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

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## Abstract

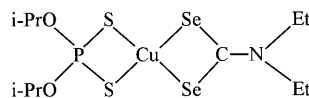
Photolysis of the ternary system consisting of diethyldiselenocarbamate (Et<sub>2</sub>dsc), diisopropyldithiophosphate (*i*-Pr<sub>2</sub>ntp) and copper(II) (1:1:1) has been studied in toluene, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub> and chloroalkane–EtOH solutions. The results obtained by EPR techniques and UV–Vis data indicate that a homolytic Cu–S bond cleavage involving ntp ligand appears as the primary photoprocess in Cu(dsc)(ntp) photolysis. Further conversion of the primary photoproduct Cu<sup>I</sup>(Et<sub>2</sub>dsc) is discussed in terms of specific interaction with the solvent. According to quantum yield data solvent efficiencies in photolysis could be related to their oxidizing power. A reaction mechanism is proposed well fitting the experimental results. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** CT photochemistry; Ternary copper(II) complexes; Diselenocarbamate and dithiophosphate ligands

## 1. Introduction

In recent papers [1,2] we have described the photochemical behaviour of bis(diethyldiselenocarbamato)-Cu(II), Cu(Et<sub>2</sub>dsc)<sub>2</sub>, and bis(diisopropyldithiophosphato)Cu(II), Cu(*i*-Pr<sub>2</sub>ntp)<sub>2</sub>, in aprotic solvents. The results obtained show that the primary photochemical act in both complexes is an intramolecular electron transfer from the equatorially bound Se (resp. 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. It was also found that upon irradiation in the corresponding charge transfer band the quantum yield of Cu(dsc)<sub>2</sub> photolysis is lower than the value obtained for Cu(dtc)<sub>2</sub> in the same solvent.

In the present paper we report our data on the photochemical properties of the ternary Cu(dsc)(ntp) complex obtained with ligands of chemically different donor sets as a part of our study on the photochemistry of copper(II) chelate complexes with different chromophores.



## 2. Experimental

### 2.1. Starting materials

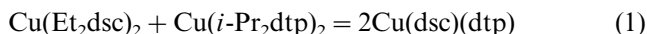
The complex bis(diethyldiselenocarbamato)Zn(II) was obtained and purified following a literature procedure [3,4]. Diisopropyldithiophosphoric acid and its sodium salt were prepared as previously described [5]. CuSO<sub>4</sub>·5H<sub>2</sub>O (p.a.) was obtained from Fluka and used without further purification. The solvents were used after distillation.

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## 2.2. Preparation of compounds

The parent complexes  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$  were prepared by standard literature methods [1,2,4,5]. The ternary complex  $\text{Cu}(\text{dsc})(\text{dtp})$  was obtained according to the reaction:



by mixing the corresponding equimolar solutions of  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$  to obtain  $\text{Cu}:\text{dsc}:\text{dtp} = 1:1:1$ . The initial solutions of the parent complexes were prepared by weighing and dissolution of the appropriate amounts.

## 2.3. Instrumentation

The EPR spectra were taken at room temperature on an X-band Bruker ER 200D-SRC spectrometer. The standard ER4202ST rectangular cavity ( $\text{TE}_{102}$  mode) was used. The microwave power was 3 mW and 2 G modulation amplitude of the magnetic field (at 100 kHz) during all experiments.

The electronic absorption spectra were recorded on a Specord UV–Vis (Carl Zeiss, Jena) spectrophotometer using quartz cells to record in the 250–750 nm region.

All measurements were performed at room temperature (293 K).

## 2.4. Irradiation and quantum yields

Photolysis experiments were performed with the full spectrum of a 250 W medium-pressure mercury lamp or through a solution filter to separate the 436 nm mercury line [5] as described previously [1,2]. 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 [5]. At least three determinations of quantum yields were made for each complex. Photolyses of all complexes were carried out at  $20 \pm 1^\circ\text{C}$ . The accuracy of the quantum yield measurements was found to be within 20–25%. 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.

## 3. Results and discussion

### 3.1. EPR spectrum of $\text{Cu}(\text{dsc})(\text{dtp})$

The isotropic EPR spectra of the ternary complex  $\text{Cu}(\text{dsc})(\text{dtp})$  in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , acetone and toluene are compared in Fig. 1 with the spectra of the parent complexes  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$ . It is seen from Fig. 1 that the newly obtained spectrum of  $\text{Cu}(\text{dsc})(\text{dtp})$  exhibits four hyperfine lines due to the interaction of the copper unpaired electron with  $^{63,65}\text{Cu}$  nucleus ( $I = 3/2$ ) which are additionally split into superhyperfine (shf) lines by one  $^{31}\text{P}$  and one  $^{77}\text{Se}$  nuclei both with nuclear spins  $I = 1/2$ . However, since the natural abundance of  $^{77}\text{Se}$  is 7.5%, only 15% of the molecules of the ternary complex contain one  $^{77}\text{Se}$  nucleus. Thus in fact the recorded spectrum of  $\text{Cu}(\text{dsc})(\text{dtp})$  is a superposition of two EPR signals, one containing  $^{77}\text{Se}$  and the other corresponding to the remaining Se isotopes ( $^{74,76,78,80,82}\text{Se}$ ). The estimated EPR parameters of  $\text{Cu}(\text{dsc})(\text{dtp})$  are:  $g_o = 2.034 \pm 0.002$ ;  $A_o(^{63,65}\text{Cu}) = 78 \pm 1$  G;  $A_o(^{77}\text{Se}) = 48 \pm 1$  G;  $A_o(^{31}\text{P}) = 7.5 \pm 0.5$  G. The obtained  $g_o$  and  $A_o(^{63,65}\text{Cu})$  values are the average of the corresponding parameters of the parent  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$  complexes which are  $g_o = 2.020 \pm 0.002$ ;  $A_o(^{63,65}\text{Cu}) = 80 \pm 1$  G;  $A_o(^{77}\text{Se}) = 46 \pm 1$  G about  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and  $g_o = 2.046 \pm 0.002$ ;  $A_o(^{63,65}\text{Cu}) = 73 \pm 1$  G;  $A_o(^{31}\text{P}) = 9.5 \pm 0.5$  G about  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$ , respectively. Therefore, the considered EPR parameters indicate an average covalence within the chromophore  $\text{CuS}_2\text{Se}_2$  of the ternary  $\text{Cu}(\text{dsc})(\text{dtp})$  complex as compared to the parent bis-chelates with  $\text{CuS}_4$  and  $\text{CuSe}_2$  chromophores according to the ‘additive rule’ [6,7]. This effect is due to the fact that unpaired electron occupies a ‘group’ orbital in which Cu and four donor atoms of the chromophore are included and the magnitudes of the EPR parameters  $g$  and  $A$  are averaged as a result. However, this is not the case with  $^{31}\text{P}$  shf split-

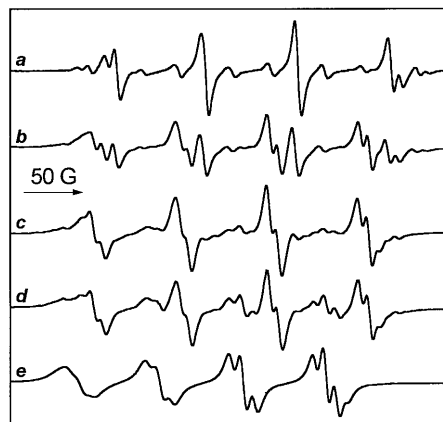


Fig. 1. EPR spectra taken after mixing of  $\text{Cu}(\text{dsc})_2$  with  $\text{Cu}(\text{dtp})_2$ . The ratio  $\text{Cu}(\text{dsc})_2/\text{Cu}(\text{dtp})_2$  is: (a) 1:0; (b) 2:1; (c) 1:1; (d) 1:2; (e) 0:1. Spectrum (c) corresponds to the  $\text{Cu}(\text{dsc})(\text{dtp})$  complex. Solvent:  $\text{CHCl}_3$ ,  $T = 298$  K.

Table 1

Values of  $\lambda_{\text{max}}$  (nm) for the complexes  $\text{Cu}(\text{Et}_2\text{dsc})(i\text{-Pr}_2\text{dtp})$ ,  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$  in various solvents

Solvent	$\text{Cu}(\text{Et}_2\text{dsc})(i\text{-Pr}_2\text{dtp})$	$\text{Cu}(\text{Et}_2\text{dsc})_2$	$\text{Cu}(i\text{-Pr}_2\text{dtp})_2$
$\text{CH}_2\text{Cl}_2$	452	495	420
$\text{CHCl}_3$	455	495	420
$\text{CCl}_4$	455	495	420
Toluene	450	495	420
Acetone	453	495	417

ting constant which may be used [8] as the probe of precise unpaired electron distribution in mixed-ligand complexes. In the case of  $\text{Cu}(\text{dsc})(\text{dtp})$  ternary complex the magnitude of  $^{31}\text{P}$  shf splitting from dtp ligand is lower than in the parent  $\text{Cu}(\text{dtp})_2$  complex, suggesting a shift of the unpaired electron density from this ligand to dsc. In the same time,  $^{77}\text{Se}$  shf splitting in the mixed-ligand  $\text{Cu}(\text{dsc})(\text{dtp})$  complex is higher than in the parent  $\text{Cu}(\text{dsc})_2$ . As seen from Fig. 1, equilibrium in reaction (1) is practically shifted to the right.

### 3.2. UV–Vis spectra of $\text{Cu}(\text{dsc})(\text{dtp})$

The visible absorption of  $\text{Cu}(\text{dsc})(\text{dtp})$  is due to the strongly allowed ligand to metal charge transfer (LMCT) band which appears near to 455 nm in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , toluene and acetone (Table 1). Similar to the corresponding EPR parameters, the obtained  $\lambda_{\text{max}}$  values of  $\text{Cu}(\text{dsc})(\text{dtp})$  are close to the average magnitudes of  $\lambda_{\text{max}}$  of the parents LMCT bands which are at 495 nm about  $\text{Cu}(\text{Et}_2\text{dsc})_2$  and 420 nm about  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$ .

### 3.3. Continuous photolysis

Solutions of  $\text{Cu}(\text{dsc})(\text{dtp})$  in toluene, acetone 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  $\lambda < 450$  nm. In general, the irradiation produces a colour change in solution, accompanied by changes in their UV–Vis and EPR absorption.

### 3.4. Photoreduction of $\text{Cu}(\text{dsc})(\text{dtp})$ in toluene

EPR spectral changes obtained upon photo-irradiation of  $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$  toluene solutions of  $\text{Cu}(\text{dsc})(\text{dtp})$  with visible light (because of the strong absorption of toluene in UV) are given in Fig. 2. The data show the decreasing intensity of the EPR spectrum of  $\text{Cu}(\text{dsc})(\text{dtp})$  because of the reduction of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$ .

When  $6 \times 10^{-5}$  mol  $\text{dm}^{-3}$  toluene solutions of  $\text{Cu}(\text{dsc})(\text{dtp})$  are photolysed with visible light at 20°C

(Fig. 3) the electronic absorption changes reveal only the bleaching of the visible LMCT absorption.

To check whether photoreduction of  $\text{Cu}(\text{II})$  is reversible the irradiated solutions were kept for 24 h in the dark and the absorption spectra were measured again after that. The obtained spectra clearly showed that photoreduction was partly reversible due to a thermal back reaction, proceeding when photolysis was limited to less than 50%. But they were continuing to bleach when the total amount of photolysis was more than 80%.

### 3.5. Photoreduction of $\text{Cu}(\text{dsc})(\text{dtp})$ in acetone

The LMCT absorption of  $\text{Cu}(\text{dsc})(\text{dtp})$  in aerated acetone and its EPR intensity gradually decrease following the reduction of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$  without any intermediate absorption or EPR signal upon irradiation with visible light (because of the strong absorption of acetone in UV). On keeping the irradiated solutions

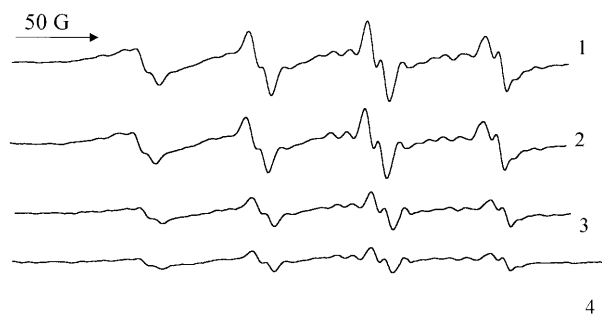


Fig. 2. Set of EPR spectra of  $\text{Cu}(\text{dsc})(\text{dtp})$  in toluene, 298 K, irradiated for 0 (1), 10 (2), 20 (3) and 40 s (4).

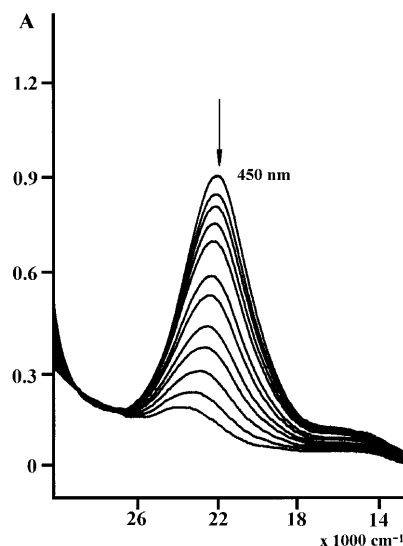


Fig. 3. Absorption spectrum of  $7 \times 10^{-5}$  M  $\text{Cu}(\text{dsc})(\text{dtp})$ , irradiated for 0–285 s in toluene.

within 24 h in the dark the original spectrum is partly restored due to a thermal back reaction, proceeding when the total amount of photolysis is less than 60%.

### 3.6. Photoreduction of $\text{Cu}(\text{dsc})(\text{dtp})$ in chloroalkanes

More complicated UV–Vis spectral changes were observed when photolysis was monitored in chloroalkanes. Fig. 4 shows the UV–Vis spectral changes obtained upon irradiation  $\lambda < 450$  nm of  $7 \times 10^{-5}$  mol  $\text{dm}^{-3}$   $\text{Cu}(\text{dsc})(\text{dtp})$  in  $\text{CH}_2\text{Cl}_2$ . It is seen that the LMCT absorption of  $\text{Cu}(\text{dsc})(\text{dtp})$  at about 450 nm gradually decreases in photolysis with the consecutive increases in absorption at 435 nm ( $22\,990\text{ cm}^{-1}$ ) and 350 nm ( $28\,750\text{ cm}^{-1}$ ). The new bands attain a maxi-

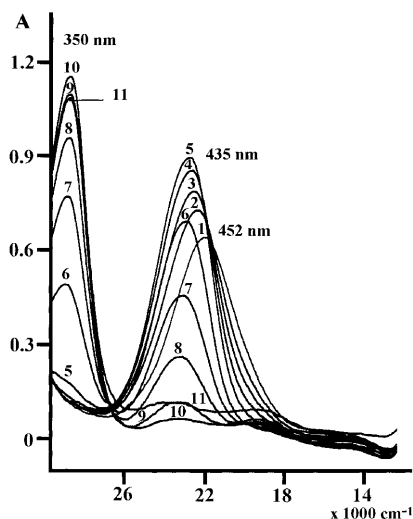


Fig. 4. Absorption spectrum of  $8 \times 10^{-5}$  M  $\text{Cu}(\text{dsc})(\text{dtp})$ , irradiated for 0–94 s in  $\text{CH}_2\text{Cl}_2$ .

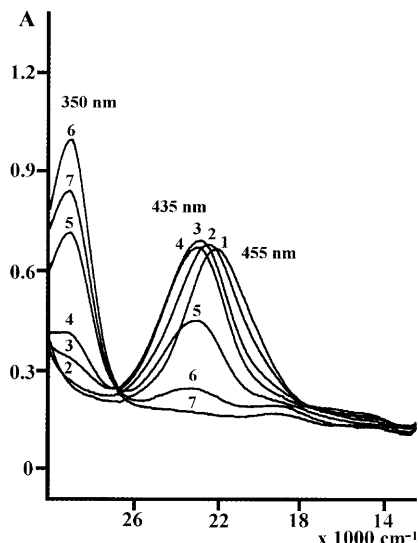


Fig. 5. Absorption spectrum of  $5 \times 10^{-5}$  M  $\text{Cu}(\text{dsc})(\text{dtp})$ , irradiated for 0–55 s in  $\text{CHCl}_3$ .

mum absorption and fade upon 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  $\text{Cu}(\text{Et}_2\text{dsc})_2$  in chloroalkanes [1] proceeding with the formation of the mixed-ligand complex  $\text{Cu}^{\text{II}}(\text{Et}_2\text{dsc})\text{Cl}$  ( $\lambda_{\text{max}} = 445$  nm) and its chloride-bridged dimeric form  $\text{Cu}_2(\text{Et}_2\text{dsc})_2\text{Cl}_2$  ( $\lambda_{\text{max}} = 350$  nm) as intermediates. Under the same experimental conditions the other parent,  $\text{Cu}(i\text{-Pr}_2\text{dtp})_2$ , exhibits a different photolysis pathway discussed before [2].

The intensity of the EPR spectrum of a  $5 \times 10^{-3}$  mol  $\text{dm}^{-3}$   $\text{Cu}(\text{dsc})(\text{dtp})$  solution in  $\text{CH}_2\text{Cl}_2$  is gradually decreasing upon photo-irradiation following the reduction of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$ .

Partially photolyzed  $\text{CH}_2\text{Cl}_2$  solutions of  $\text{Cu}(\text{dsc})(\text{dtp})$ , containing both  $\text{Cu}^{\text{II}}(\text{Et}_2\text{dsc})\text{Cl}$  and  $\text{Cu}_2(\text{Et}_2\text{dsc})_2\text{Cl}_2$ , left standing in the dark, undergo thermal back reaction as monitored by UV–Vis spectroscopy. When the total amount of photolysis is more than 80% and  $\text{Cu}^{\text{II}}(\text{Et}_2\text{dsc})\text{Cl}$  ( $\lambda_{\text{max}} = 445$  nm,  $22\,470\text{ cm}^{-1}$ ) is completely removed by a secondary photolytic process, the 350 nm band of  $\text{Cu}_2(\text{Et}_2\text{dsc})_2\text{Cl}_2$  is continuing to bleach in the dark to give a colourless solution.

Similar UV–Vis and EPR changes are observed during photo-irradiation of  $\text{Cu}(\text{dsc})(\text{dtp})$  solutions when  $\text{CH}_2\text{Cl}_2$  is replaced by  $\text{CHCl}_3$  as the solvent (Fig. 5) indicating that the same reaction mechanism is operative for both chloroalkane solvent systems. However, when irradiation is carried out in  $\text{CCl}_4$  only the absorption band at 420 nm ( $23\,800\text{ cm}^{-1}$ ) (Fig. 6) appears in the visible part of the spectrum simultaneously with the gradual decrease in intensity of the initial charge transfer band of  $\text{Cu}(\text{dsc})(\text{dtp})$  at 455 nm ( $21\,980\text{ cm}^{-1}$ ).

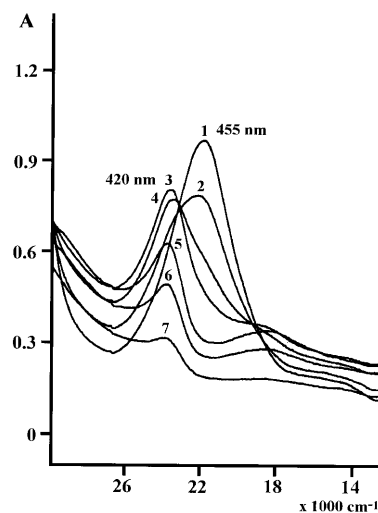


Fig. 6. Absorption spectrum of  $6 \times 10^{-5}$  M  $\text{Cu}(\text{dsc})(\text{dtp})$ , irradiated for 0–50 s in  $\text{CCl}_4$ .

### 3.7. Quantum yield

The quantum yield proved to be sensitive to the solvent. For solutions in 20°C CCl<sub>4</sub> the quantum yield of 436 nm irradiation was determined to be  $1.5 \times 10^{-3}$  mol einstein<sup>-1</sup>. In CHCl<sub>3</sub> photolysis the same light irradiation gave about  $1.0 \times 10^{-3}$  mol einstein<sup>-1</sup>, but it was much smaller in CH<sub>2</sub>Cl<sub>2</sub>. A photoredox process was also seen in acetone and toluene but it gave immeasurably small quantum yield values. Therefore, the data obtained at 436 nm irradiation decreases in the following order of solvents CCl<sub>4</sub> > CHCl<sub>3</sub> > CH<sub>2</sub>Cl<sub>2</sub> > acetone, toluene. Because of their electron acceptor properties [9] chloromethanes act as oxidants and their Cl atom donating power increases with decreasing energy of the C–Cl bond which is 75 kcal mol<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>, 71.9 kcal mol<sup>-1</sup> in CHCl<sub>3</sub> and 68 kcal mol<sup>-1</sup> in CCl<sub>4</sub> [10,11]. In view of this the observed solvent efficiencies in photolysis could be related to their oxidizing power.

### 3.8. Mechanism

The evidence about Cu<sup>II</sup>(Et<sub>2</sub>dsc)Cl and Cu<sub>2</sub>(Et<sub>2</sub>dsc)<sub>2</sub>-Cl<sub>2</sub> formation (Fig. 4) as intermediate products of Cu(dsc)(dtp) photolysis in chloroalkanes is in accordance with a scheme in which the primary photo-electron transfer to Cu(II) would occur with the participation of *i*-Pr<sub>2</sub>dtp ligand to form free *i*-Pr<sub>2</sub>dtp<sup>•</sup> radical and Cu<sup>I</sup>(Et<sub>2</sub>dsc). The subsequent reactions of Cu<sup>I</sup>(Et<sub>2</sub>dsc) 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<sup>I</sup>(Et<sub>2</sub>dsc) thermal oxidation with the chloroalkane to give Cu<sup>II</sup>(Et<sub>2</sub>dsc)Cl in equilibrium with the dimeric form Cu<sub>2</sub>(Et<sub>2</sub>dsc)<sub>2</sub>Cl<sub>2</sub> [1] and by a *i*-Pr<sub>2</sub>dtp<sup>•</sup> recombination to the stable disulphide (ds) of dithiophosphate. Furthermore, the products Cu<sup>II</sup>(Et<sub>2</sub>dsc)Cl and Cu<sub>2</sub>(Et<sub>2</sub>dsc)<sub>2</sub>Cl<sub>2</sub> undergo secondary photo-processes yielding CuCl and a free Et<sub>2</sub>dsc<sup>•</sup> radical as found before [1]. The details of this mechanism account for all of the observations made in this study as well as for the electron-acceptor properties of chloroalkanes and their oxidizing power.

The data of Fig. 2 compare well to those obtained in acetone, suggesting rather similar photochemical pathways of Cu(dsc)(dtp) in acetone and toluene.

## 4. Conclusions

The primary photo-process appearing upon UV–Vis irradiation with  $\lambda < 450$  nm of Cu(dsc)(dtp) in acetone, toluene and chloroalkane (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub>) solutions involves the homolytic cleavage of the bond between S atom of *i*-Pr<sub>2</sub>dtp and Cu(II) to give Cu<sup>I</sup>(Et<sub>2</sub>dsc) and a free *i*-Pr<sub>2</sub>dtp<sup>•</sup> radical as the primary photo-products. The solvent appears to play a major role in determining further reactions of the primary photo-products.

## Acknowledgements

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