

Oxidation of bis(dialkyldithiocarbamato)nickel(II) with bromine and iodine

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The product of bis(dialkyldithiocarbamato)nickel(II) (Ni(II)L_2) oxidation with bromine is the $\text{Ni(IV)L}_3\text{Br}$ complex (L is a dithiocarbamato ligand). Iodine oxidizes Ni(II)L_2 to the complex $\text{Ni(III)L}_2\text{I}_3$ in the nonpolar medium. The equilibrium constant of the reaction $2\text{Ni(II)L}_2 + 3\text{I}_2 \rightleftharpoons 2\text{Ni(III)L}_2\text{I}_3$ was determined spectrophotometrically. Its numerical value is $(8.7 \pm 1.5) \times 10^5$ for toluene and $(5.0 \pm 0.3) \times 10^7$ for chloroform, respectively. In the polar medium a final product of oxidation with iodine is the $\text{Ni(IV)L}_3\text{I}_3$ complex which is thought to arise due to the disproportionation of the primarily formed $\text{Ni(III)L}_2\text{I}_3$ complex.

Продукт окисления бромом бис(диалкилдитиокарбамат)никеля(II) (Ni(II)L_2) есть комплекс $\text{Ni(IV)L}_3\text{Br}$, где L — лиганд дитиокарбамата. Иод окисляет Ni(II)L_2 в комплекс $\text{Ni(III)L}_2\text{I}_3$ в неполярной среде. Константа равновесия реакции $2\text{Ni(II)L}_2 + 3\text{I}_2 \rightleftharpoons 2\text{Ni(III)L}_2\text{I}_3$ была определена спектрофотометрически. Ее численное значение $(8,7 \pm 1,5) \cdot 10^5$ для толуола и $(5,0 \pm 0,3) \cdot 10^7$ для хлороформа. В полярной среде конечный продукт окисления иодом представляет собой комплекс $\text{Ni(IV)L}_3\text{I}_3$, который, как полагают, возникает в результате диспропорционирования первично образующегося комплекса $\text{Ni(III)L}_2\text{I}_3$.

Dithiocarbamates, *i.e.* substances containing the functional group $>\text{NCS}_2$, have been vastly used in the rubber industry as vulcanization accelerators and antioxidants [1]. In recent years these substances have been increasingly applied as fungicides [2]. Both the possibility to separate metals in the form of dithiocarbamate complexes *via* liquid [3] and gas chromatography [4] and the spectrophotometric determination of metals in the form of those complexes [5] serve as additional examples for the dithiocarbamates utilization. The ability of dithiocarbamate ligands to stabilize the high-oxidation numbers of central metals contained in the complex compounds [6] aroused a great interest of coordination chemists in these substances.

A relatively easy oxidability of nickel(II) complexes with dithiocarbamato ligands to the complex nickel compounds, involving the oxidation numbers III and IV, also relates to the mentioned dithiocarbamato ligands ability [6]. The high-oxidation state stability of transition metals, contained in the dithiocarbamato complexes, is derived from the sulfur atoms ability to form the σ as well as π donor-acceptor bonds on the one hand and from the further increase in the π -electron density on sulfur atoms, caused by delocalization of the lone electron pair on the nitrogen atom [6], on the other. This can be seen in Scheme 1.



Scheme 1

An easy oxidability of the dithiocarbamato ligand to the thiuram disulfide [1] leaves one in certain doubts, whether assignment of the high-oxidation number to a nickel atom is correct. However, the X-ray structural analysis has proved [7] that the oxidation of the central atom takes place. The Ni(II) dithiocarbamato complexes may be oxidized electrochemically [8—11] and through different oxidants such as halogens [7, 12—17], thiuram disulfide [7, 18, 19], iron(III) chloride [20], nitric acid [7], etc. The products of oxidation are the Ni(III) and Ni(IV) complexes.

This paper is intended to elucidate the oxidation of Ni(II) dithiocarbamates with bromine and iodine, and moreover, to identify and characterize the oxidation products.

Experimental

The chemicals were of anal. grade purity and they did not need to be extraordinarily purified. Chloroform was purified according to [21]. Methanol was purified by means of distillation with CaO. Acetone was dried with anhydrous calcium chloride and then distilled after the addition of a small amount of potassium permanganate. Toluene was purified by means of double distillation [22].

Spectrophotometric measurements were made on the Specord UV VIS and Spekol (Zeiss, Jena) spectrophotometers with tempered cell holders. The temperature of measured solutions was maintained at (20 ± 0.1) °C. Absorption spectra in the UV VIS region were, with the exception of common registration, scanned also by the microcomputer Compucorp 610, making use of the A/D and D/A converters in the computer. The measured values of transmittance were corrected by the computer software to the transmittance of the reference solution, and thus corrected absorption spectra were tabulated and graphically recorded as the dependence of absorbance on λ or $\bar{\nu}$.

EPR spectra were measured at laboratory temperature by the Varian E-3 spectrometer operating at a frequency of 9.42 GHz.

Infrared spectra were scanned by the IR spectrometer IR-20 (Zeiss, Jena) using the KBr technique.

Preparation and analysis of reference complexes

The nickel(II) dithiocarbamates and thiuram disulfides were prepared and purified as described earlier [23, 24].

Bis(diethyl dithiocarbamato)nickel(III) triiodide, $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$:

This compound was prepared by the reaction of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ with iodine in dichloromethane at a 2:3 mole ratio. After one minute's interval n-hexane was slowly added to the mixed solutions of these compounds. The black precipitate of $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ was filtered off and dried *in vacuo*.

Tris(diethyl dithiocarbamato)nickel(IV) bromide, $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$:

0.005 mole of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ and then, on continual stirring, 10 cm³ of the chloroform solution of bromine (0.0033 mol) were slowly added to 20 cm³ of chloroform. The solution was standing for several minutes, then poured over in a separatory funnel and shaken up three times together with the small fractions of acidified water. The chloroform layer was dried with anhydrous sodium sulfate. Diethyl ether was slowly added to this solution and a black powdered material was formed. The product was filtered off and after washing by diethyl ether it was dried *in vacuo*. The complex obtained was strongly hygroscopic and, therefore, it had to be preserved in a desiccator.

Tris(di-n-butyl dithiocarbamato)nickel(IV) bromide, $[\text{Ni}(\text{Bu}_2\text{dtc})_3]\text{Br}$:

This complex was prepared similarly as the ethyl derivative (see above). The product is more air-stable than the ethyl derivative and it may be overcrystallized without any decomposition risk.

Tris(diethyl dithiocarbamato)nickel(IV) chloride, $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Cl}$:

The complex $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ was dissolved in hot acetone, and a few drops of concentrated hydrochloric acid and 30 % solution of H₂O₂ were added to this solution. The deep-brown solution obtained was poured over after several minutes' standing in a separatory funnel, and the product was extracted into chloroform. The chloroform extract was dried with anhydrous sodium sulfate. After the addition of diethyl ether, the product in the form of black amorphous substance was formed. It was considerably unstable in air.

Tris(diethyl dithiocarbamato)nickel(IV) triiodide, $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}_3$:

The solution of iodine (0.013 mol) in methanol was slowly added to 0.01 mole of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ in 20 cm³ of chloroform. When all $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ had been dissolved, one acidified water drop more was yet added to accelerate the disproportionation of Ni(III) complex (see below). After several minutes' standing the solution was poured over in a separatory funnel and repeatedly shaken up together with small fractions of acidified water to remove NiI₂. The chloroform layer was dried with anhydrous sodium sulfate. After the addition of diethyl ether the black crystals that had fallen out were separated, washed up by diethyl ether and dried *in vacuo*.

The analyses for the C, H, and N contents were made on the C. Erba (model 1102) analyzer. The metal contents in the prepared compounds were determined by the chelometric titration of mineralized samples. The results from the elemental analysis of the prepared compounds are listed in Table 1.

Table 1

Results of elemental analysis ($w_i/\%$)

Brackets: first column — relative molecular masses; other columns — theoretical contents of elements*

Compound	C	H	N	Metal
[Ni(Et ₂ dtc) ₂] (335.26)	33.01 (33.81)	5.71 (5.67)	7.80 (7.89)	16.24 (16.53)
[Ni(Bu ₂ dtc) ₂] (467.46)	46.10 (46.25)	7.70 (7.76)	6.01 (5.99)	12.38 (12.56)
[Ni(Et ₂ dtc) ₃]Cl (538.98)	30.10 (33.43)	5.15 (5.61)	7.15 (7.80)	11.40 (10.89)
[Ni(Et ₂ dtc) ₃]Br (583.44)	31.50 (30.88)	5.25 (5.18)	7.40 (7.20)	10.00 (10.06)
[Ni(Et ₂ dtc) ₃]I ₃ (884.23)	20.96 (20.38)	3.69 (3.42)	5.30 (4.75)	6.67 (6.64)
[Ni(Bu ₂ dtc) ₃]Br (751.74)	42.25 (43.14)	7.26 (7.24)	5.48 (5.59)	7.79 (7.81)
[Ni(Et ₂ dtc) ₂]I ₃ (735.94)	16.90 (16.32)	2.80 (2.74)	3.92 (3.81)	7.92 (7.98)

* Et₂dtc = (C₂H₅)₂NCS₂; Bu₂dtc = (C₄H₉)₂NCS₂.

Study of redox properties in solutions

Oxidation of the Ni(II) dithiocarbamates with bromine

The bromine solution (0.0067 mol) in chloroform was added to the [Ni(Et₂dtc)₂] solution in the same solvent (0.01 mol), and the reaction mixture was standing for 30 min. With higher molar excesses of bromine a light water-soluble precipitate was formed. The identification of components was accomplished chromatographically (TLC on the Silufol plates) using the synthesized compounds mentioned above. As the mobile phase chloroform and 20 % (v/v) of methanol in chloroform were used. The R_f values for the detected compounds are listed in Table 2.

The chromatograms obtained were evaluated also quantitatively. The spot of the [Ni(Et₂dtc)₂] complex on the chromatogram was leached by chloroform and the attained solution was filled up to an exact volume. From the absorption spectrum of that solution the concentration of the complex in the reaction mixture was calculated.

Table 2

 R_f values for compounds detected during the oxidation of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ with bromine in chloroform

Compound	Mobile phase	
	Chloroform	20 % (v/v) methanol in CHCl_3
$[\text{Ni}(\text{Et}_2\text{dtc})_2]$	0.53	0.86
tds*	0.40	0.85
NiBr_2	0	0
Reaction product	0	0.51

* N,N,N',N' -tetraethylthiuram disulfide.

The brown substance (a product of oxidation) was leached in methanol. Its electronic spectrum was identical to the spectra of compounds of the $[\text{Ni}(\text{IV})\text{dtc}_3]^+$ type (Ref. [7]) (Fig. 1). The resultant light-brown solutions were bleached with visible light. The electronic spectra showed that these solutions contained the Ni(II) dithiocarbamato complexes and thiuram disulfide.

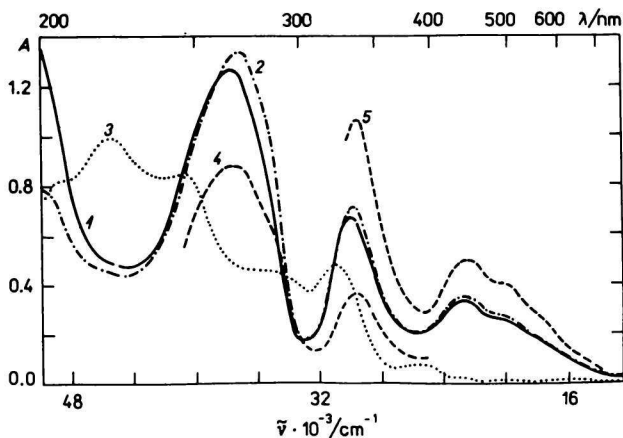


Fig. 1. Electronic spectra of: 1. $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$ in water ($c = 5.8 \times 10^{-5} \text{ mol dm}^{-3}$, $d = 0.5 \text{ cm}$); 2. $[\text{Ni}(\text{Bu}_2\text{dtc})_3]\text{Br}$ in methanol ($c = 5.8 \times 10^{-5} \text{ mol dm}^{-3}$, $d = 0.5 \text{ cm}$); 3. the same solution exposed to white light; 4. $[\text{Ni}(\text{Bu}_2\text{dtc})_3]\text{Br}$ in chloroform ($c = 1.4 \times 10^{-5} \text{ mol dm}^{-3}$, $d = 1 \text{ cm}$); 5. $[\text{Ni}(\text{Bu}_2\text{dtc})_3]\text{Br}$ in chloroform ($c = 4.5 \times 10^{-5} \text{ mol dm}^{-3}$, $d = 1 \text{ cm}$).

The dependence of the change in the amount of reaction compounds upon the amount of Br_2 added to the system is illustrated in Fig. 2. The nickel content in the brown substance found after extraction and bleaching as $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ was only a half of the theoretical amount calculated on the basis of material balance. Consequently, after bleaching two molecules of the reaction product gave rise to one molecule of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$.

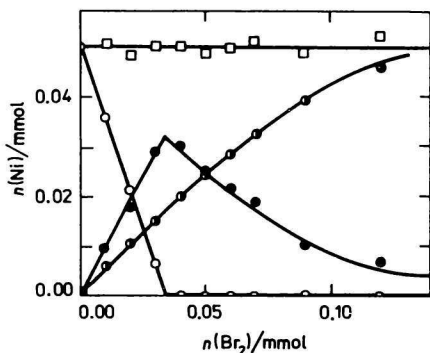
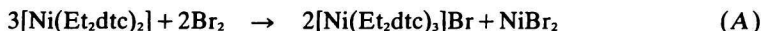
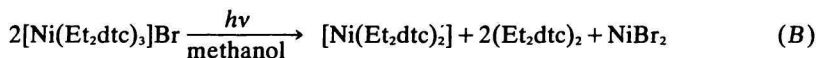


Fig. 2. Changes in the amount of nickel compounds during oxidation of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ complex by bromine in chloroform; \circ $[\text{Ni}(\text{Et}_2\text{dtc})_2]$; \bullet NiBr_2 ; \bullet $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$; \square the total nickel content in solution.

From Fig. 2 it follows that when the mole ratio of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ to bromine is not lower than 3 : 2, the complex $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$ is formed in accordance with the following equation



The complex formed decomposes due to the light influence, giving rise to $[\text{Ni}(\text{Et}_2\text{dtc})_2]$, thiuram disulfide, and NiBr_2 according to the equation



The decomposition becomes irreversible in the polar solvents, and contrary to the views of authors reported in Ref. [7], the reversible bleaching of the solution is also observed in chloroform at the lower concentrations in the complex.

After oxidation of the total $[\text{Ni}(\text{Et}_2\text{dtc})_2]$, a further bromine addition results in the concentration fall of $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$, and in the concentration growth of NiBr_2 (Fig. 2). The excess of oxidant is likely to oxidize ligands and therefore, from the aspect of synthesis of the $[\text{Ni}(\text{IV})\text{dtc}_3]\text{Br}$ type of complexes, the adherence to a mole ratio of 3 : 2, existing between the Ni(II) dithiocarbamate and the bromine, is very important.

The $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$ complex is soluble also in water where it yields a similar absorption spectrum to that in methanol and chloroform (Fig. 1). By acidifying the aqueous solution of the complex — using a small amount of hydrochloric acid — the solution stability may be prolonged. The water-solubility of the complex and its solubility in other polar solvents, or its slight solubility in the nonpolar solvents prove that the complex has a strongly ionic character. Both the $[\text{Ni}(\text{Bu}_2\text{dtc})_3]\text{Br}$ and $[\text{Ni}(\text{iBu}_2\text{dtc})_3]\text{Br}$ complexes are essentially less water-soluble, which obviously relates to the more voluminous ligands.

By oxidation of the $[\text{Ni}(\text{Bu}_2\text{dtc})_2]$ and $[\text{Ni}(\text{iBu}_2\text{dtc})_2]$ complexes with bromine performed similarly as in the case of diethyl derivative, the complexes with the Ni(IV) central atom were formed. The behaviour of these complexes was reported in paper [7].

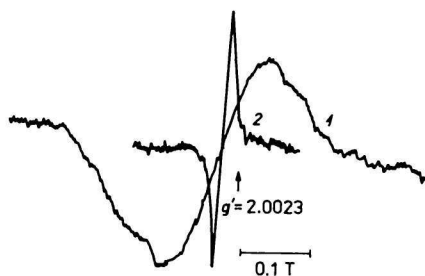


Fig. 3. EPR spectrum of powdered $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ (1) and of the solution of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ and iodine in chloroform (2).

In the electronic spectrum of the $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$ complex (Fig. 1) as well as in other types of complexes of the $[\text{NiL}_3]^+$ species, the absorption band at $\lambda = 266 \text{ nm}$ and the shoulder at $\lambda = 275 \text{ nm}$ appear. From comparisons made with other dithiocarbamates [25, 26] these bands may be assigned to the intra-ligand $\pi \rightarrow \pi^*$ transitions. Both the absorption band at $\lambda = 335 \text{ nm}$ and the wide-spread band in a visible region being characterized by the maximum absorbance at $\lambda = 440 \text{ nm}$ and by shoulders at $\lambda = 490 \text{ nm}$, 535 nm , and 625 nm , respectively, are formed due to charge transfer transitions. These bands overlap the less intensive $d-d$ transitions. The values of molar absorption coefficients could not be precisely determined because of a great solution instability and light sensitivity as well. The approximate $\log(\epsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}))$ values for $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$ in methanol and water are given in brackets beside the wavelength λ/nm : $266(4.8)$, $275(4.6)$, $335(4.4)$, and $440(4.0)$.

Oxidation of bis(diethyldithiocarbamato)nickel(II) with iodine

After mixing $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ with iodine the brown or even deep-brown solution arises with regard to the concentration of reacting compounds. In EPR spectra of the reaction mixture (Fig. 3) a rise of a relatively narrow signal is observed ($g = 2.148$). The EPR signal is measurable only at a relatively high concentration of reacting compounds ($\sim 10^{-2} \text{ mol dm}^{-3}$). The stoichiometry of reaction was studied in toluene and chloroform by the method of continual variations. As seen from Fig. 4, $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ reacts with iodine at a 2:3 mole ratio. During reaction, a paramagnetic nickel complex is formed (electronic configuration of the central metal d^7) and hence the redox process may be expressed by the equation



The results attained for chloroform were unreproducible, which was probably related to the presence of ethanol in chloroform. After the careful purification of chloroform [21] the reaction proceeded according to the same stoichiometry as in toluene. Under isolation of reaction product it was evident that the product had a more polar character than parent

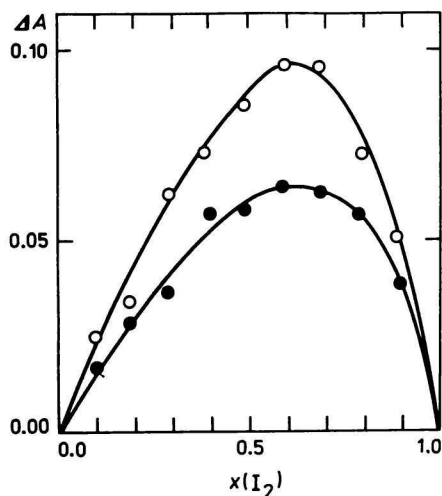


Fig. 4. Job's curves for the equilibrium system $[\text{Ni}(\text{Et}_2\text{dtc})_2] - \text{I}_2$ in chloroform (●) and in toluene (O). The total reactants concentration in chloroform is $2.9 \times 10^{-4} \text{ mol dm}^{-3}$, in toluene $5 \times 10^{-4} \text{ mol dm}^{-3}$. The wavelength of 429 nm , the light pass length of 1 cm .

compounds, and it precipitated from the solution when the solvent polarity was decreased. The elemental analysis results of the isolated material correspond to the molecular formula $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$. The EPR spectrum of its powdered sample is illustrated in Fig. 3. The signal ($g = 2.165$) is wider and more intensive than that of its chloroform solution.

The absorption spectrum of the product in chloroform (Fig. 5) represents a superposition of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ and iodine spectra, which means that the reaction product decomposes in

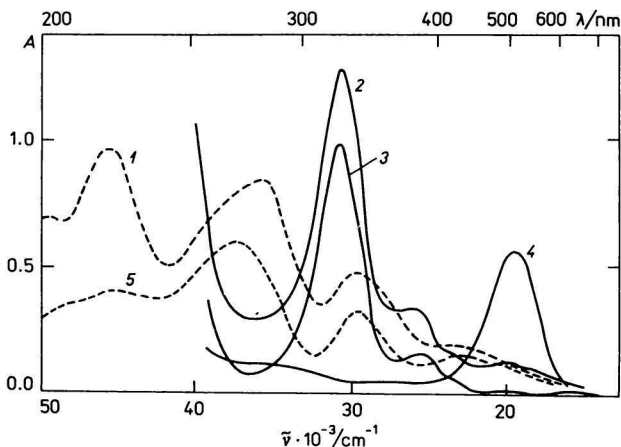
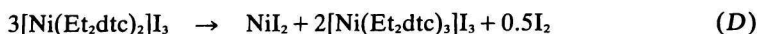


Fig. 5. Absorption spectra of: 1. $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ in methanol ($c = 1.56 \times 10^{-4} \text{ mol dm}^{-3}$, $d = 0.2 \text{ cm}$); 2. $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ in chloroform ($c = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $d = 0.2 \text{ cm}$); 3. $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ in chloroform ($c = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$, $d = 1 \text{ cm}$); 4. iodine in chloroform ($c = 6.5 \times 10^{-3} \text{ mol dm}^{-3}$, $d = 0.1 \text{ cm}$); 5. $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}_3$ in methanol ($c = 3 \times 10^{-5} \text{ mol dm}^{-3}$, $d = 0.5 \text{ cm}$).

chloroform back to these compounds. The absorption spectrum of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ complex in methanol is, with the exception of the far UV region, practically identical to the spectrum of the Ni(IV) complex $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}_3$, which is related to the disproportionation of the Ni(III) complex to the Ni(II) and Ni(IV) complexes [14] by the equation



The IR spectrum of reaction product (C) differs only slightly from the spectrum of $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ (Table 3); the band due to the $\nu(\text{C} \cdots \text{N})$ stretching vibrations was shifted slightly up to the higher wavenumbers.

The equilibrium constant of reaction (C) is expressed by the equation

$$K = [\text{NiL}_2\text{I}_3]^2 [\text{NiL}_2]^{-2} [\text{I}_2]^{-3} \quad (1)$$

where L is the Et_2dtc^- ligand and in the square brackets there are indicated equilibrium concentrations.

Table 3

Stretching vibrations of the C—N and C—S bonds of some Ni(II), Ni(III), and Ni(IV) complexes

Compound	$\nu(\text{C—N})$	$\nu(\text{C—S})$
	$\tilde{\nu}/\text{cm}^{-1}$	
$[\text{Ni}(\text{Et}_2\text{dtc})_2]$	1528	998
$[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$	1530	1000
$[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}_3$	1539	1000
$[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$	1535	999

For the total absorbance, with an assumption of the compensation of absorbance caused by iodine, the following equation is valid

$$A = \varepsilon(\text{NiL}_2) [\text{NiL}_2] d + \varepsilon(\text{NiL}_2\text{I}_3) [\text{NiL}_2\text{I}_3] d \quad (2)$$

where d is the light pass length in cm.

By using material balance for nickel ($c(\text{NiL}_2) = [\text{NiL}_2] + [\text{NiL}_2\text{I}_3]$), eqn (1) may be modified to the shape of

$$K = ((A - A_0)/(A_{00} - A))^2 [\text{I}_2]^{-3} \quad (3)$$

where

$$A_0 = \varepsilon(\text{NiL}_2) c(\text{NiL}_2) d; \quad A_{00} = \varepsilon(\text{NiL}_2\text{I}_3) c(\text{NiL}_2) d$$

This equation can be transformed to the equation of a straight line being a function of $(A - A_0)^{-1} = f([\text{I}_2]^{-1.5})$

$$(A - A_0)^{-1} = (A_{00} - A_0)^{-1} + (A_{00} - A_0)^{-1} K^{-0.5} [\text{I}_2]^{-1.5} \quad (4)$$

where the value of the intercept $((A - A_0)^{-1})$ forms a basis for the calculation of an unknown molar absorption coefficient $\varepsilon(\text{NiL}_2\text{I}_3)$ of the complex $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$. From the ratio of the intercept and the slope of dependence (4) the equilibrium constant value of reaction (C) can be calculated.

From the dependences gained experimentally (Fig. 6) the equilibrium constant value was calculated. The results are summarized in Table 4. As it is evident from the results, the rise of the Ni(III) complex is preferential in chloroform. Based on the known equilibrium constant, the absorption spectrum of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ complex in chloroform and toluene (Fig. 7) was computed. Some deviations in the absorption spectra of the complex in these solvents were caused probably by a different absorbance of the I_3^- anion in these solutions.

In a more polar medium than chloroform, the reaction between $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ and iodine proceeds via another route. On the basis of the spectrophotometric measurements it was proved that in the case of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ excess with regard to iodine the reaction product is the $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}$ complex giving practically the same spectrum as the complex $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{Br}$ (Fig. 1). After the addition of a further amount of iodine to $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}$

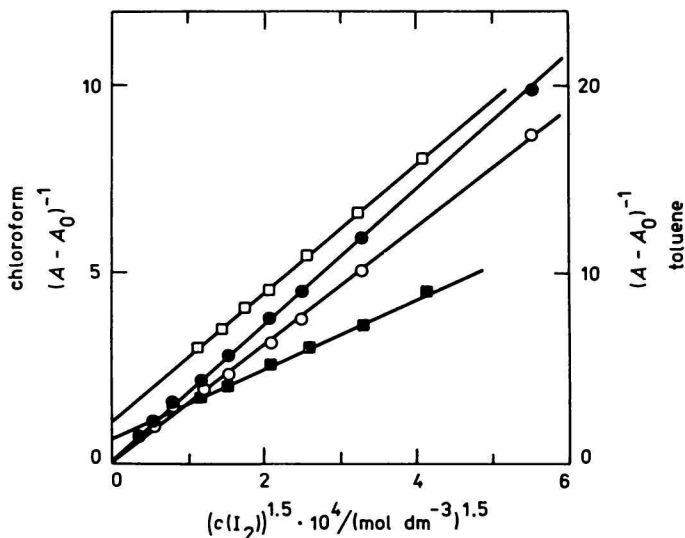


Fig. 6. The $(A - A_0)^{-1}$ dependence on the iodine concentration in the solution for the wavelengths of 288 nm (■), 390 nm (□) (chloroform solution), 410 nm (○), and 440 nm (●) (toluene solution); $\theta = 20^\circ\text{C}$, $d = 2\text{ cm}$, $c(\text{NiI}_2) = 2 \times 10^{-5}\text{ mol dm}^{-3}$.

Table 4

Calculated equilibrium constant values of reaction (C) at 20°C

Chloroform		Toluene	
λ/nm	$K/(\text{mol dm}^{-3})^{-3}$	λ/nm	$K/(\text{mol dm}^{-3})^{-3}$
288	4.9×10^7	390	9.1×10^5
390	5.0×10^7	410	7.9×10^5
440	5.1×10^7	440	9.1×10^5
Average value	$(5.0 \pm 0.3) \times 10^7$		$(8.7 \pm 1.5) \times 10^5$

a change in the absorption spectrum is noticeable, the band at $\lambda = 265\text{ nm}$ is shifted to 285 nm , and a shoulder at $\lambda = 355\text{ nm}$ appears. The spectrum of the compound formed corresponds to that of the $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}_3$ complex, its elemental composition being in accord with the composition of this complex. The mole ratio of reacting compounds determined photometrically was found to be $n([\text{Ni}(\text{Et}_2\text{dtc})]) : n(\text{I}_2) = 3 : 4$. As a result, the reaction can be expressed by the following equations



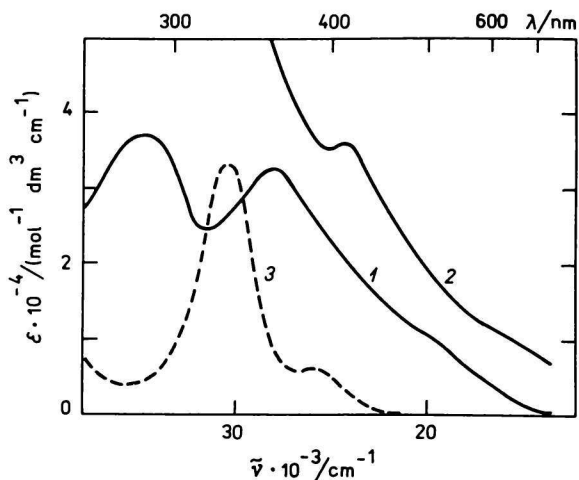
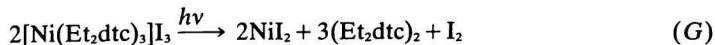


Fig. 7. The calculated absorption spectrum of $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ in chloroform (1) and in toluene (2). The absorption spectrum of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ complex in chloroform (3).

After illumination of the $[\text{Ni}(\text{Et}_2\text{dtc})_3]\text{I}_3$ methanol solution with visible light the brown solution was bleached and thiuram disulfide with iodine appeared in it



The IR spectrum of the compound (Table 3) is very similar to the spectrum of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ complex, only some of the absorption bands being less intensive; the $\nu(\text{C} \cdots \text{N})$ band is shifted by 11 cm^{-1} to higher wavenumbers with regard to an equal band in the spectrum of the Ni(II) complex. This shift relates to the increased conjugation of the lone electron pair located on the nitrogen atom with C—S bonds, which is caused by the enhanced oxidation number of the central atom.

Variations in the absorption spectrum observed during oxidation of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ complex with iodine in the mixed chloroform—methanol solution (Fig. 8) suggest that in the first reaction phase the Ni(III) complex is formed. This fact can be proved by changes at the wavelengths of $\lambda = 290 \text{ nm}$ and 380 nm , respectively, where the complex has its absorption maxima (Fig. 7). Once the maximum is being achieved, the absorbance at these wavelengths slowly decreases while that at $\lambda = 265 \text{ nm}$ and 440 nm increases, which indicates the Ni(IV) complex formation (Fig. 1). The Ni(III) complex disproportionates to the Ni(II) and Ni(IV) complexes in agreement with eqn (D).

From the dependences acquired in a similar way for both the methanol and methanol—water medium one may deduce that the more polar the medium, the higher the rate of the Ni(III) complex formation. By the polarity influence of the medium the different equilibrium constant values of reaction (C) may be explained. The more polar medium gives preference to the formation of $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ molecules which are more polar than the

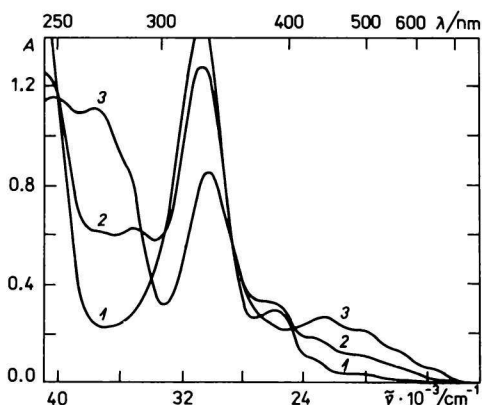
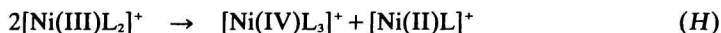


Fig. 8. Changes in the absorption spectrum of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ ($c = 4.5 \times 10^{-5} \text{ mol dm}^{-3}$) solution with iodine ($c = 3 \times 10^{-5} \text{ mol dm}^{-3}$) in the 50 % (v/v) methanol—chloroform solvent: 1 min (1), 45 min (2), and 15 h (3) after mixing the reactants; $\theta = 20^\circ \text{C}$, light pass length of 1 cm.

reactants $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ and iodine. The rate of disproportionation v_d of the Ni(III) complex is falling in dependence on the medium in the following sequence



The influencing of the rate of the Ni(III) complex disproportionation by the medium polarity can be accounted for by the elevated dissociation of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ complex to the $[\text{Ni}(\text{Et}_2\text{dtc})_2]^+$ and I_3^- ions as well as by the subsequent reaction of the $[\text{Ni}(\text{Et}_2\text{dtc})_2]^+$ ions



The $[\text{Ni}(\text{Et}_2\text{dtc})_2]^+$ complex is very quickly transformed to the $[\text{Ni}(\text{Et}_2\text{dtc})_2]$ and Ni^{2+} ion [27]. The question is why the neutral molecules $[\text{Ni}(\text{Et}_2\text{dtc})_2]\text{I}_3$ are not subjected to the disproportionation reaction. This is obviously associated with the voluminous I_3^- ligands which may prevent a charge transfer from one central Ni(III) atom to another.

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