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On the Electrochemical Reduction of Some Cr(III) Complexes in *DMSO* Investigated by Cyclic Voltammetry

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The compounds investigated were: $[Cr(en)_3]^{3+}$, $[Cr(ur)_6]^{3+}$, $[Cr(DMSO)_6]^{3+}$, $[Cr(dien)_2]^{3+}$, $[Cr(en)_2(acac)]^{2+}$, $[Cr(en)(acac)_2]^+$ and $Cr(acac)_3$.

A distinctly different behaviour is caused by the introduction of one or more *acac* ligands into the molecule. The first step is much more cathodic and quite irreversible, while it is reversible or quasi reversible for the first group of ions. This is due to a π-type interaction between the *acac* ligand and the central ion. This interaction is responsible for a third peak occurring for the second group of compounds and may be attributed to the reduction of the Cr(I) ion.

Some correlations were found e. g. between the extinction of the *d—d* band of the first group of ions and the potential of the first peak, and the number of *acac* groups introduced in the second group of compounds and the shift of the potential of the first peak.

The determined electrochemical data are tabulated.

[Keywords: Cr(III) *complexes, reduction; Cyclic voltammetry]*

Untersuchungen zur elektrochemischen Reduktion einiger Cr(III)-Komplexe in DMSO mittels zyklischer Voltammetrie

Die elektrochemischen Daten einer Reihe von Cr(III)-Komplexen mit *en-*, *ur-*, *DMSO-*, *dien-* und *acac*-Liganden werden präsentiert und einige Möglichkeiten der Korrelation der physikalischen Eigenschaften der Komplexe werden aufgezeigt.

Die erste Stufe bei der Einführung von *acac*-Liganden ist auf Grund einer π-Wechselwirkung zwischen Ligand und Zentralion irreversibel.

Introduction

The few studies on the electrochemical behaviour of Cr(III) complex compounds in non-aqueous solutions that exist[1–8], show that there are

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significant differences between the behaviour of these complexes in aqueous and non-aqueous solutions.

While the Cr(II) ions in aqueous solutions are subject to relatively fast substitution, disproportionation and dissociation reactions, in non-aqueous media, particularly in *DMSO*, the low valency states are described as "electrochemical inert"[5,6], i.e. during cyclic voltammetry no homogeneous chemical reaction could be detected or they were sufficiently slow[2,4,6,8] for elucidation. In addition to these advantages of performing electrochemical measurements in non-aqueous solutions, there is a wider potential range accessible which favours the investigation of low valency oxidation states. For these reasons we extended our previous experiments[8–11].

Experimental

We used cyclic voltammetry at a stationary electrode. The working electrode consisted of a gold disc, 0.2 cm^2 in area, a 4 cm^2 Pt foil served as counter-electrode. Gold working electrodes were poisoned less easily and gave far more reproducible results than platinum. Ag/AgCl in aqueous saturated NaCl solution was used as reference electrode and was connected with the measuring cell by a salt bridge.

All potentials mentioned refer to this electrode which had a potential of —25.1 mV versus the saturated calomel electrode.

The following complex compounds were investigated

$Cr(en)_3\,(ClO_4)_3$*	(I)
$Cr(ur)_6\,(ClO_4)_3$	(II)
$Cr(DMSO)_6\,(ClO_4)_3$	(III)
$Cr(dien)_2\,(ClO_4)_3$	(IV)
$Cr(en)_2(acac)\,(ClO_4)_2$	(V)
$Cr(en)\,(acac)_2\,ClO_4$	(VI)
$Cr(acac)_3$	(VII)

The complex compounds II, III, V, VI and VII we prepared according to[12–16].

$CrCl_3 \cdot 6\,H_2O$ was dehydrated and resolvated in *DMSO* for the preparation of the polyaminecomplexes I and IV. The coordinatively bound solvent was then substituted by adding the polyamine (*en* or *dien*) and heating the resulting mixture. The formation of the complex was fast and almost complete.

The waterfree perchlorates of I-IV were obtained and purified by adding $HClO_4$ to the aqueous solution and recrystallising from perchlorate solution, then they were vacuum dried between 80-90 °C.

Carefully dried tetraethyl- and tetrabutylammoniumperchlorate were used as supporting electrolytes.

Results and Discussion

The two types of cyclic voltammograms obtained (Fig. 1*a* and 1*b*) justify the classification of the compounds we investigated into two

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* *en* — ethylendiamine; *dien* — diethylentriamine; *DMSO* — dimethylsulfoxide; *ur* — urea; *acac* — acetylacetonato.

types. In the cyclic voltammograms there are some faint additional peaks or shoulders. They are due to an irreversible splitting off of ligand molecules from the reduced Cr(II) species as we previously described for the $[Cr(en)_3]^{3+}$ ion[8].

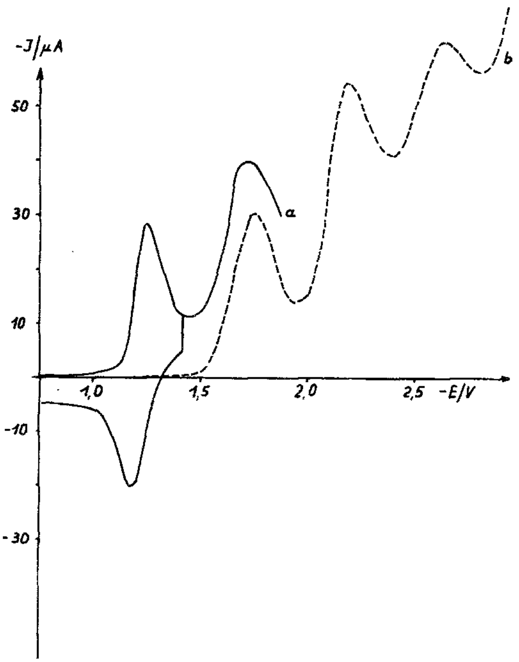

Fig. 1. Voltammograms for the reduction of *a* $[Cr(dien)_2](ClO_4)_3$: $c = 1 \cdot 10^{-3}\,mol\,l^{-1}$; $v = 0.1\,V\,s^{-1}$; 25 °C; poisoning of electrode at about 2 V; *b* $Cr(acac)_3$: $c = 1 \cdot 10^{-3}\,mol\,l^{-1}$; $v = 0.1\,V\,s^{-1}$; 25 °C

Group I Compounds

The complex compounds I-IV belong to the first group, in which the ligands are mainly linked to the central transition metal ion by a σ-bond. The following reduction mechanism may be proposed.

$$Cr(III) + e^- \rightleftharpoons Cr(II) \qquad (1\,a)$$

$$Cr(II) + 2\,e^- \rightarrow Cr(0) \qquad (1\,b)$$

First Reduction Step

Step (1 a) is reversible or quasi-reversible. Fig. 2 shows that the cathodic peak potential E_{pc} i. e. the standard redox potential of the reaction depends on the complexing ligand in such a way that it

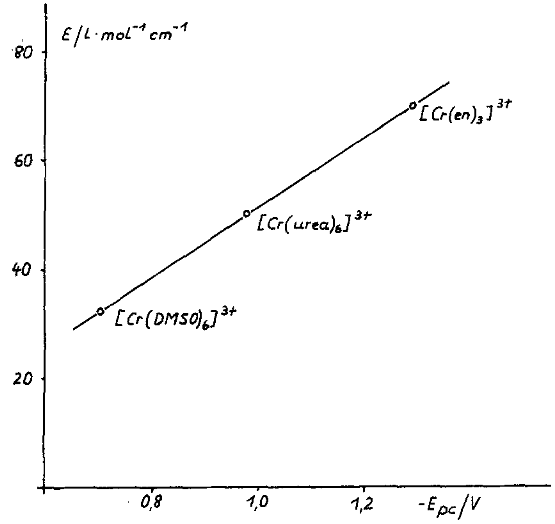

Fig. 2. Correlation between the molar extinction coefficient at the absorption maximum of the first *d*—*d* band and the reducton peak potential E_{pc} for Cr(III) → Cr(II) of the compounds I-III (25 °C)

Table 1. *The heterogenous rate constant* k_s *for the reaction* $[Cr(en)_3]^{3+} + e \rightleftharpoons [Cr(en)_3]^{2+}$ *as determined by Nicholson's method*[18, 19] *using the supplementary* ψ*-function*

v/Vs^{-1}	$\Delta E_p/V$	ψ	$10^4 k_s/cm\,s^{-1}$
0.200	0.100	0.50	4.15
0.140	0.092	0.64	4.48
0.093	0.087	0.75	4.28
0.070	0.080	0.96	4.70
0.046	0.077	1.10	4.40
0.035	0.075	1.20	4.20
0.028	0.072	1.42	4.41

$k_s = (4.37 \pm 0.07) \cdot 10^{-4}\,cm\,s^{-1}$

correlates with the molecular extinction coefficient of the first *d*—*d* band ($^4A_{2g} \rightarrow {}^4T_{1g}$ transition). In general the absorption corresponding to *d*—*d* transitions increases with ligand field strength[17], which means that the position of the first peak potential of the above Cr(III) compounds correlates with ligand field strength.

The method of *Nicholson* using a supplementary function ψ [18,19] was employed to determine k_s from the difference of the cathodic and anodic peak potentials at a given sweep rate, v (Tab. 1).

The cathodic transfer coefficient α was found to be $\alpha = 0.61$ using

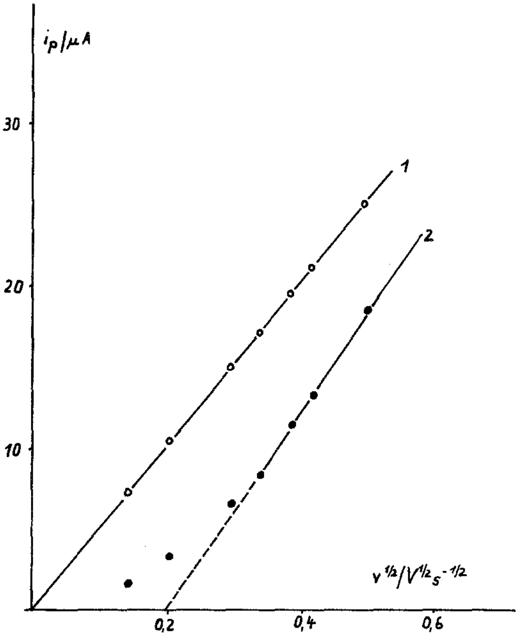

Fig. 3. Dependence of peak current on sweep rate for *1* Cr(III) → Cr(II); *2* Cr(II) → Cr(0); substrate: [Cr(*dien*)$_2$]$^{3+}$; $c = 1 \cdot 10^{-3}$ mol l^{-1}; 25 °C

the difference between peak potential and half peak potential:

$$E_p - E_{p/2} = -\frac{1.857\,RT}{\alpha\, n_a F} \tag{2}$$

and putting $n_a = 1$ (n_a—number of electrons exchanged in the rate determining step).

Second Reduction Step

For all complex compounds of the first group the second reduction process is an irreversible 2e$^-$ process in which unstable Cr(0) compounds are produced from which the ligands split off in succeeding reactions.

The irreversibility of the second reduction process shows up in a non-linear dependence of the peak current on the square root of the sweep rate particularly at low sweep rates, this is illustrated by Fig. 3, it makes a quantitative evaluation of the kinetic data of the subsequent reaction impossible.

Table 2. *Parameters for the reduction of chromium complexes of group I*

		reduction step Cr(III) → Cr(II)			
Complex	$-E_{pc}/\mathrm{V}$	$-E_{pc/2}/\mathrm{V}$	$-E_{pa}/\mathrm{V}$	α	$10^4 k_s/\mathrm{cm \cdot s^{-1}}$
I	1.304	1.225	1.216	0.61	45
II	0.950	0.892	0.690	rev.	rev.
III	0.700	0.645	0.641	rev.	rev.
IV	1.250	1.195	1.190	rev.	rev.
		reduction step Cr(II) → Cr(0)[a]			
I	1.602	1.498	irrev.	0.48	—
II	1.360	1.260	irrev.	0.48	—
III	1.320	1.218	irrev.	0.48	—
IV	1.710	1.611	irrev.	0.49	—

[a] The voltammograms obtained for this reduction step are not suitable for determining k_s.

The transfer coefficient α for the reduction of the Cr(II) compound determined by means of the relation

$$(E_{p/2})_2 - (E_{p/2})_1 = (RT/\alpha n_a F) \ln \left(\frac{v_1}{v_2}\right)^{1/2} \qquad (3)$$

for two different sweep rates v_1 and v_2 was found to be $\alpha = 0.48 \pm 0.01$ for all four complex compounds. It was assumed that only one electron is transferred in the rate determining step. This assumption is supported by the agreement found between the experimental value and the peak current calculated according to

$$i_P = 2.98 \cdot 10^5 \, (\alpha n_a)^{1/2} n A \, C_0 \, (Dv)^{1/2} \qquad (4)$$

n = number of electron transferred in the brutto reaction
A = electrode aera
D = diffusion coefficient of $[\mathrm{Cr}(en)_3]^{3+} = 1.10^{-6}\,\mathrm{cm^2\,s^{-1}}$
C_0 = concentration in mol cm^{-3}
i_P = in A cm^{-2}

Putting $n_a = 1$ and $n = 2$, i_P is found to be 27.7 μA by (4).
Changing n_a only to $n_a = 2$, i_P changes to 37.4 μA, while the experimental value was 26.1 μA.

The second reduction step always appeared in our experiments as a single peak, while *Gutmann* and *Schöber* observed two peaks for the Cr(II) → Cr(0) reduction step albeit in different systems[1].

Tab. 2 contains the experimental data found for the group I compounds.

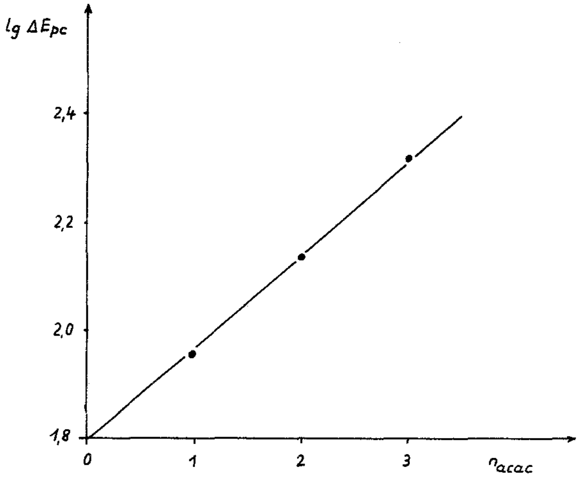

Fig. 4. Plot showing the functional relationship between ΔE_{pc} and the number of ligands, n_{acac}. E_{pc} is the potential of the first peak of the ion referred to the peak potential for the process: $[Cr(en)_3]^{3+} + e \rightarrow [Cr(en)_3]^{2+}$

Group II Compounds

Group II compounds were obtained by the stepwise introduction of one *acac* group. This group besides forming σ bonds is known to exert a strong π-type of interaction and this strongly influences the properties of the *acac* containing complexes.

The electronic structure of the *acac* chelate rings and the number of *acac* groups in the ion largely determine the electrochemical behaviour of the Cr(III) complexes. For compounds V–VIII two reduction steps are found in the potential range up to —2.7 V (Fig. 1 *b*).

First Reduction Step

Again the first step is due to the reduction of Cr(III) to Cr(II). This step becomes more negative with increasing number of *acac* groups, n_{acac}, in the complex (Tab. 3), a logarithmic relationship existing between shift of peak potential referred to $[Cr(en)_3]^{3+}$, ΔE^1_{pc}, and n_{acac} (Fig. 4).

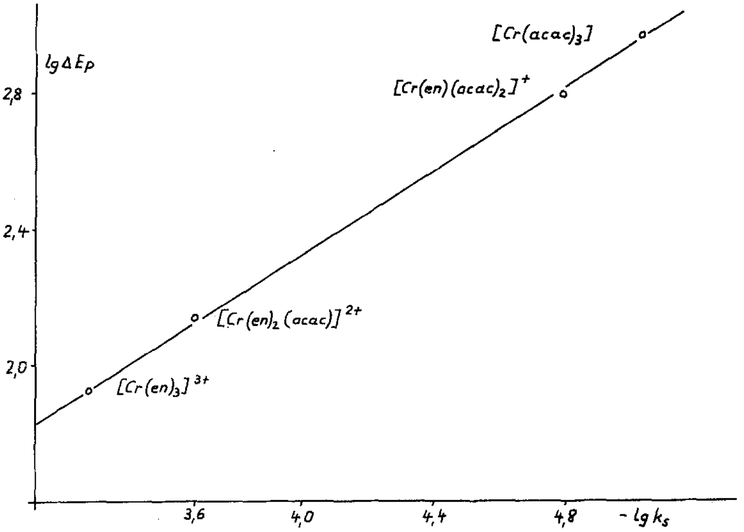

Fig. 5. Correlation between lg ΔE_{pc} (see Fig. 4) and the heterogeneous rate constant, k_s, determined by the method of *Reinmuth*[20]

Table 3. *Parameters of the reduction of the chromium(III) complexes of group II and of the* $[Cr(en)_3]^{3+}$

Complex		reduction step Cr(III) → Cr(II)			
	$-E_{pc}/V$	$-E_{pc/2}/V$	$-E_{pa}/V$	α	$10^4 k_s/cm \cdot s^{-1}$
I	1.304	1.225	1.216	0.61	45.0
V	1.376	1.283	1.252	0.54	19.6
VI	1.510	1.435	0.91	0.58	1.8
VII	1.750	1.665	0.90	0.56	1.2
		reduction step Cr(II) → Cr(I)			
I[a]	1.602	1.498	irrev.	0.48	—
V	2.100	2.015	irrev.	0.55	—
VI	2.160	2.070	irrev.	0.56	—
VII	2.182	2.101	irrev.	0.56	—

[a] Cr(II) → Cr(0).

The π-bonding in the chelate rings leads to a partial occupation of atomic orbitals of the central ion and makes a reduction more difficult. The irreversibility of the step, as demonstrated by the difference between the cathodic and the anodic peak, increases with rising number of *acac* groups.

Again a logarithmic correlation between (E_{pa} — E_{pc}) and n_{acac} exists, as well as between E^1_{pc} and k_s (Fig. 5), suggesting linear-free-energy-relationships. In correspondence with this difference in bonding between the two groups of compounds there is a presumably larger difference in the solvation shell of the oxidised and reduced form in the case of the second group, being responsible for the enhanced irreversibility of the first reduction step. α was again determined by (2)

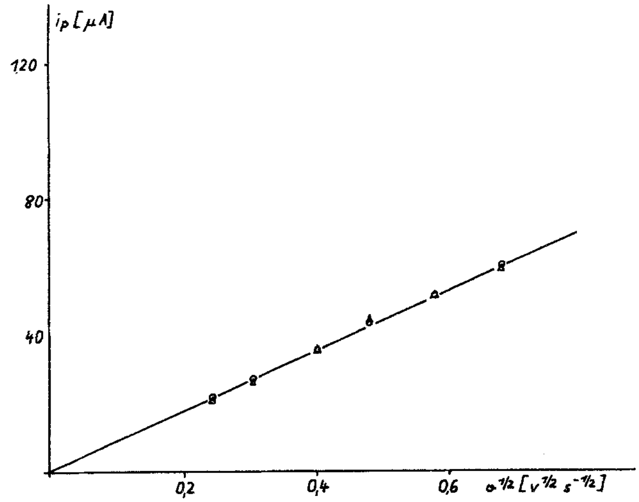

Fig. 6. Dependence of peak current, i_p, on sweep rate, v, for the reduction steps Cr(III) → Cr(II): ○ and Cr(II) → Cr(0): Δ, Substrate: Cr(*acac*)$_3$; $c = 1.2 \cdot 10^{-3}$ mol l^{-1}; 25 °C

and k_s by a method due to *Reinmuth*[20]. The current flowing is related to the potential by the following equation.

$$i = n F A\, C_0\, k_s \exp[(-\alpha\, n_a F/RT)\,(E - E_i)] \tag{5}$$

where E_i is the potential at the foot (beginning) of the peak.

A well obeyed linear relationship between log i and (E — E_i) was used to fing k_s and α according to (5). The data for all compounds of group II are collected in Tab. 3.

Second Reduction Step

The first *acac* group substituting an *en* group in [Cr(*en*)$_3$]$^{2+}$ causes the largest shift of peak potential (—500 mV) relative to [Cr(*en*)$_3$$^{2+}$]. Further substitution leads to only minor cathodic shifts (see Tab. 3).

The $i_p = f(v^{1/2})$ dependence is quite remarkable. The straight lines obtained go through the origin and are identical for both reduction steps i. e. α is the same for the two within experimental error (Fig. 6).

At the rotating disc electrode two equally high diffusion limited currents for the two reduction steps could be observed. At a stationary electrode a third voltammetric step corresponding presumably to the Cr(I) → Cr(0) reduction was observed (Fig. 1*b*). This, however, takes place at very negative potentials and decomposition of solvent and supporting electrolyte cannot be excluded. A quantitative analysis was therefore not possible. So it may be concluded that while the π-type interaction between ligand and central ion makes the reduction of the Cr(III) compound more difficult it stabilizes on the other hand the Cr(I) compound making it voltammetrically detectable under conditions used in our experiments. The following 3-step mechanism sums up our observations for the group II compounds.

$$\mathrm{Cr}(acac)_3 + \mathrm{e}^- \rightarrow \mathrm{Cr}(acac)_3^-$$
$$\mathrm{Cr}(acac)_3^- + \mathrm{e}^- \rightarrow \mathrm{Cr}(acac)_3^{2-}$$
$$\mathrm{Cr}(acac)_3^{2-} + \mathrm{e}^- \rightarrow \mathrm{Cr}(acac)_3^{3-}$$

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