

THE REACTION OF NICKEL(II) BIS(DIETHYLDITHIOCARBAMATE) WITH N,N,N',N'-TETRAETHYL THIURAMDISULPHIDE

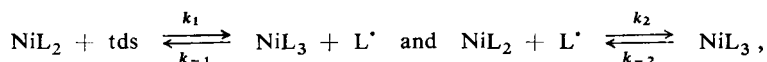
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The oxidation of nickel(II) bis(diethyldithiocarbamate) (NiL₂) by N,N,N',N'-tetraethyl thiuramdisulphide (tds) can be described by the equation $2 \text{NiL}_2 + \text{tds} \rightleftharpoons 2 \text{NiL}_3$ (NiL₃ = tris(diethyldithiocarbamate) nickel(III)). The equilibrium constant of the reaction depends on the polarity of the solvent ($4.4 \cdot 10^{-3}$ in toluene, $1.3 \cdot 10^{-3}$ in chloroform, and $8 \cdot 10^{-4}$ in acetone and methanol). The rate constants k_1 and k_{-2} and the ratio k_2/k_{-1} were found for the reaction steps



where L* is the (C₂H₅)₂NCS₂[•] radical.

The dithiocarbamate (dtc) ligand plays an important role in the stabilization of higher oxidation states of the transition metals¹ and can thus be very important in studying the pharmacological and fungicidal activity of these substances.

The oxidation reactions of the dithiocarbamate complexes of metals can be divided into three groups: 1) reactions in which the formal oxidation state of the central atom is increased, 2) reactions in which the dtc ligand is oxidized to give thiuramdisulphide (tds), where the oxidation state of the central atom does not change, and 3) reactions in which the dtc ligand is oxidized to a positive dimeric species.

The first group includes reactions in which complexes of the type $[\text{M(IV)}(\text{dtc})_3]^+ \text{X}^-$ are formed, where M = Fe, Mn, Ni, X = Cl, Br, I, I₃, etc.²⁻¹². This group includes the oxidation reactions of dithiocarbamate complexes of Cu(I), Cu(II), Ag(I), and Au(I) (ref.^{4,9,13-20}).

The second group includes the reactions of the dithiocarbamates of zinc, cadmium and mercury with the halogens with formation of complexes containing thiuramdisulphide as a ligand^{4,10,21}.

The third group corresponds to the formation of positively charged species as the result of oxidation, e.g. in the oxidation of the dtc complexes of Fe(III) with chlorine, $[\text{Fe(III)Cl}_4]^- \text{dtc}^+$ is formed^{6,22,23}.

The oxidation reactions of nickel(II) dithiocarbamates can be included in the first

two groups. The first work dealing with the preparation of complex compounds of nickel with dtc ligands with the central metal in an oxidation state higher than II was published by Brinkhoff and coworkers¹⁰. Since then, a large number of works have appeared dealing with the preparation and characterization of the dtc complexes of nickel in oxidation states of III and IV (ref.^{1,2,9-11,24-26}). The properties of the dithiocarbamates of Ni(IV) have been studied in detail. The literature contains only a few works dealing with the complexes of Ni(III). These complexes have d^7 electron configuration of the central atom and are paramagnetic; thus they can also be studied using EPR spectroscopy. Of the dithiocarbamate complexes of Ni(III), so far some properties of complexes formed during the oxidation of the dithiocarbamate complexes of nickel(II) with halogens^{5,6,27,28} and thiuramdisulphide²⁹ have been described.

Thiuramdisulphide has quite strong oxidation properties and can oxidize the dithiocarbamate complexes of Cu(I) and Ag(I) to the complexes of Cu(II) and Ag(II) (ref.^{19,20,30-34}). It is known from the literature that thiuramdisulphide can oxidize the dithiocarbamate complexes of Ni(II) to Ni(III) (ref.²⁹) or the Ni(IV) complex²⁴. This work deals with clarification of the oxidation of the dithiocarbamate complex of Ni(II) to the complex of Ni(III).

EXPERIMENTAL

Chemicals and solvents of *p.a.* purity were used in the experiments. The solvents were purified by distillation and then dried³⁵.

The complex compounds $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $[\text{Cu}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ were prepared according to the procedure given in the work³⁶. The procedure given in ref.¹⁹ for preparing and drying N,N,N',N'-tetraethyl thiuramdisulphide- $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ was followed. The results of elemental analysis are given in Table I.

TABLE I
The results of elemental analysis

Compound	M_r	Calculated/Found			
		% C	% H	% N	% metal
$[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$	355.3	33.81	5.67	7.89	16.53
		33.10	5.57	7.98	16.32
$[\text{Cu}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$	360.1	33.36	5.60	7.78	17.75
		33.10	5.65	7.81	17.30
$((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$	269.5	40.50	6.80	9.54	
		41.01	6.99	9.63	—

Spectrophotometric measurements were carried out using Specord UV VIS and Spekol spectrophotometers (Carl Zeiss, GDR) with thermostated cuvette holders. The temperature of the measured solutions was maintained with a precision of $\pm 0.1^\circ\text{C}$. EPR spectra were measured using an EPR E-3 spectrometer (Varian) with a frequency of 9.45 GHz.

The simplex method was used to calculate unknown parameters. The algorithm of the method used was similar to that used by Morgan and Deming³⁷ except that the simplex was extended in the direction of the optimum in the geometric order. Calculations were carried out using a CompuCorp 610 table-top computer with a 36 kbyte operational memory.

The calculation was carried out using the relative, *i.e.* the dimensionless values of the individual quantities. These values were given with respect to a unit of the given quantity.

RESULTS AND DISCUSSION

On mixing solutions of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ (given as NiL_2 and tds in the equations), the original green solution of the nickel(II) complex gradually changed to brown (reflected by a change in the spectrum) (Fig. 1). A signal appeared simultaneously in the EPR spectrum, that gradually increased in intensity and then remained constant (curve 1, Fig. 2). The equilibration time varied with the concentrations of the individual reactants from 10 to 30 minutes in toluene.

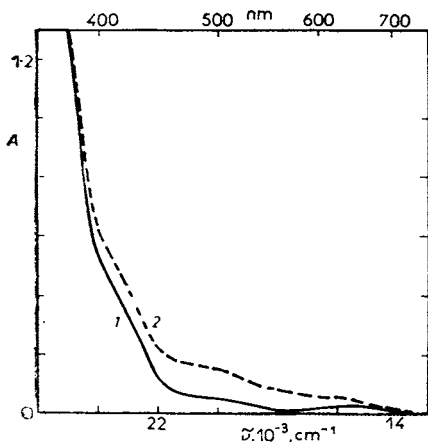


FIG. 1

The absorption spectrum of a solution of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$. 1 ($c = 5 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$) and 2 the equilibrium system $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ ($c = 5 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$) - $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ ($c = 5 \cdot 10^{-2} \text{ mol dm}^{-3}$). Solvent toluene, solution temperature 20°C , cuvette thickness 5 cm

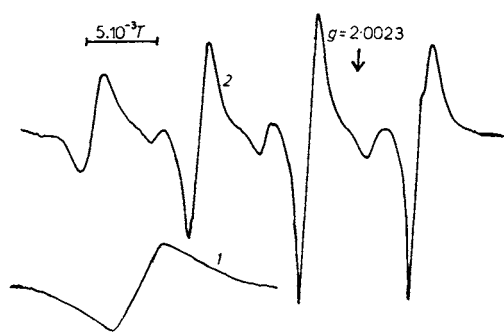


FIG. 2

The EPR spectrum of a toluene solution of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ ($c = 2.5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ ($c = 5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) 1 and of $[\text{Cu}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ ($c = 7 \cdot 10^{-5} \text{ mol dm}^{-3}$) 2

Changes can be observed in the absorption spectra only at relatively high concentrations of at least one of the reactants. As both $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ absorb strongly in the ultraviolet region, no important changes in the spectrum could be recorded at low concentrations of the reactants. Thus only changes in the visible region at 400 to 700 nm were observed.

The absorption spectra of solutions with various combinations of concentrations of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ differ qualitatively only slightly in this region. No isobestic point was observed in the spectra (Fig. 1), indicating that the reaction product has a higher molar absorption coefficient over the whole measured range than the original complex.

The EPR spectrum of the solution containing $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ consists of a simple singlet (curve 1, Fig. 2), indicating that the product is a paramagnetic substance. The g factor has a value of 2.096, in good agreement with the data in ref.²⁹. The half-width of the signal is comparable with the half-width of the EPR signal of the paramagnetic complex $[\text{Cu}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ (curve 2, Fig. 2). It follows from comparison of the intensities of the EPR signal of the reaction products of the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ complex with thiuramdisulphide and the signal of the $[\text{Cu}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ complex that the concentration of the products formed after establishment of equilibrium is an order smaller than the concentrations of the reactants.

The reaction between the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ complex and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ with formation of product R can be written as:



where p , q , and r are the stoichiometric coefficients. The equilibrium constant of reaction (A) can be expressed by the equation:

$$K = \frac{[\text{R}]^r}{[\text{NiL}_2]^p [\text{tds}]^q}, \quad (1)$$

where the square brackets indicate equilibrium concentrations.

It holds for the overall absorbance (thiuramdisulphide practically does not absorb in the studied region):

$$A = \varepsilon_{\text{NiL}_2} \cdot [\text{NiL}_2] \cdot d + \varepsilon_{\text{R}} \cdot [\text{R}] \cdot d, \quad (2)$$

where $\varepsilon_{\text{NiL}_2}$ and ε_{R} are the molar absorption coefficients of the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ complex and the reaction product, respectively, and d is the cuvette width in cm.

It follows from the EPR measurements that the concentration of reaction product R is much smaller than that of all the reactants ($[\text{R}] \ll c_{\text{NiL}_2}, c_{\text{tds}}$). Combination

of Eq. (2) and a modified form of Eq. (1) yields

$$\log(A - A_0) = \frac{1}{r} \cdot \log(K \cdot (\epsilon_R \cdot d)) + \frac{p}{r} \cdot \log c_{\text{NiL}_2} + \frac{q}{r} \cdot \log c_{\text{tds}}, \quad (3)$$

where $A_0 = \epsilon_{\text{NiL}_2} \cdot c_{\text{NiL}_2} \cdot d$.

Substitution of $Y = \log(A - A_0)$, $X_1 = \log c_{\text{NiL}_2}$ and $X_2 = \log c_{\text{tds}}$ yields the equation of a plane. Measurement of the dependence of the absorbance on the concentration of thiuramdisulphide at constant concentration of the complex of Ni(II) from the slope of the dependence $Y = \alpha + \beta X_2$ permits calculation of the ratio of stoichiometric coefficients q and r . Similarly, the ratio of stoichiometric coefficients p and r can be found by measurement of the slope of the dependence, $Y = \alpha' + \beta' \cdot X_1$ ($c_{\text{tds}} = \text{const.}$).

Fig. 3 depicts the experimentally determined dependences of Eq. (3) for three wavelengths. These dependences are, in fact, linear in a broad range of concentrations of the reactants. The slopes of these straight lines are 0.500 ± 0.005 (for a change in the concentration of thiuramdisulphide) and 1.00 ± 0.01 (for a change in the

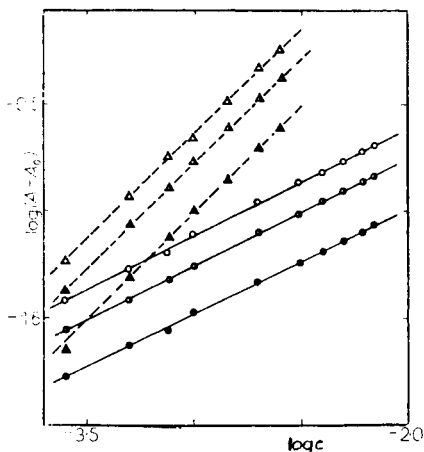


FIG. 3

The dependence of $\log(A - A_0)$ on the overall concentration of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ (Δ) and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ (\circ). Cuvette thickness 2 cm. (\bullet) 420 nm, (\blacktriangle) 440 nm, ($\circ\Delta$) 476 nm.

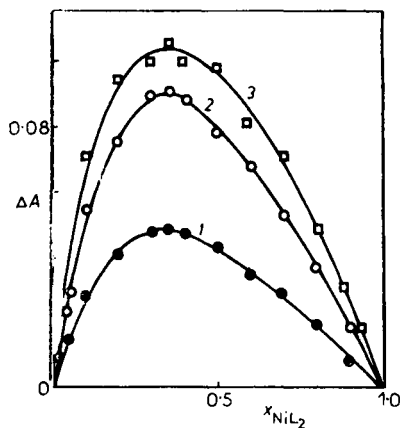


FIG. 4

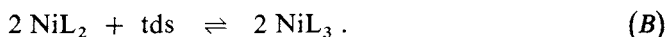
Job curves for the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2] - ((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ system in toluene. Overall reactant concentration $2.5 \cdot 10^{-3} \text{ mol dm}^{-3}$, cuvette thickness 1 cm, temperature 20°C , $\lambda = 475 \text{ nm}$ 2, 570 nm 1; the EPR signal in arbitrary units 3

concentration of the Ni(II) complex at constant concentration of the other component). It then holds for the stoichiometric coefficients in Eq. (A) that

$$p = r; \quad r = 2q.$$

The ratio of the stoichiometric coefficients of the reactants was confirmed by the method of continuous variations (the Job method) on the basis of spectrophotometric and EPR measurements of the equilibrium solutions of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ (Fig. 4).

It thus follows that the product of reaction (A) is not a paramagnetic adduct of the type $[\text{NiL}_2 \cdot \text{tds}]$, but rather the complex $[\text{Ni}^{\text{III}}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_3]$ (further NiL_3), in agreement with the authors of ref.²⁹. Thus reaction (A) can be written in the form



The equilibrium constant of this reaction can be expressed in terms of the overall absorbance using the mass balance equations:

$$c_{\text{NiL}_2} = [\text{NiL}_2] + [\text{NiL}_3] \quad (4)$$

$$c_{\text{tds}} = [\text{tds}] + \frac{1}{2}[\text{NiL}_3] \quad (5)$$

and

$$K = \frac{(A - A_0)^2}{(\varepsilon_{\text{NiL}_3} \cdot c_{\text{NiL}_2} \cdot d - A)^2 \cdot c'_{\text{tds}}}, \quad (6)$$

where $c'_{\text{tds}} = c_{\text{tds}} - (A - A_0)/(2d(\varepsilon_{\text{NiL}_3} - \varepsilon_{\text{NiL}_2}))$.

Thus the absorbance can be expressed as a function of the calculated concentrations of the Ni(II) complex and of thioamdisulphide as

$$A = \frac{A_0 + \sqrt{(K) \cdot \varepsilon_{\text{NiL}_3} \cdot c_{\text{NiL}_2} \cdot d \cdot \sqrt{(c'_{\text{tds}})}}}{1 + \sqrt{(K) \cdot c'_{\text{tds}}}}. \quad (7)$$

It follows from the experimental measurements that the dependence $A = f(\sqrt{c_{\text{tds}}}; c_{\text{NiL}_2} = \text{const.})$ is practically linear with a correlation coefficient of $r \approx 0.999$, i.e. that $c_{\text{tds}} \approx c'_{\text{tds}}$. Thus the decrease in the concentration of thioamdisulphide is negligible and it holds for the denominator of Eq. (7) that $\sqrt{(K) \cdot c'_{\text{tds}}} \ll 1$.

Fig. 5 depicts the calculated dependence of the absorbance on the concentration of thioamdisulphide for various values of equilibrium constant K . The calculations (Eq. (7)) were based on the assumption that $c'_{\text{tds}} = c_{\text{tds}}$; expression $\{\sqrt{(K) \cdot \varepsilon_{\text{NiL}_3} \cdot$

$\cdot c_{\text{NiL}_2} \cdot d$ has the value of the intercept of dependence (3) for constant initial concentration of complex $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$. It follows from the figure that the equilibrium constant of reaction (B) at 20°C is smaller than 0.01. It could not, however, be found more precisely from these calculations.

The simplex method of linear regression was used to find the values of unknown parameters K and $\varepsilon_{\text{NiL}_3}$. In the optimization, the following function was minimized:

$$U = \sum_{i=1}^s \sum_{j=1}^w [A_{ij} - f(c_{\text{NiL}_2,i}; c_{\text{tds},i}; A_{ij}; \varepsilon_{\text{NiL}_3,j}; K)]^2, \quad (8)$$

where s is the number of solutions measured, w is the number of wavelengths, A_{ij} is the absorbance of the i -th solution at the j -th wavelength, f is a function corresponding to the right-hand side of Eq. (7).

The residual standard deviation s_r of the minimum obtained was compared to the standard deviation of the measurement, with a value of $s_x = 1.7 \cdot 10^{-3}$. The absorbance values at wavelengths where the greatest changes in the spectra were observed were selected. The number of wavelengths varied from 2 to 10. The minimum value of the objective function was attained very slowly and it was found that the residual standard deviation and thus also the precision of the fitting of the calculated curve through the experimental points changed very little over a wide range of K and $\varepsilon_{\text{NiL}_3}$ values. The product $\sqrt{(K)} \cdot \varepsilon_{\text{NiL}_3}$ remains practically constant, so that the studied parameters are strongly interdependent.

Measurements in toluene at 20°C yielded a minimum value for the objective function at an equilibrium constant value of $K = (4.4 \pm 0.4) \cdot 10^{-3}$. The precision of the fitting of the calculated curve of the A vs c_{tds} dependence is very good (Fig. 6), which is also reflected in the value of the residual standard deviation, $s_r = 1.8 \cdot 10^{-3}$.

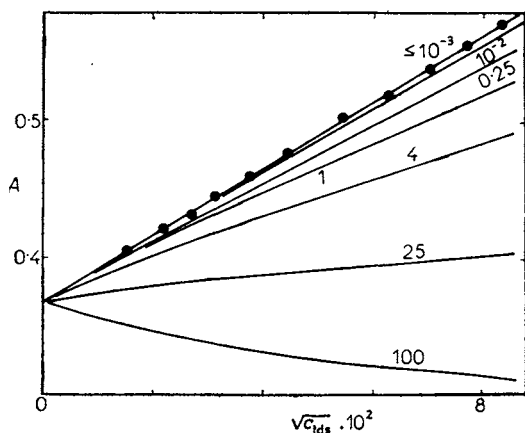


FIG. 5

The calculated dependence of the absorbance on the concentration of triuramdisulphide for various assumed values of the equilibrium constant of reaction (B); (●) experimental points $c_{\text{NiL}_2} = 7.5 \cdot 10^{-4} \text{ mol dm}^{-3}$. $\lambda = 476 \text{ nm}$, $t = 20^\circ\text{C}$, cuvette thickness 2 cm

The results of the EPR measurements were also used to independently confirm the value of equilibrium constant K . Comparison of the EPR spectra of equilibrium solutions of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ and $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ with the spectra of $[\text{Cu}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ recorded under identical conditions was used to calculate the equilibrium concentration of the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_3]$ complex from the signal intensities. The value $K = (4.9 \pm 0.2) \cdot 10^{-3}$ was then obtained from Eq. (1). A similar value was found from kinetic measurements (see below).

The calculated absorption spectrum of the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_3]$ complex in the wavelength region from 400 to 650 nm is depicted in Fig. 7. Very intense absorption apparently results from the charge transfer band from the ligand to Ni(III). The precision of determination of the molar absorption coefficient below 400 nm was very low; however, an intense absorption band can also be expected in this region, similarly as for the $[\text{Ni}^{\text{III}}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]\text{I}_3$ complex⁵.

The dependence of the equilibrium constant on temperature was also studied (Fig. 8). In the given temperature range, only a slight change in the molar absorption coefficient value for the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_3]$ complex can be expected and thus the slope of the $\log(K \cdot \varepsilon_{\text{NiL}_3}^2) = f(T^{-1})$ dependence will be practically identical with that of the $\log K = f(T^{-1})$ dependence. The value of the heat of reaction for reaction (B), $\Delta H^0 = -(1.9 \pm 0.2) \cdot 10^4 \text{ J mol}^{-1}$, was found from the slope of the dependence in Fig. 8.

In addition to toluene, reaction (B) was also studied in chloroform, acetone, and methanol. In all these solvents, similar changes in the absorption spectra were observed as in toluene, but were smaller. Table II lists the values of the equilibrium constants, K , obtained in various solvents. It follows from this survey that the equilibrium constant value decreases with increasing polarity of the solvent. Thus the formation of the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_3]$ complex is favoured in nonpolar medium.

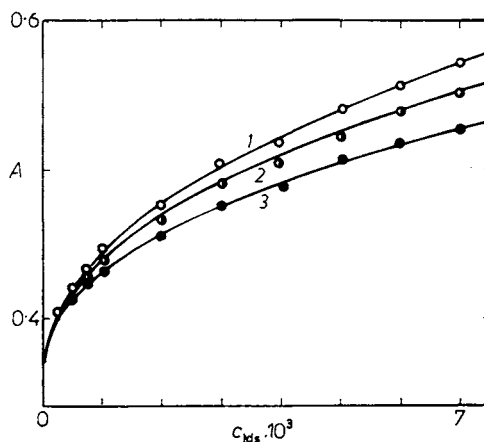


FIG. 6

The dependence of the absorbance on the concentration of $((\text{C}_2\text{H}_5)_2\text{NCS}_2)$. $c_{\text{NiL}_2} = 7.5 \cdot 10^{-4} \text{ mol dm}^{-3}$, $\lambda = 476 \text{ nm}$, cuvette thickness 2 cm, 1 20°C, 2 30°C, 3 40°C; calculated dependence (—)

The molecules of the polar solvent are coordinated more strongly around the molecule of the Ni(II) complex and probably hinder approach of the thiuramdisulphide molecule to the central atom. The negative effect of a more polar solvent may also be connected with the easier decomposition of the Ni(III) complex, similarly as for complexes of the $[\text{Ni(IV)L}_3]^+$ type^{5,8}. The exothermic nature of the reaction could explain the disappearance in the EPR spectrum of the signal of a solution of Ni(II) dithiocarbamate and thiuramdisulphide on heating²⁵, where the equilibrium in reaction (B) is shifted almost completely to the left.

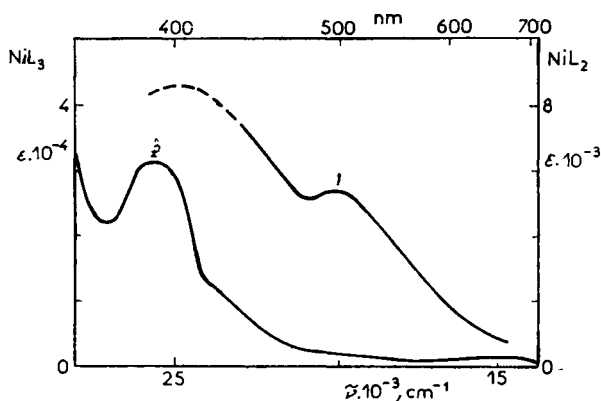


FIG. 7

The calculated absorption spectrum of the $[\text{Ni}^{\text{III}}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_3]$ complex- NiL_3 1 and the experimentally obtained spectrum of the $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ complex- NiL_2 2 in toluene

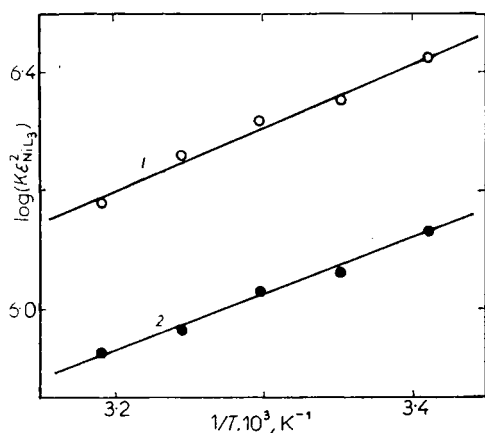
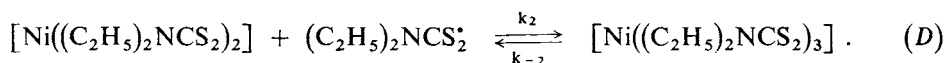
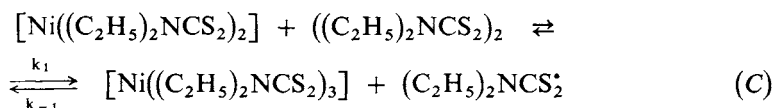


FIG. 8
The dependence of $\log(K\epsilon_{\text{NiL}_3}^2)$ on temperature; 1 476 nm, 2 556 nm

The kinetics of the reaction of the Ni(II) complex with thiuramdisulphide was studied in the temperature range 16 to 50°C. As a measurable concentration of free radicals $(C_2H_5)_2NCS_2^*$, which could be formed by homolytic splitting of thiuramdisulphide, was not found by EPR spectroscopy even in very concentrated thiuramdisulphide solutions⁶, the first step in the reaction mechanism probably involves reaction of the $[Ni((C_2H_5)_2NCS_2)_2]$ molecule with a thiuramdisulphide molecule. A $(C_2H_5)_2NCS_2^*$ radical is formed during the formation of the Ni(III) complex. This radical then reacts with a further molecule of the Ni(II) complex. Because of the low value of the equilibrium constant of reaction (B), both reaction steps are reversible:



Assuming very low, stable concentration of the radicals formed, $(C_2H_5)_2NCS_2^*$, the following relationship can be derived for the change in the concentration of the $[Ni((C_2H_5)_2NCS_2)_3]$, (*i.e.*) $[NiL_3]$ complex:

$$d[NiL_3]/dt = \frac{2k_1k_2[NiL_2]^2[tds] - 2k_{-1}k_{-2}[NiL_3]^2}{k_2[NiL_2] + k_{-1}[NiL_3]}, \quad (9)$$

where the square brackets refer to instantaneous concentrations.

As follows from the above measurements, only a small portion of the Ni(II) complex is oxidized to the Ni(III) complex. Thus the decrease in the concentrations of $[Ni((C_2H_5)_2NCS_2)_2]$ and $((C_2H_5)_2NCS_2)_2$ during the reaction will be negligible ($[NiL_2] \doteq c_{NiL_2}$; $[tds] \approx c_{tds}$). When the concentration of the reaction product

TABLE II

The values of the equilibrium constant of reaction (B) in various solvents at 20°C and the residual standard deviations of objective function (δ)

Solvent	$K \cdot 10^3$	$s_r \cdot 10^3$
Toluene	4.4 ± 0.4	1.8
Chloroform	1.3 ± 0.2	2.1
Acetone	0.8 ± 0.1	2.2
Methanol	0.8 ± 0.1	2.0

is expressed in terms of the absorbance, equation (9) can be modified to give:

$$dA/dt = (1 - a \Delta A^2)/(b + c \Delta A), \quad (10)$$

where $\Delta A = A - \varepsilon_{\text{NiL}_2} \cdot c_{\text{NiL}_2} \cdot d$.

$$a = k_{-1} \cdot k_{-2} / (k_1 \cdot k_2 \cdot \varepsilon_{\text{NiL}_3}^2 \cdot d \cdot c_{\text{NiL}_2}^2 \cdot c_{\text{tds}})$$

$$b = (2 \cdot \varepsilon_{\text{NiL}_3} \cdot d \cdot k_1 \cdot c_{\text{NiL}_2} \cdot c_{\text{tds}})^{-1}$$

$$c = a(2k_{-2})^{-1}.$$

Solution of differential equation (10) yields the relationship:

$$(2a)^{-1} \cdot \ln \frac{(1 + \sqrt{(a) \Delta A})^{\sqrt{(a)b-c}}}{(1 - \sqrt{(a) \Delta A})^{\sqrt{(a)b+c}}} = t \quad (11)$$

which expresses the dependence of the change in absorbance on time.

Of coefficients a , b and c , only coefficient a is known; its value can be calculated from the value of the absorbance for equilibrium solutions, for which it holds that $dA/dt = 0$. It then follows from Eq. (10) that $a = \Delta A^{-2}$ at $t \rightarrow \infty$. Coefficients b and c were found by the nonlinear regression method.

The dependence $A = f(t)$ was calculated using these parameters and is depicted in Fig. 9. The precision of the fitting of the calculated curve to the experimental points is satisfactory (the correlation coefficient for optimized function (11) has a value of $r \sim 0.999$).

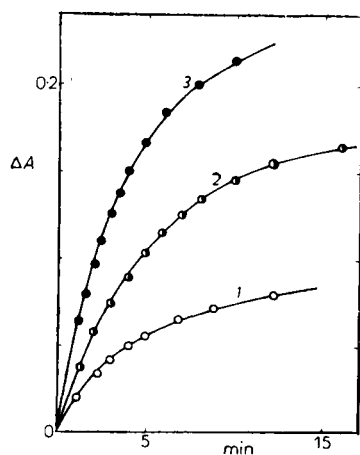


FIG. 9

The dependence of the change in absorbance on time during the oxidation of $[\text{Ni}((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2]$ by $((\text{C}_2\text{H}_5)_2\text{NCS}_2)_2$ in toluene. 1 $c_{\text{NiL}_2} = 2.5 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{tds}} = 10^{-2} \text{ mol dm}^{-3}$; 2 $c_{\text{NiL}_2} = 5 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{tds}} = 2 \cdot 10^{-2} \text{ mol dm}^{-3}$; 3 $c_{\text{NiL}_2} = 5 \cdot 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{tds}} = 10^{-2} \text{ mol dm}^{-3}$; $t = 20^\circ\text{C}$, $\lambda = 475 \text{ nm}$, cuvette thickness 2 cm, (—) calculated dependence

The dependence of coefficient b on the reciprocal of the value of the product of the initial concentrations of the Ni(II) complex and thiuramdisulphide is linear, as expected, with practically zero intercept value and with a slope of $\text{tg } \alpha = 1.8 \cdot 10^{-4}$ (at 20°C). The slope of this dependence can be used to calculate the value of rate constant k_1 ($(5.6 \pm 0.3) \cdot 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ at 20°C).

Rate constant k_{-2} was calculated using coefficients a and c ($k_{-2} = (0.23 \pm 0.05) \text{ min}^{-1}$ at 20°C). The rate constants k_2 and k_{-1} cannot be calculated, but their ratio can be found:

$$k_{-1}/k_2 = (k_1 \cdot a \cdot \varepsilon_{\text{NiL}_3}^2 \cdot d^2 \cdot c_{\text{NiL}_2}^2 \cdot c_{\text{tds}}) / k_{-2} \quad (12)$$

At 20°C, $k_{-1}/k_2 = 58 \pm 6$.

These values can then be used to find the equilibrium constant of reaction (B) using the following relationship:

$$K = k_1 \cdot k_2 (k_{-1} \cdot k_{-2})^{-1} \quad (13)$$

The value obtained in this way ($K = (4.2 \pm 0.6) \cdot 10^{-3}$ at 20°C) is, within experimental error, equal to the value obtained in the preceding section on the basis of study of equilibrium systems.

The temperature dependence of the equilibrium constant k_1 was used to determine the activation energy of the first reaction step ($E_A = (3 \pm 1) \cdot 10^4 \text{ J mol}^{-1}$). Because of the large scatter of parameter c , the temperature dependences of the other rate constants could not be found.

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