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Charge-transfer photochemistry of the ternary complex (dithiocarbamato, dithiophosphato)copper(II)

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Abstract—The mixed ligand complex Cu(dtc)(dtp) where dtc is diethyldithiocarbamate and dtp is diisopropyldithiophosphate has been studied in air-saturated acetone, toluene and chloroalkane ($CHCl_3$ and CCl_4) solutions. The results obtained by EPR and UV–vis absorption together with quantum yield data about the photochemical behaviour of the complex Cu(dtc)(dtp) indicate that a homolytic Cu—S bond cleavage involving the dtp ligand appears as the primary photoprocess. The observed strong solvent effect on the conversion of the primary photoproduct $Cu^I(Et_2dtc)$ is discussed in terms of specific donor-acceptor interaction and coordination. A reaction mechanism is proposed to fit the experimental results. © 1997 Elsevier Science Ltd

Keywords: CT photochemistry; copper(II)dithiophosphate; dithiocarbamate; ternary complex.

In a recent paper we have described the photochemical behaviour of bis(diethyldithiocarbamato)Cu^{II}–$Cu(Et_2dtc)_2$ and bis(diisopropyldithiophosphato)Cu^{II}–$Cu(i\text{-}Pr_2dtp)_2$ in aprotic solvents [1]. The results obtained show that the primary photochemical act in both complexes is an intramolecular electron transfer from the equatorially bound S atom of the ligand to copper(II) yielding the corresponding complex of copper(I) and the free radical from the ligand. Further reactions of the primary photoproducts are related to the redox properties of both ligands and solvents [1].

We now report the data obtained about the photochemical properties of the ternary Cu(dtc)(dtp) complex obtained with ligands of similar but chemically different donor sets as a part of our study on the photochemistry of complexes with the chromophore CuS_4.
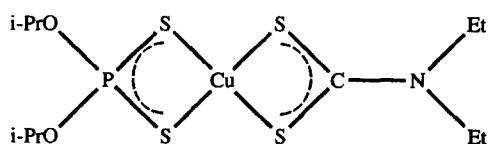

EXPERIMENTAL

Starting materials

The ligand $NaEt_2dtc$ and p.a. grade $CuCl_2 \cdot 2H_2O$ were obtained from Fluka and were used without further purification. Diisopropyldithiophosphoric acid and its sodium salt were prepared as previously described [2]. The solvents were used after distillation.

Preparation of the coordination compounds

The pure parent complexes $Cu(Et_2dtc)_2$ and $Cu(i\text{-}Pr_2dtp)_2$ were prepared by standard literature methods [1]. The mixed ligand Cu(dtc)(dtp) complex was obtained according to the reaction:

$$Cu(Et_2dtc)_2 + Cu(i\text{-}Pr_2dtp)_2 = 2\,Cu(dtc)(dtp) \quad (1)$$
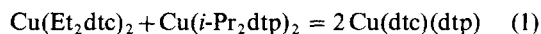
by mixing the corresponding equimolar solutions of $Cu(Et_2dtc)_2$ and $Cu(i\text{-}Pr_2dtp)_2$ to obtain Cu : dtc : dtp = 1 : 1 : 1. The initial solutions of the parent complexes were prepared by weighing and dissolution of the appropriate amounts.

Instrumentation

The EPR spectra were taken on an X-band BRUKER ER 200D-SRC spectrometer using 100

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kHz modulation of the magnetic field. The electronic absorption spectra were recorded on a SPECORD UV–vis (Jena) spectrophotometer using quartz cells to record in the 250–750 nm region.

Irradiation and quantum yields

Photolysis experiments were performed with the full spectrum of a 250 W medium-pressure mercury lamp or through a 436 nm solution filter [3] as previously described [4]. For quantum yield determination the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to measure the quantum yield of the primary photoprocess. No correction was made for internal filter effects. The absorption values at the visible LMCT band were used to determine the concentration change of the complex during the photolysis. The incident light intensity was determined immediately after each photolysis by a ferrioxalate actinometric method [3]. At least three determinations of quantum yields were made for each complex. Photolyses of all complexes were carried out at $25 \pm 1°C$. The accuracy of the quantum yield measurements was found to be within 20–25%. The previously reported [5,6] 'self-redox' behaviour of $Cu(i\text{-}Pr_2dtp)_2$ made its quantum yield data subject to higher error. Photolysis reactions were also monitored by measuring the UV–vis and EPR spectra directly in the photolysis cell or by removing aliquots at various intervals to record UV–vis absorption.

RESULTS AND DISCUSSION

UV–vis spectra of Cu(dtc)(dtp)

The UV–vis spectrum of the mixed ligand Cu(dtc)(dtp) complex is dominated by two main absorptions in the regions 260–300 nm and 430 nm in $CHCl_3$. The first band could be ascribed to the intraligand dtc transitions since the spectrum of the non-coordinated Et_2dtc anion consists of two bands at 273 nm ($\varepsilon = 33{,}000$ dm^3 mol^{-1} cm^{-1}) and 290 nm ($\varepsilon = 20{,}000$ dm^3 mol^{-1} cm^{-1}) respectively [7], similar to those observed in the complex, while the non-coordinated $i\text{-}Pr_2dtp^-$ anion exhibits only a very low intensity band at about 350 nm. The visible absorption of Cu(dtc)(dtp) at 430 nm is due to the strongly allowed ligand to metal charge transfer (LMCT) band having a log ε value ~ 4.1 which appears in $CHCl_3$ solutions of the parent $Cu(Et_2dtc)_2$ at 435 nm ($\varepsilon = 13{,}000$ dm^3 mol^{-1} cm^{-1}) as well as at 420 nm in the corresponding $Cu(i\text{-}Pr_2dtp)_2$ solutions with $\varepsilon = 6350$ dm^3 mol^{-1} cm^{-1} in the 5×10^{-5}–5×10^{-4} mol dm^{-3} range, gradually decreasing at higher $Cu(i\text{-}Pr_2dtp)_2$ concentrations [5,6]. The electronic spectrum of Cu(dtc)(dtp) in all other solvents used exhibits only

Table 1. LMCT absorption of Cu(dtc)(dtp) and of the parent $Cu(Et_2dtc)_2$ and $Cu(i\text{-}Pr_2dtp)_2$ in different solvents

Complex solvent	Cu(dtc)(dtp) (nm)	$Cu(Et_2dtc)_2$ (nm)	$Cu(i\text{-}Pr_2dtp)_2$ (nm)
Acetone	426	432	417
Toluene	429	435	420
CCl_4	428	433	420
$CHCl_3$	429	435	420

the visible LMCT absorption at about 430 nm (Table 1) because of their strong absorption in the UV region.

EPR spectra of Cu(dtc)(dtp)

The EPR parameters of Cu(dtc)(dtp) listed in Table 2 agree well with those previously reported [8]. The most significant feature of the EPR spectrum of Cu(dtc)(dtp) are the ^{31}P satellites in the relative intensities expected for one coordinated dtp ligand (Fig. 1). The value of ^{31}P shfs in the spectra of the mixed ligand complex is lower compared to that of the parent $Cu(i\text{-}Pr_2dtp)_2$ [9]. Although the chromophore is the same, changes in the electron density of the donor atoms can have a noticeable effect decreasing the covalency of the coordinate bond.

Only the hyperfine lines of Cu(dtc)(dtp) are seen in Fig. 1 indicating a quantitative ligand exchange between $Cu(Et_2dtc)_2$ and $Cu(i\text{-}Pr_2dtp)_2$ in their equimolar mixtures in acetone, toluene, $CHCl_3$ and CCl_4 to yield exclusively Cu(dtc)(dtp) in reaction (1).

Solutions of Cu(dtc)(dtp) in acetone, toluene and chloroalkanes could be kept for several days in the dark without any changes in their UV–vis and EPR spectra. The complex undergoes photolysis when irradiated with UV or visible light of $\lambda < 440$ nm. In general, the irradiation produces a colour change in solution, accompanied by changes in their UV–vis and EPR absorption.

Photoreduction of Cu(dtc)(dtp) *in acetone*

The EPR spectral changes obtained upon photoirradiation of air-saturated 1×10^{-3} mol dm^{-3} acetone

Table 2. EPR parameters of the ternary complex Cu(dtc)(dtp) obtained in the reaction of $Cu(Et_2dtc)_2$ with $Cu(i\text{-}Pr_2dtp)_2$ (1 : 1) in acetone, toluene and chloroalkanes ($CHCl_3$ and CCl_4), 300 K

Solvent	g_0 (± 0.001)	$^{Cu}A_0$ ($\pm 1G$)	$^{P}A_0$ ($\pm 0.5G$)
Acetone	2.044	77	7.0
Toluene	2.044	77	7.3
CCl_4	2.044	77	7.3
$CHCl_3$	2.045	77	7.4
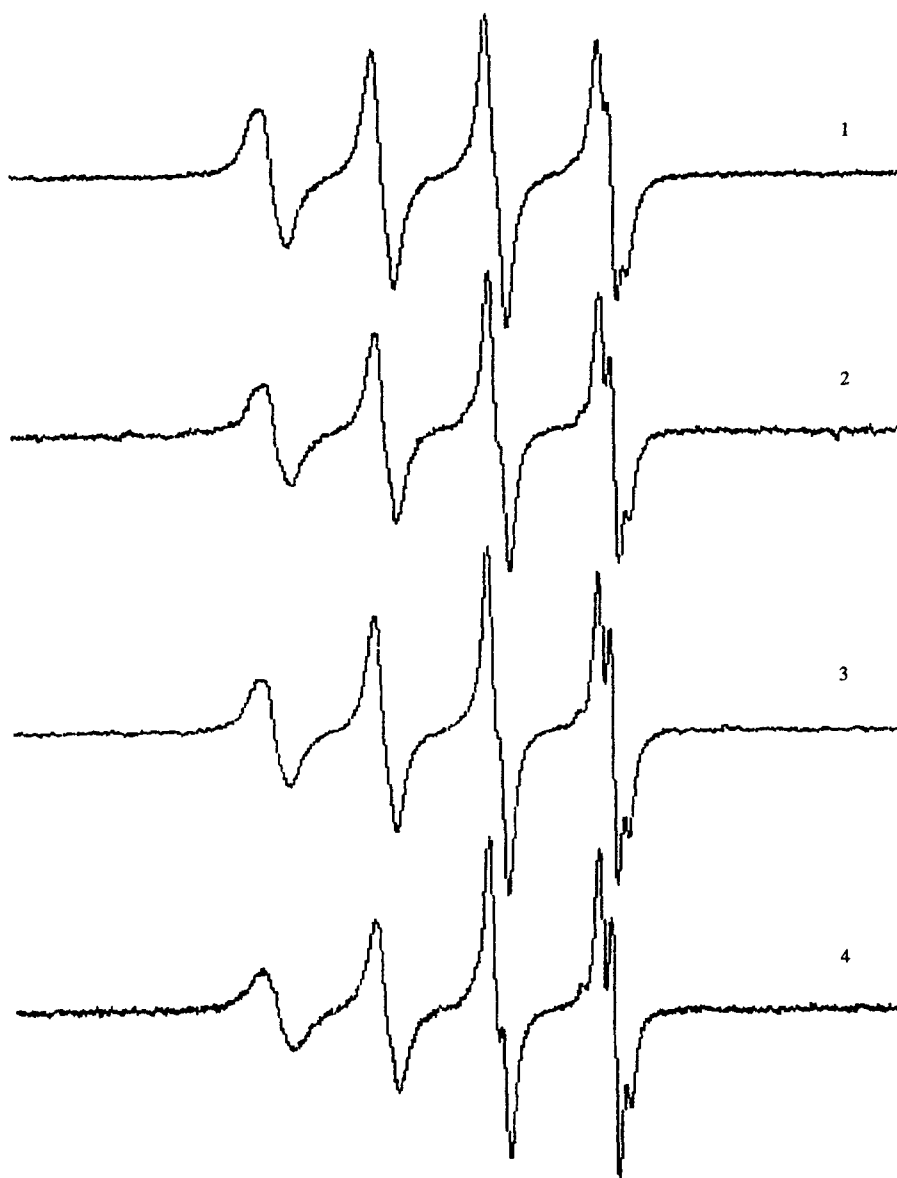
Fig. 1. EPR spectra of equimolar $(1 \times 10^{-3} \text{ mol dm}^{-3})$ mixtures of $Cu(Et_2dtc)_2$ and $Cu(i\text{-Pr}_2dtp)_2$ in acetone (1); toluene (2); $CHCl_3$ (3) and CCl_4 (4), 300 K.

solutions of Cu(dtc)(dtp) with visible light (because of the strong internal filter effect of acetone in UV) are given in Fig. 2. The data show that in addition to the decreasing intensity of the EPR spectrum the relative intensities of the ^{31}P shf lines gradually invert (spectra 2–5 in Fig. 2) following the transformation of Cu(dtc)(dtp) EPR spectrum into the spectrum of $Cu(Et_2dtc)_2$, which also fades on further irradiation (spectra 6 to 8 in Fig. 2) because of the reduction of Cu^{II} to Cu^{I}.

When 8×10^{-5} mol dm^{-3} air-saturated acetone solutions of Cu(dtc)(dtp) are photolysed with visible light at 20°C (Fig. 3a) the electronic absorption changes reveal only the bleaching of the visible LMCT absorption.

To check whether photoreduction of Cu^{II} is revers-

ible the irradiated solutions were kept for 24 h in the dark and the absorption spectra were then measured again. The spectra obtained clearly showed that photoreduction was partly reversible due to a thermal back reaction, proceeding when photolysis was limited to less than 60%. But they were continuing to bleach when the total amount of photolysis was more than 75%.

Photoreduction of Cu(dtc)(dtp) *in toluene*

The LMCT absorption of Cu(dtc)(dtp) in aerated toluene (Fig. 3b) and its EPR intensity (Fig. 4) gradually decrease following the reduction of Cu^{II} to Cu^{I} without any intermediate absorption or EPR signal
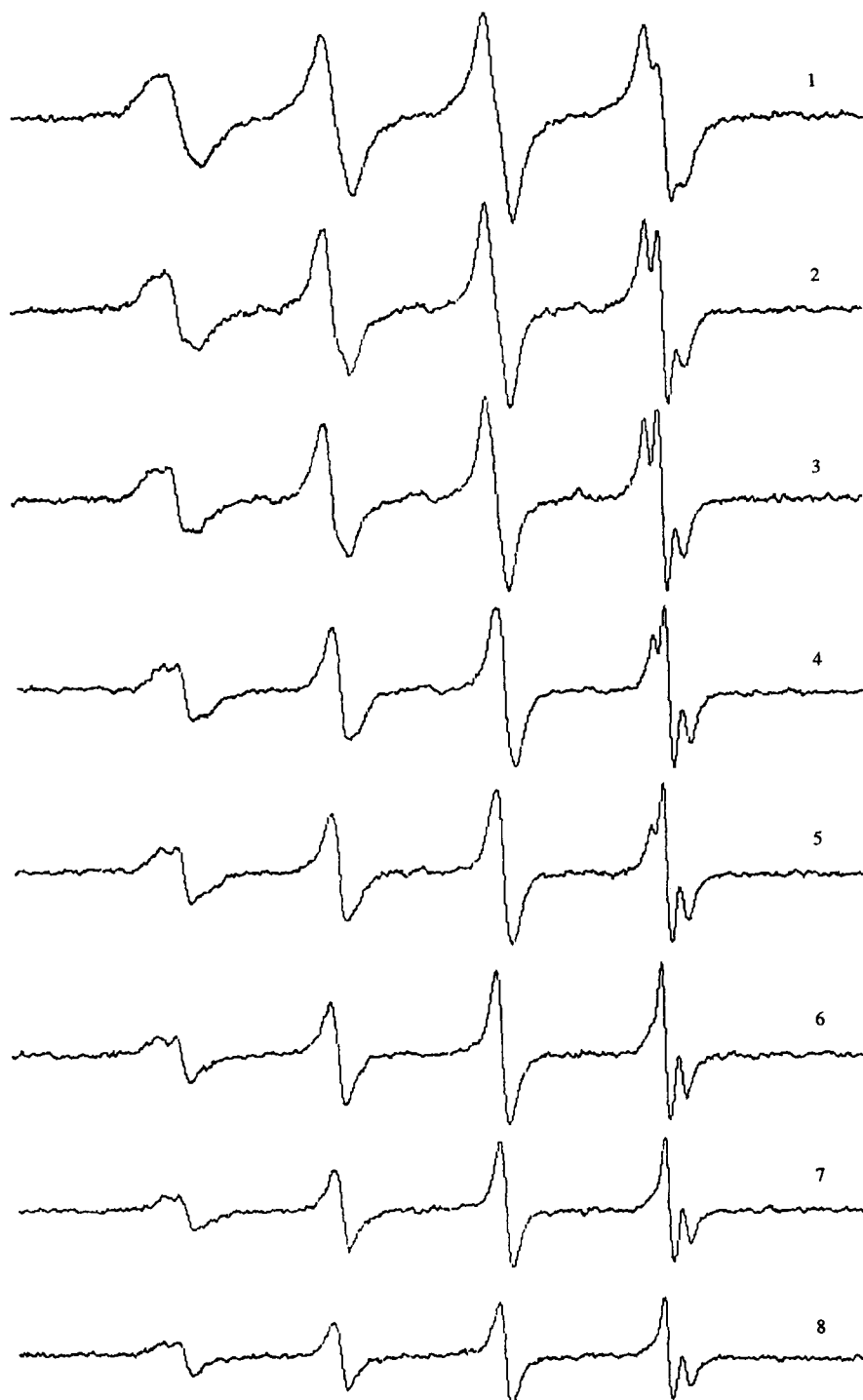
Fig. 2. Changes in the room temperature EPR spectrum of an aerated acetone solution of Cu(dtc)(dtp) complex $(1 \times 10^{-3}$ mol dm$^{-3})$ following visible light irradiation in the spectrometer cavity. Spectra before (1) and after 4.5 min (2) ; 5.5 min (3) ; 6.5 min (4) ; 7.5 min (5) ; 11.5 min (6) ; 12.5 min (7) and 15 min (8) of irradiation.

upon irradiation with visible light (because of the strong internal filter effect of toluene in UV). A gradual invertion of the ^{31}P shf lines relative intensities (spectra 2–4 in Fig. 4) is also observed. The LMCT absorption band fades upon longer irradiation to give a nearly colourless solution. On keeping the irradiated solutions within 24 h in the dark, the original spectrum is partly restored due to a thermal back reaction, proceeding even when the total amount of photolysis is more than 75%.

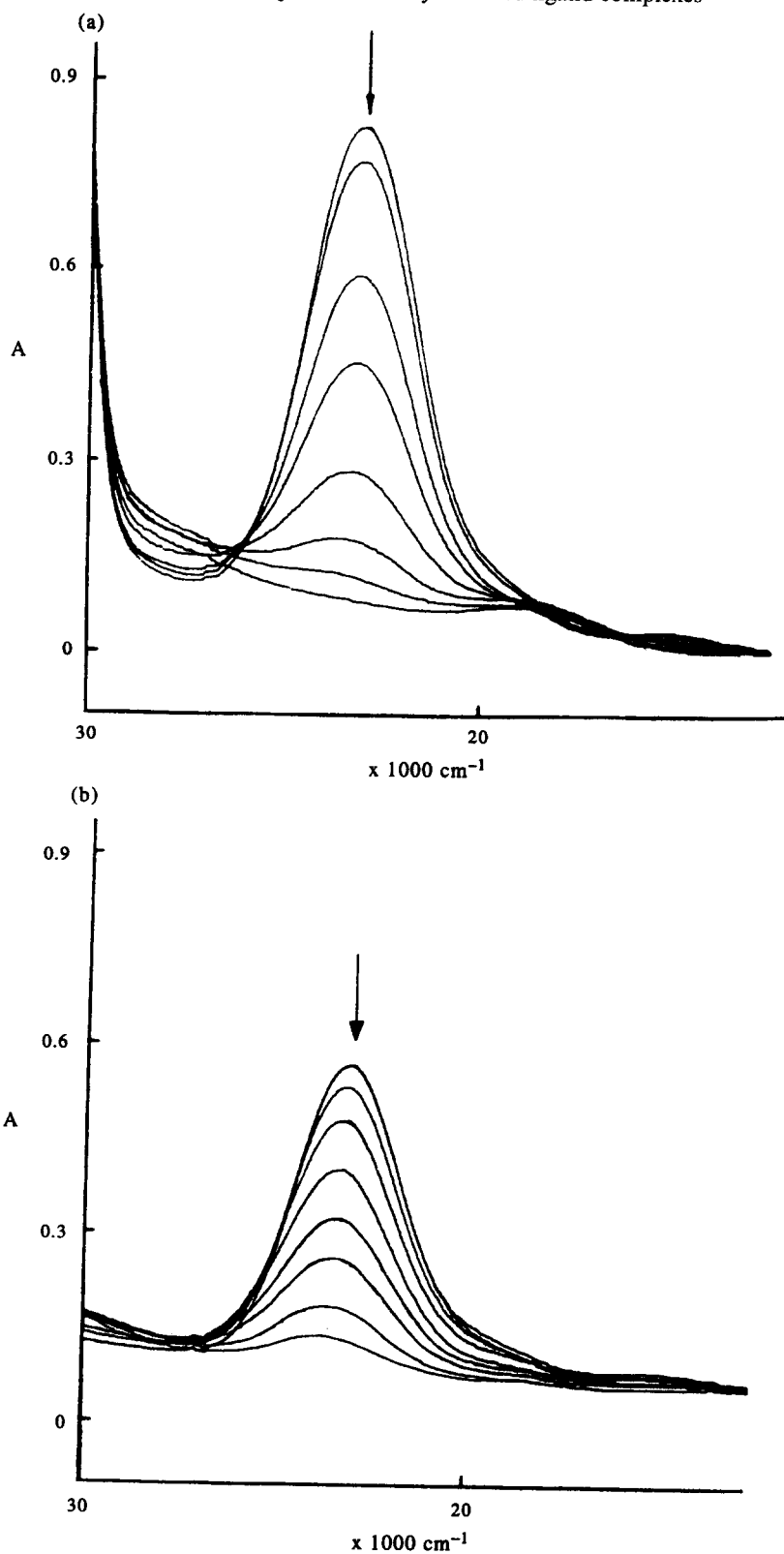(a)

A

x 1000 cm^{-1}

(b)

A

x 1000 cm^{-1}

Fig. 3. Visible spectral changes in aerated solutions of Cu(dtc)(dtp) during consecutive visible light irradiations for 0, 1, 3, 5, 8, 11, 14 and 17 min in acetone, 8×10^{-5} mol dm^{-3} (a) and 0, 0.7, 1.5, 2.5, 4, 5, 6.5 and 8 min in toluene, 6×10^{-5} mol dm^{-3} (b) in the spectrophotometer cavity.

Fig. 4. Changes in the EPR spectrum of an aerated toluene solution of Cu(dtc)(dtp) complex (1×10^{-3} mol dm^{-3}) following visible light irradiation. Spectra before (1) and after 0.3 min (2); 1 min (3) and 2 min (4) of irradiation.

Photoreduction of Cu(dtc)(dtp) *in chloroalkanes*

More complicated UV–vis spectral changes are observed when photolysis is monitored in chloro-alkanes (both in the neat solvent and in the presence of small amounts of ethanol). Figure 5 shows the UV–vis spectral changes obtained upon irradiation $\lambda < 440$ nm of $7 \cdot 10^{-5}$ mol dm^{-3} Cu(dtc)(dtp) in CHCl$_3$/EtOH (150/1). It is seen that the LMCT absorption of Cu(dtc)(dtp) at about 430 nm gradually decreases in photolysis with the consecutive increases in absorption at 350 nm and 284 nm. The 350 nm band attains a maximum absorption and fades upon

Pr$_2$dtp)$_2$, exhibits a different photolysis pathway, illustrated by the UV–vis spectral changes in Fig. 6 and discussed before [1].

The intensity of the EPR spectrum of a 5×10^{-3} mol dm^{-3} Cu(dtc)(dtp) solution in CHCl$_3$/EtOH (150/1) is gradually decreasing upon photoirradiation following the reduction of Cu^{II} to Cu^{I} with the appearance of a low intensity EPR signal [1] of Cu^{II}(Et$_2$dtc)Cl as intermediate. The other complex, Cu$_2$(Et$_2$dtc)$_2$Cl$_2$, which is the only intermediate product of Cu(dtc)(dtp), resp. Cu(Et$_2$dtc)$_2$, photolysis in neat CHCl$_3$, is EPR silent [10], but it changes to Cu^{II}(Et$_2$dtc)Cl in the presence of EtOH (reaction 2):
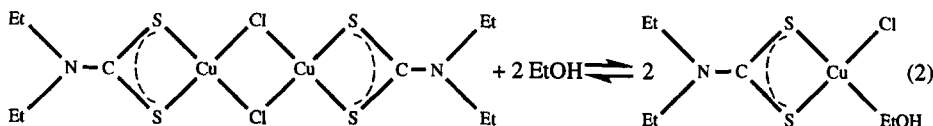
longer irradiation to give a nearly colourless solution. The observed spectral changes are rather similar to those previously reported about the photolysis of the parent Cu(Et$_2$dtc)$_2$ in chloroalkanes [1,10] proceeding with the formation of the mixed-ligand complex Cu^{II}(Et$_2$dtc)Cl ($\lambda_{max} = 406$ nm) and its chloride-bridged dimeric form Cu$_2$(Et$_2$dtc)$_2$Cl$_2$ ($\lambda_{max} = 350$ nm) as intermediates and the disulfide from Et$_2$dtc ($\lambda_{max} = 282$ nm) as a final product. Under the same experimental conditions the other parent, Cu(i-

Partially photolyzed CHCl$_3$/EtOH (150/1) solutions of Cu(dtc)(dtp) containing both Cu^{II}(Et$_2$dtc)Cl and Cu$_2$(Et$_2$dtc)$_2$Cl$_2$, left standing in the dark, undergo reaction (2), as monitored by UV–vis spectroscopy. When the total amount of photolysis is more than 75% and Cu^{II}(Et$_2$dtc)Cl ($\lambda_{max} = 406$ nm) is completely removed by a secondary photolytic process, the 350 nm band of Cu$_2$(Et$_2$dtc)$_2$Cl$_2$ is continuing to bleach in the dark to give a colourless solution.

Similar UV–vis and EPR changes were observed

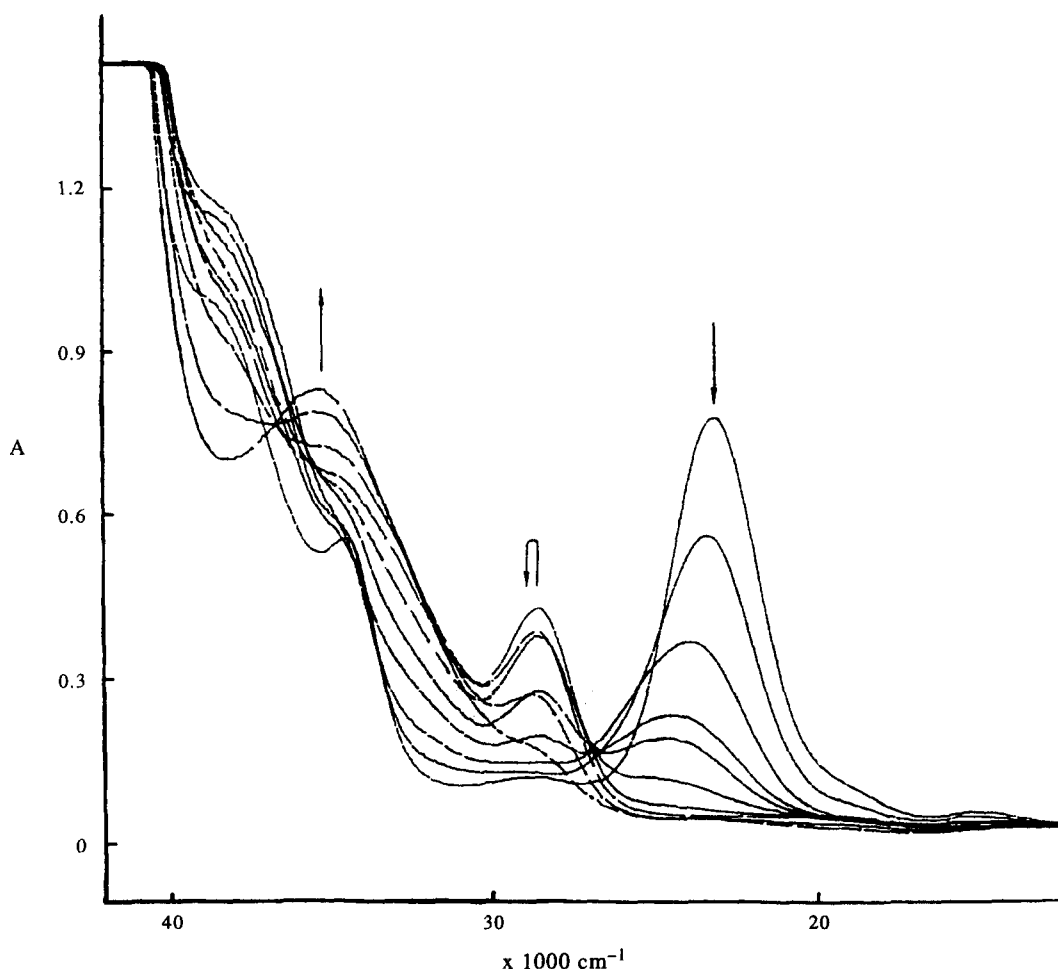Fig. 5. UV–vis spectral changes in $CHCl_3$/EtOH (150:1) solution of Cu(dtc)(dtp) (7×10^{-5} mol dm^{-3}) during irradiation with $\lambda < 400$ nm at 0, 5, 10, 15, 20, 25, 30, 35, 45 and 55 s in the spectrophotometer cavity.

during photo-irradiation of Cu(dtc)(dtp) solutions when $CHCl_3$ was replaced by CCl_4 indicating that the same reaction mechanism is operative for both chloroalkane solvent systems.

Quantum yield

Cu(dtc)(dtp) has been irradiated in acetone, toluene and chloroalkanes ($CHCl_3$ and CCl_4) at room temperature with the 436 nm line of the mercury lamp [3]. The absorbance in the LMCT band was found to decrease linearly for the first 30–40 min of 436 nm irradiations suggesting a zero-order kinetics of the photo-reduction process. The decreasing intensity of this band indicated that the photo-redox reaction between the metal and the ligand occurred *via* a LMCT excitation. The absorbance values obtained at the LMCT band were used to calculate the photo-reduction quantum yields (ϕ_{red}) in all solvents used. The results in Table 3 show that the quantum yield increases in the order of solvents used :

$$\text{acetone} \ll \text{toluene} < CHCl_3 < CCl_4$$
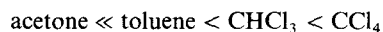
following their strongly decreasing donor and increasing acceptor properties. As a rule, the ϕ_{red} values of the primary photo-process in Cu(dtc)(dtp) are higher than in Cu(Et$_2$dtc)$_2$, but they are lower compared to Cu(i-Pr$_2$dtp)$_2$. The very low ϕ_{red} values associated with the irradiation of acetone solutions of Cu(dtc)(dtp) are consistent with its conversion to Cu(Et$_2$dtc)$_2$ (see Fig. 2), which replaces the initial 426 nm LMCT band with a band at 432 nm and maintains the higher measured absorbance values at the early stages of photolysis.

Mechanism

The evidences about Cu(Et$_2$dtc)$_2$ in Fig. 2 and both Cu^{II}(Et$_2$dtc)Cl and Cu$_2$(Et$_2$dtc)$_2$Cl$_2$ in Fig. 5 as intermediate products of Cu(dtc)(dtp) photolysis in acetone and chloroalkanes respectively, are in accordance with a scheme in which the primary photo-electron
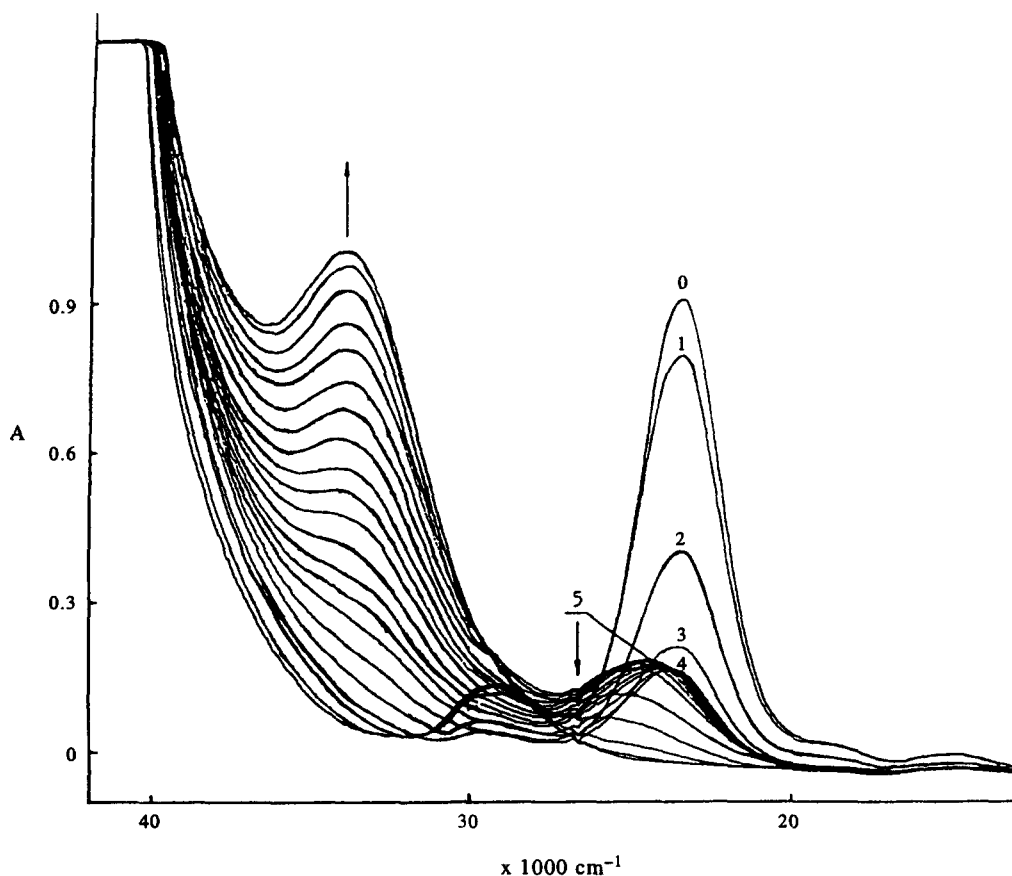
x 1000 cm⁻¹

Fig. 6. UV–vis spectral changes in $CHCl_3/EtOH$ (150:1) solution of $Cu(i\text{-}Pr_2dtp)_2$ (1×10^{-4} mol dm⁻³) during irradiation with $\lambda < 400$ nm. Spectra before (0) and after 10 s (1); 30 s (2); 40 s (3); 50 s (4); 60 s (5), followed by consecutive 20 s irradiations in the spectrophotometer cavity.

Table 3. Quantum yields ($\phi_{red} \times 10^2$ mol/einstein) of $Cu(dtc)(dtp)$, $Cu(Et_2dtc)_2$ and $Cu(i\text{-}Pr_2dtp)_2$ CT-Photolysis in Different Solvents ($\lambda_{irr} = 436$ nm)

Complex	Acetone	Toluene	$CHCl_3$	CCl_4
$Cu(dtc)(dtp)$	0.1	0.5	0.8	0.9
$Cu(Et_2dtc)_2$	0.1	0.2	0.3	0.5
$Cu(i\text{-}Pr_2dtp)_2$	0.2	0.6	0.6	1.6

transfer to Cu^{II} would occur with the participation of i-Pr_2dtp ligand to form free i-Pr_2dtp radical and $Cu^I(Et_2dtc)$. The character of the primary homolytic Cu—S bond cleavage is supported by the quantum yield data for $Cu(dtc)(dtp)$, $Cu(Et_2dtc)_2$ and $Cu(i\text{-}Pr_2dtp)_2$ (Table 3).

The subsequent reactions of $Cu^I(Et_2dtc)$ following the primary homolytic Cu—S bond cleavage are strongly solvent dependent as found before [1]. In chloroalkanes the primary photo-process is followed by a rapid $Cu^I(Et_2dtc)$ thermal oxidation [11] with $CHCl_3$ (or CCl_4) to $Cu^{II}(Et_2dtc)Cl$ or $Cu_2(Et_2dtc)_2Cl_2$, respectively [10], and by a i-Pr_2dtp recombination to

the stable disulphide (ds) of dithiophosphate ($\lambda_{max} = 294$ nm in Fig. 6). Furthermore, the products $Cu^{II}(Et_2dtc)Cl$ and $Cu_2(Et_2dtc)_2Cl_2$ undergo secondary photo-processes yielding CuCl and a free Et_2dtc radical as found before [1,10,12].

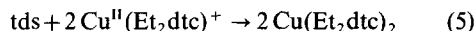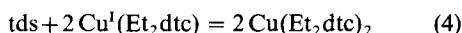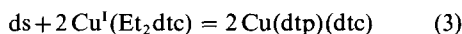The oxidation of the primary photo-product $Cu^I(Et_2dtc)$ by chloroalkane and the secondary LMCT-photolyses of $Cu^{II}(Et_2dtc)Cl$ and $Cu_2(Et_2dtc)_2$ Cl_2 are best explained if we assume that the primary photochemical act in $Cu(dtc)(dtp)$ proceeds within its donor–acceptor complex with $CHCl_3$ (CCl_4). The existence of DA interactions of the parent $Cu(dtc)_2$ and $Cu(dtp)_2$ with chloroalkanes has been found in previous studies [13–15] and the geometric and electronic structures of the corresponding DA adducts have been the object of much research during past years. Because of the weak electron acceptor properties of $CHCl_3$, CCl_4 molecule, they were assumed to co-ordinate to the sulphur atoms of the chromophore CuS_4, and this was observed in the ENDOR detected $CHCl_3$ adduct of $Cu(i\text{-}Pr_2dtp)_2$ [14,15].

Tetraethylthiuramdisulphide, tds, detected by its UV-absorption [16,17] at 282 nm (see Fig. 5), is obtained by recombination of Et_2dtc radicals.

The EPR data in Fig. 2 lead us to propose a some-

what different model of Cu(dtc)(dtp) photolysis in acetone. The photochemistry through this model would involve the same primary homolytic photo-cleavage generating $Cu^I(Et_2dtc)$ and i-$Pr_2dtp^{\cdot}$, followed by a rapid free radical recombination and $Cu^I(Et_2dtc)$ thermal oxidation to $Cu^{II}(Et_2dtc)^+$. Several oxidants are present in these solutions that could react with $Cu^I(Et_2dtc)$. The oxidant present in highest concentration in acetone solutions open to the air is dissolved dioxygen, reacting spontaneously with Cu^I compounds to yield the compounds of Cu^{II}. Other potentially oxidizing species include ds (dtp–dtp) and tds (dtc–dtc) which exhibit different reactivities towards Cu^I and Cu^{II}. It has been found before that only the compounds of Cu^I react with ds (reaction 3) [18], whereas both Cu^I and Cu^{II} compounds react with tds to give $Cu(Et_2dtc)_2$ according to equations (4) and (5) respectively [16].

$$ds + 2\,Cu^I(Et_2dtc) = 2\,Cu(dtp)(dtc) \qquad (3)$$

$$tds + 2\,Cu^I(Et_2dtc) = 2\,Cu(Et_2dtc)_2 \qquad (4)$$

$$tds + 2\,Cu^{II}(Et_2dtc)^+ \rightarrow 2\,Cu(Et_2dtc)_2 \qquad (5)$$

Therefore, on the basis of the present results we could propose that $Cu^I(Et_2dtc)$, when produced photo-chemically, would be rapidly oxidized with dissolved dioxygen to $Cu^{II}(Et_2dtc)^+$, which would further react with the disulphide of Et_2dtc (reaction 5) to give $Cu(Et_2dtc)_2$ [16]. Both intermediate copper complexes are stabilized by the coordination of acetone [19–21]. The appearance of $Cu(Et_2dtc)_2$ in Fig. 2 could not be attributed to the disproportionation of $Cu^{II}(Et_2dtc)^+$ (reaction 6):

$$2\,Cu^{II}(Et_2dtc)^+ \rightleftharpoons Cu(Et_2dtc)_2 + Cu^{II} \qquad (6)$$
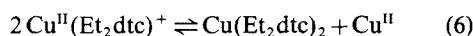
since the equilibrium (6) is shifted strongly to the left in acetone [22].

The data of Fig. 2 and Fig. 3a compare well to those in Fig. 3b and Fig. 4, suggesting similar photochemical pathways of Cu(dtc)(dtp) in acetone and toluene. However, Cu(dtc)(dtp) converts completely to $Cu(Et_2dtc)_2$ in acetone (Fig. 2), whereas the EPR spectral changes in Fig. 4 illustrate only a partial conversion of Cu(dtc)(dtp) to $Cu(Et_2dtc)_2$ in toluene, with gradually decreasing concentrations of both species upon photo-irradiation. In our opinion, the coordination inertness of toluene poorly stabilizing the intermediate copper complexes could be the reason for that.

The details of both mechanisms account for all of the observations made in this study as well as for the

donor–acceptor properties of acetone and chloro-alkanes, and the coordination inertness of toluene.

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