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Femtosecond spectroscopy of the dithiolate Cu(II) and Ni(II) complexes

Victor F. Plyusnin,[a,b] Ivan P. Pozdnyakov,[a,b] Vjacheslav P. Grivin,[a] Aleksey I. Solovyev,[b] Helge Lemmetyinen,[c] Nikolai V. Tkachenko,[c] Stanislav V. Larionov[d]

[a]*Institute of Chemical Kinetics and Combustion Siberian Branch of Russian Academy of Sciences, 3, Institutskaya str., Novosibirsk, 630090, Russia*
[b]*Department of Natural Sciences, Novosibirsk State University (National Research University), 2, Pirogova str., Novosibirsk, 630090, Russia*
[c]*Department of Chemistry and Bioengineering, Tampere University of Technology, Finland, 33101 Tampere, Finland*
[d]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Akad. Lavrentiev Ave., Novosibirsk, 630090, Russia.*

Abstract

Femtosecond spectroscopy was applied to study the ultrafast dynamics for the excited states of dithiolate Cu(II) and Ni(II) complexes. The detailed information of initial steps after the absorption of a photon by the metal complexes is of fundamental importance to understand the mechanism of photochemical reactions. The fast processes for the dithiolate complexes have hardly been studied. In this review the spectra of transients and its lifetimes will be presented. For example, the xanthogenate $Ni(S_2COEt)_2$ complex in acetonitrile and CCl_4 after the pulse of second harmonic (100 fs, 400 nm) of Ti:S laser moves to excited ^{1}LMCT state which decays during 0.76 ps to excited ^{3}LF state. With the time 6.8 ps the ^{3}LF state undergoes vibrational cooling and then it slowly decays during 550 ps to the ground state. However, for many dithiolate complexes the kinetics curves can be well treated in two-exponential approximation. A short time (less 1 ps) may include several processes (relaxation of the Franck-Condon state, redistribution of vibrational energy (IVR), internal conversion (IC) and intersystem crossing (ISC)). A long time (a few picoseconds) usually reflects the vibrational cooling of ground state. The quantum yields of the dithiolate and dithiolene complexes disappearance in halogencontaining solvents have a strong dependence on wavelength of irradiation. It is very likely that an electron transfer to the acceptor becomes effective when the electron in excited complex moves to an antibonding ligand orbitals localized at the periphery of complex close to acceptor molecule (halogenated solvent).

Keywords: dithiolate Ni(II) and Cu(II) complexes, femtosecond spectroscopy, photophysics, ultrafast processes

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*Corresponding author at: Institute of Chemical Kinetics and Combustion SB RAS, 630090, Novosibirsk, Russian Federation. Tel.: +7 383 3332385; Fax: +7 383 3307350.
E-mail address: plyusnin@kinetics.nsc.ru (V. F. Plyusnin).

Introduction

The dithiolate Ni(II) and Cu(II) complexes, containing a flat coordination MS_4 unit, are widely applied in analytical chemistry[1-3] organic synthesis,[4,5] medicine,[6] biology,[7,8] as radiation protectors,[9,10] antioxidants[11] and polymer photostabilizers.[12] Dithiolate ligands are used to extract metals,[13] their complexes serve as precursors of sulfides in modern electronics.[14-17] Dithiocarbamate ligands can stabilize metal ions at high oxidation levels. Well known are the following dithiocarbamate complexes: Ru(IV),[18] Au(III),[19,20] Cu(III),[21] Ni(IV)[21-23] and Fe(IV).[24]

Copper-sulfur interactions have been of marked interest in the different research fields such as the copper-thiolate chemistry,[25] "blue" copper electron transfer proteins,[26] Cu-thiolate proteins,[27,28] synthesis of coordination polymers[29] and solar cell.[30] A new focus of interest in copper-sulfur coordination chemistry is derived from the recent discovery of a tetra copper-sulfide cluster at so-called CuZ active site of nitrous oxide reductase.[31] Diethyl dithiocarbamates are also known to inhibit the activity of Cu/Zn-superoxide dismutase (SOD) through the withdrawal of copper from the protein.[32] Some dialkyl-substituted dithiocarbamates have proved to be efficient anti-alkylating, anti-HIV and froth-floatation agents.[33] The optical and electrochemical properties of dithiocarbamates can effectively be used to construct sensors for guest molecules and macromolecules.[34-36]

The photophysics and photochemistry of emissive and photoactive coordination compounds attract a high attention due to potential application in optoelectronic devices. From this point of view the study of fast photophisical processes for the different metal complexes takes special significance. In literature many review on photophysics of various coordination compounds published in latest years.[37,38] Unfortunately, the fast photophysics and photochemistry of dithiolate transition metal complexes have the weak presentation in literature in spite of their wide chemical applications.

The excited state dynamics of many organic molecules can usually be predicted from rules that relate the rate constants of internal conversion, intersystem crossing, fluorescence, and phosphorescence. In contrast, with the exception of $[Ru(bpy)_3]^{2+}$,[39-41] a fundamental understanding of the ultrafast excited state processes of transition metal complexes is still lacking.

In the literature, the work on the photophysics of metal complexes mainly with nitrogen-containing ligands[42-45] are presented. Among the works devoted to the complexes with a sulfurcontaining ligands can be mentioned[46] which considers the photophysics and photochemistry of the $Ni(mnt)_2^{2-}$ complex (mnt = maleonitriledithiolate = $S_2C_2(CN)_2)_2^{2-}$) in CH_3CN and $CHCl_3$ mixtures. The authors demonstrate that the quantum yield of $Ni(mnt)_2^{2-}$ photolysis increases with increasing concentration of chloroform whose molecules are an electron acceptor. Besides, the

quantum yield increases substantially with the decreasing irradiation wavelength. This increase was assigned to the existence of weak bands of charge transfer to a solvent (CTTS) in the range 200-300 nm that are masked by the bands related to intraligand transitions (LL*) and ligand-metal charge transfer (LMCT). The picosecond excitation (355 nm, 30 ps) of $Ni(mnt)_2^{2-}$ gives rise to a broad absorption band over the range 426-675 nm with a dip at 475 nm caused by the disappearance of absorption from the ground state of the complex.[46] The intermediate absorption is independent of the solvent (CH_3CN or $CHCl_3$) and almost vanishes during 100 ps. In this paper the results on the study of ultrafast processes for the dithiolate Cu(II) and Ni(II) complexes will be presented.

Experimental section

A pump-probe spectroscopy was used to study transient absorption in femto- and picosecond time domains. The experimental setup was described in details elsewhere.[47] The samples were excited by ~ 60 fs pulses at ~ 390 - 410 nm (second harmonic of a Ti:Sapphire generator - amplifier system, CDP Ltd., Moscow, Russia). The excitation pulse repetition rate was 10 Hz, and 200 pulses were used to record a single time-resolved spectrum. The samples were placed in a 1 mm rotating cuvette to provide uniform irradiation of the sample and to avoid thermal effects from the heating of sample by the pumping pulse. The typically time-resolved spectra were collected with a delay displacement of 100 fs during the first 3 ps after excitation and with exponentially increasing delay times at longer delays. Usually, 60-70 spectra were collected for each sample. The fitting program performed corrections of the group velocity dispersion and calculated the response time of the instrument. The overall time resolution was 150-200 fs. All pump-probe measurements were carried out at room temperature.

The stationary irradiation of solutions was performed either with the pulses of YAG:Nd (355 nm), excimer XeCl lasers (308 nm), by the lines of high-pressure mercury lamp (290, 313, 365 nm) or using a set of light emitting diodes (275, 306, 375 and 405 nm). The optical absorption spectra were recorded using an HP 8453 spectrophotometer. When determining the quantum yield, the laser pulse energy was measured using a ferrioxalate actinometer and Gentec-EO system (Canada) (SOLO-2 monitor and pyroelectric measuring QE25SP-H-MB head). Intensities of the mercury lamp light and the light emitting diode radiation were measured with the same system using a photodiode PH100-SiUV head. Solutions were prepared using spectrally pure solvents.

Results and discussion

The structures, optical spectra and quantum yields of photolysis for the dithiolate complexes in CCl₄

All dithiolate Cu(II) and Ni(II) complexes have a flat MS_4 unit with the distance M-S 2.2-2.3 A and angle S-M-S about 77-88 degrees for one dithiolate ligand (Table 1). Beyond the plane

4

there are only the atoms of the alkyl groups. The Cu(II) dithiolate complexes have the ligand to metal charge transfer (LMCT) bands at 425-437 nm.[48,49] For example, the optical absorption spectrum of the $Cu(Et_2dtc)_2$ complex in acetonitrile contains absorption bands from 217 to 605 nm (Figure 1ab, Table 1). A weak absorption in the range of 507Sh and 605Sh nm refers to the d-d transitions. In CCl_4 the optical spectrum of the complex exhibits the same parameters with the exception of a small shifts of bands.

The dithiolate Ni(II) complexes have a high intensive LMCT bands at 316-334 nm (Figure 1a, Table 1). In a far UV region the intraligand (LL*) transitions can contribute to absorption.[50-55] For all nickel dithiolate complexes in the visible spectrum have absorption bands corresponding to d-d transitions (Figure 1b and Table 1).

A broad weak band of the $Ni(S_2COEt)_2$ complex with a maximum at 637 nm is determined by the forbidden d-d transitions. For the Ni(II) ion with electron configuration $3d^8$, the orbital d_{xy} is the low unoccupied molecular orbital (LUMO). Therefore, in the spectrum, four d-d transitions should be manifested. However, due to the overlapping of broad bands, only one maximum is observed. The stronger bands at 469 – 316 nm refer to the bands of charge transfer from ligand to metal (LMCT).[15] The bands in the region shorter than 316 nm belong to intraligand excitation (LL*), because this region contains the absorption bands of the free Et-xan⁻ ligand.[2,57,58]

Table 1. Structure and parameters of optical spectra of the dithiolate Cu(II) and Ni(II) complexes in acetonitrile.

Complex	Distance M-S / Å	Angle S-M-S	Maxima of optical bands / nm Absorption coefficients / $M^{-1}cm^{-1}$								Ref.
$Cu(S_2CN(Et)_2)_2$	2.31	77	217 12000	243Sh 11400	270 33000	287 18000	356Sh 1000	435 13100	507Sh 3100	605Sh 1050	49, 59, 60
$Ni(S_2CN(n-Bu)_2)_2$	2.21	79	229 30200	246 32900	324 39000	378Sh 5900	393 6200	424 1300	470 380	627 140	50, 51, 61
$Ni(S_2P(OEt)_2)_2$	2.23	88	211 12300	227 12600	279Sh 4400	317 16800	382 750	521 140	684 120		52-55, 62
$Ni(S_2P(i-Bu)_2)_2$	2.23	88	206 8800	230 14100	332 21000	393Sh 1760	557 120	724 93			63
$Ni(S_2COEt)_2$	2.22	78	217 35800	252 20600	316 30000	412 2860	469 1800	637 62			64-70

The photochemical transformation of dithiolate complexes occurs only in halogenated solvents (e.g. in CCl_4, $CHCl_3$ and so on). These molecules are the good electron acceptors, and therefore the photoreaction is due to an electron transfer from the excited complex to acceptor. The absence of photochemical activity in acetonitrile allows one to determine the dependence of quantum yield of the complex disappearance on CCl_4 concentrations for all dithiolate complexes presented in this paper. As usual, the quantum yield is observed to increase linearly with CCl_4 concentration passing at high concentrations to saturation.[71,72] For the $[Ni(mnt)_2]^{2-}$ complex, the quantum yield increases with increasing mole fraction of chloroform in a $CH_3CN – CHCl_3$ mixture.[46]

When the lifetime of the excited state is about 2-3 ps, a diffusion can deliver an electron acceptor (for example a CCl_4 molecule) to the excited complex over a distance less than 1 Å. Thus, the electron transfer is possible if the molecule of acceptor is in the first (along the axial axis of the flat complex with MS_4 unit) coordination sphere of the excited complex. In these conditions, the data on the quantum yield can be processed by Perrin's "black sphere" model.[71,72] used usually to determine the distance of energy transfer upon molecule luminescence quenching in either polymer films or frozen matrices in the absence of diffusion. The processing of quantum yield dependences on CCl_4 concentration in frame of "black sphere" model leads really to the distances of electron transfer about 4-6 A. Taking into account the size of CCl_4 (radius is about 3.6 Å[73]), it means that the CCl_4 molecule must be located above the flat complex, more probably, at the fifth free coordination position.

Another interesting fact is that the quantum yield of photolysis of the dithiolate and dithiolene complexes in halogenated solvents has strong dependence on the wavelength of irradiation (Figure 1c)[49,71,72,74] For example, for the $Cu(S_2CN(Et)_2)_2$ complex in CCl_4 in range of the longwave charge transfer band (LMCT) at 437 nm the quantum yield is less than 10^{-2} and begins to grow up at $\lambda < 400$ nm. For the dithiolate Ni(II) complexes quantum yield sharply increases only in range $\lambda < 350$ nm (Figure 1b) where the ligand-ligand (LL*) bands is located. For the $[Ni(mnt)_2]^{2-}$ complex, the quantum yield in chloroform at 313 nm is 0.25, and decreases to 0.001 at 405 nm.[75] It is very likely that an electron transfer to the acceptor becomes effective when the electron in excited state transfers to antibonding ligand orbitals localized at the periphery of complex close to acceptor molecule. It is not excluded also that in UV region the weak charge transfer to solvent bands (CTTS) are located. Shirom et al. suggested that the electron ejection is rapid enough to occur from higher vibrational levels of the CTTS excited state.[76,77] Such a hot excited-state mechanism may account for the observed a wavelength quantum yield dependence.

Ultrafast photophysical processes for the dithiolate Cu(II) and Ni(II) complexes

Ultrafast relaxation processes of the excited $Cu(S_2CN(Et)_2)_2$ complex. As the quantum yields of photochemical decomposition for the dithiolate complexes at the wavelength of second harmonic of Ti:S laser (390 - 405 nm, 100 fs) is very small ($10^{-2} – 10^{-5}$), therefore, the femtosecond spectroscopy with this wavelength allows to study only the fast photophysical processes. The excitation of $Cu(S_2CN(Et)_2)_2$ complex in acetonitrile at 390 nm leads to a change in the initial absorption which vanishes during several picoseconds[71]. 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 (Table 2).

For the $Cu(S_2CN(Et)_2)_2$ complex 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 nm to 400 nm.[49,74]

Ultra-fast relaxation processes of the excited $Ni(S_2CN(n-Bu)_2)_2$ complex. The excitation of $Ni(S_2CN(n-Bu)_2)_2$ complex at 405 nm (100 fs) leads to the appearance of intermediate wide absorption band with maximum at 460 nm which during 1 ps transforms to new band with maximum at 430 nm. The last vanishes for two tens of picoseconds. For $Ni(S_2CN(n-Bu)_2)_2$ in CCl_4, the spectral and kinetic characteristics are close to those obtained for acetonitrile. Figure 3a shows the intermediate spectra recorded at various times after the pulse for $Ni(S_2CN(n-Bu)_2)_2$ in CCl_4. The kinetic curve at 470 nm is presented in Figure 3b. A global treatment of kinetic curves at all wavelengths gives satisfactory results in the framework of a two-exponential model with characteristic times of 0.63 ± 0.08 and 14.9 ± 3.3 ps in CCl_4. For acetonitrile solutions, these times are 0.75 ± 0.09 and 7.5 ± 1.6 ps.

Processes of the excited $Ni(S_2P(i-Bu)_2)_2$ and $Ni(S_2P(OEt)_2)_2$ complexes. The transient spectra and kinetics after laser pulse for the $Ni(S_2P(i-Bu)_2)_2$ complex in acetinitrile are very similar to that observed for the $Ni(n-Bu_2dtc)_2$ complex. At the initial moment a wide structureless absorption band appears with a maximum at 510 nm which is transformed during 1 ps into a new band centered at 435 nm. The new band decays within 3 - 4 ps (Table 2). For the $Ni(S_2P(OEt)_2)_2$ complex initial wide absorption band has maximum at 485 nm, and second band at 430 nm. In CCl4 spectral and kinetic parameters for both complexes have the close values (Table 2).

Femtosecond spectroscopy of the $Ni(S_2COEt)_2$ complex in acetonitrile and CCl_4. The $Ni(S_2COEt)_2$ complex, unlike other dithiolate Ni(II) complexes, has enough intensive absorption band at 476 nm. In these conditions it is expected that both the disappearance of absorption from the ground state and the dynamics of its recovery will be manifested in transient spectra. The radiation of the second harmonic of the Ti:S laser (400 nm) excites the $Ni(S_2COEt)_2$ complex to the second LMCT state (the band maxima at 414 nm in acetonitrile and at 421 nm in CCl_4). In both solvents,

no photochemical processes are observable at this wavelength, therefore, the fast relaxation of excited states is likely to occur.

Figure 4a shows the kinetics of optical density change after the laser pulse for the Ni(S$_2$COEt)$_2$ solution in acetonitrile. A global treatment of all kinetics with regard to the instrument response indicates that the calculated curves are in good agreement with the experimental ones in the three-exponential approximation (solid lines in Figure 4a)

$$\Delta A(\lambda, t) = A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} + A_3(\lambda)e^{-\frac{t}{\tau_3}} \tag{1}$$

The characteristic times of the exponents of transient absorption disappearance are $\tau_1 = 0.59 \pm 0.05$ ps, $\tau_2 = 3.6 \pm 0.6$ ps, and $\tau_3 = 540 \pm 50$ ps. The spectra of $A_1(\lambda)$, $A_2(\lambda)$ and $A_3(\lambda)$ are presented in Figure 4b. The laser pulse is immediately followed by wide absorption over the entire spectral range from 440 to 550 nm (Figure 4c). Against the background the wide dip with minimum at 476 nm is due to the disappearance of absorption from the ground state of Ni(S$_2$COEt)$_2$. The spectrum 7 in Figure 4c shows that the shapes of the dip and the absorption band of Ni(S$_2$COEt)$_2$ are the same. Absorption decreases considerably during 1 ps and the dip with the same depth moves to the negative region (bleaching of sample in region of 476 nm). The existence of dip with the conservation of its shape and size during time interval 0-3 ps indicates that the complex is in the excited state (no absorption recovery from the ground state). Due to the decrease of transient absorption the dip center (476 nm) reaches its maximal negative value at 3 ps. Thereafter, the dip with negative optical density and positive absorption at other wavelengths are decreased with time $\tau_3 = 540 \pm 50$ ps. So, the fast relaxation processes stop completely to 1-2 ns. It should be noted that the relative depth of the dip allows to estimate the concentration of photolysised Ni(S$_2$COEt)$_2$ complex ($\sim3.8\times10^{-4}$ M) and the absorption coefficient of transient absorption ($\varepsilon \approx 2100$ M^{-1}cm^{-1} at 515 nm and at zero time).

Table 2. Times of fast processes of the dithiolate Cu(II) and Ni(II) complexes.

Complex	λ_{ex} / nm	Solvent	Times of exponents / ps			Ref
			τ_1	τ_2	τ_3	
Cu(S$_2$CN(Et)$_2$)$_2$	390	CH$_3$CN	0.39 ± 0.05	2.9 ± 0.35		71
		CCl$_4$	0.33 ± 0.04	2.2 ± 0.25		
Ni(S$_2$CN(n-Bu)$_2$)$_2$	405	CH$_3$CN	0.75 ± 0.09	7.5 ± 1.6		72
		CCl$_4$	0.63 ± 0.08	14.9 ± 3.3		
Ni(S$_2$P(OEt)$_2$)$_2$	405	CH$_3$CN	0.55 ± 0.05	1.46 ± 0.25		this work
		CCl$_4$	0.60 ± 0.05	1.6 ± 0.3		
Ni(S$_2$P(i-Bu)$_2$)$_2$	405	CH$_3$CN	0.50 ± 0.10	1.4 ± 0.3		this work
		CCl$_4$	0.58 ± 0.08	2.0 ± 0.5		
Ni(S$_2$COEt)$_2$	400	CH$_3$CN	0.59 ± 0.05	3.6 ± 0.6	550 ± 150	56
		CCl$_4$	0.76 ± 0.05	6.8 ± 0.9	540 ± 50	

Figure 3a shows the kinetics of the absorption change after the laser pulse for the $Ni(S_2COEt)_2$ in CCl_4. In this case, the global treatment of kinetics was also performed in the three-exponential approximation (eq. 1). Figure 3b shows the spectra of $A_1(\lambda)$, $A_2(\lambda)$ and $A_3(\lambda)$ amplitudes of exponents. The characteristic times of exponents in this case are $\tau_1 = 0.76 \pm 0.08$ ps, $\tau_2 = 6.8 \pm 0.9$ ps and $\tau_3 \sim 550 \pm 150$ ps. The change of the transient absorption spectra are presented in Figures 3c. As in acetonitrile solutions, after the laser pulse a wide absorption band appears which contains a dip with minimum at 485 nm due to the disappearance of absorption from the ground state of the complex in this solvent. The dip center reaches its maximal negative value at 2.5-3 ps after the laser pulse.

The possible photophysical processes for the dithiolate complexes

The processes for the excited $Cu(S_2CN(Et)_2)_2$ complex. The excitation of $Cu(S_2CN(Et)_2)_2$ complex at 390 nm corresponds to the long-wave LMCT transition. After excitation the transient absorption appears in a wide spectral range (550-750 nm) and the bleaching in area of absorption from the ground state (425-550 nm, Figure 2a). All changes in the transient spectrum are described by two times (Table 2). The first fast time 0.39 ps in acetonitrile corresponds likely to a whole combination of processes involving vibrational relaxation in the LMCT Franck-Condon state, the transition to excited ^{2}LF (Ligand Field) state and further transition into the "hot" ground state. In this case the second time 2.9 ps can fit to the vibrational cooling of "hot" ground state.[78] The alternative pathway would be a slow transition of ^{2}LF state to ground state during 2.9 ps with the fast vibrational cooling (significantly shorter than 2.9 ps) of this "hot" ground state, however, for the excited states of coordination compounds the vibrational cooling takes as usual the times in range 2-10 ps.[78-80] So, we consider that the first case of processes is realized. For the $Cu(Et_2dtc)_2$ in CCl_4 the spectral and kinetic parameters of the intermediate absorption upon femtosecond photolysis are practically the same as in acetonitrile (Table 2).

The processes for the excited $Ni(S_2CN(n-Bu)_2)_2$ complex. For the $Ni(S_2CN(n-Bu)_2)_2$ complex a 405 nm quanta fall in long-wave side of the ^{1}LMCT band with maximum at 393 nm (Table 1). The excitation leads to the appearance of intermediate wide absorption (400-750 nm) with maximum at 475 nm which during 1 ps transforms to a new band with maximum at 465 nm (Fig. 3). The Ni(II) ion has $3d^8$ electron configuration and may have a singlet and triplet states (LMCT and LF types). Since the kinetics of absorption change show only two characteristic times, one may assume the same mechanism of photophysical processes, as for the $Cu(Et_2dtc)_2$ complex. The fast times 0.75 ps in acetonitrile and 0.63 ps in CCl_4 correspond to a whole set of processes which ended by the transition to "hot" ground state. Vibration cooling of "hot" ground state in this case takes 7.5 and 14.9 ps in acetonitrile and CCl_4, respectively. A similar explanation of

photophysical processes can be offered for the $Ni(S_2P(n\text{-}Bu)_2)_2$ and $Ni(S_2P(OEt)_2)_2$ complexes. The times of fast and more slow processes are presented in Table 2.

The processes for the excited $Ni(S_2COEt)_2$ complex. In the $Ni(S_2COEt)_2$ optical spectrum the first four components (14990, 16010, 17330 and 19100 cm^{-1}) are due to the forbidden d-d transitions. The next four components (20700, 22150, 23700 and 24950 cm^{-1}) can be explained as the LMCT transitions according to.[67] The dispositions of $Ni(S_2COEt)_2$ molecular orbitals bears a strong resemblance to the positions of orbitals for dithioacetylacetone Ni(II) complex with the same D_{2h} symmetry.[81] So, the femtosecond pulse with the wavelength at 400 nm (25000 cm^{-1}) falls in the region of an eighth gaussian component, therefore the $Ni(S_2COEt)_2$ complex is excited to the state which we denote as the S_8 (^1LMCT) state.[56]

Recent works on the femtosecond dynamics show that the fast intersystem crossing (ISC) in transition metal complexes can be exceedingly fast and the transitions $^1LMCT \rightarrow {}^3LMCT$ can occur with $\tau < 30$ -100 fs.[43,49,82,83] The role of low-lying ligand-field states as highly efficient deactivation pathways for higher-lying charge-transfer states was demonstrated in low-spin Fe^{II} polypyridyl complexes. Following ground state (GS) $\rightarrow {}^1LMCT$ excitation, the ligand-field manifold is accessed with a time constant of $\sim$100 fs.[82]

In accordance with these results in the photophysics of coordination compounds, we can assume that the first change of transient absorption ($A_1(\lambda)$, $\tau_1 = 0.6$-0.8 ps) for the $Ni(S_2COEt)_2$ complex can be the sequence of fast processes involving internal conversion (IC) in the charge transfer manifold, the intersystem crossing ^1LMCT to ^3LMCT and the transfer to triplet ligand field manifold (^3LF). The alternative pathway is the transfer $^1LMCT \rightarrow {}^1LF$ and the following fast intersystem crossing in ligand field manifold ($^1LF \rightarrow {}^3LF$). In both cases the triplet ^3LF state is the final state of these processes.

The second ($A_2(\lambda)$, $\tau_2 = 3.6$-6.8 ps) process can be determined by the vibration cooling of the "hot" ^3LF state. In[82] it was found that the vibration relaxation for the $[Fe(tren(py)_3)]^{2+}$ complex in the $^5T_2$ ligand field state takes about 8 ps. For $Cr(acac)_3$ the vibration cooling in the ^2E excited LF state having a time constant of 1.1 ps. The vibration relaxation of ^3LF state for the Ni(II)Pc (Pc – phthalocyanine) complex which contains a flat coordination NiN_4 unit takes 20 ps.[84] For the popular $[Ru(bpy)_3]^{2+}$ complex it is shown that the excited singlet ^1MLCT state changes due to the fast intersystem crossing to the vibrationally excited triplet ^3MLCT state whose vibrational cooling takes 10 ps.[85] The vibrationally excited triplet state of the $W(CO)_5(4\text{-cyanopyridine})$ complex cools off during 1-10 ps depending on excitation wavelength, solvent and oscillation frequency of CO and CN groups.[86] In the $[W(CO)_5(solvent)]$ complex, the vibrationally excited CO group cools off for

16-22 ps through an anharmonicity of vibration which provides a communication with low-frequency vibration modes.[86] So, the times of vibration cooling for the $Ni(S_2COEt)_2$ complex in ^3LF state ($\tau_2 = 3.6$-6.8 ps) fall in the region is quite normal for the triplet states of different coordination compounds.

In this mechanism of photophysical processes for the $Ni(S_2COEt)_2$ complex the third slow ($A_3(\lambda)$, $\tau_3 \approx 550$ ps) process is the decay of triplet ^3LF state to the ground state. It is worth noting that the excited triplet ^3LF state for the Ni(II)Pc complex converts, rather slowly, for 300 ps, to the ground state.[85] The time of $^3LF \rightarrow {}^1GS$ transition can vary over a wide range from hundreds of picoseconds to nano- and microseconds. For the Ni(II) octaethyl porphyrin (OEP), the LF excited state was formed in <350 fs.[87] The relaxation of this LF state was found to be biexponential. The first component of this decay, $\tau_1 \approx 10$ ps, was attributed to the equilibration of LF excited state. The second component, $\tau_2 = 250$ ps, accounted for the decay of the excited state to the ground state.[87] It can be noted that for the transition $^3MLCT \rightarrow {}^1GS$ the times also varies in a wide region. For the $[Ru(bpy)_2(dppp_2)]^{2+}$ complex in CH_3CH_2OH it takes about 1.7 ns, in CH_3CN – 35 ns, and in CH_2Cl_2 – 273 ns.[79] Thus, the $\tau_3 \approx 550$ ps in the $Ni(S_2COEt)_2$ complex can be satisfactorily explained by the $^3LF \rightarrow {}^1GS$ transition.

Figure 5 schematically depicts the probable relaxation processes for the excited dithiolate Cu(II) and Ni(II) complexes with the participation of excited charge transfer and ligand field manifolds (spin multiplicity is different for Cu(II) and Ni(II) ions) similarly to the figure presented in.[82] For the $Cu(S_2CN(Et)_2)_2$, $Ni(S_2CN(n\text{-}Bu)_2)_2$, $Ni(S_2P(i\text{-}Bu)_2)_2$ and $Ni(S_2P(OEt)_2)_2$ complexes, where we have found only two characteristic times, under the proposed scheme in Figure 5 the ratio of times $\tau_1 \approx \tau_2 \ll \tau_3$ can be assumed. In this case the τ_3 time corresponds to $^3LF \rightarrow$ "hot" $^1GS \rightarrow$ "cold" ^1GS transitions. For the $Ni(S_2COEt)_2$ complex the kinetics display three times with the ratio $\tau_1 < \tau_2 \ll \tau_3$. It is presented the fast internal conversion in the charge transfer manifold, then the transfer to ligand field manifold and the next transfer to triplet ^3LF state with the following vibration cooling. The final process is the transition of excited triplet ^3LF state to ground state with the time τ_3.

Conclusions

The ultrafast photophysical processes for the dithiolate Cu(II) and Ni(II) complexes are considered. The kinetic and spectroscopic femtosecond measurements have shown that for all dithiolate Ni(II) complexes the first fast process with time 0.4-07 ps includes apparently a lot of processes – the vibrational relaxation in the LMCT Franck-Condon state, internal conversion (IC), possible transition to a ^1LF state and further transition into the "hot" ground state. We consider that

11

the second time in interval 1.4 -15 ps for different complexes corresponds to vibration cooling of "hot" ground state.

For the $Ni(S_2COEt)_2$ complex an excitation in the region the [1]LMCT band causes the all mentioned fast processes and the intersystem crossing to [3]LF excited state (0.6-0.8 ps). With the time 3.6-6.8 ps the triplet [3]LF state undergoes vibrational cooling and then it slowly decays (~550 ps) to the ground state. For the $Cu(S_2CN(Et)_2)_2$ complex a first processes slightly faster than for nickel complexes. May by this is due to the $3d^9$ electronic configuration of Cu(II) ion and to the absent of set of singlet and triplet states.

Acknowledgements

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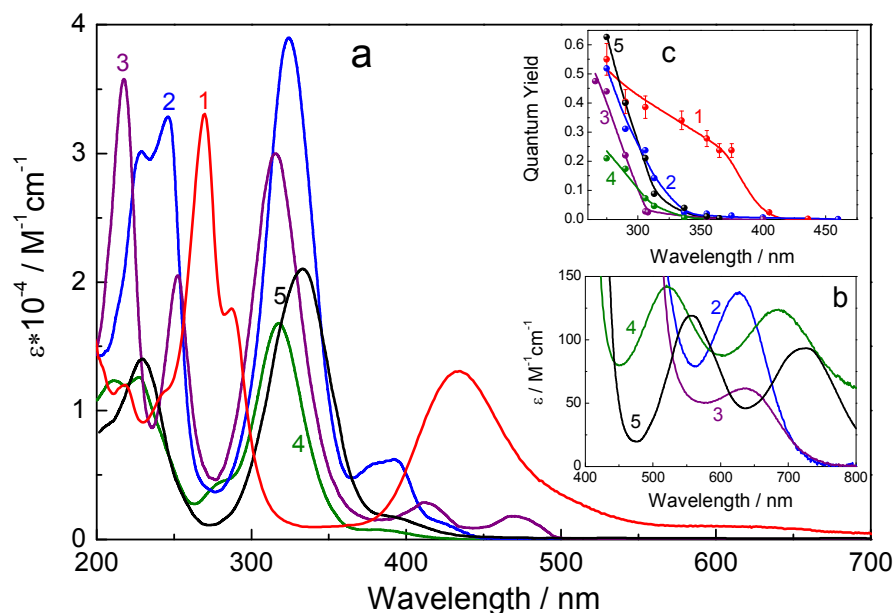87 J. Rodriguez and D. Holton, *J. Chem. Phys*., 1989, **91**, 3525.

Figure Captions

Figure 1. Optical spectra (**a, b**) in CH_3CN and dependence of quantum yield of photolysis on wavelengths (**c**) for the dithiolate Cu(II) and Ni(II) complexes in CCl_4. In all figures the complexes: 1 – $Cu(S_2CN(Et)_2)_2$; 2 – $Ni(S_2CN(n-Bu)_2)_2$; 3 – $Ni(S_2COEt)_2$; 4 – $Ni(S_2P(OEt)_2)_2$; 5 – $Ni(S_2P(i-Bu)_2)_2$.

Figure 2. Intermediate spectra (**a**) and kinetics at 500 and 440 nm (**b**) upon femtosecond flash photolysis (390 nm) of $Cu(S_2CN(Et)_2)_2$ in CCl_4. Spectra **1-7** – 0, 0.2, 0.5, 1, 2, 5 and 30 ps after the laser pulse.[71]

Figure 3. The spectra of intermediate absorption (**a**) and experimental kinetics (dots) at 460 nm (**b**), recorded by femtosecond flash photolysis (405 nm) of the $Ni(S_2CN(n-Bu)_2)_2$ in CCl_4. Spectra 1-7 - 0, 0.3, 0.6, 1, 5, 10, 20, 40 ps after the laser pulse. The solid line (**b**) – approximation in the framework of a two-exponential model with times of 0.63 and 14.9 ps. (**c**) – the spectra of fast (1) and slow (2) exponents are obtained by global treatment of kinetic curves at all wavelengths in the framework of a two-exponential model.[72]

Figure 4. Fast photophysical processes for the $Ni(S_2COEt)_2$ complex in CCl_4 after the femtosecond pulse (100 fs, 400 nm). **a** – the kinetics at 440, 480 and 590 nm; **b** – the spectra of $A_1(\lambda)$ (1), $A_2(\lambda)$ (2) and $A_3(\lambda)$ (3) amplitudes of exponents (eq.1); **c** – 1-6 – the transient spectra at 0, 0.3, 1, 3, 10, 300 ps after the laser pulse; 7 – the inverse spectrum of the $Ni(S_2COEt)_2$ complex in CCl_4.[56]

Figure 5. The scheme of photophysical processes for the dithiolate Cu(II) and Ni(II) complexes upon the femtosecond excitation at 400 nm. This scheme is close to the scheme presented in.[82]

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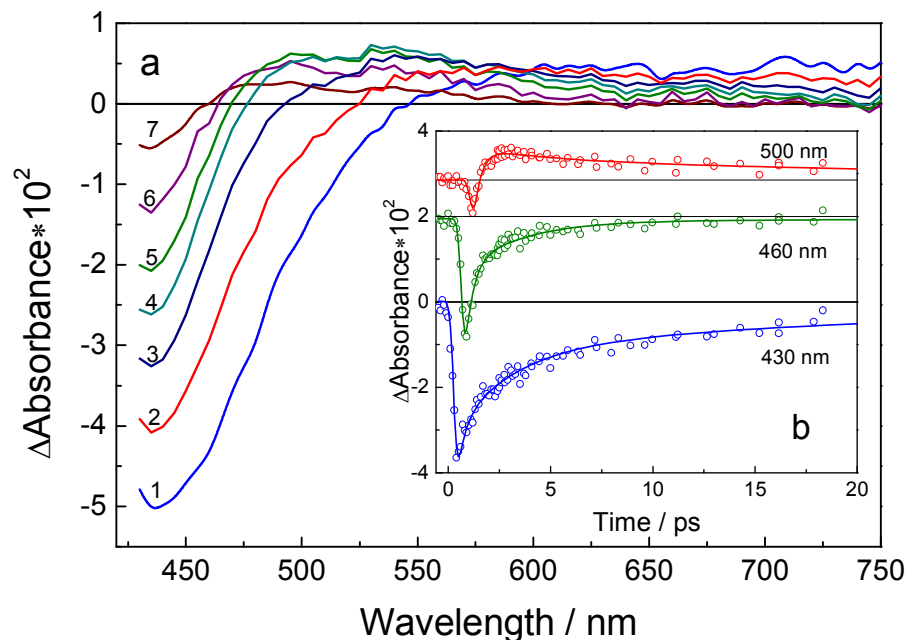**Figure 2.** Transient spectra (**a**) and kinetics of absorption change (**b**) upon femtosecond flash photolysis (390 nm) of $Cu(S_2CN(Et)_2)_2$ in CCl_4. Spectra **1-7** in (**a**) – 0, 0.2, 0.5, 1, 2, 5, and 30 ps after laser pulse.[71]
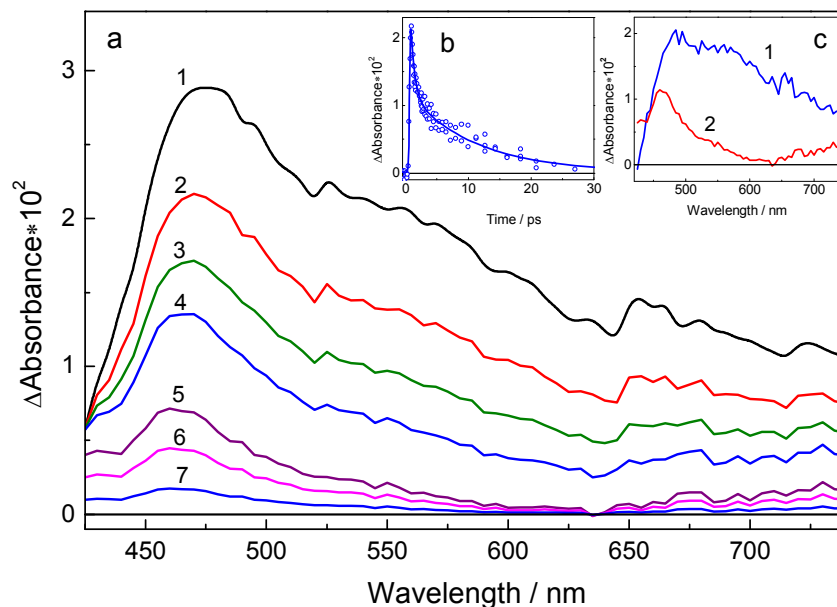

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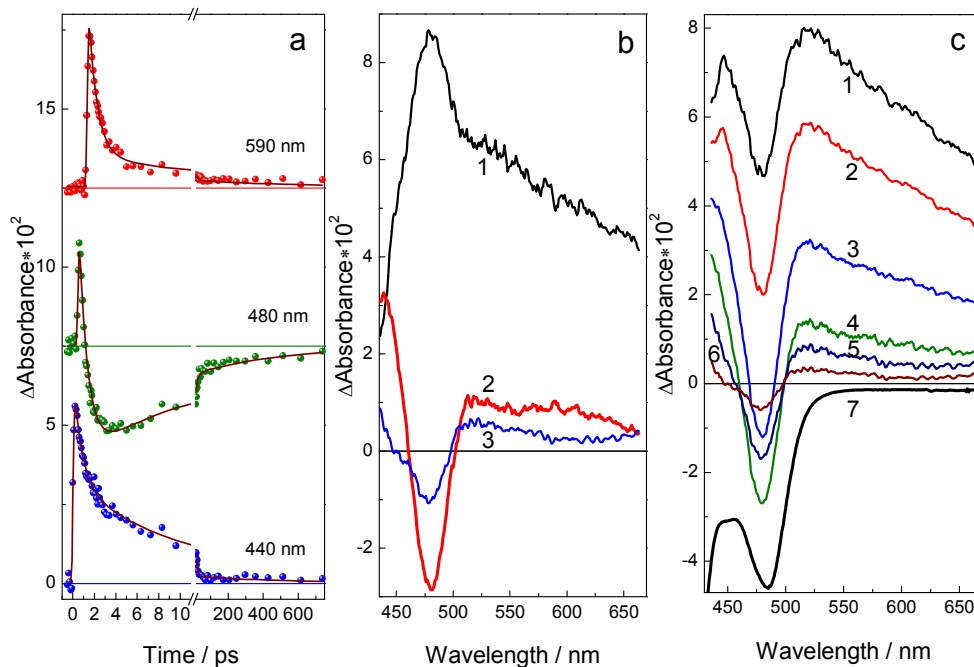
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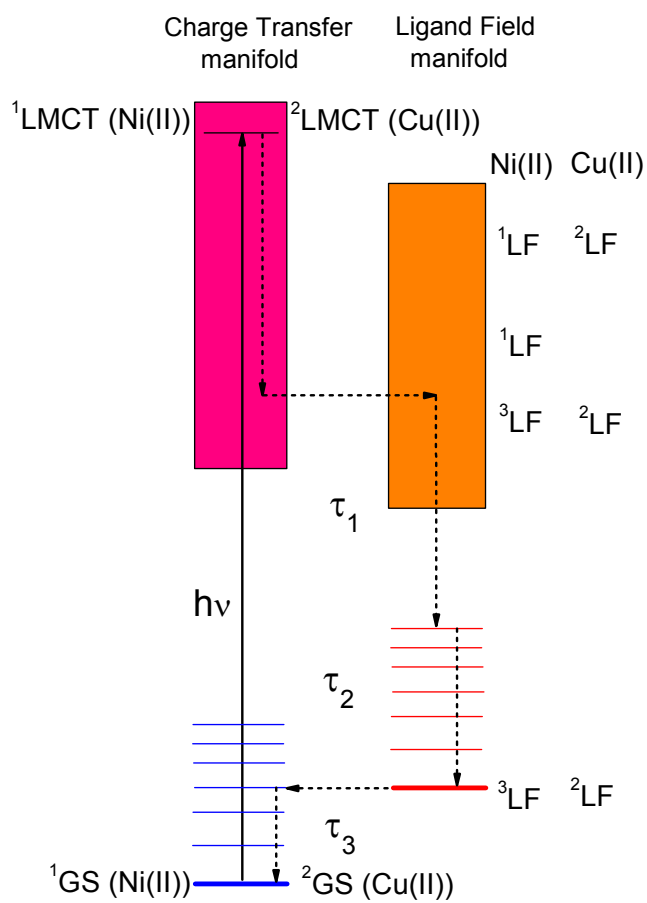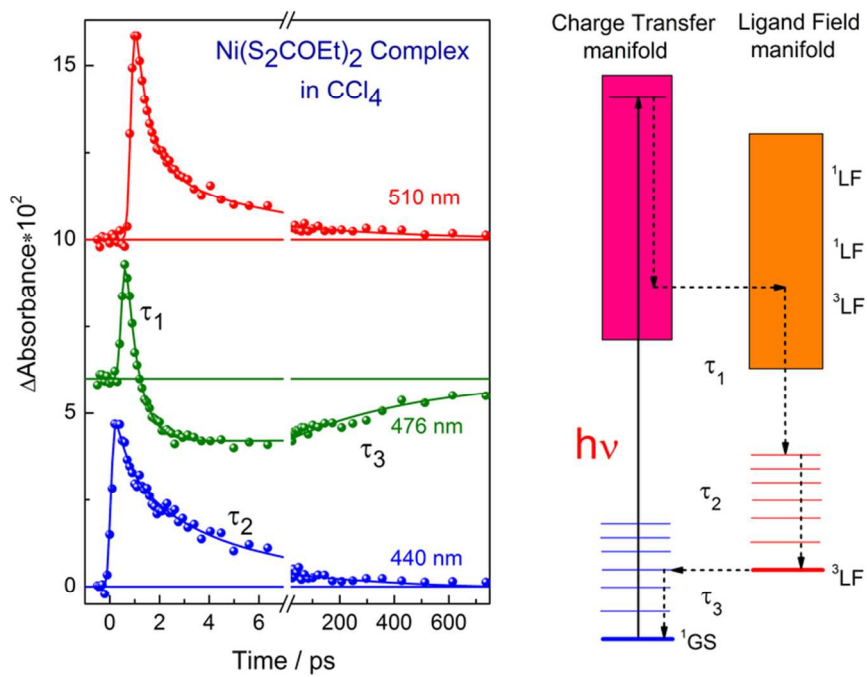
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