

# Preparation, spectral and electrochemical characterization of dithiocarbamate nitrosyl chromium complexes

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Complexes of  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  and  $\text{Cr}[(\text{CH}_2)_4\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  were prepared. Nitrosyl coordination was verified by chemical analysis and by electronic absorption, infrared, and e.p.r. spectra. Voltammetric and coulometric characteristics were determined on platinum and dropping mercury electrodes in dimethylformamide and acetonitrile. Electrode reduction and oxidation of complexes are associated with changes in the coordination sphere. Results were compared with conclusions drawn from studies of analogous chromium(III) tris(dithiocarbamate) complexes.

Получены комплексы  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  и  $\text{Cr}[(\text{CH}_2)_4\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$ . Координация нитрозила подтверждена химическим анализом, электронным, инфракрасным и ЭПР спектрами. Изучены вольтамперометрические и кулонометрические характеристики комплексов на платиновом и ртутном электродах в диметилформамиде и ацетонитриле. Электродное восстановление и окисление комплексов связано с изменениями в координационной сфере. Результаты сравнены с заключениями полученными для аналогичных трис(дитиокарбаминатов) хрома(III).

Of all the dithiocarbamate complexes with a heterogeneous coordination sphere, nitrosyl complexes with one or two nitrosyl groups are among those that have been most intensively studied. This is evidently because of the practical importance and theoretical interest of both ligands. Investigation into mononitrosyl dithiocarbamate chromium complexes has so far been exclusively aimed at examining the e.p.r. spectra [1—6]. Information on the preparation and stability of these species has been fragmentary and all too inconsistent. Data on electronic and vibration spectra and their redox properties that might contribute to characterization of oxidation states and the reactivity of the mentioned group of species are entirely missing. In the present paper, two complexes have been studied from the above aspects and our attention has been concentrated on detailed examination of spectral properties and processes of electrode reduction and oxidation in the complex with a diethyldithiocarbamate ligand.

## Experimental

Cupral,  $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ , was of anal. grade (Lachema, Brno); sodium tetramethylenedithiocarbamate was prepared as described elsewhere [7].

For the preparation of the complex we used  $Cr(H_2O)_5NO^{2+}$  ( $c = 0.01 \text{ mol dm}^{-3}$ ), obtained through the reaction of  $K_2CrO_4$  with  $NH_2OH$ , according to the procedure described in Ref. [8]. The value of pH was adjusted to 5 using NaOH and the aqueous solution ( $0.05 \text{ mol dm}^{-3}$ ) of a sodium salt of the corresponding dithiocarbamate was added (in 10-fold molar excess with respect to  $Cr(H_2O)_5NO^{2+}$ ). The resulting solution gradually got turbid at room temperature and after standing a precipitate was formed, which was then filtered and washed several times with distilled water.

Electronic absorption spectrum was obtained on a Specord UV VIS spectrophotometer (Zeiss, Jena).

Infrared spectrum was recorded in a chloroform solution, contained in an infrared KBr cell, 0.06 cm thick, on a UR-20 apparatus (Zeiss, Jena).

E.p.r. spectrum was registered on a Varian E 3 spectrometer of a 9.08 GHz working frequency.

Voltammetric measurements were made with a three-electrode polarograph, Model OH-102 (Radelkis, Budapest). The working electrodes used were a platinum disc microelectrode, a hanging mercury-drop electrode (HMDE), and a dropping mercury electrode (DME). The reference electrode consisted of a calomel electrode in an aqueous LiCl solution of  $4 \text{ mol dm}^{-3}$  (4 M-CE). All the potentials mentioned in this paper relate to this reference electrode. Unless otherwise stated in the text, scan rate used in stationary electrode voltammetry was  $v = 0.1 \text{ V s}^{-1}$  and in polarography  $v = 4.1 \times 10^{-3} \text{ V s}^{-1}$ . Coulometric measurements were made with a universal OH-404 coulometric analyzer (Radelkis, Budapest). Characteristics of all the electrodes as well as their arrangement were the same as those given in paper [9].

Acetonitrile (Avondale Laboratories, England) and dimethylformamide (Reachim, USSR) were purified as described in [10, 11]. Base electrolyte consisted of tetrabutylamine tetrafluoroborate of  $0.1 \text{ mol dm}^{-3}$  (Southwestern Analytical Chemicals, Austin, Texas). Incandescent lamp nitrogen, dried with anhydrous  $CaCl_2$  and saturated with the vapours of the used solvent, was used as inert gas.

## Results and discussion

Preparation procedure, described in Experimental, has materialized and simplified concise references to the synthesis mentioned in literature. In order to ensure the formation of the bis(dithiocarbamate) complex we have worked with an excess of the dithiocarbamate anion in the reaction mixture. Unlike in literature mentioned above, our preparations were carried out solely in an aqueous medium, at room temperature, and with air access (parallel to those in  $CO_2$  inert atmosphere).

For  $Cr[(C_2H_5)_2NCS_2]_2(H_2O)NO$  calculated: 30.29 % C, 5.59 % H, 10.59 % N,

32.34% S, 13.12% Cr; found: 30.52% C, 5.36% H, 10.04% N, 32.60% S, 13.35% Cr.

For  $\text{Cr}[(\text{CH}_2)_4\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  calculated: 30.60% C, 4.62% H, 10.70% N, 32.67% S, 13.24% Cr; found: 30.51% C, 4.40% H, 10.03% N, 32.01% S, 13.00% Cr.

The chemical analysis and properties of the reference sample prepared in  $\text{CO}_2$  atmosphere were practically identical. The obtained products are powdery, brown in colour, stable when exposed to air even for weeks, water-insoluble but soluble in organic solvents such as chloroform, acetone, acetonitrile, dimethylformamide, and just a little in ethanol.

Chemical analysis confirms the view that the products contain two dithiocarbamate ligands and one NO and  $\text{H}_2\text{O}$  ligand each per complex particle. In nonaqueous solvents, depending on electron-donor ability, the coordination  $\text{H}_2\text{O}$  molecule may be substituted by a solvent molecule, but no detailed investigation has been done in this direction.

### *Spectral properties*

Coordination of nitrosyl has also been confirmed by electronic absorption, infrared and e.p.r. spectra, all pertaining to the  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  complex. Electronic spectrum, identical both in chloroform and dimethylformamide solutions, respectively, shows bands characterized by the maxima positions at  $\lambda_{\text{max}} = 625 \text{ nm}$  ( $\epsilon = 150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 470 (380), and 260 ( $3.7 \times 10^4$ ). The 470 nm absorption band occurs in all nitrosyl complexes (with a  $\text{CrNO}^{2+}$  unit) and is characteristic of  $\text{CrNO}^{2+}$  chromophore [12–14].

The infrared spectrum in a chloroform solution runs as follows (data given in  $\text{cm}^{-1}$ ): 863 w, 921 w, 1008 m, 1154 s, 1284 s, 1309 m, 1362 m, 1387 m, 1448 m, 1467 s, 1509 vs, 1610 m, 1699 vs, 1817 s, 3688 m. In the region between 836 and  $1509 \text{ cm}^{-1}$ , the shape of the spectrum is identical with that of the  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_3$  complex infrared spectrum obtained under the same conditions. Important is the position of  $\nu(\text{C}=\text{S})$  bond vibrations at  $1008 \text{ cm}^{-1}$  and that of  $\nu(\text{C}-\text{N})$  at  $1284 \text{ cm}^{-1}$  and the so-called  $\nu(\text{C}-\text{N})$  thioureide peak at  $1509 \text{ cm}^{-1}$  in the case of the nitrosyl complex or at  $1508 \text{ cm}^{-1}$  in that of the chromium(III) tris(dithiocarbamate) complex [15, 16]. The  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  spectrum in addition includes further four peaks, namely those at 1610, 1699, 1817, and  $3688 \text{ cm}^{-1}$ .

A very strong peak at  $1699 \text{ cm}^{-1}$  is assigned to stretching vibration  $\nu(\text{N}-\text{O})$ . In nitrosyl complexes this vibration reflects the NO ligand electron density — of  $\text{Na}_2[\text{Cr}(\text{EDTA})\text{NO}]$  at  $1632 \text{ cm}^{-1}$  [14], of  $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$  at  $1645 \text{ cm}^{-1}$  [12], of  $\text{Na}_3[\text{Cr}(\text{CN})_5\text{NO}]$  at  $1660 \text{ cm}^{-1}$  [17], of  $[\text{Cr}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$  at  $1670 \text{ cm}^{-1}$  [12], of  $[\text{CrCl}(\text{das})_2\text{NO}]\text{ClO}_4$  at  $1690 \text{ cm}^{-1}$  [18], of  $[\text{Cr}(\text{C}_2\text{H}_5\text{OH})_5\text{NO}]\text{Cl}_2$  at  $1718 \text{ cm}^{-1}$ , of

[Cr(CH<sub>3</sub>OH)<sub>5</sub>NO]Cl<sub>2</sub> at 1719 cm<sup>-1</sup> [12], of Cr(CN)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>NO at 1720 cm<sup>-1</sup> [13], and of [Cr(H<sub>2</sub>O)<sub>5</sub>NO]Cl<sub>2</sub> at 1747 cm<sup>-1</sup> [12].

Position  $\nu(\text{N—O})$  1699 cm<sup>-1</sup> of the complex under study at the same time indicates that the nitrosyl ligand oxidation state (and therefore that of Cr as well) is, within the scope of the CrNO<sup>2+</sup> structural unit, the same as in all the cases stated for comparison purposes. On the other hand, in the K<sub>4</sub>[Cr(CN)<sub>5</sub>NO] complex containing CrNO<sup>1+</sup>, *i.e.* the reduced form of CrNO<sup>2+</sup>,  $\nu(\text{N—O})$  is at 1515 cm<sup>-1</sup> [12], therefore, the shift towards lower wavenumbers is markedly pronounced. Differences in  $\nu(\text{N—O})$  values in the series of above-mentioned complexes in the order from EDTA- to pentaquo-nitrosyl complex groups are due to the change in the strength of the coordination sphere ligand field.

Peaks at 1610 and 3688 cm<sup>-1</sup> pertain to coordinated H<sub>2</sub>O. They belong to the deformation  $\delta(\text{HOH})$  and the stretching  $\nu(\text{O—H})$  vibration, respectively; in the case of the Cr(CN)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>NO complex,  $\delta(\text{HOH})$  was observed at 1626 cm<sup>-1</sup> [13].

An e.p.r. spectrum of a Cr[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub>(H<sub>2</sub>O)NO solid sample was recorded both in a chloroform and a toluene solution. Value  $g_{\text{aver}} = 2.002$ , which may be expected in nitrosyl complexes [19], has been found from an isotropic signal.

### *Electrochemical behaviour*

Voltammetric characteristics of both synthesized complexes, obtained in dimethylformamide, are given in Table 1. Dependence of oxidation peak current at Pt electrode and of the first reduction peak at Pt and HMDE electrodes on the square root of polarization rate (in the range  $\nu = 0.0125\text{—}0.1$  V s<sup>-1</sup>) was linear. Since the dependence of polarographic limiting current on the square root of mercury head height (in the range of  $h = 25\text{—}100$  cm) was also linear, the process can be regarded as a diffusion-controlled. At the same time it has been verified that cathodic currents, registered by the three used indicating electrodes, as well as the anodic current at the platinum stationary electrode, linearly depend on the concentration of the complexes under study and are, therefore, analytically utilizable in the concentration range of 10<sup>-4</sup> to 10<sup>-2</sup> mol dm<sup>-3</sup>. The lower limit is characterized by a relatively high value of residual current.

### *Electrochemical reduction*

The reduction of nitrosyl complexes is a two-step process (Fig. 1) just as that of analogous chromium(III) tris(dithiocarbamate) complexes [9]. Both reduction steps in the case of nitrosyl complexes, however, take place at more negative potentials and their potential separation, compared with that of tris(dithiocarba-

*Table 1*  
 Voltammetric characteristics of dithiocarbamate nitrosyl chromium complexes  
 0.1 mol dm<sup>-3</sup> (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub> in dimethylformamide, all potentials expressed in V vs. 4 M-CE

Complex	Reduction Step 1			Reduction Step 2			Oxidation
	DME <i>E</i> <sub>1/2</sub>	HMDE <i>E</i> <sub>p</sub>	Pt <i>E</i> <sub>p</sub>	DME <i>E</i> <sub>1/2</sub>	HMDE <i>E</i> <sub>p</sub>	Pt <i>E</i> <sub>p</sub>	Pt <i>E</i> <sub>p</sub>
Cr[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> (H <sub>2</sub> O)NO	-1.70	-1.82	-1.85	-2.65	-2.70	-2.80	1.10
Cr[(CH <sub>2</sub> ) <sub>4</sub> NCS <sub>2</sub> ] <sub>2</sub> (H <sub>2</sub> O)NO	-1.67	-1.78	-1.92	-2.56	-2.70	-2.75	1.00

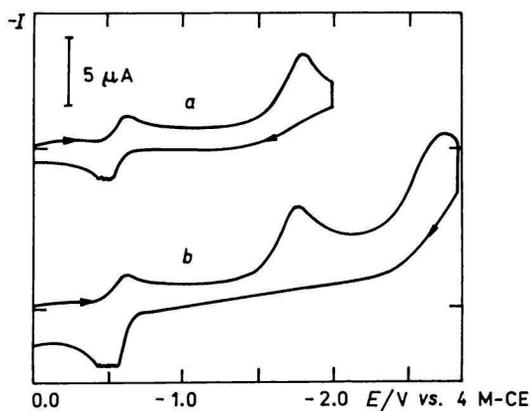


Fig. 1. Cyclic voltammograms of  $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$ , HMDE, scan rate  $0.1 \text{ V s}^{-1}$ ,  $0.1 \text{ mol dm}^{-3} (\text{C}_4\text{H}_9)_4\text{NBF}_4$  in dimethylformamide.

mate), is greater. The change in the complex reduction potential, when the type of the dithiocarbamate ligand has been substituted, is less pronounced when compared with that of chromium(III) tris(dithiocarbamate) complexes, particularly at Step 2 of the reduction.

Fig. 1a, b shows a cyclic voltammogram of  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  reduction, Step 1 and Step 2, recorded by an HMDE in dimethylformamide. Neither step had an anodic counterpeak. In the broader region of the potential at about  $-0.5 \text{ V}$  there is an anodic peak pertaining to Hg electrooxidation in the presence of a free dithiocarbamate anion [20, 21]. The peak current of this anodic peak is dependent on the reduction degree of the complex. Following the reversal of the polarization direction after the second step reduction peak ( $-2.8 \text{ V}$ ) it becomes twice as large in comparison with its recording after the reversal of the polarization direction at  $-2.0 \text{ V}$ .

Likewise, on the platinum electrode, both reduction steps were irreversible, without an anodic counterpeak (in acetonitrile, the first step of the reduction was at  $-1.75 \text{ V}$ , difference  $|E_p - E_{p/2}| = 80 \text{ mV}$ ). On a cyclic voltammogram, after the polarization direction reversal at  $-1.8 \text{ V}$ , anodic peaks, associated with the reduction of the samples at  $-0.8 \text{ V}$  and at  $-1.2 \text{ V}$  (see below), could be seen in the region between  $-0.1$  and  $+0.1 \text{ V}$ ; in this case, however, the maximum current of the anodic peak at  $+0.1 \text{ V}$  in dimethylformamide (or at  $+0.05 \text{ V}$  in acetonitrile) was markedly greater (Fig. 2a) thus confirming the presence of a free dithiocarbamate anion [21, 22].  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  reduction is, therefore, like the reduction of  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_3$  [9], associated with dithiocarbamate ion liberation from the Cr coordination sphere.

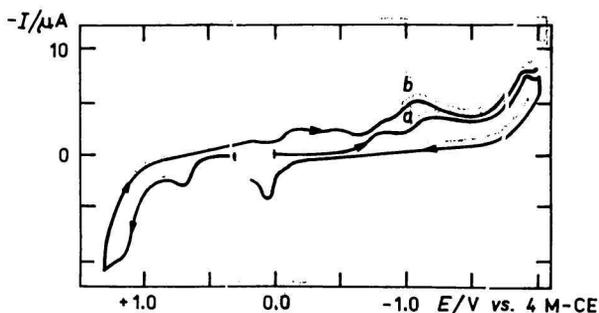


Fig. 2. Cyclic voltammograms of  $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$ , Pt electrode, scan rate  $0.1 \text{ V s}^{-1}$ ,  $0.1 \text{ mol dm}^{-3} (\text{C}_4\text{H}_9)_4\text{NBF}_4$  in dimethylformamide.

The one-electron character of the first reduction step of the  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  complex has been confirmed by coulometric reduction at  $-1.9 \text{ V}$  (solution electrolyzed after preelectrolysis at  $-0.9 \text{ V}$ ). On the voltammogram, recorded by Pt and HMDE electrodes after electrolysis, there was no current in the region of the reduction Step 1 of the complex at  $-1.7 \text{ V}$  (a small cathodic peak, however, remained at  $-0.8 \text{ V}$ ), which proves that the reduction was complete. Following the polarization direction reversal, an anodic oxidation peak of the liberated ligand was registered. The maximum current value of this peak, compared with that of the cupral peak current under given conditions, is responsible for the liberation of one dithiocarbamate ligand per complex particle.

Maximum currents of the second reduction peak of complexes as well as the corresponding polarographic limiting currents were distinctly higher than those of Step 1, without ever reaching twice their value. Coulometric reduction, carried out at a potential which was  $100 \text{ mV}$  more negative than the peak potential of Step 2, was influenced by the base electrolyte current and could not be evaluated quantitatively. Associated with the complex reduction Step 2 is the liberation of another dithiocarbamate ligand as can be deduced from the increase in its anodic peak on the cyclic voltammogram.

In the potential region before reduction Step 1, further low cathodic peaks of both nitrosyl complexes under examination were observed. At the DME and the HMDE it was at  $-0.7 \text{ V}$ , at the platinum electrode at  $-0.80 \text{ V}$  (with a prepeak at  $-0.65 \text{ V}$ ) in dimethylformamide, or at  $-0.85 \text{ V}$  (with a prepeak at  $-0.7 \text{ V}$ ) in acetonitrile. Samples of a few weeks standing further exhibited poorly resolved cathodic peaks at  $-1.1$  and  $-1.25 \text{ V}$ . A cyclic voltammogram of  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$ , recorded at a platinum electrode in dimethylformamide (Fig. 3), after polarization direction reversal at  $-1.0 \text{ V}$ , contained an anodic counterpeak (separation  $|E_{p, \text{cat}} - E_{p, \text{an}}| = 100 \text{ mV}$ , maximum current ratio of peaks

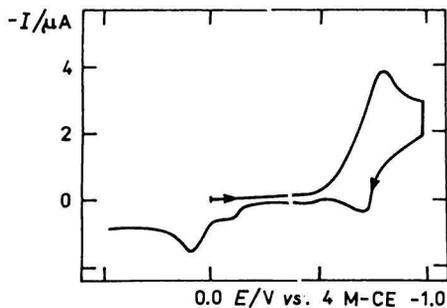


Fig. 3. Cyclic voltammogram of  $4 \times 10^{-3}$  mol  $\text{dm}^{-3}$   $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$ , Pt electrode, scan rate  $0.1 \text{ V s}^{-1}$ ,  $0.1 \text{ mol dm}^{-3}$   $(\text{C}_4\text{H}_9)_4\text{NBF}_4$  in dimethylformamide.

$I_{p, \text{an}}/I_{p, \text{cat}} \approx 0.7$ ) and further two anodic peaks, the lower at  $-0.1 \text{ V}$  and the higher at  $+0.1 \text{ V}$ . In acetonitrile these anodic peaks were observed at somewhat more negative potentials ( $-0.15$  and  $+0.05 \text{ V}$ ). Much the same was the voltammetric picture after the reduction down to  $-1.4 \text{ V}$  and the subsequent reversal of the polarization direction towards positive potential values. Only a small charge (0.4 mole of an electron per 1 mole of complex particle) was transferred in coulometric electrolysis at a  $-0.85 \text{ V}$  constant potential. Cathodic peaks in question are those of decomposition products of the examined species. On the basis of the voltammetric picture it is evident that sulfur or some products of deeper oxidation of the dithiocarbamate anion are present [21, 22]. Slight contamination, which had no effect on the result of elemental analysis, may have occurred during the preparation of the complex. Other changes in the preparations that take place in storage, under common laboratory conditions lasting a few months, are revealed in elemental analysis by percentage drop in C and N content.

### *Electrochemical oxidation*

Oxidation of complexes under study takes place only at potentials that are almost 3 V more positive than their reduction Step 1 potential (Table 1, Fig. 2b) and simultaneously 1 V more positive than the oxidation potential of the free dithiocarbamate anion [21, 22]. The oxidation process takes place in the same potential region as that of analogous chromium(III) tris(dithiocarbamate) complexes [9]. From the obtained characteristics and from the mutual comparison of both series of complexes it follows that even in the case of chelates containing nitrosyl, primary redox changes are localized on the chromium atom.

The oxidation of nitrosyl complexes is associated with the occurrence of several anodic peaks. In acetonitrile the  $\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2(\text{H}_2\text{O})\text{NO}$  oxidation peak at  $+1.10 \text{ V}$  is preceded by a smaller peak at  $+0.75 \text{ V}$ ; in dimethylformamide, before the  $+1.10 \text{ V}$  peak, there are smaller peaks at  $+0.70 \text{ V}$  and at  $+1.00 \text{ V}$ . The

maximum peak current at +0.70 V varied in often repeated experiments but was rather more expressive in concentrated solutions, reaching a value equal to one-fifth of that of the main peak maximum current. In the case of a newly prepared complex, in acetonitrile, it reached, however, an up to 100 % value of the main peak current. Cyclic voltammetry in acetonitrile has shown that a similar reduction pattern corresponds to both anodic peaks at +0.75 and +1.1 V (a small cathodic peak at -0.05 V). If the platinum indicating electrode was polarized up to +1.4 V, it was even possible, after the reversal of the polarization direction, to record cathodic peaks at +0.6 and +0.35 V pertaining to  $(C_2H_5)_2NCS_2^-$  deep oxidation products, the stability of which was higher in acetonitrile than in dimethylformamide [21]. In dimethylformamide the +0.70 V anodic peak had no cathodic counterpeak and in the reduction part of the cyclic voltammogram, peaks at -0.1 and -0.50 V (Fig. 2b) corresponded to the main oxidation peak.

Coulometric electrolysis, carried out at a +0.8 V potential, required a charge corresponding to 0.2—0.4 of a theoretical electron per complex particle and caused a slight increase in the cathodic peak at -1.2 V (Fig. 4a). Follow-up coulometric oxidation, performed at +1.2 V, yielded a value of the number of exchanged electrons averaging 1.1 per complex particle. The anodic peak current at +1.1 V fell low, to 10% of its original value. Reduction peaks on a voltammogram, recorded in acetonitrile at the end of coulometric oxidation, were as follows: at -0.05 V, in wider region from -0.3 to -0.6 V, at -0.8 V (lower than in the original complex), at -1.2 V (higher than originally), and at -1.8 V (almost without change). On a record, obtained in dimethylformamide at the end of electrolysis (Fig. 4b) there was a small reduction peak at -0.1 V, a large peak at -0.55 V, another small peak at -0.8 V, a large peak at -1.2 V and a partly lowered peak at -1.75 V. Peaks in the region between -0.1 and -0.5 V had no anodic counterpeaks and were decreasing with time, while the peak current at -1.2 V (or -1.1 and -1.25 V) grew higher. The addition of NaOH into a dimethylformamide solution resulted in removing cathodic peaks down to -1.0 V.

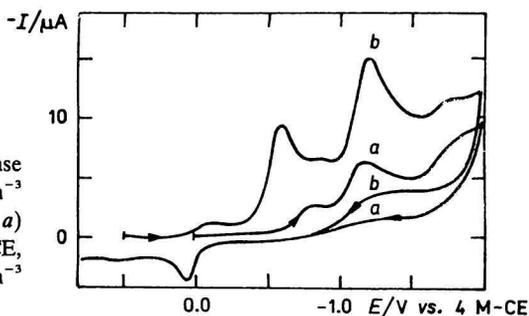


Fig. 4. Cyclic voltammograms of bulk-phase electrooxidation products of  $4 \times 10^{-3} \text{ mol dm}^{-3}$   $Cr[(C_2H_5)_2NCS_2]_2(H_2O)NO$ , electrolysis at: a) +0.8 V vs. 4 M-CE; b) +1.2 V vs. 4 M-CE, Pt electrode, scan rate  $0.1 \text{ V s}^{-1}$ ,  $0.1 \text{ mol dm}^{-3}$   $(C_4H_9)_4NBF_4$  in dimethylformamide.

On the basis of the described behaviour and after comparing the results of the studies on  $(C_2H_5)_2NCS_2^-$  [21] and on  $Cr[(C_2H_5)_2NCS_2]_3$  [9] we propose the following explanation of the electrochemical oxidation process: The +0.70 V anodic peak is the prepeak of the oxidation peak of the complex (+1.1 V). In view of the considerable potential separation it is unlikely that the more negative peak is an adsorption prepeak. The oxidation process at +1.1 V raises the oxidation state of chromium by 1. A dithiocarbamate ligand can only temporarily withstand this state. As in  $Cr[(C_2H_5)_2NCS_2]_3$  so analogously in this case, follow-up chemical reactions, in which the coordination sphere gets oxidized at the expense of the oxidation state of the central atom, take place relatively quickly. The cathodic peak at -0.1 V, disappearing more rapidly in dimethylformamide than in acetonitrile, pertains to one of the steps of this reaction sequence. This was the reason why attempts at an electrochemical preparation of a complex of a higher chromium oxidation state were unsuccessful.

The value of the  $Cr[(C_2H_5)_2NCS_2]_2(H_2O)NO$  oxidation potential is close to that of the thiuram disulfide oxidation potential which represents a product of the first oxidation step of the dithiocarbamate anion. This accord in potentials is the cause of profound changes taking place in the coordination sphere, as it has also been confirmed by cathodic peaks at +0.6, +0.3, and -1.2 V [21, 22]. The process of the coordination sphere deeper oxidation evidently takes place already during the coulometric electrolysis and, together with the partial oxidation of the solvent (confirmed by reduction peak of  $H^+$  at -0.5 V) is the cause of the increased charge, transferred in electrolysis.

The results of electrochemical study lead to the conclusion that the presence of a nitrosyl ligand, with the exception of a shift in reduction potential values, does not essentially change redox properties of chromium dithiocarbamate complexes. The same type and close energy of redox orbitals may be assumed, therefore, both in tris(dithiocarbamate) and bis(dithiocarbamate) nitrosyl complexes.

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