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Photochemistry of Fe(III), Fe(IV), Ru(III), Mo(VI), and Ni(IV) dithiocarbamate complexes

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Contents

Abstract

Experimental results on the photochemical transformations and structure of some Fe(III), Fe(IV), Ru(IV), Mo(IV) dithiocarbamate complexes have been considered. Attention is paid to the photochemistry of the Ni(IV) dithiocarbamate complexes. The solutions of these complexes show high photochemical activity even in the red spectral range, which is very unusual for photochemical systems. Moreover, these solutions are photochromic systems. Using laser flash photolysis, it has been shown that some phototransformation steps occur

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inside the coordination sphere of the nickel ion. The reverse dark reactions are bimolecular processes.

Keywords: Photochemistry; Dithiocarbamate complexes

1. Introduction

Dithiocarbamate complexes have been extensively studied owing to their applications in analytical chemistry [1,2], organic synthesis [3], medicine [4], biology [5], and as vulcanization accelerators [6,7], flotation agents [8], fungicides and pesticides [7], radiation protectors [9,10], antioxidants [11] and photostabilizers of polymers [12].

Dithiocarbamate ligands form coordination compounds with all transition metals and many other elements (Ge, Sn, Pb, As, Sb, Bi, Se, Te, etc.) [3]. Moreover, they can stabilize metal ions at high degrees of oxidation [13– 34]. Dithiocarbamate complexes of Ru(IV) [13], Au(III) [14–17], Cu(III) [16,18–22], Ni(IV) [19–24], Fe(IV) [25,26], and U(IV) [27] are well known.

The unusual degree of oxidation of the central ion determines the unique properties of the complex as a whole. For example, $Ni(R_2dtc)_3^+$ complexes have intense charge transfer bands in both the UV and visible spectral ranges [24]. This is also the case for the dithiocarbamate complexes of other metal ions [28]. In addition, such complexes often exhibit fairly high photochemical activity [24,25,29–34], which for $Ni(R_2dtc)_3^+$ is accompanied by photochromic properties [24,29].

2. The structure of the dithiocarbamate complexes of metal ions

Transition metal complexes with two dtc ligands have a planar structure ($M^{II}dtc_2$), or a structure in which the metal ion protrudes from the plane formed by four sulphur atoms (complexes $M^{III}dtc_2X$, where X = halogen atom). $Ni^{II}(dtc)_2$ [35–39], $Zn^{II}(dtc)_2$ [40], $Pt^{II}(dtc)_2$, and $Mo^{VI}O_2(dtc)_2$ [3] complexes belong to the first type, and $Fe^{II}(dtc)_2$ [3], $Fe^{III}(dtc)_2Cl$ [41], $Cu^{II}(dtc)_2$ [16,42], $Au^{III}(dtc)_2^+Au^IBr_2^-$ [14], $Au^{III}(dtc)_2Br$, $Au^{III}(dtc)_2^+Au^{III}Br_4^-$ [15] belong to the second type of complex. The characteristic S–M–S angle is 72–80°, the characteristic lengths of the M–S bonds lie in the range of 2.19–2.35 Å, and the S–C and C–N bond lengths lie in the range 1.70–1.72 Å and 1.30–1.35 Å [14,15,35,40,41], respectively.

In addition, Zn(II), Cd(II), Hg(II) and Pt(II) complexes exist, with the general formula $M^{II}X_2(dtc)_2$ (X = Cl, Br, I) and a different structure from usual. They include two dtc radicals linked in one thiuramdisulphide molecule (tds) [43–45], which in the literature are designated more often as $MX_2(tds)$.

X-ray analysis [23,24] shows that the $Ni(n\text{-}Bu_2dtc)_3Br$ complex has a structure where the coordination sphere of the nickel ion contains six sulphur atoms located in an octahedron. The Ni–S distance is equal to 2.261 Å [24], and the S–Ni–S angle, with both sulphur atoms belonging to one dtc ligand, equals 76.3°.

Some other metal complexes with three dtc ligands, such as $Au^{III}(dtc)_3$, $Ga^{III}(dtc)_3$, $In^{III}(dtc)_3$, $Cu^{III}(dtc)_3$, $Fe^{III}(dtc)_3$, $Mn^{IV}(dtc)_3ClO_4$, and $Mn^{IV}(dtc)_3BF_4$ [3], have similar octahedral structures. The S–M–S angle values lie in the range 72–90°, and a value of 90° is observed in the $Fe^{III}(dtc)_3$ complex.

In some cases, multi-ligand dithiocarbamate metal complexes may have a very complex structure [46–49], and clusters occur rather frequently [32,46,49].

3. Photochemistry of the dithiocarbamate complexes of metal ions

3.1. Photochemistry of Fe(III) and Fe(IV) dithiocarbamate complexes

Studies on the photochemistry of Fe(III) and Fe(IV) dithiocarbamate complexes have shown [25,30,31,50] that they display practically no photochemical activity in solutions which are free from halogenated hydrocarbons (RX); however, the addition of even small quantities of such species results in an increase for the quantum yield of initial product disappearance. The principal products of $Fe^{III}(dtc)_3$ photolysis are the $Fe^{III}(dtc)_2X$ complex and Rdtc molecule.

In a pioneering photochemical paper, Miessler et al. [31] suggested a photolysis scheme with electron transfer from ligand to central ion being the first step, followed by reaction of the halogenated hydrocarbon with the excited complex

$$[Fe^{III}(dtc^-)_3] \xrightarrow{h\nu} [(dtc^-)_2Fe^{II}(dtc^\cdot)]^* \tag{1}$$

$$[(dtc^-)_2Fe^{II}(dtc^\cdot)]^* + RX \rightarrow [Fe^{III}(dtc^-)_2X] + Rtdc \tag{2}$$

A similar scheme was proposed in Ref. [30] to interpret results of the photolysis of $Fe^{III}(dtc)_3$ in benzene and acetonitrile solutions in the presence of $CHCl_3$, CCl_4, C_6H_5Cl and CBr_4.

However, it is known, that the halogenated hydrocarbons are good electron acceptors, and therefore the photolysis scheme was revised in a further paper by Miessler et al. [25]. It is assumed that the primary process is electron transfer from the excited complex to the halogenated hydrocarbon.

$$[Fe^{III}(dtc^-)_3] \xrightarrow{h\nu} [Fe^{III}(dtc^-)_3]^* \tag{3}$$

$$[Fe^{III}(dtc^-)_3]^* + RCl \rightarrow [Fe^{IV}(dtc^-)_3^+ \; RCl^{\cdot -}] \tag{4}$$

$$[Fe^{IV}(dtc^-)_3^+ ...RCl^{\cdot -}] \rightarrow [\{Fe^{III}(dtc^-)_2Cl^-\}...dtc^\cdot ...R^\cdot] \tag{5}$$

$$[\{Fe^{III}(dtc^-)_2Cl^-\}...dtc^\cdot ...R^\cdot] \rightarrow Fe(dtc)_2Cl + Rdtc \tag{6}$$

The quantum yield depends on the concentration of RX, the nature of the R′ group in the ligands (Et [25,31], Bz [30,50]), and the wavelength of irradiation. In the absence of the halogen-containing additives, the quantum yield of $Fe(dtc)_3$

disappearance is less than 0.002 and formation of the $Fe(dtc)_2Cl$ complex is not observed. For $R'=Bz$ in pure $CHCl_3$ ($\lambda_{irr}=320$–360 nm), the quantum yield is equal to 0.048 and increases to 0.87 in the presence of CBr_4 (0.239 M) [30].

In the $Fe(dtc)_2Cl$ complex [41,51] four S atoms lie in one plane, and the Fe ion protrudes above it by 0.63 Å. The lengths of the Fe–S (2.32 Å) and Fe–Cl (2.27 Å) bonds are usual for dtc complexes. This complex is also formed in photolysis of $Fe^{IV}(dtc)_3BF_4$ in chlorinated solvents [25], but with a significantly lower quantum yield (for $CHCl_3$, $\phi(265\,\mathrm{nm})=0.06$). A possible photolysis scheme [25] includes two-electron transfer from dtc ligand to Fe ion with the formation of a dtc^+ cation. Further, this cation escapes into the bulk with consequent recombination, loss of the sulphur atom, and transformation to product 1 (Eq. (11)) identified by NMR and IR spectroscopy:

$$[Fe^{IV}(dtc^-)_3]^+ \xrightarrow{h\nu} [Fe^{II}(dtc^-)_2...dtc^+]^* \tag{7}$$

$$[Fe^{II}(dtc^-)_2...dtc^+]^* \rightarrow [Fe^{II}(dtc^-)_2]+dtc^+ \tag{8}$$

$$[Fe^{II}(dtc^-)_2]+RCl \rightarrow Fe(dtc)_2Cl+R^{\cdot} \tag{9}$$

$$dtc^+ + dtc^+ \rightarrow (dtc)_2^{2+} \tag{10}$$

$$(dtc)_2^{2+} \rightarrow [Et_2NCS(S)SCNEt_2]^{2+}(\text{product 1})+S \tag{11}$$

A mechanism with one-electron transfer and dtc radical abstraction is not discussed because the spectrum of the tds molecule, the product of two-dtc radical recombination, is not found in stationary photolysis.

3.2. Photochemistry of Ru(III) dithiocarbamate complexes

Ru(III) dithiocarbamate complexes also display noticeable photochemical activity only in the presence of chlorinated solvents. In Ref. [32], the photoprocess scheme for the complexes $Ru(R_2dtc)_3$ (where $R=CH_3$, C_2H_5) in $CHCl_3$, CH_2Cl_2, and C_6H_5Cl solutions is proposed:

$$[Ru^{III}(dtc)_3] \xrightarrow{h\nu} [(dtc^-)_2Ru^{II}(dtc^{\cdot})]^* \tag{12}$$

$$[(dtc^-)_2Ru^{II}(dtc^{\cdot})]^* + RCl \rightarrow [(Cl^-)Ru^{IV}(dtc^-)_3](\text{product 1})+R^{\cdot} \tag{13}$$

$$[(dtc^-)_2Ru^{II}(dtc^{\cdot})]^* + RCl \rightarrow [(Cl^-)Ru^{III}(dtc^-)_2]+Rdtc \tag{14}$$

$$[(Cl^-)Ru^{III}(dtc^-)_2]+[Ru^{III}(dtc)_3] \rightarrow \alpha-[Ru_2^{III}(dtc^-)_5]^+Cl^-(\text{product 2}) \tag{15}$$

Two products are formed during the photolysis. Product 1 appears as a result of Cl atom abstraction by the excited complex from a solvent molecule, and product 2 arises from the reaction of intermediate species $[(Cl^-)Ru^{III}(dtc^-)_2]$, which has lost one dtc ligand, with the initial complex. The identification of the resulting products was made on the basis of their electronic and NMR spectra [13,33]. X-ray studies of product 1 [13,33] have confirmed its structure as having five sulphur atoms lying in one plane, and have shown that the length of the Ru–S bond changes from 2.352 up to 2.428 Å, the S–Ru–S angle varies from 69.3 to 72.9°, and the S–C–S angle is equal to 108 and 110°.

The molar yield ratio of the products (1:2) [32], which does not depend on the solvent, is 80:20. The quantum yield of $Ru(Et_2dtc)_3$ disappearance in $CHCl_3$, measured at 30° C for $\lambda = 265$, 313, 366 nm, is equal to 0.29, 0.071 and 0.01, respectively.

3.3. *Photochemistry of the Mo(VI) dithiocarbamate complex*

The $Mo(VI)O_2(Et_2NCS_2)$ complex in 1,2-dichloroethane has three intense absorption bands with maxima at 258, 300 and 380 nm (with extinction coefficients of 28 100, 12 600 and 3700 M^{-1} cm^{-1}, respectively). The irradiation of the solution in the 380 nm range [34] results in loss of the yellow colour of the solution, disappearance of the initial complex absorption bands and the occurrence of a new absorption at 290 nm with isosbestic points at 295, 268 and 242 nm. Superposition of the spectra of the $Mo(VI)O_2(Et_2NCS_2)$ complex and of the tds molecule shows that the crossing points coincide with isosbestic points, testifying to the formation of a tds molecule as a single product absorbing in this spectral range. Stationary photolysis results in MoO_2 sedimentation.

Irradiation of the solution in the ESR spectrometer probe results in an ESR signal containing six lines of Mo(V) ion (MoO_2dtc complex) ($g_{iso} = 1.952$, $A_{iso} = 4.2$ mT). The termination of irradiation leads to disappearance of the ESR signal. A photolysis scheme has been proposed [34], and calculations of the quantum yield dependence on concentration and irradiation time have been performed.

$$MoO_2(dtc)_2 \xrightarrow{h\nu} [MoO_2(dtc)_2]^* \quad (16)$$

$$[MoO_2(dtc)_2]^* \rightarrow MoO_2(dtc) + dtc^{\cdot} \quad (17)$$

$$MoO_2(dtc)_2 + dtc^{\cdot} \rightarrow MoO_2(dtc) + tds \quad (18)$$

$$MoO_2(dtc) + dtc^{\cdot} \rightarrow MoO_2(dtc)_2 \quad (19)$$

$$MoO_2(dtc) + dtc^{\cdot} \rightarrow MoO_2 + tds \quad (20)$$

$$dtc^{\cdot} + dtc^{\cdot} \rightarrow tds \quad (21)$$

These calculations allow the determination of the reaction rate constants which agree well with the experimental data on quantum yield. The calculations use the value $k_{21} = 2.0 \times 10^5$ M^{-1} s^{-1} taken from Ref. [52] on the electrochemical oxidation of the $(S_2CNEt_2)^-$ anion in acetonitrile. It is supposed [52] that in this process dtc radicals are formed and recombine, resulting in a thiuramdisulphide molecule. However, laser flash photolysis of tds solutions [53] has shown that dtc radicals recombine with a rate constant close to the diffusion rate constant

($k_{21} = 5.4 \times 10^9$ M^{-1} s^{-1}). Thus, the mechanism of the photolysis of Mo(VI) dithiocarbamate complexes [34], as well as the reaction rate constant values for different stages of the process remain uncertain.

3.4. Photochemistry and photochromism of Ni(IV) dithiocarbamate complexes

3.4.1. Photochemical studies by stationary methods

In the first papers on the photochemical and photochromic activity of Ni(IV) dithiocarbamate complexes, the investigations were conducted by steady-state methods in the range $\lambda > 350$ nm. In this spectral range, solutions of the $Ni(dtc)_3^+$ complex in $CHCl_3$ [19,24] and CH_3CN [24,29] have absorption bands with maxima at 18 200 (5.1–5.6), 20 200 (7.7–8.4) and 22 800 cm^{-1} (10.4) (the magnitude of $\epsilon{*}10^{-3}$ (M^{-1} cm^{-1}) is specified in the parentheses).

$Ni(dtc)_3^+$ solutions have a very deep red–brown colour which, during irradiation with UV or visible light, changes to a pale yellow color [24,29]. Some dozens of minutes after the termination of irradiation, in the dark, the red–brown colour is completely restored. It is possible to divide the solvents into three groups on the basis of the results of treatment of the solution with light [24]. Solvents in which photolysis does not proceed are $CHCl_3$, CH_2Cl_2, $CHBr_3$, $CHCl_2CHCl_2$, and C_6H_5Br; those in which photolysis proceeds reversibly are CH_3CN, C_2H_5OH, CH_3OH, CH_3NO_2, and acetone; and solvents in which photolysis proceeds irreversibly are pyridine, triethylamine, chloroform, and H_2SO_4.

It is supposed that the products of Ni(IV)(*n*-Bu$_2$dtc)$_3$Br photolysis are Ni(II)(*n*-Bu$_2$dtc)$_2$ and $NiBr_2$ complexes, and the tds molecule according to the following equation [24]:

$$\mathrm{Ni^{IV}(dtc)_3^+ + Br^- \xrightarrow{h\nu} \tfrac{1}{2}Ni^{II}(dtc)_2 + \tfrac{1}{2}Ni^{II}Br_2 + tds} \qquad (22)$$

The final products are proposed on the basis of PMR spectroscopy data. During irradiation the methylene proton signals in the complex $Ni^{IV}(Bz_2dtc)_3^+$ ($\delta = 4.88$) disappear. Two new signals with $\delta = 5.28$ and $\delta = 4.72$, assigned to methylene protons of the free tds molecule ($\delta = 5.27$) and ligands in the complex $Ni^{II}(Bz_2dtc)_2$ ($\delta = 4.70$) are formed.

$NiBr_2$ formation is assumed, based on an approximately 50% drop in the conductance of the solution during photolysis. The quantum yield measured in the 330–460 nm range [29] has practically no dependence on wavelength, temperature, and light intensity, and is equal to about 0.19. Although a mechanism for the photoprocess [24] was not proposed, the appearance of the tds molecule allows one to propose that the mechanism should be described by the following sequence of reactions:

$$\mathrm{[Ni^{4+}(dtc^-)_3]^+ \xrightarrow{h\nu} [Ni^{3+}(dtc^-)_2]^+ + dtc^{\cdot}} \qquad (23)$$

$$\mathrm{dtc^{\cdot} + dtc^{\cdot} \rightarrow tds} \qquad (24)$$

$$\mathrm{[Ni^{3+}(dtc^-)_2]^+ + [Ni^{3+}(dtc^-)_2]^+ \rightarrow [Ni^{4+}(dtc^-)_3]^+ + [Ni^{2+}(dtc^-)]^+} \qquad (25)$$

$$[Ni^{2+}(dtc^-)]^+ + [Ni^{2+}(dtc^-)]^+ \rightarrow [Ni^{2+}(dtc^-)_2] + [Ni^{2+}(Br^-)_2] \qquad (26)$$

Studies of the reverse dark reaction, ensuring the photochromism of $Ni(dtc)_3^+$ complexes, have shown that this is a second-order process with $E_a = 88$ kJ mol^{-1}, and $k = 5.4$ M^{-1} s^{-1} at room temperature. The dark process is offered as the sequence of reactions [24]

$$Ni(dtc)_2 + NiBr_2 \rightarrow 2Ni(dtc)Br \qquad (27)$$

$$Ni(dtc)Br \rightarrow Ni(dtc)^+ + Br^- \qquad (28)$$

$$Ni(dtc)^+ + tds \rightarrow Ni(dtc)_3^+ \qquad (29)$$

The detection of intermediate Ni(III) complexes employed ESR [54] for $Ni(R_2dtc)_3^+$ in a frozen acetonitrile (120 K). After irradiation, the observed ESR signal with an anisotropic g-factor ($g_x = 2.136$, $g_y = 2.126$ and $g_z = 2.037$) is assigned to the paramagnetic Ni(III) complex. Unfortunately, the relative yield of Ni(III) (in relation to the quantity of decomposed $Ni(R_2dtc)_3^+$) is not measured, and therefore it is impossible to assert that under these conditions Ni(III) formation is a principal channel of $Ni(R_2dtc)_3X$ photoreduction.

3.4.2. *The steady-state photolysis of $Ni(dtc)_3^+$ solution in the 200–800 nm spectral range [55]*

Fig. 1 shows evolution of the optical spectrum during irradiation of $Ni(dtc)_3^+$ solution in acetonitrile at room temperature, with a set of isosbestic points at 30 640, 34 100, 40 530, and 48300 cm^{-1}. The photoreaction is observed to form the bivalent nickel complex $Ni(dtc)_2$. Most typical is the appearance of bands with maxima at

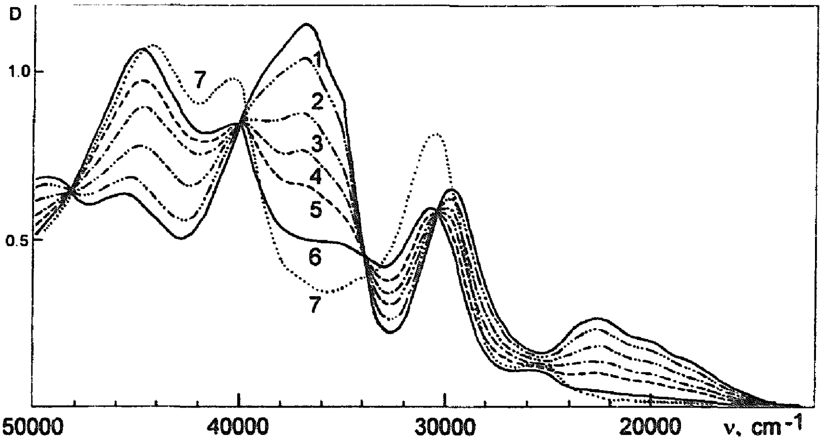

Fig. 1. Change in the optical spectrum of $Ni(n\text{-}Bu_2dtc)_3Br$ solution in acetonitrile (2.2×10^{-4} M, cuvette 1 mm) on irradiation with $\lambda > 600$ nm: (1–6) irradiation for 0, 4, 15, 30, 60, 300 s respectively; (7) spectrum of $Ni(n\text{-}Bu_2dtc)_2$ + tds solution (the concentration of each component being 2.2×10^{-4} M). Adapted from Ref. [55].

30 720 and 40 300 cm^{-1}. However, in the spectrum of the solution, containing only the Ni(dtc)$_2$ complex, there is a deep gap between these bands, which is absent after photolysis (Fig. 1). This indicates the appearance of additional absorption, which is probably due to thiuramdisulphide. Spectrum 7 in Fig. 1 shows the total spectrum of Ni(dtc)$_2$ and tds.

3.4.3. Photolysis of Ni(dtc)$_3^+$ in a frozen matrix [55]

The data on Ni(dtc)$_3^+$ photolysis in a frozen matrix are very important for the determination of the primary mechanism of the photoprocesses. The change in the Ni(dtc)$_3^+$ optical spectrum during photolysis in a methanol matrix is depicted in Fig. 2. During the irradiation the spectrum displays isosbestic points at 41 340, 34 480, 30 640, 27 200, and 24 480 cm^{-1}. The location of the points is similar to that observed for Ni(dtc)$_3^+$ photolysis in liquid solution (Fig. 1).

Of great importance is the formation of the characteristic absorption bands of the Ni(dtc)$_2$ complex and tds molecule. Spectrum 6 in Fig. 2 represents the total spectrum of the (Ni(dtc)$_2$+tds) system at 77 K. The methanol matrix is very rigid; therefore, the appearance of the Ni(II) ion and tds molecule can only be explained by intracoordination reactions. The appearance of the tds molecule must involve several stages. First, according to the nature of absorption bands, the electron is transferred from the dtc$^-$ ligand to the central ion with breaking of one of the Ni–S bonds. This is followed by electron transfer from the second dtc$^-$ ion and, as a result, two coordinated dtc radicals appear which recombine to form the –S–S– bond between free sulphur atoms:

$$\mathrm{Ni(dtc)_3^+} \xrightarrow{h\nu} [\mathrm{Ni^{4+}(dtc^-)_3}]^{+*} \rightarrow [(\mathrm{dtc^-})_2\mathrm{Ni^{3+}} - \mathrm{SC(^{\bullet}S)NR_2}]^+ \qquad (30)$$

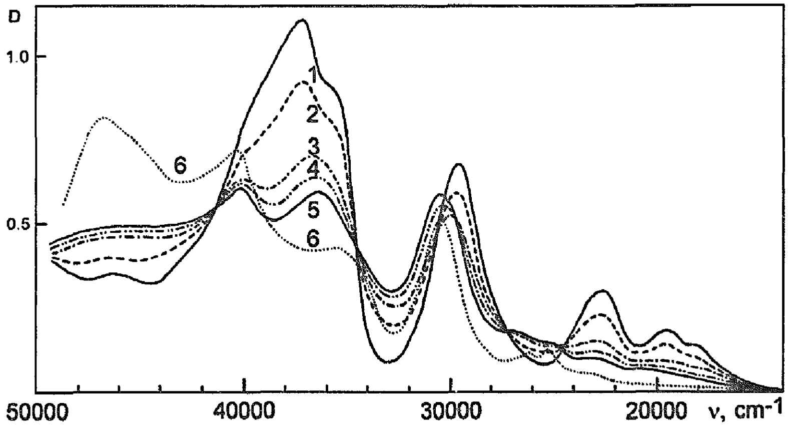

Fig. 2. Change in the optical spectrum of Ni(n-Bu$_2$dtc)$_3$Br in a methanol matrix (2.44 × 10^{-3} M, cuvette 50 μm) on irradiation: (1–5) irradiation for 0, 5, 15, 30 and 45 min, respectively; (6) spectrum of the (Ni(n-Bu$_2$dtc)$_2$ + Et$_2$tds) system in a matrix (the concentration of each component being 2.44 × 10^{-3} M). Adapted from Ref. [55].

$$[(\mathrm{dtc}^-)_2\mathrm{Ni}^{3+}-\mathrm{SC}(^\cdot\mathrm{S})\mathrm{NR}_2]^+ \rightarrow [(\mathrm{dtc}^-)\mathrm{Ni}^{2+}-\{\mathrm{SC}(^\cdot\mathrm{S})\mathrm{NR}_2\}]^+ \qquad (31)$$

$$[(\mathrm{dtc}^-)\mathrm{Ni}^{2+}-\{\mathrm{SC}(^\cdot\mathrm{S})\mathrm{NR}_2\}]^+ \rightarrow [(\mathrm{dtc}^-)\mathrm{Ni}^{2+}=\mathrm{tds}]^+ \qquad (32)$$

The discrepancy between the position of the isosbestic points and the crossings of $\mathrm{Ni(dtc)}_3^+$ and $(\mathrm{Ni(dtc)}_2+\mathrm{tds})$ spectra can be attributed to the fact that the final product is a complex containing a coordinated tds molecule.

Thus, the observation of photochemical transformations for $\mathrm{Ni(dtc)}_3^+$ in a rigid frozen matrix and the similarity between the spectral changes in the matrix and liquid solution testify that the photoprocesses for this complex are limited to intracoordination reactions in both cases.

3.4.4. *Laser flash photolysis of $\mathrm{Ni(dtc)}_3^+$ solutions [55]*

The formation of the tds molecule in the coordination sphere of the complex must be accompanied by transfer of two electrons, cleavage of two Ni–S bonds and the formation of a new –S–S– bond. The kinetic changes, occurring after laser flash photolysis, indeed involve several stages.

At room temperature, after the laser pulse, a stepwise decrease in the optical density is observed in the range 400–700 nm, which coincides with the spectrum of the $\mathrm{Ni(dtc)}_3^+$ complex. The time of the decrease at 240 K is about 1 μs (Fig. 3). The difference between the spectrum after the laser pulse and the spectrum at 3 μs (Fig. 3, curve 3) is probably due to the spectrum of the excited state of the complex, which causes cleavage of the first Ni–S bond and the formation of the coordinated dtc radical. The presence of oxygen has no effect on the process kinetics. According to extrapolation, the characteristic time of bond cleavage at room temperature is in the range 25–30 ns.

The absence of free dtc radical formation has been demonstrated both in a frozen matrix and in liquid solutions. In a separate experiment [53], we have shown that the optical spectrum of this radical is a wide absorption band with a maximum at 16 660 cm^{-1} (600 nm) and an extinction coefficient of about 3250 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. However, both matrix photolysis and laser flash photolysis of the $\mathrm{Ni(dtc)}_3^+$ complex fail to give rise to the absorption band at 600 nm.

The processes occurring after cleavage of the first Ni–S bond manifest themselves in the spectral range $\lambda<420$ nm. Fig. 4 shows the kinetic curves of the change in optical density after the laser pulse for $\mathrm{Ni(dtc)}_3^+$ solutions in acetonitrile at ambient temperature. The absorption spectra of the intermediates are also shown in Fig. 4. The first is the absorption spectrum of the initial $\mathrm{Ni(dtc)}_3^+$ complex. The second is the spectrum of the particle appearing 1 μs after the laser pulse, when the excited state of the complex has disappeared and the first Ni–S bond cleavage has been completed. This spectrum could be assigned to the Ni^{3+} ion with a coordinated dtc radical. The third spectrum appears at 50 μs and can be attributed to the Ni^{2+} ion with two coordinated dtc radicals. The kinetic curves in Fig. 4 reflect the process of the second Ni–S bond cleavage. The third spectrum does not coincide with final spectrum (spectrum 4). Thus, there is at least one more process that can be represented by the reaction of –S–S– bond closure between two dtc radicals and the

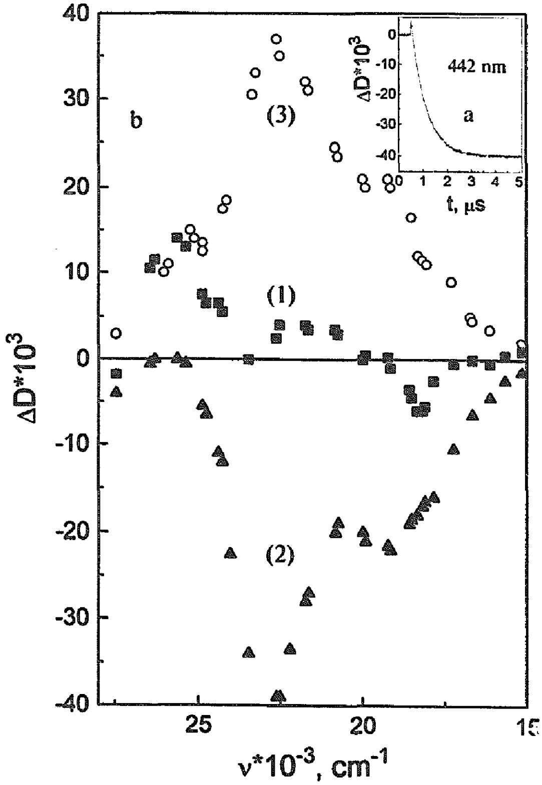

Fig. 3. Change in the optical spectrum of $Ni(n\text{-}Bu_2dtc)_3Br$ solution (4.93×10^{-4} M) in acetonitrile after the laser pulse (308 nm) (cuvette 1.17 mm) at 240 K: (1,2) 50 ns and 3 μs after the pulse, respectively; (3) the difference between spectra 2 and 1. Adapted from Ref. [55].

formation of the tds molecule, coordinated with the central Ni^{2+} ion. The time of appearance of the final spectrum is about 1 ms.

3.4.5. Dark reaction of $Ni(dtc)_3^+$ spectrum reconstruction [56]

At room temperature, the kinetics of the reverse dark reduction of the spectrum in acetonitrile can be described by an exponential law up to sufficiently large transformation depths (greater than 90%). However, this reaction is a pseudo-first-order process because the observed first-order rate constant is linearly dependent on the initial concentration of $Ni(dtc)_3^+$ complex with zero intersect on the ordinate. The observed rate constant is also dependent on the decrease in optical density after irradiation. This result shows that the photoreaction product reacts with both the initial complex and itself.

$$[(dtc^-)Ni^{2+}{=}tds]^+ + [Ni^{4+}(dtc^-)_3]^+ \rightarrow 2Ni(dtc)_3^+ \qquad (33)$$

$$[(dtc^-)Ni^{2+}{=}tds]^+ + [(dtc^-)Ni^{2+}{=}tds]^+ \rightarrow 2Ni(dtc)_3^+ \qquad (34)$$

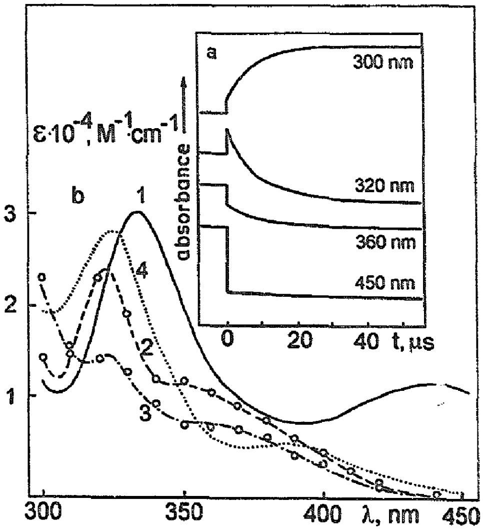

Fig. 4. (a) Kinetic changes in the optical density of $Ni(dtc)_3^+$ solution (3×10^{-4} M) in acetonitrile at 295 K after the laser pulse (532 nm; cuvette 1 mm). (b) Spectra of the intermediates arising in succession: (1) spectrum before the pulse (initial spectrum); (2,3) spectra 1 μs and 50 μs after the pulse, respectively; (4) final spectrum. Adapted from Ref. [55].

The activation energies for Eqs. (33) and (34) in acetonitrile are 54 and 78 kJ mol^{-1}, respectively. At room temperature (293 K), their rate constants are about 1.2 and 1.5 $M^{-1}\ s^{-1}$, respectively. Thus, if phototransformation of the $Ni(dtc)_3^+$ complex involves only an intracomplex, monomolecular processes, the reverse dark reaction is probably determined by the interaction between different complexes, i.e. a bimolecular process.

3.4.6. The number of photochromic transformation cycles [56]

The number of cyclic transformations of the molecule can be determined using the efficient rate constants of optical density decrease ($k_{h\nu}$) and increase (k_{dark}) when the laser is switched on and off:

$$N = \frac{k_{h\nu}k_{dark}}{k_{h\nu}+k_{dark}} \tag{35}$$

For fairly high complex concentrations, the time of the transition to the stationary state after the laser is switched on ($1/(k_{h\nu}+k_{dark})$) may by 1 s or less, and the time of optical density recovery ($1/k_{dark}$) may reach about 2 s. Thus, according to Eq. (35) each complex molecule in the sample undergoes about 10^3 transformation cycles during 1 h of irradiation. Permanent irradiation of the $Ni(dtc)_3^+$ solution in acetonitrile for about 10 h caused no changes in the optical density of the solution after the laser has been switched off. Thus, the complex can endure more than 10^4 transformation cycles.

4. Conclusions

A number of dithiocarbamate complexes of transition metals have intense absorption bands in both the UV and visible ranges, and display high photochemical activity. For complexes of Fe(III), Fe(IV), and Ru(IV), the primary process is an electron transfer to the appropriate acceptor, e.g. frequently used halogenated hydrocarbons. For Mo(VI) complexes, photochemical changes affect only the coordination sphere. To establish the nature of the intermediate species, further research using laser flash photolysis is necessary.

The combination of stationary photolysis of the $Ni(dtc)_3^+$ complex in liquid solutions and frozen matrices with laser flash photolysis demonstrates that all phototransformations occur within the coordination sphere of the complex. The reverse dark reactions which lead to photochromic transformations of $Ni(dtc)_3^+$ solutions are shown to be due both to the reactions of disproportionation of the Ni(II) complex (photolysis product) and to its reaction with the initial $Ni(dtc)_3^+$ complex.

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