Inorganica Chimica Acta, 203 (1993) 201–204

Charge transfer photochemistry of bis(diethyldithiocarbamato)copper(II) and bis(diisopropyldithiophosphato)copper(II) complexes

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(Received May 27, 1992; revised August 21, 1992)

Abstract

The photochemistry of bis(diethyldithiocarbamato)copper(II) and bis(diisopropyldithiophosphato)copper(II) complexes characterized by strongly allowed ligand to metal charge transfer transition in the visible spectra is reported. The reaction from the lowest LMCT state is reduction of Cu(II) to Cu(I) proceeding via an intramolecular electron transfer from an equatorially bonded S atom of the ligand to copper(II). Both complexes show solvent independent photochemistry when irradiated in acetone, toluene, $CHCl_3$ and CCl_4. UV irradiation of $Cu(dtc)_2$ in mixed chlorohydrocarbon–ethanol solvents gives rise to $Cu^{II}(dtc)Cl$ with equatorially coordinated chloride ion as an intermediate and $CuCl_2$ as a final reaction product. The photoproduct of the dithiophosphate complex is partially reconverted into the initial $Cu^{II}(dtp)_2$ by thermal reaction. These assignments are supported by EPR data and by UV–Vis spectra of the complexes.

Introduction

Sulfur containing metal complexes are known as antioxidants [1], rubber vulcanization accelerators [2] and in some cases are recommended as photostabilizers in patent literature [3]. However apart from this application the mechanism of their action is still unknown and only a few studies have been concerned with this problem [4–13]. In the present paper we report the results of our study on the charge-transfer photochemistry of bis(*N*,*N*′-diethyldithiocarbamato)copper(II), [$Cu(dtc)_2$], and bis(*O*,*O*′-diisopropyldithiophosphato)copper(II), [$Cu(dtp)_2$], dissolved in non-polar solvents. Because of the recently obtained evidence for a charge-transfer to solvent complex between $CHCl_3$ and $Cu(dtp)_2$ [14], the photoredox process is studied in CCl_4 and $CHCl_3$ and compared with the data obtained in acetone and toluene.

Experimental

Preparation of compounds

The ligand Nadtc was commercially obtained and used without further purification. The sodium salt of diisopropyldithiophosphoric acid was prepared according to the literature procedure [15]. The complexes bis(*N*,*N*′-diethyldithiocarbamato)copper(II) and bis-(*O*,*O*′-diisopropyldithiophosphato)copper(II) were prepared by mixing aqueous solutions of $CuCl_2$ and the appropriate sodium salts of the ligands. The precipitates were separated, dried and twice recrystallized from $CHCl_3$. The purity of the $Cu(dtc)_2$ complex thus obtained was checked by elemental analysis. *Anal.* Calc. for $CuC_6N_2H_2O$: 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. In view of the fact that $Cu(dtp)_2$ exhibits some peculiarities in the solid state [16], its purity and therefore the elemental analysis cannot be considered as definitive. It has been confirmed by spectrophotometric measurements of $CHCl_3$ solutions of weighed quantities (accuracy ± 0.00001 mg) of both complexes ($\epsilon = 13\,000$ at 437 and 425 nm for $Cu(dtc)_2$ and $Cu(dtp)_2$, respectively) [17].

The solvents were all of spectroscopic grade and were twice distilled and deoxygenated before use.

Instrumentation

The electronic absorption spectra were taken using a SPECORD UV–Vis spectrophotometer. The EPR spectra were recorded at room temperature on an X-

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band BRUKER ER 200D-SRC spectrometer using 100 kHz modulation of the magnetic field.

Irradiation and quantum yields

All quantum yields were done on an optical bench using a 1000 W super-high pressure mercury lamp as light source. The 313, 436 and 578 nm bands were isolated with filters described in the literature [18]. The quantum yields were determined by following changes in the electronic absorption spectra.

The light intensity was measured by a ferric oxalate actinometric method [19].

Sample solutions (5 cm^3 with 8×10^{-5} M concentration) for long-term photolysis in quartz cells were deaerated by solvent saturated nitrogen (N_2) gas.

The samples were housed in the thermostated block at room temperature under the same geometrical restraints as the actinometer solutions. During photolysis UV–Vis spectra as well as absorption values at 437 nm for $Cu(dtc)_2$ and 425 nm for $Cu(dtp)_2$ were taken at regular intervals. Each calculation of quantum yield was based on two actinometry determinations performed before and after a photochemical run. The quantum yields at wavelengths less that 313 nm were not measured because of the complication of light absorption by the solvents. The accuracy of the quantum yield measurements was found to be within 20–25%.

For EPR measurements 5×10^{-3} M sample solutions were irradiated with the full spectrum of the mercury lamp directly in the spectrometer cavity.

Results and discussion

Solutions of $Cu(dtc)_2$ and $Cu(dtp)_2$ in acetone, toluene and chlorohydrocarbon solvents ($CHCl_3$ and CCl_4) could be kept for several days in the dark without any changes in their UV–Vis and EPR spectra and particularly in their LMCT absorption bands at 437 and 425 nm, respectively, as well as their EPR signals with $g = 2.049$, $^{Cu}a = 79$ G for $Cu(dtc)_2$ and $g = 2.046$, $^{Cu}a = 75$ G, $^{P}a = 9.5$ G for $Cu(dtp)_2$ in all solvents.

Photoreduction of Cu(dtc)$_2$

The UV–Vis absorption of $Cu(dtc)_2$ in acetone, toluene and chlorohydrocarbon ($CHCl_3$ and CCl_4) solutions gradually decreases upon irradiation with the appearance of one time dependent isosbestic point at 408 nm (Fig. 1). Under the same experimental conditions the intensity of the EPR spectrum decreases (Fig. 2) following the reduction of Cu(II) to Cu(I). A low intensity EPR signal similar in shape and parameters ($g = 2.064$, $^{Cu}a = 72$ G) to the mixed-ligand Cu(II) complexes [20] appears as an intermediate. In all EPR experiments the photoreactions are followed by the formation of a fine green precipitate. The precipitate dissolves when ethanol is added to the irradiated solutions. Immediately after that the EPR spectrum of the complex Cu(dtc)Cl with equatorially coordinated chloride ion appears (Fig. 3) in chlorohydrocarbon/ethanol mixed solvents. The same complex is the intermediate photoproduct obtained during the UV irradiation of $Cu(dtc)_2$ in chlorohydrocarbon/ethanol solvent mixtures from 9/1 to 3/7 vol./vol. with $CuCl_2$ observed as a final product.

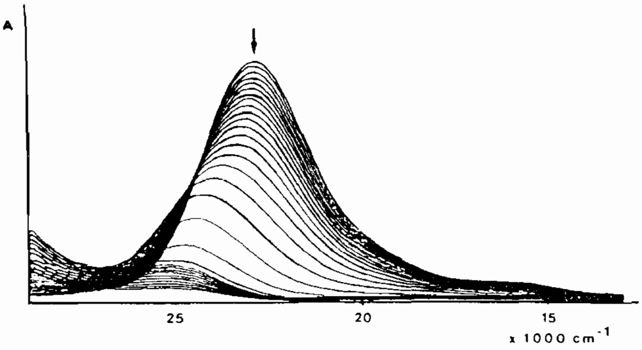

Fig. 1. UV–Vis spectra taken after consecutive 15 min irradiations of the $Cu(dtc)_2$ complex dissolved in $CHCl_3$.

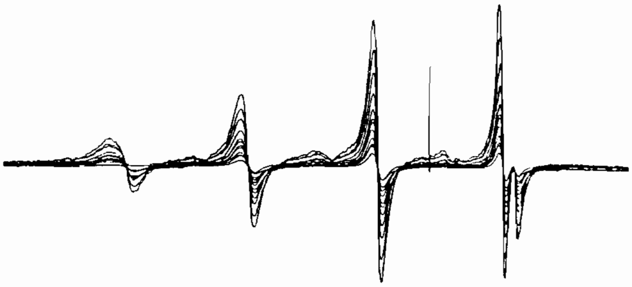

Fig. 2. EPR spectra taken after consecutive 15 min irradiations of the $Cu(dtc)_2$ complex in toluene.

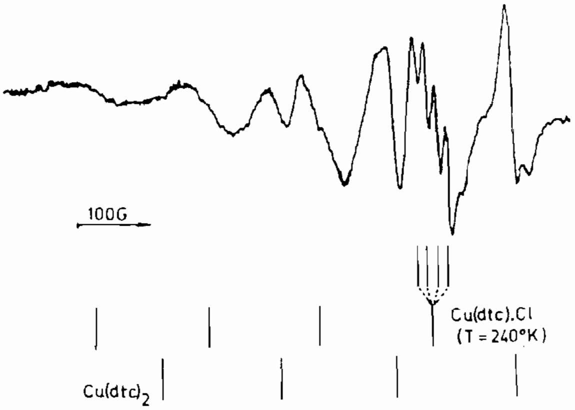

Fig. 3. EPR spectrum of Cu(dtc)Cl mixed-ligand complex ($T = 240$ K).

Photoreduction of Cu^{II}(dtp)$_2$

Irradiation of acetone, toluene and chlorohydrocarbon (CCl_4 and $CHCl_3$) solutions of $Cu(dtp)_2$ resulted in reduction to Cu(I) with gradually decreasing UV–Vis and EPR spectra (Fig. 4) and without any isosbestic point or intermediate EPR signal. When the irradiated solutions containing the photoproduct $Cu^{I}(dtp)$ are kept for 24 h in the dark the electronic and EPR spectra show partial reconversion into $Cu(dtp)_2$.

Quantum yield

The values of the quantum yield were measured for the reduction of $Cu(dtp)_2$ and $Cu(dtc)_2$ complexes upon irradiation. The data obtained under different conditions are presented in Table 1.

As seen from the data reported in Table 1 the ϕ_{red} values of both complexes are very similar which implies that the LMCT excited state responsible for the photoreduction of Cu(II) to Cu(I) has energy and redox reactivity which depends only on the chromophore CuS_4. On the other hand both complexes $Cu(dtc)_2$ and $Cu(dtp)_2$ show solvent independent photochemistry upon irradiation. A possible explanation for this unexpected behaviour should be found in the weakness of the CTTS complex between $Cu(dtp)_2$ and $CHCl_3$ [14] or CH_3OH [21]. It is obvious that the equilibrium concentration of this complex detected by ENDOR in frozen solutions is too low at room temperature and could not exhibit any influence on the quantum yield.

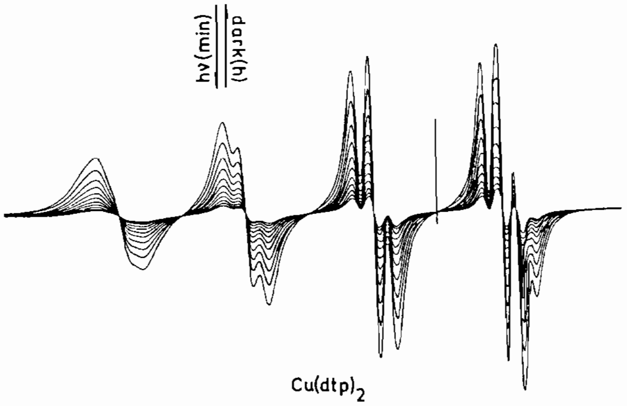

Fig. 4. EPR spectra taken after consecutive 15 min irradiations of the $Cu(dtp)_2$ complex in toluene and then taken every 2 h on keeping the irradiated sample in the dark.

TABLE 1. Quantum yields of Cu(I) formation (10^2 ϕ_{red}) by irradiation of $Cu(dtp)_2$ and $Cu(dtc)_2$ in different solvents[a]

Solvent	$Cu(dtc)_2$			$Cu(dtp)_2$		
	313 nm	436 nm	578 nm	313 nm	436 nm	578 nm
CCl_4	3.1	3.7	0.024	3.8	4.2	0.03
$CHCl_3$	2.8	3.7	0.023	4.6	3.2	0.036
Toluene	2.6	3.3	0.022	3.4	3.7	0.031
Acetone	3.6	3.4	0.027	4.0	3.8	0.036

[a] With $Cu(dtc)_2$ and $Cu(dtp)_2$ concentration 8×10^{-5} M.

Mechanism

The experimental results reported about the photoinduced reduction of $Cu(dtc)_2$ and $Cu(dtp)_2$ are in accordance with the following scheme in which the primary photochemical act is an intramolecular electron transfer from an equatorially bonded S atom of the ligand to copper(II).

$$2Cu^{II}(SR)_2 \overset{h\nu}{\rightleftarrows} 2Cu^{I}(SR) + RS\text{–}SR \qquad (1)$$

where SR = dtc, dtp.

The data obtained before [22] about the interaction of $Cu^{I}(dtc)$ with halogen-containing hydrocarbons in the presence of ethanol could be used to explain the formation of Cu(dtc)Cl according to the reaction

$$Cu^{I}(dtc) + RX \longrightarrow Cu^{II}(dtc)X + RX(n-1) \qquad (2)$$

where $RX = CCl_4$, $CHCl_3$.

The photoproduct $Cu^{I}(dtc)$ is stable in toluene and acetone since thermal oxidation to Cu(II) does not take place in them [22].

The partial reconversion of the photoproduct $Cu^{I}(dtp)$ into $Cu^{II}(dtp)_2$ is due to the following thermal reaction already studied [16, 23]

$$2Cu^{I}(dtp) + RS\text{–}SR \rightleftarrows 2Cu^{II}(dtp)_2 \qquad (3)$$

where RS = dtp.

The initial $Cu^{II}(dtp)_2$ complex is not completely reconverted since the disulfide obtained is also included in a photochemical reaction as has been pointed out for thiuramdisulfide [7].

Our previous study [23] could also be used to explain the difficulties in detecting the mixed-ligand complex of $Cu(dtp)_2$ as intermediate photoproduct.

Conclusions

The results obtained from the investigation on the photoredox properties of $Cu(dtc)_2$ and $Cu(dtp)_2$ in acetone, toluene and chlorohydrocarbon (CCl_4 and $CHCl_3$) solvents show that the energy and reactivity of the LMCT excited state responsible for the primary photoreduction process is determined by the chromophore CuS_4.

The mechanism of the primary photochemical act is discussed in terms of an intramolecular electron transfer from an equatorially bonded S atom of the ligand to copper(II).

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