Electrochemical study of some chromium(III) tris(dithiocarbamate) complexes

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Study has been made of redox behaviour of CrL_3 complexes (L = diethyl-, tetramethylene-, and pentamethylenedithiocarbamate) at platinum and mercury electrodes in dimethylformamide and acetonitrile. The reduction of complexes is a two-step reaction. The first step $Cr(III) \rightarrow Cr(II)$ is connected with the liberation of one ligand, the second two-electron reduction step leads to chromium(0) and to a complete decomposition of the coordination sphere. During the primary oxidation one electron is transferred on to the complex particle and then the oxidation is followed by the intramolecular redox process. The ability of the dithiocarbamate ligand to stabilize a high oxidation state of metal has been proved to be rather lower in the case of complexes with high values of oxidation potential.

Изучено окислительно-восстановительное поведение комплексов CrL_3 (L = диэтил-, тетраметилен- и пентаметилендитиокарбаминат) на платиновом и ртутном электродах в диметилформамиде и ацетонитриле. Восстановление комплексов происходит в 2 этапа: реакция $Cr(III) \rightarrow Cr(II)$ связана с отщеплением одного лиганда, второй двухэлектронный этап приводит к $Cr(0)$ и полному разрушению координационной сферы. Первичное окисление протекает с потерей одного электрона на комплексную частицу и потом доходит к последовательным внутримолекулярным окислительно-восстановительным процессом. Подтверждено, что способность дитиокарбаминатного лиганда стабилизировать более высокую степень окисления металла в комплексах с высоким потенциалом окисления значительно понижена.

Dithiocarbamate complexes have attracted widespread attention of research workers in view of their possible use in industry and agriculture, their significant analytical application, no less than from theoretical aspects of coordination chemistry. Many properties of these species are specifically given by their redox behaviour. It is from this aspect that the dithiocarbamate ligand ability to stabilize

formally higher oxidation states of the central ion, is chiefly being studied. Shorter redox series were observed in dithiocarbamate complexes of Cu [1, 2], Ag [3, 4], Au [4, 5], Mn [6], Fe [7, 8], Ni [1, 9—13], Ru [14, 15], Os [16, 17], Pd and Pt [9, 18] and the stability of a higher oxidation state was shown to depend on the type of the central ion and on the medium (solvent). Owing to the easy oxidability of the ligand and as a consequence of it, intramolecular redox may take place in complexes of a higher oxidation state [12, 13]. Such reactions may be expected especially in complexes of high oxidation potential values. Chromium(III) tris(dithiocarbamate) complexes are characterized just by such values. Their reduction has, to some extent, been studied only by a mercury electrode [19] but the oxidation process is still but poorly understood [20, 21].

The present work treats of the characterization of tris(dithiocarbamate) CrL_3 complexes (L = diethyl-, tetramethylene-, and pentamethylenedithiocarbamate) with a more profound examination of $Cr[(C_2H_5)_2NCS_2]_3$ redox processes. The investigation has been directed at evaluating the coordination sphere stability of the complex after the electron is received or lost.

Experimental

Complexes, prepared according to the published procedure [22], were recrystallized twice from chloroform. The composition of the preparations was verified by chemical analysis as well as by electronic and infrared spectra, which agreed with the published data [23, 24].

Voltammetric measurements were made with a three-electrode polarograph, Model OH-102 (Radelkis, Budapest). The working electrodes used were a platinum disc electrode (surface area 1.150 mm^2), sealed in soft glass, a hanging mercury drop electrode (HMDE), Kemula E-69b Model (Radiometer, Copenhagen), and for polarographic measurements a dropping mercury electrode (DME) with constants $t_1 = 4.8$ s, $m = 1.4$ mg s^{-1}. The reference electrode consisted of a calomel electrode in an aqueous LiCl solution of 4 mol dm^{-3} (4 M-CE) with a 0.1 M salt bridge filled with tetrabutylamine tetrafluoroborate in an appropriate nonaqueous solution. The auxiliary electrode was a large-surface platinum electrode. Unless otherwise stated in the text, scan rate used in stationary electrode voltammetry was $v = 0.1$ V s^{-1} and in polarography $v = 4.1 \times 10^{-3}$ V s^{-1}.

Coulometric measurements were made with a universal OH-404 coulometric analyzer (Radelkis, Budapest). The working electrode consisted of a double circular platinum gauze, placed parallel to a frit separating the anodic from the cathode compartment in the electrolytic cell. The auxiliary electrode was a platinum coil. The reference electrode was constituted as for voltammetric measurements.

Acetonitrile (Avondale Laboratories, England) and dimethylformamide (Reachim, USSR) were purified as described in literature [25, 26]. Tetrabutylamine tetrafluoroborate (Southwestern Analytical Chemicals, Austin, Texas), in 0.1 mol dm^{-3} concentration, was used as base electrolyte.

Inert gas employed was incandescent lamp nitrogen dried with anhydrous $CaCl_2$ and saturated with the vapours of the used solvent.

Results and discussion

The reduction of chromium(III) tris(dithiocarbamate) complexes under study is a two-step process with potential separation between the two steps equal to a few hundred millivolts (Table 1). The potentials of the two reduction steps do not essentially depend upon the type of the indicating electrode used. Oxidation of complexes on a Pt electrode takes place solely at potentials which are over 2.5 V more positive than the potentials of the first reduction step and simultaneously almost 1 V more positive than the oxidation potential of the free dithiocarbamate anion (more exactly the anion bonded to an ion pair with Na^+ [27, 28]; the oxidation potential value of the ligand may change by coordination).

Full voltammetric characteristics of the complexes under examination, determined in dimethylformamide, are given in Table 1. They demonstrate the dependence of redox potential on donor-acceptor properties of the dithiocarbamate ligand, similarly as has been determined for Cr(III) and other transition metal complexes in acetonitrile [19, 20] or in acetone [7]. In general, the conclusion stated in Ref. [7], *viz.* that the easier the reduction of the dithiocarbamate complex, the more difficult is its oxidation, has also been confirmed.

Considerable differences in redox potentials of individual transition dithiocarbamate metal complexes [20] and the comparison of structural parameters of oxidized and reduced forms of complexes have led to the conclusions concerning the localization of redox processes on metal atoms [7]. The authors of paper [21], while establishing correlation between E_{ox} and the properties of the ligand (ionization potential), have, nevertheless, also noted the effect of metal on the value of oxidation potential of the complex. In Cr(III) complexes under discussion, there exists an exceptionally great difference in oxidation potentials of complexes and of free dithiocarbamate anions. Moreover, oxidation peak currents of Cr(III) complexes (*vide infra*) confirm the view that the number of exchanged electrons (n) in reaction is equal to 1. We are inclined, therefore, to think that the redox reaction centre has the character of a metal.

The controlled process study of electrode reactions was done on the basis of $Cr[(C_2H_5)_2NCS_2]_3$ reduction and oxidation Pt and HMDE electrode peak current dependence on the square root of the scan rate (the range of $v = 0.0125—0.1$ V s^{-1}) and of the dependence of DME polarographic limiting current of the first reduction step of the complex on the square root of the mercury head height (the range of $h = 25—100$ cm). Linear graphs of all these functions go to confirm that the current is diffusion-controlled.

Cathodic currents on the three indicating electrodes used, as well as the anodic current at the Pt electrode, are all linearly dependent on the $Cr[(C_2H_5)_2NCS_2]_3$ concentration and can be analytically employed in concentration range from 10^{-4} to 10^{-2} mol dm^{-3}. The lower limit is given by the residual faradayic current, which

Table 1

Voltammetric characteristics of chromium(III) tris(dithiocarbamate) complexes
0.1 mol dm^{-3} (C$_4$H$_9$)$_4$NBF$_4$ in dimethylformamide, all potentials expressed in V vs. 4 M-CE

| Complex | Reduction Step 1 | | | Reduction Step 2 | | | Oxidation |
	DME $E_{1/2}$	HMDE E_p	Pt E_p	DME $E_{1/2}$	HMDE E_p	Pt E_p	Pt E_p
Cr[(C$_2$H$_5$)$_2$NCS$_2$]$_3$	-1.60	-1.70	-1.75	-2.25	-2.35	-2.35	0.95
Cr[(CH$_2$)$_4$NCS$_2$]$_3$	-1.58	-1.66	-1.72	-2.00	-2.08	-2.05	0.93
Cr[(CH$_2$)$_5$NCS$_2$]$_3$	-1.61	-1.72	-1.78	-2.05	-2.15	-2.14	0.85

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cannot be eliminated in the ordinary manner of cleaning solvents and indifferent electrolyte.

Voltammetric peaks, obtained at stationary electrodes, have sometimes been split up and then the potential difference between the prepeak and the peak is 100—200 mV. Similar split in peaks or reduction waves at the DME was noted in the case of $(C_2H_5)_2NCS_2^-$ ion, tetraethylthiuram disulfide and sulfur [28], which is evidently connected with the adsorption of sulfur compounds at certain concentration levels [29] and even perhaps with traces of water content. The observed increased irreversibility of processes further points to such a complication.

In studying the $Cr[(C_2H_5)_2NCS_2]_3$ reduction process by cyclic voltammetry at HMDE (both in dimethylformamide and acetonitrile) we recorded an anodic counterpeak proving quasireversibility in the first reduction step only (Fig. 1a). Cathodic peak A is characterized by difference $|E_p - E_{p/2}| = 150$ mV, potential separation $|E_{p, A} - E_{p, B}| = 200$ mV, ratio of the maximum peak currents $I_{p, B}/I_{p, A} = 0.7$. According to [19], reduction is associated with the coordination sphere decomposition. The proof of it is peak C, observed on the cyclic voltammogram in further HMDE polarization towards more positive potentials, which is associated with electrode material oxidation in the presence of the free dithiocarbamate anion. This assignment has, in addition to the proof provided by the comparison with the behaviour of cupral [28], been further substantiated by the fact that, on recurrent changes in the polarization direction of the indicating electrode towards
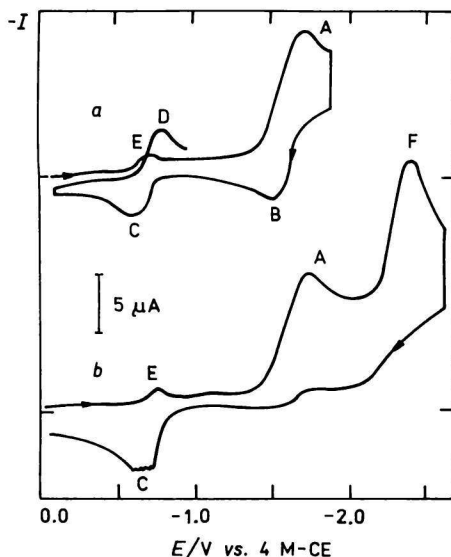

Fig. 1. Cyclic voltammograms of 2×10^{-3} mol dm^{-3} Cr[(C₂H₅)₂NCS₂]₃, HMDE, scan rate 0.1 V s^{-1}, 0.1 mol dm^{-3} (C₄H₉)₄NBF₄ in dimethylformamide.

negative potentials (Fig. 1a), a new cathodic peak D appeared at -0.8 V, corresponding to the reduction of the newly formed $[(C_2H_5)_2NCS_2]Hg$ [30]. Logarithmic analysis of the polarographic wave of reduction Step 1 of the complex in dimethylformamide yielded a value of $(\alpha\, n_a) = 0.57$.

In cyclic voltammetry at a platinum electrode, cathodic peak G, pertaining to the $Cr[(C_2H_5)_2NCS_2]_3$ reduction Step 1 (Fig. 2a), is characterized, both in dimethyl-formamide and acetonitrile, by a difference $|E_p - E_{p/2}| = 130$ mV (in acetonitrile $E_p = -1.85$ V). No anodic counterpeak to peak G has been noticed. Peak H (Fig. 2a) is potentially identical with oxidation peak J of the $(C_2H_5)_2NCS_2^-$ free ion (Fig. 2b) and thus confirms the liberation of a dithiocarbamate anion from the coordination sphere during the reduction of Cr(III) to Cr(II).

Coulometric reduction of $Cr[(C_2H_5)_2NCS_2]_3$ took place at a potential of -1.9 V. Peak G was still observed on the voltammogram obtained with a platinum electrode after the charge (one electron per complex particle) had been transferred to the complex, the peak current being, however, considerably lower (ca. 20 %) than before electrolysis. Continued presence of reduced peak G on records taken during further electrolytic reduction is a proof of partial reoxidation of the Cr(II) complex by solvate. Voltammetric determination of free dithiocarbamate anion concentration in electrolyzate after prolonged reduction at -1.9 V, using the method of standard addition, has shown that the reduction of the Cr(III) complex to Cr(II) is associated with one dithiocarbamate ligand liberation per complex particle.

Cyclic voltammetry, using an HMDE, has shown no difference in $Cr[(C_2H_5)_2NCS_2]_3^-$ and $Cr[(C_2H_5)_2NCS_2]_2$ oxidation potentials nor in $Cr[(C_2H_5)_2NCS_2]_2^+$ and $Cr[(C_2H_5)_2NCS_2]_3$ reduction potentials, as reported in some cases in Ref. [31].

The reduction second step of $Cr[(C_2H_5)_2NCS_2]_3$ is characterized by peaks at platinum and HMDE electrodes, the peak current of which is significantly higher than that of the reduction Step 1 peaks and is almost twice as high (Fig. 1b). The ratio of diffusion limiting currents of both reduction steps, ascertained at a DME, is similar. This ratio, however, has been affected by shortening drop time due to high negative potentials. If we consider values $I_{lim}/t_1^{1/6}$, their ratio in the reduction Steps 2 and 1 is close to 2.

Cr(II) complex reduction at an HMDE increases the anodic peak C current (Fig. 1b) as well as that of peak H (Fig. 2a), when a platinum electrode is used. This may well be explained by increased concentration of the free dithiocarbamate ion in the solution. On the basis of these facts we are inclined to believe that the reduction of $Cr[(C_2H_5)_2NCS_2]_2$ is an irreversible two-electron process connected with complete coordination sphere decomposition and the transition of chromium into solid phase.

Minor increase in cathodic current, observed at an HMDE at -0.7 V (peak E, Fig. 1) or at a platinum electrode at -1.1 V (peak I, Fig. 2a) has been caused by impurities that were in dithiocarbamate sodium salt reagents [28] or which are the result of oxidation during the preparation of complexes.

The oxidation of the three studied complexes at a platinum electrode was in both solvents electrochemically irreversible ($E_p - E_{p/2} = 90$—100 mV). Peak currents of anodic peaks are equal to those of reduction Step 1 peaks of complexes (e.g. for diethyl derivative peak K and peak G, Fig. 2c, 2a), which shows that the number of exchanged electrons (n) in the electrochemical oxidation is equal to that of the reduction first step, i.e. one electron per complex particle.

After primary $Cr[(C_2H_5)_2NCS_2]_3$ oxidation, cathodic peak L was recorded on a cyclic voltammogram (at -0.05 V in dimethylformamide, at 0.0 V in acetonitrile) and in addition, the original reduction Step 1 peak (peak G) of the complex appeared (Fig. 2c). From the comparison of such cyclic voltammograms, obtained at three different scan rates v (0.1, 0.05, and 0.025 V s^{-1}) it follows that the peak L maximum current decreases considerably more rapidly than the value $v^{1/2}$, which indicates instability of the oxidation product. When the platinum electrode is polarized at potentials of $+1.1$ V for about 30 s, peak M markedly becomes more evident at -0.55 V, especially in dimethylformamide, and in acetonitrile there are, in addition, cathodic peaks at $+0.35$ and -0.85 V.

No reversible cathodic counterpeak, pertaining to anodic peak K, has been recorded, contrary to what has been reported in [20, 21]. This is evidently due to the fact that relatively lower scan rates have been used with regard to the instability of the oxidation primary product of the Cr(III) complex.

Deeper understanding of electrode oxidation is based on coulometric electrolysis (in the bulk solution phase), performed at a potential of $+1.1$ V, combined with cyclic voltammetry and spectrophotometric study. The number of electrons taking part in electrode reaction, determined coulometrically, used to be somewhat higher than 1, or after the transfer of the charge corresponding to one electron per particle, peak K maximum current dropped to 1/3—1/4.

Electrolyzate voltammogram points to the presence of several electroactive species but the picture changes with time. The course of changes recorded at a platinum electrode in dimethylformamide is given in Fig. 2d. On a record, obtained after 24 h, cathodic peak M (-0.55 V) itself disappeared and a new cathodic peak was recorded at -1.95 V. Changes registered in acetonitrile were as follows: the cathodic peak dropped at $+0.3$ V and so did peak L at 0.0 V; peak M (-0.6 V) remained without marked alteration; peak N (-0.85 V) increased and so did the peak at -1.0 V (later at -1.25 V); peak G (-1.85 V) remained unchanged. On electrolyzate polarograms, recorded with a DME, there were cathodic waves with half-wave potentials of -0.05, -0.4, -0.7, and -1.6 V. The wave limiting current at -0.7 V was significantly greater than before the electroly-

tic oxidation (Fig. 1a). Wave $E_{1/2} = -0.05$ V was already missing on the record made after 2 h but the remaining part of the polarogram was essentially unaltered.

Incidental to the electrolytical oxidation of the complex was a colour alteration of the solution from blue-violet to yellowish brown. This change, as well as other alterations in the visible spectrum at the end of electrolysis, is shown in Fig. 3 (behaviour was found to be identical in dimethylformamide and acetonitrile alike). Time change of spectrum and of the voltammetric image reveals the existence of follow-up chemical reactions. Absence of isosbestic points indicates that a large number of coloured species with comparable absorbances can be found in the reaction sequence. Half-time of spectrum alterations was approximately the same as that of cathodic peak L drop at -0.05 V.
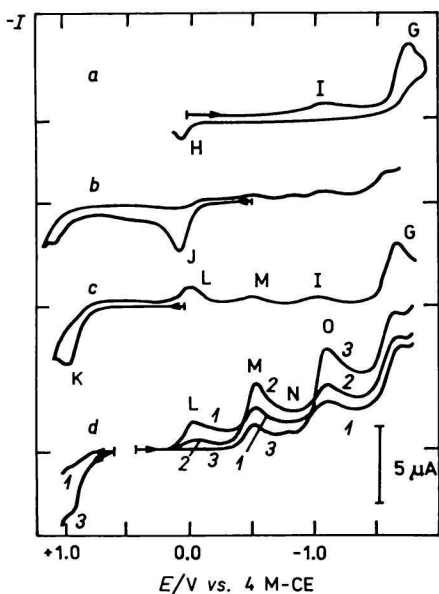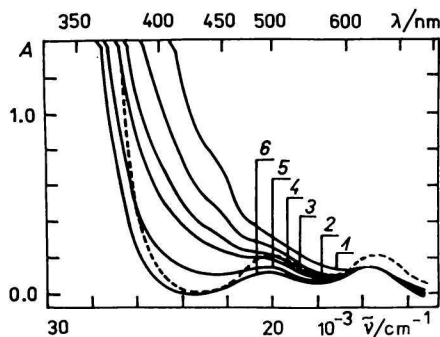

Fig. 2.

Fig. 3.

Fig. 2. Cyclic voltammograms of: *a*) 1×10^{-3} mol dm^{-3} Cr[(C$_2$H$_5$)$_2$NCS$_2$]$_3$, *b*) 1×10^{-3} mol dm^{-3} (C$_2$H$_5$)$_2$NCS$_2$Na, *c*) as *a*), *d*) bulk-phase electrooxidation products of 1×10^{-3} mol dm^{-3} Cr[(C$_2$H$_5$)$_2$NCS$_2$]$_3$, electrolysis at $+1.0$ V *vs.* 4 M-CE finished after the charge corresponding to one electron oxidation was supplied by potentiostat, time after electrolysis — 5 min (*1*), 25 min (*2*), and 300 min (*3*). Pt electrode, scan rate 0.1 V s^{-1}, 0.1 mol dm^{-3} (C$_4$H$_9$)$_4$NBF$_4$ in dimethylformamide.

Fig. 3. Time change of visible spectrum after bulk-phase electrooxidation of 3×10^{-3} mol dm^{-3} Cr[(C$_2$H$_5$)$_2$NCS$_2$]$_3$ at $+1.1$ V *vs.* 4 M-CE (electrolysis finished after the charge corresponding to one electron oxidation was supplied by potentiostat). Dashed line: solution before electrolysis, full lines: time after electrolysis — 10 min (*1*), 20 min (*2*), 30 min (*3*), 40 min (*4*), 70 min (*5*), and 120 min (*6*). 0.1 mol dm^{-3} (C$_4$H$_9$)$_4$NBF$_4$ in dimethylformamide, light-pass length 0.2 cm.

Cathodic peaks at $+0.3$, -0.55, -0.85, and -1.25 V, *i.e.* all new peaks except peak L, recorded on voltammograms after the $Cr[(C_2H_5)_2NCS_2]_3$ electrolytical oxidation, as well as their time changes, are all consistent with the behaviour of deep oxidation products of the $(C_2H_5)_2NCS_2^-$ ion itself [27, 28]. The peak at $+0.3$ V is that of the reduction of the 3,5-bis(diethyliminum)trithiolane 1,2,4-dication (denoted as Et_4bitt^{2+}), the decomposition of which has been slower in acetonitrile than in dimethylformamide. Peak M at -0.55 V is that of the reduction of proton originating from partial solvent oxidation or derived from residual water after OH^- ions have bonded on to cations [32], peak N at -0.85 V is that of sulfur, freed on Et_4bitt^{2+} formation and peak O at -1.2 V (isopotential with peak I) belongs to the stable product of Et_4bitt^{2+} particle chemical decomposition.

Cathodic peak L evidently pertains to the reduction of a Cr complex oxidized form. From the electrochemical viewpoint it is irreversible and at a platinum electrode is characterized by a difference $|E_p - E_{p/2}| = 90$ mV without having an anodic counterpeak. This oxidized form of the complex has a markedly altered electronic absorption spectrum (Fig. 3) and has also been demonstrated by DME reduction.

The disappearance of peak L reveals the existence of a medium-rate chemical intramolecular redox process or possibly indicates reaction with the solvent. Chromium oxidation state reverts to Cr(III) since cathodic peak G, reflecting the reduction of the Cr(III) complex to Cr(II) (with the original value of the maximum peak current), can still be observed on voltammograms and the anodic peak reappears in the region of the Cr(III) complex oxidation. The coordination sphere in processes, taking place after primary electrochemical oxidation, changes evidently under the formation of the disulfide bond. This is proved by the electronic absorption spectrum (Fig. 3) which is similar to the spectrum of Cr(III) tetraethylthiuram disulfide complex [33] and by the polarographic wave at -0.7 V corresponding to the S—S bond reduction [28]. The result is formation of a mixed ligands complex (dithiocarbamate, thiuramdisulfide, product of further oxidation, solvent). From the electron balance point of view, even Cr(III) binuclear complexes with an S—S bond formation, may be produced.

Intramolecular processes partly take place already during the electrolytic oxidation of the complex lasting a few minutes when Cr(III) regeneration raises charge consumption. $Cr[(C_2H_5)_2NCS_2]_3$ oxidation is further complicated by the proximity of the oxidation potential of this complex and the potential of tetraethylthiuram disulfide deeper oxidation [27, 28]. This further contributes to the consumption of electrolytic charge and leads to the coordination sphere deep oxidation (the formation of free sulfur, Et_4bitt^{2+}, and this dication chemical decomposition products) as can be seen from the voltammetric reduction picture. This process is probably connected with the Cr—S bond breaking and leads to significant changes

in the coordination sphere. In case the electrolysis ends after the charge, corresponding to the loss of one electron per complex particle, has passed, as was the case in experiments described above, only some complex units and only a part of their coordination sphere are affected by the mentioned redox changes.

Studies of $Cr[(C_2H_5)_2NCS_2]_3$ have thus confirmed the assumption that in dithiocarbamate complexes of high oxidation potential value, the stability of a higher oxidation state of the central metal (especially in a solution) is significantly reduced. It is from this aspect that the stabilizing effect, generally attributed to a ligand, must be viewed.

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