in the reaction mechanism which occur on addition of small amounts of ethanol (EtOH) or isopropanol (i-PrOH) to the solvent; (c) a clear explanation of the change in mechanism.

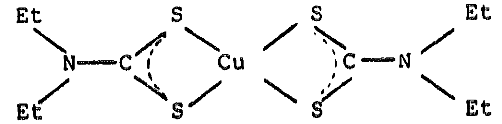
2. Experimental details

2.1. Materials

The ligand $NaEt_2dtc$ was obtained from Merck and was used as received. The solvents were used after distillation. $CHCl_3$ was washed thoroughly with bidistilled water and dried over Na_2SO_4 before use.

2.2. Preparation of the compounds

The complex $Cu(Et_2dtc)_2$



was prepared by mixing aqueous solutions of $CuCl_2$ and the sodium salt of the ligand. The precipitate formed was separated, washed with bidistilled water, dried and twice recrystallized by dissolution in $CHCl_3$, filtration and partial evaporation in air to induce precipitation. The purity of the $Cu(Et_2dtc)_2$ complex thus obtained was checked by elemental analysis. Analysis (%): calculated for $CuC_{10}N_2H_{20}S_4$: Cu, 17.6; C, 33.3; N, 7.8; S, 33.6; H, 5.5; found: Cu, 18.0; C, 33; N, 7.5; S, 33.4; H, 5.3.

2.3. Instrumentation

The electronic absorption spectra were obtained on a Specord UV–visible (Carl Zeiss, Jena) spectrophotometer using quartz cells to record in the 250–750 nm region. The electron paramagnetic resonance (EPR) spectra were recorded at room temperature on an X-band Bruker ER 200D-SRC spectrometer using 100 kHz modulation of the magnetic field.

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2.4. Photolysis experiments

Photolysis experiments were performed with a 250 W medium-pressure mercury lamp as described previously [1]. The sample was irradiated with the full spectrum of the lamp or through 254, 313 and 436 nm solution filters [2] for irradiation at selected wavelengths. The light intensity was measured by a ferrioxalate actinometric method [3]. In all photolysis experiments, the concentrations of the reactant and products were monitored throughout the reaction by recording the EPR spectra directly in the photolysis cell or by removing aliquots periodically to record the UV–visible absorption.

3. Results and discussion

The most interesting feature of the electronic spectrum of $Cu(Et_2dtc)_2$ is the intense visible band [4] at 437 nm (ϵ = 13 000 dm^3 mol^{-1} cm^{-1}) due to the equatorial ligand-to-metal charge transfer (LMCT) transition involving the CS_2 group bound to copper.

The complex also exhibits ligand-centred π–π^* transitions at higher energy giving rise to UV absorptions at 273 nm (ϵ = 33 000 dm^3 mol^{-1} cm^{-1}) and 290 nm (ϵ = 20 000 dm^3 mol^{-1} cm^{-1}) [5]. The EPR parameters of $Cu(Et_2dtc)_2$ obtained at 20 °C in $CHCl_3$ ($g_0 = 2.049 \pm 0.003$, $a(^{63}Cu) = 79 \pm 2$ G) are in good agreement with the previously reported values [6].

3.1. Photoreduction of $Cu(Et_2dtc)_2$ in $CHCl_3$–EtOH (150:1)

The visible charge transfer absorption of $Cu(Et_2dtc)_2$ in $CHCl_3$–EtOH (150:1) gradually decreases on irradiation, with the consecutive appearance of two isosbestic points at 408 nm and 370 nm (Fig. 1). The spectral changes are similar to those previously reported for the formation of an intermediate mixed-ligand complex $Cu^{II}(Et_2dtc)Cl$ as photoproduct (λ_{max} = 406 nm) [1] during the irradiation of $Cu(Et_2dtc)_2$ in chloroalkane–EtOH mixed solvent (9:1 to 3:7). Under the same experimental conditions, the intensity of the initial EPR spectrum of $Cu(Et_2dtc)_2$ decreases (Fig. 2) following the reduction of Cu^{II} to Cu^{I}, and a low intensity EPR signal of $Cu^{II}(Et_2dtc)Cl$ [1] appears as an intermediate. The typical spectral difference here is the new absorption band at 350 nm which increases with irradiation. In a separate experiment (Fig. 3), it was established that this disappears after longer irradiation times (340 s) to give a nearly colourless solution. The appearance of the second isosbestic point at 370 nm indicates that $Cu^{II}(Et_2dtc)Cl$ is smoothly converted into a second intermediate (λ_{max} = 350 nm) which disappears on further irradiation. These observations suggest the same photochemical process as the primary step for both intermediates; moreover, the original spectrum is partly restored when the irradiated solutions are kept for 24 h in the dark.

3.2. Photoreduction of $Cu(Et_2dtc)_2$ in pure $CHCl_3$

Irradiation of $Cu(Et_2dtc)_2$ solution in pure $CHCl_3$ results in a gradual decrease in intensity of the initial EPR spectrum

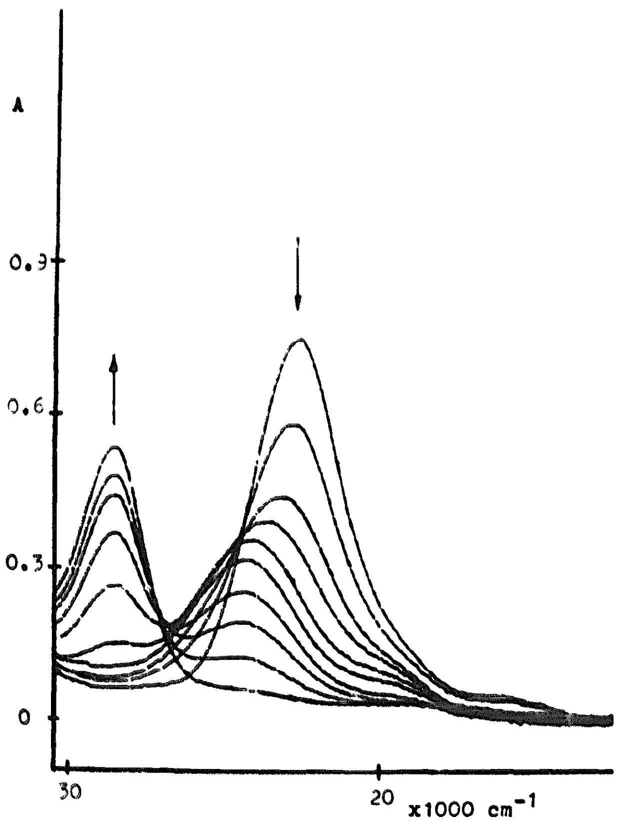


Fig. 1. Visible absorption spectra taken before and after consecutive 10–160 s UV irradiation of 5.7×10^{-5} M $Cu(Et_2dtc)_2$ in $CHCl_3$–EtOH (150:1).

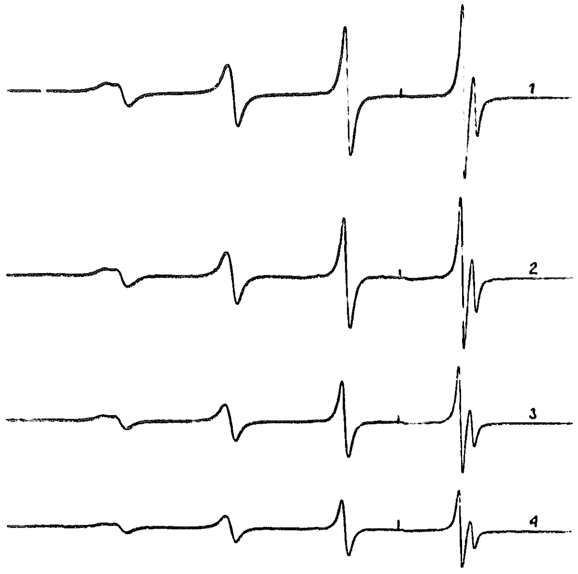


Fig. 2. EPR spectra taken before (1) and after consecutive 15 s (2), 30 s (3) and 60 s (4) UV irradiation of a 1×10^{-3} M solution of $Cu(Et_2dtc)_2$ in $CHCl_3$–EtOH (150:1).

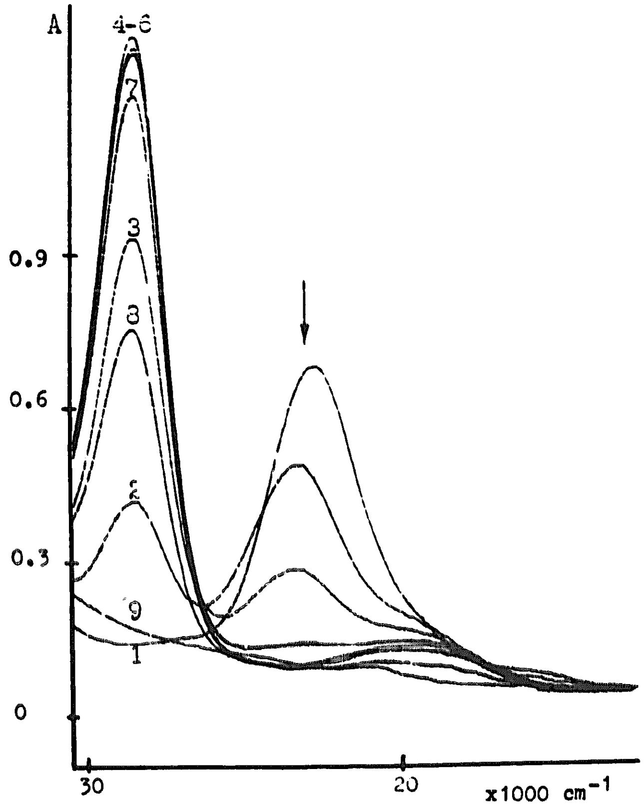


Fig. 3. Visible absorption spectra taken before (1) and after consecutive 30 s (2), 60 s (3), 90 s (4), 100 s (5), 130 s (6), 160 s (7), 220 s (8) and 340 s (9) UV irradiation of 5.2×10^{-5} M $Cu(Et_2dtc)_2$ in pure $CHCl_3$.

of $Cu(Et_2dtc)_2$ and the visible charge transfer band at 437 nm, with a corresponding strong increase in absorption at 350 nm (Fig. 3), but without any distinctive isosbestic point or intermediate EPR signal. It seems from the data obtained that the conditions in pure $CHCl_3$ are not favourable for the formation of the mixed-ligand $Cu^{II}(Et_2dtc)Cl$ complex as an intermediate. Attempts to measure the EPR of the second intermediate ($\lambda_{max} = 350$ nm) in the experimental conditions corresponding to its maximum concentration suggest that it is essentially diamagnetic. When irradiated solutions containing this product were kept for 24 h in the dark, and the absorption spectra were then measured again, the spectra obtained clearly showed that the photoreduction was partly reversible due to a backward dark reaction which yielded the initial $Cu(Et_2dtc)_2$ complex.

3.3. Photoreduction of $Cu(Et_2dtc)_2$ in $CHCl_3$–EtOH (10:1 and 50:1)

In contrast with the previous experiments (illustrated by Figs. 1 and 3), on irradiation in $CHCl_3$–EtOH (10:1), the electronic absorption changes in the visible part of the spectrum (Fig. 4) only reveal the formation of the intermediate $Cu^{II}(Et_2dtc)Cl$ ($\lambda_{max} = 406$ nm). In $CHCl_3$–EtOH (50:1), the time course of the reaction clearly shows the decay of the initial $Cu(Et_2dtc)_2$ band at 437 nm through the intermediate $Cu^{II}(Et_2dtc)Cl$ band at 406 nm with the appearance of a new band at 350 nm with a very low intensity. Therefore irradiation in solvent mixtures of $CHCl_3$–EtOH > 50:1 seems to be favourable for the appearance of the 350 nm absorption in photolysis.

The 282 nm absorption in Fig. 4 due to the appearance of tetraethylthiuramdisulphide [7,8] is typical of the UV spectral changes in all the experiments. Therefore the changes in the electronic and EPR spectra are fully consistent with the photolysis products Cu^{I} and tetraethylthiuramdisulphide.

3.4. Photoreduction of $Cu(Et_2dtc)_2$ in $CHCl_3$–i-PrOH (15:1)

Fig. 5 illustrates the electronic absorption spectral changes on irradiation of $Cu(Et_2dtc)_2$ in a $CHCl_3$–i-PrOH (15:1) solvent mixture. This experiment was performed in order to determine the effect of other alcohols on the processes following the photoreduction of $Cu(Et_2dtc)_2$. The data in Fig. 5 are similar to the spectral changes observed in Fig. 1 for the $CHCl_3$–EtOH mixture (150:1).

3.5. Quantum yields

The absorbance of the charge transfer band decreases linearly for the first 15–20 min of 254, 313 and 436 nm irradiation, indicating that the photoreduction process follows zero-order kinetics. Thus we can calculate the photoreduction quantum yields (ϕ_{red}) for all the solvent compositions used. The results (Table 1) show that the ϕ_{red} values of $Cu(Et_2dtc)_2$ obtained in $CHCl_3$–EtOH mixtures (150:1 and 10:1) are no different from those obtained in pure $CHCl_3$. This suggests that EtOH has no influence on the redox reactivity of the LMCT excited state responsible for the photoreduction of Cu^{II} to Cu^{I} and does not participate in the primary photoprocess. This conclusion differs from recent investigations on the Fe^{III} porphyrin-catalysed photoreduction of CCl_4 by EtOH [9], in which the primary photoprocess involves intramolecular electron transfer from the axially coordinated EtOH to iron, leading to the reduction of Fe^{III} to Fe^{II} and the formation of a free EtOH radical.

Special experiments carried out with different initial concentrations of the irradiated $Cu(Et_2dtc)_2$ complex (1×10^{-5} to 1×10^{-4} M) give concentration-independent ϕ_{red} values.

3.6. Mechanism

According to the recently proposed mechanism [1] of $Cu(Et_2dtc)_2$ charge transfer photolysis, the primary photoproduct is formed by photoinduced electron transfer from an equatorially bound S atom of Et_2dtc to copper. The intramolecular character of the photoelectron transfer is supported by the observed independence of the quantum yields on the initial concentration of the irradiated complex. Once formed, $Cu^{I}(Et_2dtc)$ is further oxidized by $CHCl_3$ [1,10] to give $Cu^{II}(Et_2dtc)Cl$.

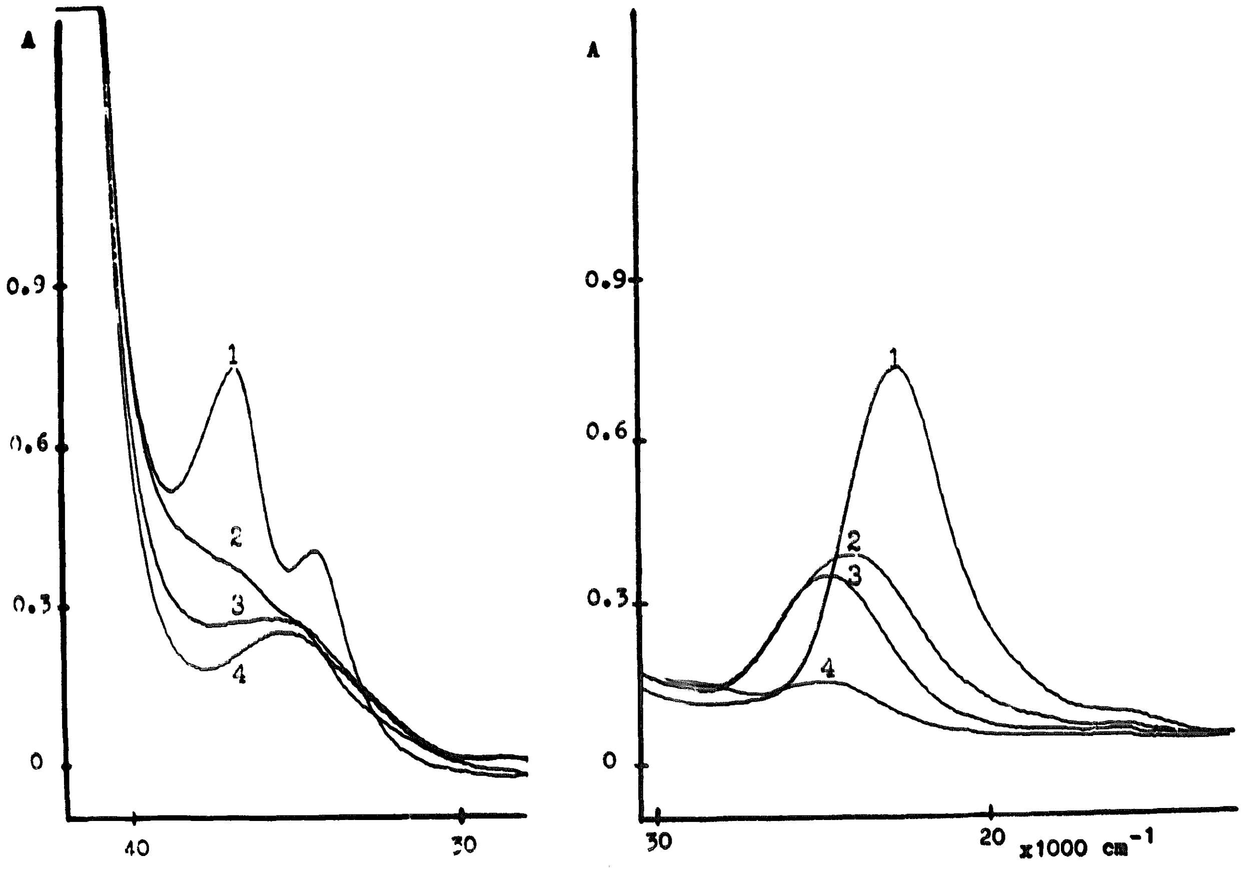
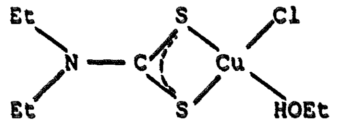


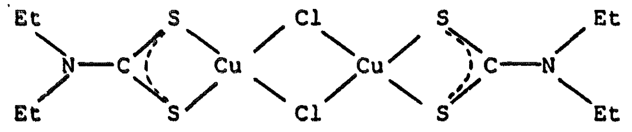
Fig. 4. UV–visible absorption spectra taken before (1) and after consecutive 20 s (2), 60 s (3) and 120 s (4) UV irradiation of $Cu(Et_2dtc)_2$ in $CHCl_3$–EtOH (10:1).

An important conclusion of the present study is that the intermediate complex $Cu^{II}(Et_2dtc)Cl$ cannot be obtained in the absence of EtOH, and its formation occurs via coordination of an EtOH molecule in the plane *xy* giving rise to the species



The stabilizing effect of EtOH on the complex $Cu^{II}(Et_2dtc)Cl$ is made evident by the failure to obtain this intermediate on irradiation of $Cu(Et_2dtc)_2$ in pure $CHCl_3$ (Fig. 3). In the experiments in which a $CHCl_3$–EtOH (150:1) mixture is used as solvent (Fig. 1), the molar ratio of EtOH to $Cu(Et_2dtc)_2$ is 1400:1 ([complex] $=5.7\times10^{-5}$ M). Under these conditions, there seems to be sufficient EtOH to coordinate and stabilize $Cu^{II}(Et_2dtc)X$. In the presence of i-PrOH, the same favourable conditions (Fig. 5) are obtained at an i-PrOH to $Cu(Et_2dtc)_2$ ratio of 9000:1 because of the weaker coordinating properties of i-PrOH in comparison with EtOH.

In view of the above considerations, the EPR silence of the intermediate product ($\lambda_{max}=350$ nm) obtained in the absence of EtOH can be explained by the formation of a dimeric species with two chloride bridging ligands



Halide- or pseudo-halide-bridged dimeric structures are well known for Cu^{II} [11,12] and are thought to be the reason for the failure to obtain EPR spectra of $Cu^{II}(Et_2dtc)Cl$ in the solid state [13]. When photolysis is carried out in pure $CHCl_3$, the dimeric complex $Cu_2(Et_2dtc)_2Cl_2$ is the only observed intermediate product (Fig. 3) and is characterized by antiferromagnetic properties and visible absorption at 350 nm. However, on addition of small portions of EtOH to a freshly photolysed solution containing this product, the features of the monomeric species $Cu^{II}(Et_2dtc)Cl$ appear in solution. Moreover, when photolysis is carried out in mixed $CHCl_3$–EtOH solvent, the lower the EtOH content in the mixture, the higher the $Cu_2(Et_2dtc)_2Cl_2$ yield.

A reaction mechanism which fits the experimental results is given in Scheme 1. The primary photoprocess proceeds within the donor–acceptor (DA) complex between copper(II) dithiocarbamate and $CHCl_3$. The formation of this complex has been deduced in previous studies [14] on reactions between $Cu(dtc)_2$ adducts and halocarbons. Because of the weak electron acceptor properties of the $CHCl_3$ molecule, it is assumed to coordinate to the sulphur atoms of

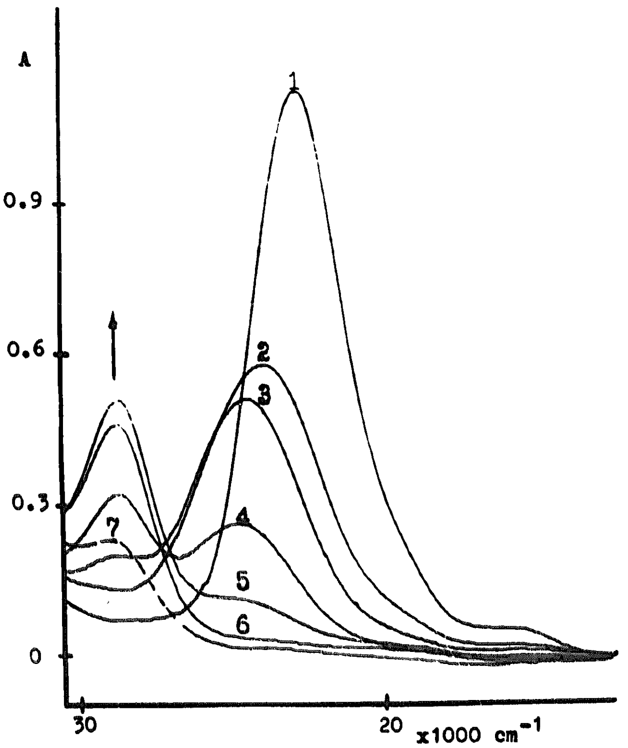


Fig. 5. Visible absorption spectra taken before (1) and after consecutive 15 s (2), 25 s (3), 45 s (4), 55 s (5), 65 s (6) and 75 s (7) UV irradiation of 8.6×10^{-5} M $Cu(Et_2dtc)_2$ in $CHCl_3$–i-PrOH (15:1).

Table 1
Quantum yields ($\phi_{red}\times10^2$ mol einstein^{-1}) of $Cu(Et_2dtc)_2$ photolysis in different $CHCl_3$–EtOH solvent mixtures

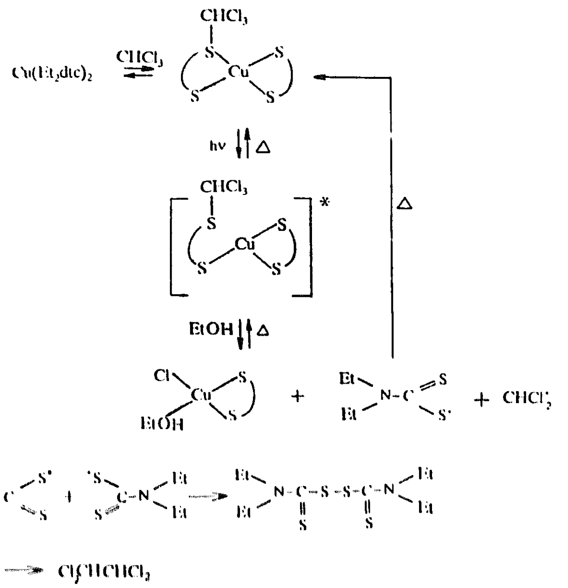
Solvent	λ_{irr} (nm)		
	254	313	436 [a]
Pure $CHCl_3$	2.6	2.4	0.3
$CHCl_3$–EtOH (150:1)	3.6	3.0	0.4
$CHCl_3$–EtOH (10:1)	3.3	2.4	0.2

[a] The order of magnitude for 436 nm photolysis has been reported previously [1] as 10^{-2} instead of the correct value of 10^{-3}.

$Cu(Et_2dtc)_2$ in a similar manner to the ENDOR detected $CHCl_3$ adduct of $Cu(dtp)_2$ [15,16]. In view of this, the oxidation of the primary photoproduct $Cu^I(Et_2dtc)$ by $CHCl_3$ may be considered to take place within the DA complex. Tetraethylthiuramdisulphide, detected in all experiments by its UV absorption at 282 nm (Fig. 4), is obtained by free dtc$^•$ radical recombination.

4. Conclusions

On irradiation in mixed $CHCl_3$–EtOH solvent, the photoreduction of $Cu(Et_2dtc)_2$ proceeds within its DA complex with $CHCl_3$, and the primary photoproduct is further oxidized in a dark reaction with $CHCl_3$ producing the corresponding mixed-ligand monomeric $Cu^{II}(Et_2dtc)Cl$ complex (λ_{max} = 406 nm) and/or the chloride-bridged dimeric $Cu_2(Et_2dtc)_2Cl_2$ complex (λ_{max} = 350 nm). The formation of the monomeric species occurs by coordination of an EtOH molecule in the *xy* plane of the complex. The results obtained indicate that EtOH does not take part in the primary photoreduction of $Cu(Et_2dtc)_2$ or reduction of $CHCl_3$ by the primary photoproduct.



Scheme 1.

Acknowledgements

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