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Photochemistry of Dithiocarbamate Cu(II) Complex in CCl_4

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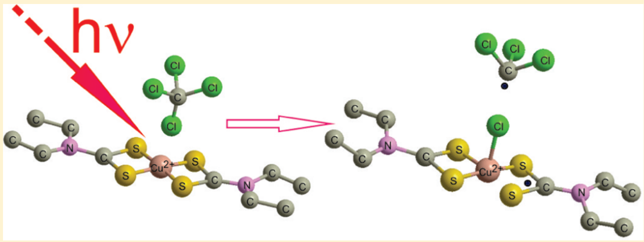
ABSTRACT: Laser pulse photolysis was used to study the nature and reactions of intermediates in the photochemistry of the flat dithiocarbamate complex $Cu(Et_2dtc)_2$ in CCl_4. A nanosecond laser pulse (355 nm) is shown to induce intermediate absorption bands of bivalent copper complex whose coordination sphere contains a dithiocarbamate radical $Et_2dtc^\bullet$ and a chloride ion at the axial position ($[(Et_2dtc)Cu(Et_2dtc^\bullet)Cl_a]$). At room temperature during some microseconds after the laser pulse, this intermediate interacts with the initial complex to form presumably a dimer $[Cu_2(Et_2dtc)_3(Et_2dtc^\bullet)Cl]$. The latter vanishes in the second-order reaction. Analysis of kinetic and spectral features gives the arguments for the formation of a cluster $[Cu_2(Et_2dtc)_3Cl\text{-tds-}Cu_2(Et_2dtc)_3Cl]$, which produces a new absorption band at 345 nm. The cluster decomposes in ∼5 ms into final products, a binuclear complex $[Cu_2(Et_2dtc)_3Cl]$ and tetraethylthiuramdisulfide (Et_4tds).



1. INTRODUCTION

Copper−sulfur interactions have been of marked interest in the different research fields such as the copper-thiolate chemistry,[1] "blue" copper electron transfer proteins,[2] Cu-thiolate proteins,[3,4] synthesis of coordination polymers,[5] and solar cell.[6] A new focus of interest in copper−sulfur coordination chemistry is derived from the recent discovery of a tetra-copper-sulfide cluster at a so-called CuZ active site of nitrous oxide reductase.[7]

Copper(II) dithiocarbamate is successfully used as a single source precursor for the growth of semiconducting copper sulfide thin films.[8] The iron(II) and iron(III) dithiocarbamates have been studied for their spin crossover phenomenon,[9] radical traps for NO,[10] and as antioxidants and pro-oxidants in biological systems.[11] Diethyl dithiocarbamates are also known to inhibit the activity of Cu/Zn-superoxide dismutase (SOD) through the withdrawal of copper from the protein.[12] Some dialkyl-substituted dithiocarbamates have proved to be efficient antialkylating, anti-HIV, and froth-floatation agents.[13] The optical and electrochemical properties of dithiocarbamates can effectively be used to construct sensors for guest molecules and macromolecules.[14−16]

The dithiocarbamate ligand wide ranging coordination chemistry has led to the formation of an array of novel and complex supramolecular architectures.[17] Macrocycles, cages, catenanes, and nanodimensional assemblies can be generated using a variety of oligomeric dithiocarbamate constructs in combination with transition metals. The use of the dithiocarbamate ligand has recently expanded to stabilizing gold nanoparticles and preparing multimetallic wires and arrays.[18]

It should be noted that dithiocarbamate complexes of metal ions are widely employed in analytical chemistry,[19,20] organic synthesis,[21] medicine,[22] biology,[23] as radiation protectors,[24,25] antioxidants[26] and polymer photostabilizers.[27] Dithiocarbamate ligands form complexes with all transition metals. Moreover, they can stabilize metal ions at high oxidation levels. Well known are the following dithiocarbamate complexes: Ru(IV),[28] Au(III),[29,30] Cu(III),[31] Ni(IV),[31−33] and Fe(IV).[34]

The photochemistry of dithiocarbamate complexes is poorly known despite a great number of works on the chemistry and spectroscopy of these particles. These publications are devoted mainly to stationary photolysis.[35−38] Therefore, for many dithiocarbamate complexes the mechanisms of photochemical reactions and the nature of intermediates remain unknown.

The steady-state photochemistry of both the dithiocarbamate complex $Cu(II)(Et_2dtc)_2$ in chloroform and its mixtures with ethanol is analyzed in.[39,40] This complex displays an absorption band at 437 nm ($\varepsilon = 13000\ M^{-1}cm^{-1}$). When the $Cu(Et_2dtc)_2$ solution in chloroform is irradiated with the light of mercury lines at 313, 436, and 578 nm, the absorption band at 437 nm vanishes to form a less intense band at 420 nm with the appearance of an isosbestic point at 408 nm.[39] Further irradiation leads to a decrease in band intensity at 420 nm and the formation of a new band at 350 nm. Continuous irradiation causes the complete disappearance of the band at 350 nm and the complete bleaching of the solution. Small additions of ethanol to chloroform (1:150) decrease the manifestation of the band at 350 nm, and when the ethanol-to-chloroform ratio is 1:10, it fails to appear.[40] In[39] it is

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assumed that a new band at 420 nm refers to the Cu(II)(Et$_2$dtc)Cl$_e$ complex which results from the reactions (from now on in chemical reactions the Et$_2$dtc$^-$ ligand, the Et$_2$dtc$^\bullet$ radical and tetraethylthiuramdisulfide Et$_4$tds will be denoted as dtc$^-$, dtc$^\bullet$ and tds, respectively)

$$\mathrm{Cu(II)(dtc)_2} \xrightarrow{h\nu,\,\mathrm{CHCl_3}} \mathrm{(dtc)Cu(I)(dtc^\bullet \cdots CHCl_3)} \quad (1)$$

$$\mathrm{(dtc)Cu(I)(dtc^\bullet \cdots CHCl_3)} \rightarrow \mathrm{Cu(II)(dtc)Cl_e} + \mathrm{dtc^\bullet} + {}^\bullet\mathrm{CHCl_2} \quad (2)$$

$$\mathrm{dtc^\bullet} + \mathrm{dtc^\bullet} \rightarrow \mathrm{tds} \quad (3)$$

In the intermediate complex (dtc)Cu(I)(dtc$^\bullet$$\cdots$CHCl$_3$), the dithiocarbamate radical dtc$^\bullet$ is coordinated with the copper ion by one sulfur atom and the second sulfur atom is bound via the donor−acceptor bond to a chloroform molecule. This complex transforms to the Cu(II)(dtc)Cl$_e$ complex to which the band at 420 nm belongs. It is worth noting that the authors assume that the chloride ion is coordinated in the equatorial plane. When chloroform contains no ethanol additive, Cu(II)(dtc)Cl$_e$ is dimerized to form the Cu$_2$(dtc)$_2$Cl$_2$ complex, which gives an absorption band at 350 nm.[40]

$$2\mathrm{Cu(II)(dtc)Cl_e} \rightarrow \mathrm{Cu_2(dtc)_2Cl_2} \quad (4)$$

Ethanol molecules are assumed to block coordination place in the equatorial plane. Therefore, no dimers are formed in the presence of ethanol and, thus, no band is recorded at 350 nm. The free dithiocarbamate radicals dtc$^\bullet$, resulting from decomposition of the (dtc)Cu(I)(dtc$^\bullet$$\cdots$CHCl$_3$) complex, recombine to thiuramdisulfide.[40]

Upon irradiation the intensity of the Cu(Et$_2$dtc)$_2$ complex lines in the ESR spectrum ($g = 2.049$, $a_{\mathrm{Cu}} = 79$ G) decreases due to copper ion reduction to the monovalent state.[39] In the presence of ethanol, continuous irradiation gives rise to a weaker ESR signal of the Cu(II)(dtc)Cl$_e$ complex. In pure ethanol-free chloroform, the ESR spectrum vanishes completely owing to the formation of the diamagnetic dimer Cu$_2$(dtc)$_2$Cl$_2$.

The quantum yield of Cu(Et$_2$dtc)$_2$ disappearance is close to 3×10^{-2} upon irradiation at 254 and 313 nm and is actually independent of ethanol concentration in chloroform. Changing to a wavelength of 436 nm leads to a decrease in quantum yield by order of magnitude.

Thus, the Cu(II)(dtc)Cl$_e$ complex is the final product of the irradiation of Cu(Et$_2$dtc)$_2$ solutions. This complex (Cu(II)(dtc)Cl$_e$) displays two optical absorption bands with maxima at 264 and 420 nm (ε = 3350 and 5800 M^{-1} cm^{-1}, respectively) and the ESR spectrum with parameters $g = 2.074$, $a_{\mathrm{Cu}} = 75$ G, and $a_{\mathrm{Cl}} = 7.6$ G. It can also be subjected to the photochemical transformation whose mechanism is schematically depicted in[41−43]

$$\mathrm{Cu(II)(dtc)Cl_e} \xrightarrow{h\nu} [\mathrm{Cu(I)(dtc^\bullet)Cl_e}]^* \quad (5)$$

$$[\mathrm{Cu(I)(dtc^\bullet)Cl_e}]^* \rightarrow \mathrm{Cu(I)Cl} + \mathrm{dtc^\bullet} \quad (6)$$

$$\mathrm{Cu(I)Cl} + \mathrm{CHCl_3} \rightarrow \mathrm{Cu(II)Cl_2} + {}^\bullet\mathrm{CHCl_2} \quad (7)$$

$$\mathrm{dtc^\bullet} + \mathrm{dtc^\bullet} \rightarrow \mathrm{tds} \quad (8)$$

$${}^\bullet\mathrm{CHCl_2} + {}^\bullet\mathrm{CHCl_2} \rightarrow \mathrm{Cl_2HCCHCl_2} \quad (9)$$

The final products of Cu(II)(dtc)Cl$_e$ phototransformation are thiuramdisulfide and the complex of monovalent copper ion which is transformed in the reaction with chloroform into the Cu(II)Cl$_2$ complex. Upon lasting irradiation of the Cu(Et$_2$dtc)$_2$ solution, the initial complex is first transformed into Cu(II)(dtc)Cl$_e$ and then into Cu(I)Cl and, finally, into Cu(II)Cl$_2$. The latter has low solubility in nonpolar solvents and often gives a light-green precipitate.

The aforementioned schemes of the phototransformations of the Cu(Et$_2$dtc)$_2$ and Cu(II)(dtc)Cl$_e$ complexes are based on the results obtained only by stationary optical spectroscopy and ESR. Therefore, the nature and reactions of intermediates remain actually unknown. The goal of the present work is to study the mechanism of the photochemical transformations of the Cu(Et$_2$dtc)$_2$ complex in CCl$_4$ and to determine the spectra, kinetics, and rate constants of the reactions of excited states and intermediates upon femto- and nanosecond laser flash photolysis.

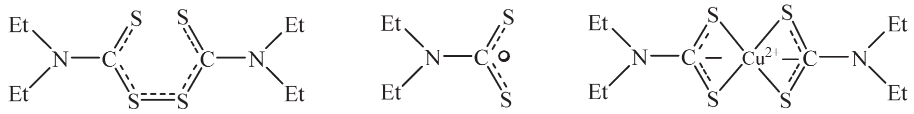
2. EXPERIMENTAL DETAILS

The laser flash photolysis of solutions was performed using a setup with a neodymium laser (third harmonic, 355 nm, 7 ns, 10−50 mJ).[44,45] The exciting and probing light beams intersect at a small angle (~2°) in a sample. Some experiments were fulfilled using a similar setup for laser flash photolysis[46] with perpendicular geometry of exciting and probing light beams. After photomultiplier the signal was recorded by a digital Tektronix 7912AD oscillograph, connected to a computer.

When the initial concentration of Cu(Et$_2$dtc)$_2$ in CCl$_4$ was about $3{-}7 \times 10^{-5}$ M, the optical density at the band maximum at 435 nm did not exceed unity, which made it possible to measure the kinetics of absorption variations in the region of this band as well. At a wavelength of laser radiation of 355 nm, the absorption coefficient of the band ε = 1300 M^{-1} cm^{-1}. Therefore, the optical density was close to 0.1 and about 20% of laser radiation was absorbed by solution. A special cryostat with quartz optical windows and a system of automated temperature maintenance to within ±0.5 C were used in the measurements performed at temperatures differing from the room one. When necessary, oxygen was removed by blowing argon through solution for 15−20 min. For determining of quantum yields, the laser pulse energy was measured using the ferrioxalate actinometer and the system of a firm Gentec-EO (Canada)-(SOLO-2 monitor and pyroelectric measuring cap QE25SP-H-MB). The intensity of mercury lines was measured by means of the same system with a photodiode measuring cap PH100-SiUV.

The ultrafast relaxation processes of the Cu(Et$_2$dtc)$_2$ excited states have been studied using a setup for femtosecond flash photolysis (pump−probe spectroscopy).[47] The samples were excited by pulses of a duration of 100 fs at a wavelength of 390 nm (second harmonic of the Ti:sapphire generator with an amplifier, CDP Ltd., Moscow, Russia) with a pulse repetition frequency of 10 Hz. The accumulation of about 200 repeating pulses was used to record one spectrum. The Cu(Et$_2$dtc)$_2$ solution was placed in a rotating cuvette 1 mm thick to irradiate it more uniformly and to exclude thermal heating. For the first 3 ps, the time-resolved spectra were recorded with a shift of 100 fs and then with logarithmically increasing delay times. Usually, about 60−70 spectra were recorded over the range of 20−30 ps. The program for processing experimental data introduced corrections for the group velocity dispersion and an instrumental response function.

Scheme 1



Thiuramdisulfide Et_4tds

Dithiocarbamate radical $Et_2dtc^{\bullet}$

Dithiocarbamate Cu^{2+} complex $Cu(Et_2dtc)_2$

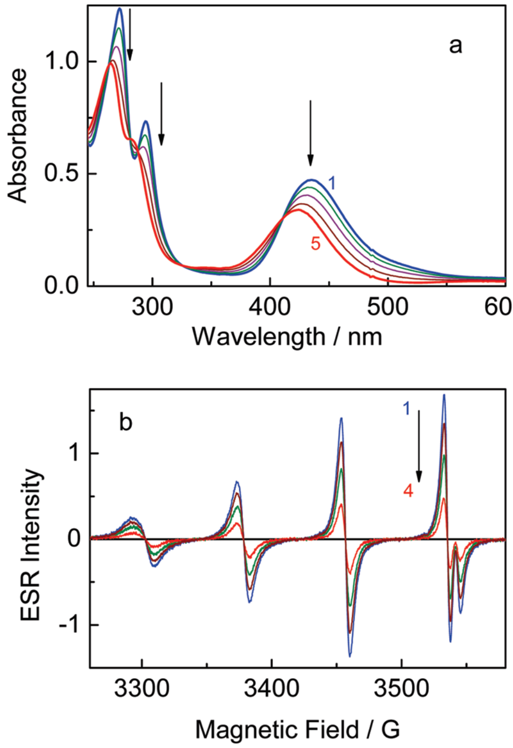


Figure 1. Changes in optical (a) and ESR (b) spectra of $Cu(Et_2dtc)_2$ (3.6×10^{-4} M) complex in CCl_4 under irradiation with light of mercury line at 365 nm. Optical and ESR spectra detected for same solution at same time of irradiation; **1**−**4**: 0, 6, 15, and 45 s of irradiation. Spectrum **5** is the calculated spectrum of final product. Optical spectra were registrated in 1 mm cuvette.

The total time resolution varied over the range of 150−200 fs. All femtosecond experiments were carried out at room temperature.

Stationary irradiation was performed using either the pulses of a neodymium laser (third harmonic, 355 nm) or the light of high-pressure mercury lamp (DRSh-500). Single lines of the mercury lamp were isolated by means of an interferential filter (436 nm), a combination of UFS-8 and BS-7 filters (365 nm). The optical absorption spectra were recorded using HP 8453 and Shimadzu UV-2501 spectrophotometers in quartz cuvettes with a length of optical path of 0.01−1 cm. The $Cu(Et_2dtc)_2$ complex was synthesized, purified, and analyzed as described in ref 48. Solutions were prepared by means of spectrally pure solvents.

The numerical calculations of the kinetics of intermediate optical absorption disappearance including differential equations were solved using a particular program based on the fourth-order Runge−Kutta method. The program allows calculations and fitting to experimental kinetic curves simultaneously at many wavelengths.

3. RESULTS

3.1. Stationary Photolysis of $Cu(Et_2dtc)_2$ Solutions. $Cu(Et_2dtc)_2$ is a flat complex with Cu−S distances of about 2.31 Å and S−Cu−S angles of about 77° (sulfur atoms belong to the same ligand).[49,50] Beyond the plane there are the atoms of the ethyl groups only. The structures of $Cu(Et_2dtc)_2$ complex, thiuramdisulfide and dithiocarbamate radical are shown in Scheme 1. The optical absorption spectrum of the $Cu(Et_2dtc)_2$ complex in chloroform contains absorption bands with maxima at 437, 294, and 272 nm and extinction coefficients of 13000, 20000, and 33000 $M^{-1} \times cm^{-1}$, respectively.[40] A weak absorption in the range of 500−650 nm refers to d−d transitions. In CCl_4, the optical spectrum of the complex exhibits the same parameters.

Figure 1a shows the optical spectrum of the $Cu(Et_2dtc)_2$ complex in CCl_4 and its variations under irradiation with the light of the mercury line at 365 nm. Under initial irradiation, the intensity of the bands at 435 and 294 nm decreases. As a result, a new spectrum is formed with the bands at 424, 341sh, 281, and 264 nm upon retention of isosbestic points at 411, 326, 287, 281, and 263 nm. This change caused by initial irradiation is in agreement with the data given in ref 39 for the $Cu(Et_2dtc)_2$ photolysis in chloroform where the isosbestic point was observed at 408 nm. Under longer irradiation, the isosbestic points vanish due to the further photolysis of products.

A similar change in optical spectrum is caused by irradiating the $Cu(Et_2dtc)_2$ solution in CCl_4 with pulses of a neodymium laser (third harmonic, 355 nm). Because the radiation power in the latter case is by ~8 orders of magnitude higher, the similar spectral variations indicate the absence of two quantum processes upon laser excitation.

Figure 1b shows changes in the ESR spectrum of $Cu(Et_2dtc)_2$ solution under irradiation with the light of the mercury line at 365 nm. The ESR spectra were recorded at the same solutions and the same times of irradiation as in Figure 1a. Thus, irradiation of the $Cu(Et_2dtc)_2$ solution causes the initial ESR spectrum to disappear without forming any new signals, which indicates either the diamagnetic nature of the product or the product with more wide lines are spread in major range of the magnetic field. The comparison of ESR and optical data allows to calculate the optical spectrum of final product presented as spectrum 5 in Figure 1a.The absorption coefficient of 424 nm band is 9350 M^{-1} cm^{-1} if to calculate it on one copper ion.

At low concentration of the initial $Cu(Et_2dtc)_2$ complex (~10^{-4} M), the product of photolysis with new bands at 424, 341sh, 281, and 264 nm is stable in solution. However, the increase of $Cu(Et_2dtc)_2$ concentration up to 4×10^{-4} M leads to slow disappearance of optical spectrum of photolysis product and to formation of black precipitate. Time of its formation at room temperature is more than 3 h. At higher concentrations (up to

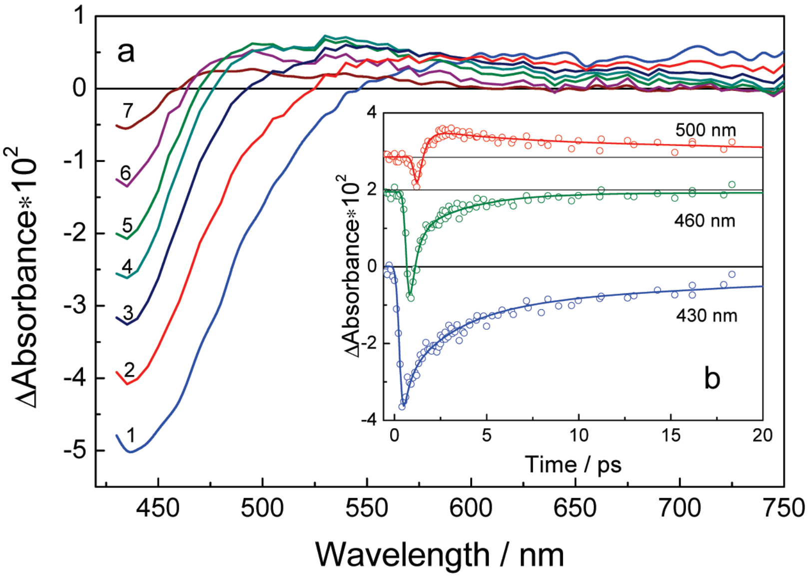


Figure 2. Intermediate spectra (a) and kinetics of absorption change at 500 and 440 nm (b) upon femtosecond flash photolysis (390 nm) of $Cu(Et_2dtc)_2$ (3.4×10^{-4} M, 1 mm cuvette) in CCl_4. Spectra **1**−**7**: 0, 0.2, 0.5, 1, 2, 5, and 30 ps after the laser pulse.

4×10^{-3} M), the optical spectrum of $Cu(Et_2dtc)_2$ disappears under irradiation without any isosbestic points with the immediate formation of black precipitates (the photolysis was performed in 0.01 cm cuvette). In this case, the absorption bands of thiuramdisulfide (Et_4tds) remain in the spectrum. The yield of Et_4tds is one-quarter of the initial concentration of the $Cu(Et_2dtc)_2$ complex. So, the thiuramdisulfide is one of the products of $Cu(Et_2dtc)_2$ photolysis in parallel with the compound, which has low solubility in CCl_4 and falls out as precipitate at $[Cu(Et_2dtc)_2] \geq 4 \times 10^{-4}$ M. The presence of Et_4tds as the photolysis product can also be detected by thin layer chromatography (TLC).

3.2. Ultrafast Relaxation Processes of the Excited $Cu(Et_2dtc)_2$ Complex. The $Cu(Et_2dtc)_2$ complex in acetonitrile solution exhibits no photochemical activity, probably due to fast relaxation processes. The time characteristics of these processes were determined by femtosecond flash photolysis. Exciting the $Cu(Et_2dtc)_2$ complex in acetonitrile by the pulse of the second Ti:sapphire laser harmonic (100 fs, 390 nm) leads to a change in the initial absorption, which vanishes during several picoseconds. A global treatment of kinetic curves at all wavelengths provides satisfactory results in the framework of a two-exponential model with characteristic times of 0.39 and 2.9 ps. The excitation at 390 nm corresponds to the long-wave LMCT transition. The first process of 0.39 ps can correspond to the fast vibrational relaxation in the excited state, and the second one (2.9 ps) can correspond to the return of the complex to its ground state.[51] Thus, the fast relaxation to the ground state prevents development of photochemical processes.

For $Cu(Et_2dtc)_2$ in CCl_4, the spectral and kinetic parameters of the intermediate absorption upon femtosecond photolysis are presented in Figure 2. They almost coincide upon femtosecond pulse with the values obtained for acetonitrile. The pulse in the long-wave part of the spectrum ($\lambda > 530$ nm) is immediately followed by additional absorption. In a more short-wave region ($\lambda < 530$ nm), the bleaching is formed due to absorption disappearance from the ground state of the complex (Figure 2a). The global treatment of the kinetic curves using the two-exponential model provides characteristic times of 0.33 and 2.2 ps (solid line in the kinetic curve, Figure 2b). In this case, at times exceeding 20−30 ps, a broad absorption band is observed in the region of 500−600 nm. Its intensity is substantially weaker than the initial bleaching in the band (435 nm) of the initial complex because the quantum yield decreases by order of magnitude upon irradiation wavelength shift from ∼300−350 to 400 nm.[39,40] The excited state almost fully relaxes to the ground state and only a small part of the molecules is involved in the photochemical reaction. The consequences of these initial processes will be discussed below using results from nanosecond laser flash photolysis.

3.3. Quantum Yield of $Cu(Et_2dtc)_2$ Disappearance. The absence of $Cu(Et_2dtc)_2$ photochemical activity in acetonitrile allows one to determine the dependence of the quantum yield of complex disappearance on CCl_4 concentration (at 365 nm in Figure 3a). Initially, the quantum yield is observed to increase linearly with CCl_4 concentration passing at high concentrations to saturation. When the lifetime of the excited state is about 2−3 ps, diffusion can bring an electron acceptor (in our case, a CCl_4 molecule) to the excited complex over a distance of about 1 Å. Thus, the electron transfer is possible if the CCl_4 molecule is in the first (along the axial axis of the flat complex) coordination sphere of the excited complex. In these conditions, the data on the quantum yield are processed (Figure 3a) by Perrin's "black sphere" model used to determine the distance of energy transfer upon molecule luminescence quenching in either polymer films or frozen matrices in the absence of diffusion. The Perrin formula modified for our case is of the form

$$\varphi(C) = \varphi_\infty(1 - e^{-\Omega C}) \qquad (10)$$

where C is the CCl_4 concentration, φ_∞ is the quantum yield at the infinitely high concentration of the acceptor, $\Omega = (4/3)\pi R^3 N_0$ is the volume of the "black sphere" in which electron transfer occurs, R is the black sphere radius, and N_0 is the Avogadro number. The solid line in Figure 3 denotes calculations according to the modified Perrin formula with $R = 5.7$ Å.

Thus, the photochemical transformation of $Cu(Et_2dtc)_2$ is possible only if the CCl_4 molecule is close to the complex. The

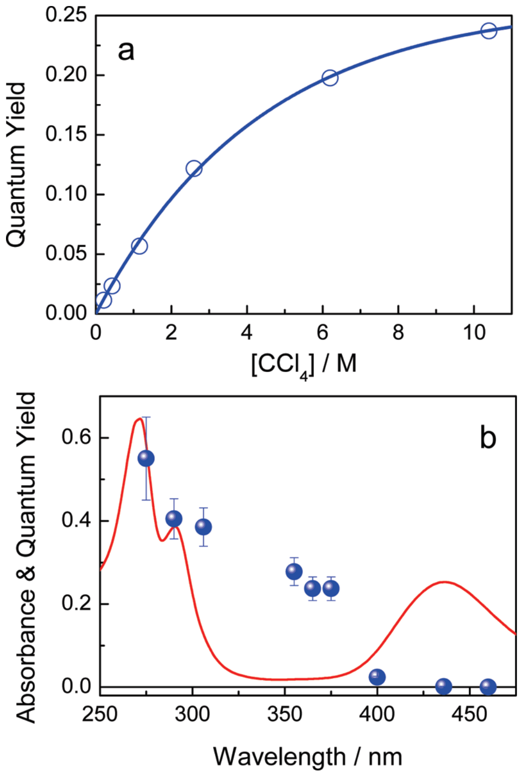


Figure 3. Dependence of the quantum yield of Cu(Et$_2$dtc)$_2$ disappearance on CCl$_4$ concentration in acetonitrile at 365 nm (a) and on wavelength (b). Solid line in (a): calculations according to the modified Perrin formula with the "black sphere" radius *R* = 5.7 Å (see text).

CCl$_4$ radius is about 3.57 Å (the length of the C−Cl bond is 1.77 Å and the chlorine atom radius is 1.8 Å[52]). About 2 Å of the black sphere radius account for the complex, that is, the CCl$_4$ molecule must be located above the flat complex, more probably, at the fifth free coordination position.

Figure 3b demonstrates the dependence of quantum yield on wavelength of irradiation. A considerable decrease of quantum yield in the range $\lambda > 350$ nm shows the low photochemical activity of excitation to the band with 435 nm maximum. It is most probable that bands that are related to intraligand excitation demonstrate higher quantum yields. As the 435 nm band is LMCT band it means that photochemical process is more effective with the electron transfer from excited dithiocarbamate ligand to CCl$_4$ molecule.

3.4. Nanosecond Laser Flash Photolysis of Cu(Et$_2$dtc)$_2$ Solutions. A nanosecond laser pulse (7 ns, 355 nm) in the Cu(Et$_2$dtc)$_2$ solution in CCl$_4$ gives rise to intermediate absorption in the form of two broad absorption bands with maxima at 400 and 560 nm (Figure 4a). During the first microsecond, the absorbance of these bands increases with the exception of the range 435−480 nm where the absorbance decreases. After that, these bands vanish with different rates (kinetics are shown in Figure 4b). After 20 μs, the band at 390−410 nm almost fully vanishes to form a new absorption band at 350 nm. Absorption at 560−570 nm decreases much slower.

To study the spectral ranges of fast and slow processes as the first step of analysis of kinetic data, the global fitting with three exponential approximation (eq 11) of all kinetic curves at different wavelengths in the time interval 0−20 μs was made.

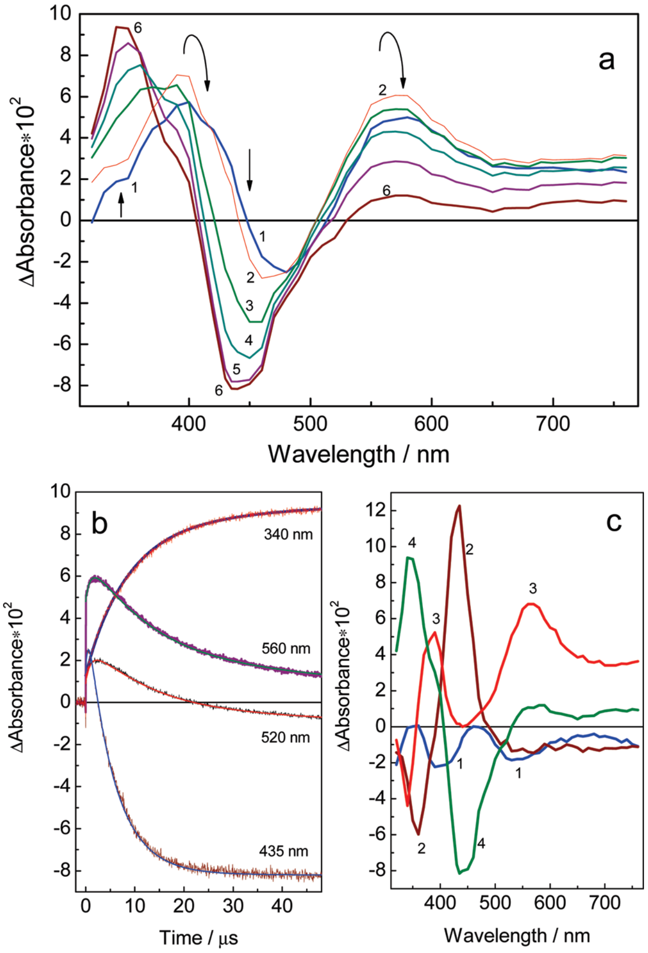


Figure 4. Spectra (a) and kinetics (b) of intermediate absorption arising from laser flash photolysis of Cu(Et$_2$dtc)$_2$ (1.26×10^{-4} M) in CCl$_4$; (c) **1**−**3**: amplitudes of exponents, obtained by global fitting of kinetics in the range 310−770 nm with three exponential approximation (see text). Times of exponents are 0.64, 6, and 14.8 μs; **4**: spectrum of A_∞; in (a), spectra **1**−**6**: 0, 1, 5, 10, 20, and 50 μs after laser pulse.

$$\Delta D(\lambda, t) = A_1(\lambda)e^{-t/\tau_1} + A_2(\lambda)e^{-t/\tau_2} + A_3(\lambda)e^{-t/\tau_3} + A_\infty(\lambda) \qquad (11)$$

This fitting has shown three characteristic times $\tau_1 = 0.63$, $\tau_2 = 6$, and $\tau_3 = 14.8$ μs (concentration of Cu(Et$_2$dtc)$_2$ complex is 1.26×10^{-4} M). The spectra of $A_1(\lambda)$, $A_2(\lambda)$, $A_3(\lambda)$, and $A_\infty(\lambda)$ amplitudes are shown in Figure 4c. First negative amplitude (increase of absorption) $A_1(\lambda)$ has a maximum near 400 and 530 nm. Second amplitude $A_2(\lambda)$ with a time of 6 μs has a maximum at 435 nm and exceeds the amplitude of the third slow exponent $A_3(\lambda)$ in order of value. At 560 nm, the situation is reverse, the A_3 amplitude considerably exceeds the rest of the amplitudes. Therefore, we have studied the dependence of relatively fast process on experimental conditions at 435 nm and more slow process at 560 nm. Amplitude $A_\infty(\lambda)$ shows a transient spectrum at long times, which begins to change only in millisecond time scale.

The first shortest time $\tau_1 = 0.63$ μs shows no dependence on amplitude of signal (laser intensity) and Cu(Et$_2$dtc)$_2$ concentration. It means that the first transient species (T1) is transformed in the first-order reaction with the rate constant $k = 1.6 \times 10^7$ s^{-1}

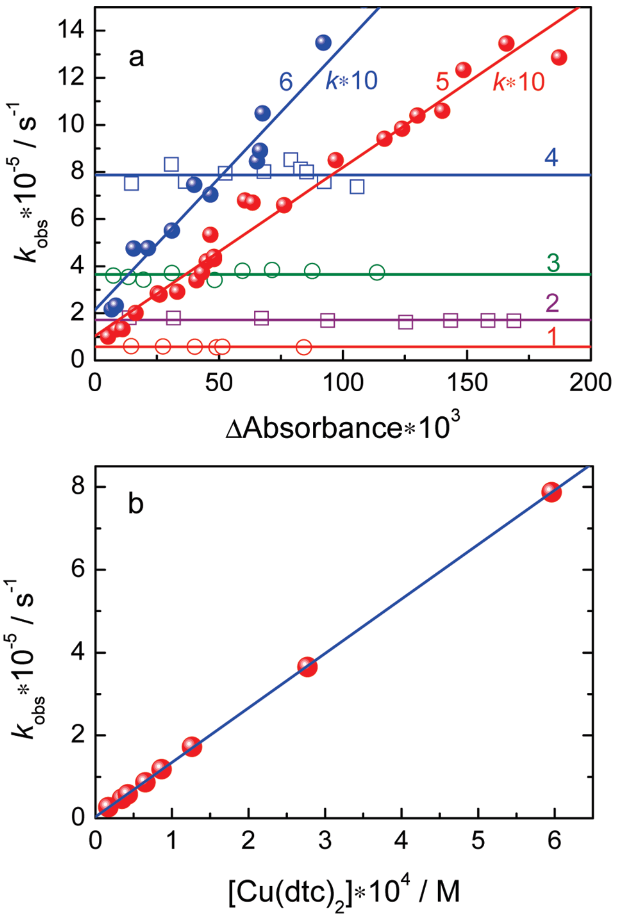


Figure 5. Dependence of k_{obs} at 345, 435, and 560 nm (a) on signal amplitude (ΔA) upon laser flash photolysis of $Cu(Et_2dtc)_2$ in CCl_4 and dependence of k_{obs} at 435 nm on $Cu(Et_2dtc)_2$ concentrations (b). In (a) for k_{obs} at 435 nm **1**−**4**, $[Cu(dtc)_2] \times 10^5 = 4.2, 12.6, 27.7, 59.6$ M; for visualization k_{obs} at 560 (**5**) and 345 (**6**) are multiplied by a factor of 10 and they practically are not dependent on $Cu(Et_2dtc)_2$ concentrations.

to the T2 transient. Figure 5a displays the dependence of the observed rate constant (k_{obs}) on the absorption amplitude (ΔA_0) at various concentrations of the initial $Cu(Et_2dtc)_2$ complex and at different wavelengths. The observed rate constant at 435 nm (lines 1−4) shows no dependence on the initial absorption amplitude (indication of the first-order or pseudofirst-order reaction) and linearly increases with the concentration of the initial complex (Figure 5b). This rise corresponds to the typical pseudo-first-order reaction of the T2 particle (the concentration of $Cu(Et_2dtc)_2$ is much higher than that of this intermediate) with the $Cu(Et_2dtc)_2$ complex and the formation of a third transient species (T3) with a bimolecular rate constant of $k = (1.31 \pm 0.01) \times 10^9$ M^{-1} s^{-1}.

The absorption at 560 nm changes more slowly as compare with absorption at 435 nm and the observed rate constant (k_{obs}) at 560 nm practically shows no dependence on the concentrations of $Cu(Et_2dtc)_2$ complex and increases linearly with the initial absorption amplitude (Figure 5a, line 5), which indicates the determined contribution of second-order reaction to decay of this absorption. It means that all transient species (T1, T2, T3) have comparable absorption in this spectral region (560 nm), and the T3 intermediate decays in second-order reaction with the formation of next T4 particle. The appearance of 345 nm absorption due to the formation of T4 species also is not depended on $Cu(Et_2dtc)_2$ concentrations and is close to second-order reaction. Really, the k_{obs} in this case increases linearly with the initial absorption amplitude (Figure 5a, line 6). It should be noted that, in Figure 5a, k_{obs} at 345 and 560 nm is multiplied by a factor of 10 for more clear presentation.

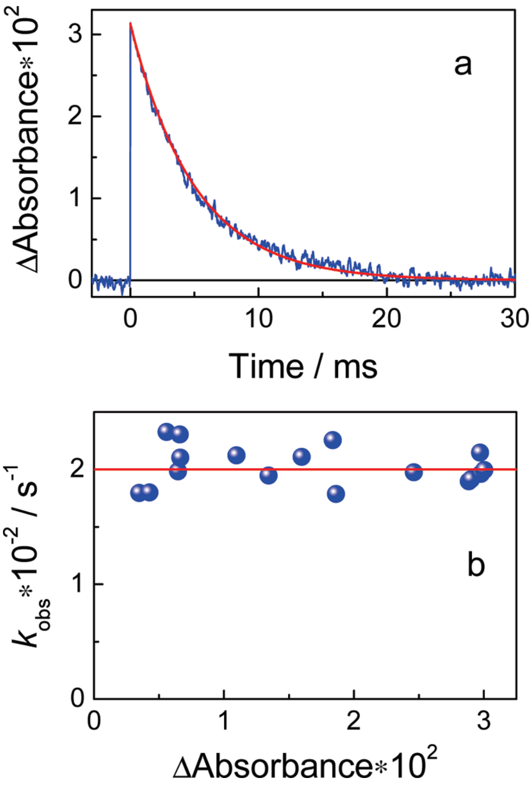


Figure 6. Kinetics (a) and dependence of k_{obs} on signal amplitude (ΔA) and (b) of intermediate absorption disappearance at 345 nm upon flash photolysis of $Cu(Et_2dtc)_2$ (1.26×10^{-4} M) solution in CCl_4.

The absorption band at 345 nm belongs to a relatively long living T4 particle, which disappears during some milliseconds (Figure 6a). The observed rate constant of absorption disappearance at 345 nm shows no dependence on the initial absorption amplitude (Figure 6b), which indicates that this particle vanishes in the first-order reaction ($k_{obs} = 200 \pm 30$ s^{-1}). Thus, the kinetics of absorption change upon laser pulse indicates the appearance of several intermediates. According to the set of characteristic times, four transients (T1−T4) appeared in consecutive order after laser pulse.

It is assumed in refs 39 and 40 that the excited $Cu(Et_2dtc)_2$ complex dissociates upon electron transfer from ligand to the central ion to form a free dithiocarbamate radical $Et_2dtc^{\bullet}$ (see Introduction). In acetonitrile, this radical displays the absorption band at 590 nm and the extinction coefficient $\varepsilon = 3100$ M^{-1} cm^{-1}.[53,54] The recombination rate constant of $Et_2dtc^{\bullet}$ radicals $2k_{rec} = 1.5 \times 10^{10}$ M^{-1} s^{-1} for acetonitrile solutions at room temperature is close to the diffusion rate constant calculated by the Debye−Smoluchowski formula ($k_{diff} = 1.92 \times 10^{10}$ M^{-1} s^{-1}).

3.5. Laser Flash Photolysis of Thiuramdisulfide (Et_4tds) in CCl_4.

A broad band with a maximum near 560 nm formed by flash photolysis of $Cu(Et_2dtc)_2$ could belong to the free $Et_2dtc^{\bullet}$ radical in CCl_4. In addition, it vanishes according to the second-order kinetic

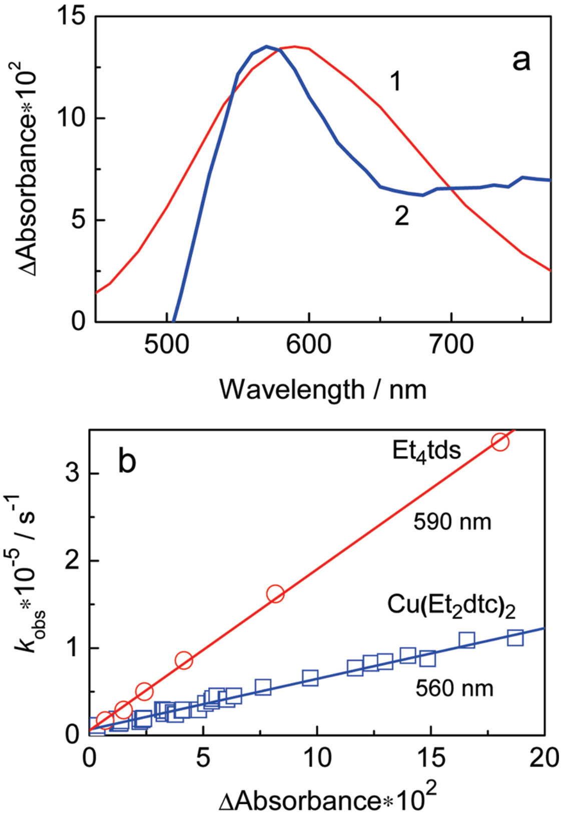


Figure 7. Spectra (a) and dependence of k_{obs} on signal amplitude (ΔA) and (b) of intermediates arising in laser flash photolysis of solutions of thiuramdisulfide (**1**) and $Cu(Et_2dtc)_2$(**2**) in CCl_4. Spectrum (**1**) belongs to free dithiocarbamate radical ($Et_2dtc^•$).

law (Figure 5a, line 5) which is in agreement with the reaction of recombination typical of the process of sulfur-containing radicals disappearance.[54] This assumption was verified by recording intermediate spectra and the kinetics of absorption changes upon laser flash photolysis of thiuramdisulfide (Et_4tds) in CCl_4. This molecule absorbs at 355 nm (ε = 3100 M^{-1} cm^{-1}) and can dissociate into two dithiocarbamate radicals.[53]

$$Et_4tds \xrightarrow{h\nu} 2Et_2dtc^• \tag{12}$$

Figure 7a shows the $Et_2dtc^•$ spectrum whose absorption band maximum in CCl_4 (590 nm) coincides with the position of a maximum in acetonitrile.[53] The band absorption coefficient in CCl_4 (ε = 3100 ± 300 $M^{-1}cm^{-1}$) was determined using the reaction between the $Et_2dtc^•$ radical and a stable nitroxyl radical.[54] Thus, the band (560 nm) arising from the $Cu(Et_2dtc)_2$ photolysis shifts to a more short-wave part of the spectrum (Figure 7a). Figure 7b shows also the dependence of the observed rate constant (k_{obs}) of the free $Et_2dtc^•$ radical disappearance in CCl_4 arising from the tds photolysis. The free radical is observed to vanish much faster than the particle to which the band at 560 nm belongs. The difference in the spectral and kinetic parameters indicates that the $Cu(Et_2dtc)_2$ photolysis gives rise to the particle which differs from the free dithiocarbamate radical. Therefore, the scheme of primary processes, given in refs 39 and 40 and described by reactions (1−3), should be modified.

4. DISCUSSION

4.1. Model of Photochemical Transformations. To explain the photochemical transformations for the $Cu(Et_2dtc)_2$ complex it is necessary to build up a model in which a new optical spectrum with a number of isosbestic points and ESR signal disappearance take place. Laser flash photolysis shows that the primary T1 intermediate is quickly converted ($\tau_1 \approx$ 630 ns) to the second T2 transient particle. The rate constant of this process shows no dependence on the $Cu(Et_2dtc)_2$ concentration and amplitude of initial transient absorption. The fact that the secondary T2 intermediates vanish in the reaction with the initial complex (the formation of T3 particle) should be taken into consideration. And at last we need to take into account that the more slow disappearance of absorption band at 560 nm (T3) is going on in second-order reaction.

The optical spectrum of $Cu(Et_2dtc)_2$ is independent of the nature of a solvent, and the absorption at 355 nm (laser wavelength) corresponds to the excited state in which charge transfer from ligands to a metal ion occurs (LMCT absorption). Of course, in this spectral range the intraligand transitions (LL band) can give the contribution to total absorption, as free dithiocarbamate ligand has absorption on this wavelength. As the quantum yield is much lower than unity, in both cases the excited state relaxes mainly to the ground state via electron transfer back to the ligand or by relax of excited ligand. As shown above, these processes end 2−3 ps after the laser pulse.

Because photochemical activity manifests itself only in the presence of CCl_4 molecules, if the excited complex has the CCl_4 molecule in first coordination sphere, the electron transfer competes with relaxation processes. In both cases, regardless of the nature of the excited state in the primary photochemical reaction, the complex with dithiocarbamate radical is formed

$$\begin{aligned} &Cu(II)(dtc)_2 \xrightarrow{h\nu} [Cu(I)(dtc)(dtc^•)]^*(LMCT) \\ &\quad \text{or} \quad Cu(II)(dtc)(dtc^*)(LL) \end{aligned} \tag{13}$$

$$\begin{aligned} &[Cu(I)(dtc)(dtc^•)]^* \cdots CCl_4 \\ &\rightarrow [Cu(II)(dtc)(dtc^•)]^+ \cdots CCl_4^{-•} \end{aligned} \tag{14}$$

$$\begin{aligned} &[Cu(II)(dtc)(dtc^*)] \cdots CCl_4 \\ &\rightarrow [Cu(II)(dtc)(dtc^•)]^+ \cdots CCl_4^{-•} \end{aligned} \tag{15}$$

If the cleavage one of the Cu−S bond occurs, the fast reverse electron transfer becomes impossible. As follows from the data on the radiation chemistry of halogen-containing solvents, the $CCl_4^{-•}$ radical ion dissociates rapidly (from the dissociation term) into the Cl^- ion and the $CCl_3^•$ radical.[55] The Cl^- ion and the $[Cu(II)(dtc)(dtc^•)]^+$ complex are located in the cage of the nonpolar solvent and can form the next generation of intermediates $[ClCu(II)(dtc)(dtc^•)]$.

$$CCl_4^{-•} \rightarrow Cl^- + CCl_3^• \tag{16}$$

$$[Cu(II)(dtc)(dtc^•)]^+ + Cl^- \rightarrow [ClCu(II)(dtc)(dtc^•)] \quad (T1) \tag{17}$$

The chloride ion in the $[ClCu(II)(dtc)(dtc^•)]$ complex occupies the axial position (as the parent CCl_4 molecule). Equations 13−17 are the fast processes and occur probably within subpico- or picosecond time range. Thus, at the moment of registration with nanosecond time resolution the $[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]$ complex is likely to be already formed (the T1 intermediate). In this case, the absorption band at 400 nm of this complex corresponds to electron transfer from the dtc^{-} ligand, and the band at 560 nm belongs to the $\mathrm{dtc}^{\bullet}$ radical coordinated with the copper ion via one sulfur atom (free radical $\mathrm{dtc}^{\bullet}$ has absorption band with maximum at 590 nm).

Fast kinetics with the characteristic time of τ_1 = 0.63 μs most likely is due to intramolecular rearrangement of $\mathrm{dtc}^{\bullet}$ radical in coordination sphere (denote this change of coordination sphere as transition S1 → S2)

$$[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]_{S1} \rightarrow [\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]_{S2} \quad (\mathrm{T2}) \tag{18}$$

Time τ_1 = 0.63 μs (the T1 → T2 transformation) shows no dependence on concentration both $\mathrm{Cu(Et_2dtc)_2}$ complex (in range 4×10^{-5} to 6×10^{-4} M) and transient species, and it is quite short for the second order reaction, even with diffusion rate constant. In our experiments, only the initial complex has a concentration of about 10^{-4} M, which could provide a short time of second order reaction.

The next process is the pseudo-first-order reaction, and its rate constant increases with the initial concentration of $\mathrm{Cu(Et_2dtc)_2}$. This dependence corresponds to the bimolecular rate constant $k = (1.31 \pm 0.02) \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$ (by 1 order of magnitude lower than the diffusion rate constant). The various mechanisms of the interaction between $[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]$ and the initial complex can be suggested. The reaction in which the $\mathrm{dtc}^{\bullet}$ radical is transferred from $[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]$ into the $\mathrm{Cu(Et_2dtc)_2}$ coordination sphere may be ignored, because the laser flash photolysis of a system containing $\mathrm{Cu(Et_2dtc)_2}$ and thiuramdisulfide (tds) has demonstrated that the $\mathrm{dtc}^{\bullet}$ radical disappears (recombines) independently of the presence of $\mathrm{Cu(Et_2dtc)_2}$. The electron transfer from the ligand of the initial complex to the radical of the intermediate is a degenerate reaction causing almost no changes in the system:

$$\begin{aligned}[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]_{S2} + \mathrm{Cu(dtc)_2} &\rightarrow \mathrm{Cu(II)(dtc)_2} \\ &+ [\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]\end{aligned} \tag{19}$$

More favorable seems the formation of the dimer **D** containing either two Cu(II) ions (the third transient species T3)

$$\begin{aligned}&[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]_{S2} + \mathrm{Cu(dtc)_2} \rightarrow \\ &[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})Cu(II)(dtc)_2}] \quad (\mathrm{D} \equiv \mathrm{T3})\end{aligned} \tag{20}$$

or Cu(I) and Cu(III) ions

$$\begin{aligned}&[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})}]_{S2} + \mathrm{Cu(dtc)_2} \rightarrow \\ &[\mathrm{ClCu(I)(dtc)(dtc^{\bullet})Cu(III)(dtc)_2}] \quad (\mathrm{D} \equiv \mathrm{T3})\end{aligned} \tag{21}$$

The formation of the Cu(I) and Cu(III) ions is attractive assumption explaining the fast disappearance of the band of charge transfer in range 400−435 nm from the dtc^{-} ligand to Cu(II). In addition, the formation of the Cu(I) and Cu(III) ions helps to explain the vanishing of the ESR spectrum of $\mathrm{Cu(Et_2dtc)_2}$ in $\mathrm{CCl_4}$ under irradiation (Figure 1b).

It is worth noting that dithiocarbamate complexes of copper ions can frequently form dimeric structures. It is known that the initial complex $\mathrm{Cu(Et_2dtc)_2}$ in the solid state forms dimers with additional Cu−S bonds between copper ions and "alien" ligands.[49,56] In solution, however, those dimers dissociate into monomeric complexes.

The absorption band at 560 nm more probable belongs to the coordinated radical $\mathrm{dtc}^{\bullet}$ and, thus, changes little in the fast reactions (eqs 20 or 21; the radical remains in coordinated position in transients T1−T3). This absorption disappears in a second-order reaction and it could be assumed that $\mathrm{Cu_2(dtc)_3(dtc^{\bullet})Cl}$ dimer disappears in reaction of the coordinated $\mathrm{dtc}^{\bullet}$ radicals recombination

$$\begin{aligned}&\mathrm{Cu_2(dtc)_3(dtc^{\bullet})Cl} + \mathrm{Cu_2(dtc)_3(dtc^{\bullet})Cl} \\ &\qquad \rightarrow \mathrm{tds} + 2\mathrm{Cu_2(dtc)_3Cl}\end{aligned} \tag{22}$$

with the formation of final thiuramdisulfide and two $\mathrm{Cu_2(dtc)_3Cl}$ dimeric complexes. However, the 560 nm band decays simultaneously with the formation of new 345 nm transient absorption band. which disappears only in the millisecond time domain (Figure 5a). The second order kinetics of the $\mathrm{Cu_2(dtc)_3(dtc^{\bullet})Cl}$ dimer decay can be also explained by the reaction of coordinated $\mathrm{dtc}^{\bullet}$ radical with the $^{\bullet}\mathrm{CCl_3}$ radical, which appears in the reaction of the $\mathrm{CCl_4}^{\bullet-}$ dissociation (eq 16)

$$\mathrm{Cu_2(dtc)_3(dtc^{\bullet})Cl} + {}^{\bullet}\mathrm{CCl_3} \rightarrow \text{dtc-CCl}_3 + \mathrm{Cu_2(dtc)_3Cl} \tag{23}$$

However, in this case, it is difficult to explain the formation of 350 nm transient absorption band. In addition, in the final product by the optics and thin layer chromatography (TLC) we have found the thiuramdisulfide.

In this case it is reasonable to assume that the second-order reaction of the $\mathrm{Cu_2(dtc)_3(dtc^{\bullet})Cl}$ dimer (**D**) decay can be explained by the formation of $\mathrm{(dtc)_3ClCu_2\text{-}tds\text{-}Cu_2Cl(dtc)_3}$ tetramer (**D-D**), which has the absorption band at 350 nm. In this tetramer two $\mathrm{dtc}^{\bullet}$ radicals recombine by free sulfur atoms to form thiuramdisulfide, which is still coordinated with the different copper ions.

$$\begin{aligned}&2[\mathrm{ClCu(II)(dtc)(dtc^{\bullet})Cu(II)(dtc)_2}] \rightarrow \\ &[\mathrm{(dtc)_3Cu(II)ClCu(II)}(\mathbf{tds})\mathrm{Cu(II)ClCu(II)(dtc)_3}] \\ &(\mathbf{D\text{-}D} \equiv \mathrm{T4})\end{aligned} \tag{24}$$

Similar to the formation of dimers, the process of clusterization is typical of the dithiocarbamate compounds of copper ions. For instance, $[\mathrm{Cu(I)(Et_2dtc)}]_4$ is a well-known cluster, containing four monovalent copper ions and four dithiocarbamate anions.[57]

Simultaneously with the absorption band at 560 nm disappearance a new band at 345 nm is formed, which belongs to the cluster **D-D** (T4). This cluster is a long-lived particle and decays in first order reaction approximately for 5 ms (k_{decay} = 200 ± 50 $\mathrm{s^{-1}}$), regardless of initial complex concentration and amplitude of absorption (Figure 6). So, the disappearance of the absorption band at 345 nm is due to the dissociation of the cluster into a free thiuramdisulfide (tds) molecule and two new dimeric complexes:

$$\mathbf{D\text{-}D} \rightarrow 2[\mathrm{ClCu(II)(dtc)Cu(II)(dtc)_2}] + \mathrm{tds} \tag{25}$$

4.2. Spectral Properties of Transients. Full scheme of reactions allows to calculate the kinetic curves at different wavelengths. The comparison of calculated and experimental kinetics gives possibility to calculate the absorption coefficients and spectra of all transient species. In Figure 4b the solid lines are the result of global fitting with the same rate constants at all wavelengths. All experimental kinetics can be described with good accuracy. Figure 8 shows these calculated spectra (initial $\mathrm{Cu(Et_2dtc)_2}$ complex (1), first transient complex

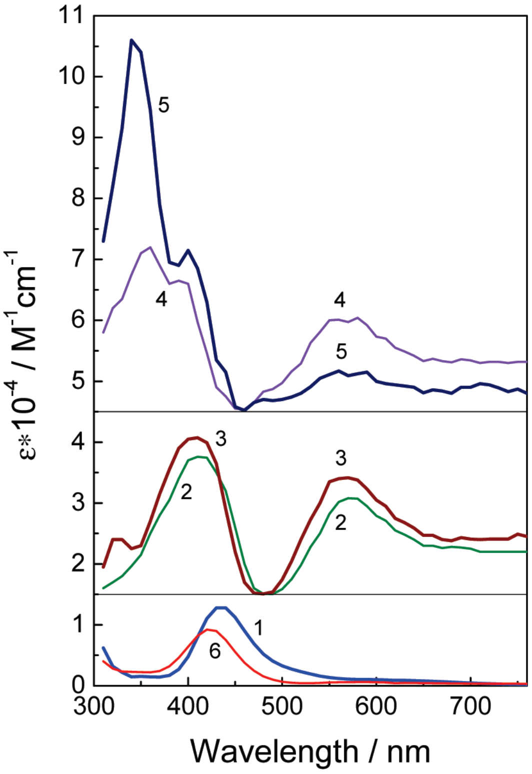


Figure 8. Spectra of intermediate particles successive arising in photochemistry of $Cu(Et_2dtc)_2$ complex in CCl_4. Absorption coefficients were calculated by fitting of kinetics on base of suggested scheme of photochemical transformations. At all wavelengths, fittings were made with the same rate constants and initial change of $Cu(Et_2dtc)_2$ concentration. Solid lines in kinetics in Figure 4 are the result of these calculations. Spectra: **1**, initial $Cu(Et_2dtc)_2$ complex; **2**, complex $(Et_2dtc)ClCu(Et_2dtc^{\bullet})$ appearing after nanosecond laser pulse; **3**, second transient complex after transformation of coordination sphere during 0.63 μs; **4**, dimer forming in reaction of second transient with initial $Cu(Et_2dtc)_2$ complex; **5**, cluster which is the result of two dimer reaction; **6**, final product, dimer containing two Cu(II) ions (or Cu(I) and Cu(III) ions).

$[ClCu(II)(dtc)(dtc^{\bullet})]_{S1}$ (2), second transient complex after the rearrangement of coordination sphere $[ClCu(II)(dtc)(dtc^{\bullet})]_{S2}$ (3), dimer **D** after reaction with initial complex (4), cluster **D-D** after recombination of two dimers (5), and spectrum of final products (6)). In Figure 9 the full scheme of photochemical transformations for $Cu(Et_2dtc)_2$ complex are presented in graphic view.

The first transient product $[ClCu(II)(dtc)(dtc^{\bullet})]_{S1}$ has absorption bands with maxima at 400 and 560 nm and it turns into second species $[ClCu(II)(dtc)(dtc^{\bullet})]_{S2}$ with small shift of maxima to blue. The third transient particle, dimer **D**, has an absorption band with a maximum at 350 and 560 nm. The band of next species, cluster **D-D** at 345 nm, has the increased absorption coefficient due to double decrease of concentration of **D-D** versus of dimer **D**. At the same time, the formation **D-D** leads to a decrease of absorption at 560 nm owing to recombination of coordinated $dtc^{\bullet}$ radicals to thiuramdisulfide in cluster **D-D**. The decay of cluster **D-D** to final products in the millisecond time scale (Figure 7) results in the disappearance of absorption at 345 nm.

The formation of a final dimeric complex explains the disappearance of ESR spectrum. If in dimeric complex both copper ions exist in two-valent states with spins $S_i = 1/2$, the total spin can be zero (singlet state) or one (triplet state). This system can be described as composed of two coupled spins with the effective Hamiltonian

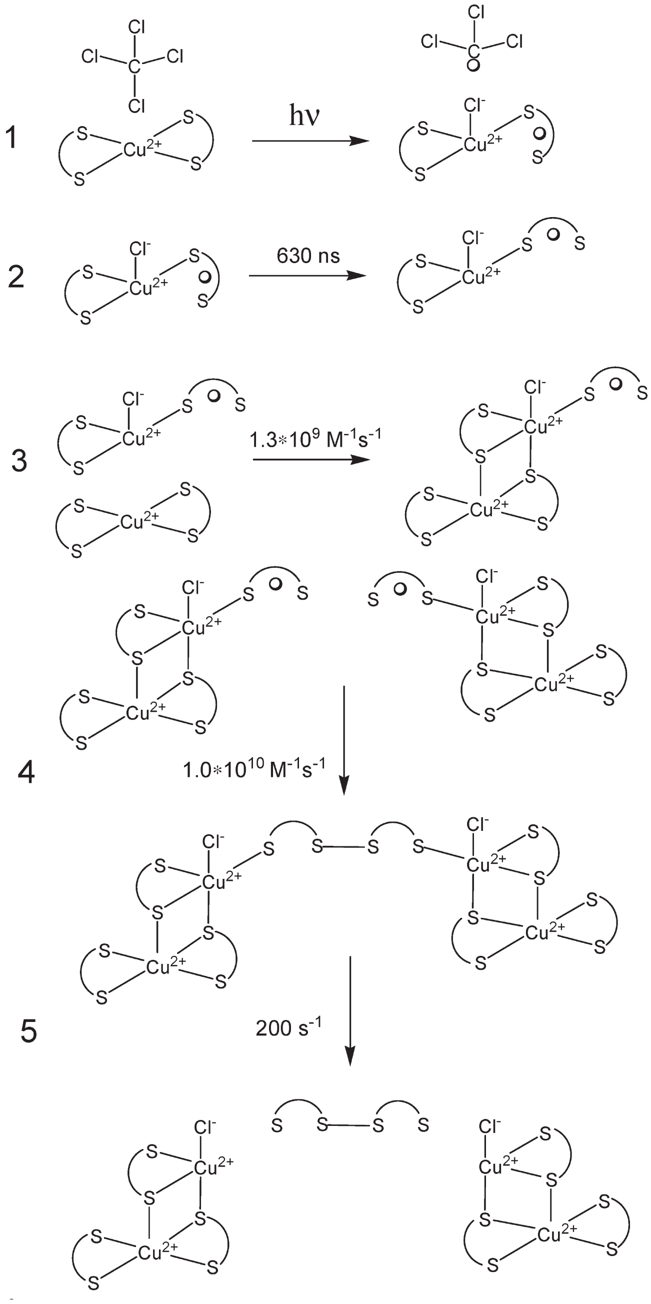


Figure 9. Scheme of photochemical transformations of $Cu(Et_2dtc)_2$: (**1**) photochemical formation of primary transient complex, (**2**) fast change of geometry of primary transient complex, (**3**) formations of dimer in reaction with initial complex, (**4**) formation of cluster bounded by thiuramdisulfide, (**5**) dissociation of cluster to two final dimers and thiuramdisulfide.

$$H = -2J(S_1 \bullet S_2)$$

where $2J$ is the energy separation between the triplet and singlet states and S_i are the respective spins of the copper ions. It should be noted that a positive $2J$ value is indicative of a triplet ground state.

It is well-known that the Cu(II) diethyldithiocarbamate, Cu(Et$_2$dtc)$_2$, in crystal composed of dimers, [Cu(Et$_2$dtc)$_2$]$_2$, where the sulfur atoms act as bridges and the Cu−Cu distance is 3.54 A.[48] The study of magnetic properties of this compound points to a triplet ground state $2J$ = 24.0 cm^{-1} below the singlet.[58,59] The reaction of copper(II) dithiocarbamates, Cu(dtc)$_2$, with copper(II) chloride, CuCl$_2$, in anhydrous solvents produces dimer [Cu(dtc)Cl]$_2$ with a Cu$_2$Cl$_2$ bridging unit and negative value $2J = -50$ cm^{-1} and a singlet ground state.[60]

For Cu(II) dimers in triplet state in ESR spectra the allowed $\Delta M_S = \pm 1$ transitions near $g \approx 2$ and forbidden $\Delta M_S = \pm 2$ transitions near $g \approx 4$ can be registrated.[61−63] Careful analysis has not shown the lines in range $g \approx 2$ and $g \approx 4$ for the final dimer upon the Cu(Et$_2$dtc)$_2$ photolysis in CCl$_4$ during the keeping of isosbestic points. It means that the final dimer has the singlet ground state with large separation of triplet state ($|2J| > kT$).

Another explanation of the absence of final dimer ESR spectrum is the formation two copper ions in Cu(I) and Cu(III) valent states. An electrochemical study of the Cu(R$_2$dtc)$_2$ system in aprotic solvents defines the electron transfer relationships between bis-chelated complexes of copper in the three oxidation states I, II, and III. The Cu(R$_2$dtc)$_2$ complex undergoes single one-electron oxidation and reduction steps at a platinum electrode[64]

$$\mathrm{Cu^{III}(R_2dtc)_2} \overset{\pm e^-}{\rightleftharpoons} \mathrm{Cu^{II}(R_2dtc)_2} \overset{\pm e^-}{\rightleftharpoons} \mathrm{Cu^{I}(R_2dtc)_2}$$

At oxidative electrolysis, the formed Cu^{III}(R$_2$dtc)$_2$ complex has the absorption band with maximum at 425 nm, which coincides with the position of the absorption band of the final dimer upon the Cu(Et$_2$dtc)$_2$ photolysis (425 nm, Figure 1). At reductive electrolysis, the generated Cu^{I}(R$_2$dtc)$_2$ complex arises with a low-intensity absorption band at 364 nm.[64] If to take into account that one-half of Cu^{II}(dtc)$_2$ transforms to the Cu^{III}(dtc)$_2$ and the other half to the Cu^{I}(R$_2$dtc)$_2$ at photolysis, the data on spectral change at the electrochemical oxidation and reduction of Cu^{II}(dtc)$_2$ in ref 64 shows the similarity of optical spectra change at the electrolysis and photolysis. Some difference in final spectra can be explained by the entry of Cu(I) and Cu(III) ions into dimer at photolysis.

Quantum yield of Cu(Et$_2$dtc)$_2$ disappearance has strong dependence on wavelength of irradiation (Figure 3b). In range of the longwave charge transfer band (CTLM) at 435 nm quantum yield is less than 10^{-2} and begins to grow up at $\lambda <$ 400 nm. The same behavior of quantum yield for Cu(Et$_2$dtc)$_2$ was observed in refs 39 and 40. It should be noted that in photochemistry of many dithiolate and dithiolene complexes in halogencontaining solvents the quantum yield sharply increases in range $\lambda <$ 360−400 nm where the ligand−ligand (LL) or charge transfer to solvent (CTTS) bands are located.[65] Shirom et al. suggested that the electron ejection is rapid enough to occur from higher vibrational levels of the CTTS excited state.[66,67] Such a hot excited-state mechanism may account for the observed wavelength dependence.

5. CONCLUSIONS

The femto- and nanosecond laser flash photolysis were used to study the mechanism of photochemical transformations of the flat Cu(Et$_2$dtc)$_2$ complex in CCl$_4$ solutions. The photochemical process is shown to compete with the fast relaxation of the excited state, which lasts for several picoseconds. In halogen-containing solvents, the photochemical activity is determined by feasible electron transfer from the excited Cu(Et$_2$dtc)$_2$ complex to a solvent molecule. In the case of CCl$_4$, the electron capture leads to molecule dissociation into the CCl$_3^•$ radical and a chloride ion, which coordinates to the copper ion at the axial position. This is followed by the interaction between the intermediate and the initial complex to form the dimer containing the coordinated Et$_2$dtc$^•$ radical. For several microseconds the coordinated dithiocarbamate radicals of these dimers recombine to give the tetranuclear cluster. At the last stage, the cluster dissociates for several milliseconds into thiuramdisulfide and two final binuclear copper complexes. Thus, the mechanism of photochemical transformations of the Cu(Et$_2$dtc)$_2$ complex turned out to be more complicated and interesting than assumed in the works on stationary photolysis.

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REFERENCES

(1) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993–2998.
(2) Randall, D. W.; Gamelin, D. R.; LaCroix, L. B.; Solomon, E. I. *J. Biol. Inorg. Chem.* **2000**, *5*, 16–29.
(3) Brown, K. R.; Keller, G. L.; Pickering, I. J.; Harris, H. H.; George, G. N.; Winge, D. R. *Biochemistry* **2002**, *41*, 6469–6476.
(4) Romero-Isart, N.; Vasak, M. *J. Inorg. Biochem.* **2002**, *88*, 388–396.
(5) Okubo, T.; Kawajiri, R.; Mitani, T.; Shimoda, T. *J. Am. Chem. Soc.* **2005**, *127*, 17598–17599.
(6) Hattori, S.; Wada, Yu.; Yanagida, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 9648–9654.
(7) Chen, P.; Cabrito, I.; Moura, J. J. G.; Moura, I.; Solomon, E. I. *J. Am. Chem. Soc.* **2002**, *124*, 10497–10507.
(8) Ngo, S. C.; Banger, K. K.; DelaRosa, M. J.; Toscano, P. J.; Welch, J. T. *Polyhedron* **2003**, *22*, 1575–1583.
(9) Nigam, H. L.; Pandey, K. B.; Singh, R. *J. Indian Chem. Soc.* **2001**, *78*, 525–532.
(10) Law, N. A.; Dietzsch, W.; Duffy, N. V. *Polyhedron* **2003**, *22*, 3423–3432.
(11) Nagano, T.; Yoshimura, T. *Chem. Rev.* **2002**, *102* 1235–1270.
(12) Cocco, D.; Calabrese, L.; Rigo, A.; Argese, E.; Rotillo, G. *J. Biol. Chem.* **1981**, *256*, 8983–8986.
(13) Gringeri, A.; Keng, P. C.; Borch, R. F. *Cancer Res.* **1988**, *48*, 5708–5712.
(14) Beer, P. D.; Berry, N.; Drew, M. G. B.; Fox, O. D.; Padilla-Tosta, M. E.; Patell, S. *Chem. Commun.* **2001**, 199–200.
(15) Nami, S. A. A.; Siddiqi, K. S. *Synth. React. Inorg. Met.-Org. Chem.* **2004**, *34*, 1581–1590.
(16) Siddiqi, K. S.; Afaq, H.; Nami, S. A. A.; Umar, A. *Synth. React. Inorg. Met.-Org. Chem.* **2003**, *33*, 459–468.
(17) Cookson, J.; Beer, P. D. *Dalton Trans.* **2007**, 1469–1472.
(18) Vickers, M. S.; Cookson, J.; Beer, P. D.; Bishopb, P. T.; Thiebautb, B. *J. Mater. Chem.* **2006**, *16*, 209–215.

(19) Morrison, J.; Freizer, G. *Extraction in Analytical Chemistry*; Goskhimizdat: Moscow, 1960.
(20) Stari, I. *Extraction of Chelates*; Mir: Moscow, 1966.
(21) Birko, I. M. *Analytical Reagents: Dithiocarbamates*; Nauka: Moscow, 1984.
(22) Korablev, M. V. *Derivative of Dithiocarbamine Acids: Chemistry, Toxicology, Pharmacology and Clinical Application*; Minsk: Belarus, 1971.
(23) Thorn, G. D.; Ludwig, R. A. *The Dithiocarbamates and Related Compounds*; Elsevier: Amsterdam, 1962.
(24) Rachinskii, F.Yu.; Mozhuchin, A. S.; Slovachevskaya, N. M.; Tank, L. I. *Usp. Khim.* **1959**, *28*, 1488–1522.
(25) Tomson, J. *Protection of Mammalia from Ionization Irradiations*; Atomizdat: Moscow, 1964.
(26) *Developments in Polymer Stabilization*; Scott, G., Ed.; Applied Sci. Publ.: London, 1979; Part 1.
(27) Goldfarb, Yu.L.; Ostapenko, E. G.; Ivanov, V. B.; Efremkin, A. F.; Litvinov, V. L. *Khim. Geterotsikl. Soedin.* **1982**, 1482–1488.
(28) Given, K. W.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 3152–3156.
(29) Beurskens, P. T.; Cras, J. A.; van der Linden, J. G. M. *Inorg. Chem.* **1970**, *9*, 475–479.
(30) Bardaji, M.; Laguna, A.; Laguna, M.; Merchan, F. *Inorg. Chim. Acta* **1994**, *215*, 215–218.
(31) Barbier, J. P.; Hugel, R. P.; Kappenstein, C. *Inorg. Chim. Acta* **1983**, *77*, L117–L118.
(32) Avdeef, A.; Fackler, J. P.; Fischer, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 6972–6974.
(33) Fackler, J. P.; Avdeef, A.; Fischer, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 774–782.
(34) Raston, C. L.; White, A. H.; Petridis, D.; Taylor, D. *J. Chem. Soc., Dalton Trans.* **1980**, 1928–1931.
(35) Miessler, G. L.; Stuk, G.; Smith, T. P.; Given, K. W.; Palazzotto, M. C.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 1982–1985.
(36) Schwendiman, D. P.; Zink, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 4439–4443.
(37) Given, K. W.; Mattson, B. M.; McGuiggan, M. F.; Miessler, G. L.; Pignolet, L. H. *J. Am. Chem. Soc.* **1977**, *99*, 4855–4857.
(38) Plyusnin, V. F.; Grivin, V. P.; Larionov, S. V. *Coord. Chem. Rev.* **1997**, *159*, 121–133.
(39) Jeliazkova, B. G.; Yordanov, N. D. *Inorg. Chim. Acta* **1993**, *203*, 201–204.
(40) Jeliazkova, B. G.; Sarova, G. C. *J. Photochem. Photobiol., A* **1996**, *97*, 5–9.
(41) Jeliazkova, B. G.; Doicheva, M. A.; Miltchovska, K. *Polyhedron* **1998**, *17*, 4553–4566.
(42) Jeliazkova, B. G.; Dimitrova, A.; Doicheva, M. A. *Spectrochim. Acta, Part A* **2004**, *60*, 1291–1297.
(43) Doytcheva, M. A.; Jeliazkova, B. G. *Spectrochim. Acta, Part A* **2004**, *60*, 1299–1305.
(44) Grivin, V. P.; Plyusnin, V. F.; Khmelinski, I. V.; Bazhin, N. M.; Mitewa, M.; Bontchev, P. R. *J. Photochem. Photobiol., A* **1990**, *51*, 371–377.
(45) Pozdnyakov, I. P.; Plyusnin, V. F.; Grivin, V. P.; Vorobyev, D. Yu.; Bazhin, N. M.; Pages, S.; Vauthey, E. *J. Photochem. Photobiol., A* **2006**, *182*, 75–81.
(46) Lemmetyinen, H.; Ovaskanien, R.; Nieminen, K.; Vaskonen, K.; Sychtchikova, I. *J. Chem. Soc., Perkin Trans. 2* **1992**, *2*, 113–119.
(47) Tkachenko, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121*, 9378–9387.
(48) Larionov, S. V.; Kosareva, L. A.; Malikova, A. F.; Shklyaev, A. A. *J. Inorg. Chem. (Russ.)* **1977**, *23*, 2401–2406.
(49) Bonamico, M.; Dessyt, M.; Mugnolit, A. *Acta Crystallogr.* **1965**, *19*, 886–897.
(50) O'Connor, B. H.; Maslen, E. N. *Acta Crystallogr.* **1966**, *21*, 828–830.
(51) Vlcek, A., Jr. *Coord. Chem. Rev.* **2000**, *200—202*, 933–978.
(52) Basolo, F.; Pearson, R. G. *Mechanism of Inorganic Reactions: A Study of Metal Complexes in Solution*; John Wiley and Sons: New York, 1967.
(53) Plyusnin, V. F.; Kuznetzova, E. P.; Bogdanchikov, G. A.; Grivin, V. P.; Kirichenko, V. N.; Larionov, S. V. *J. Photochem. Photobiol., A* **1992**, *68*, 299–308.
(54) Plyusnin, V. F.; Ivanov, Yu.V.; Grivin, V. P.; Vorobjev, D.Yu.; Larionov, S. V.; Maksimov, A. M.; Platonov, V. E.; Tkachenko, N. V.; Lemmetyinen, H. *Chem. Phys. Lett.* **2000**, *325*, 153–162.
(55) Klassen, N. V.; Ross, C. K. *J. Phys. Chem.* **1987**, *91*, 3668–3672.
(56) Hogard, G. *Prog. Inorg. Chem.* **2005**, *53*, 138–595.
(57) Kita, H.; Miyake, S.; Tanaka, K.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3532–3538.
(58) Villa, J. F.; Hatfield, W. E. *Inorg. Chem.* **1971**, *10*, 2038–2041.
(59) McGregor, K. T.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1973**, *12*, 731–735.
(60) Furneaux, R. H.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 1809–1812.
(61) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 2422–2431.
(62) Addison, A. W.; Landee, C. P.; Willett, R. D.; Wicholas, M. *Inorg. Chem.* **1980**, *19*, 1921–1923.
(63) Chasteen, N. D.; Belford, R. L. *Inorg. Chem.* **1970**, *9*, 169–175.
(64) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1976**, *15*, 2115–2119.
(65) Vogler, A.; Kunkely, H. *Inorg. Chem.* **1982**, *21*, 1172–1175.
(66) Shirom, M.; Weiss, M. *J. Chem. Phys.* **1972**, *56*, 3170–3173.
(67) Shirom, M.; Siderer, Y. *J. Chem. Phys.* **1973**, *58*, 1250–1252.