The effect of N-methylation on the spectroscopical and electrochemical properties of 1,4,8,11-tetraazacyclotetradecane chromium(III) complexes

Dirk Guldi, F. Wasgestian*
Institute of Inorganic Chemistry, University of Cologne, Greinstrasse 6, D-5000 Cologne (FRG)

and Dan Meyerstein
Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva (Israel)

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Abstract

trans-[Cr(tmc)X_2] complexes (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, X = F, Cl, Br, H_2O, OH, NO_3) have been prepared and spectroscopically characterized. The redox potentials of the tmc complexes and of the analogous cyclam complexes (cyclam = 1,4,8,11-tetraazacyclotetradecane) were determined by cyclic voltammetry. The potentials of the tmc complexes are 1.1 ± 0.1 V more positive. Their long wavelength absorption is red-shifted by 50 to 100 nm with respect to that of the analogous cyclam complexes. The shift was consistent with a linear dependence of the polarographic half-wave potentials on the transition energies of the first spin allowed ligand field bands, observed on a series of chromium(III) amine complexes. The reaction entropies for the reduction of *trans*-[Cr(cyclam)$(H_2O)_2]^{3+}$, *trans*-[Cr(cyclam)$(OH)_2]^{+}$, and *trans*-[Cr(tmc)$(OH)_2]^{+}$, $\Delta S = 88 \pm 2$, 200 ± 40 and 53 ± 8 J mol^{-1} K^{-1}, respectively, were obtained from the temperature dependence of the redox potential. It was shown that *trans*-[Cr(cyclam)$(H_2O)_2]^{3+}$ catalyzes the electroreduction of nitrate.

Introduction

The methylation of the nitrogen atoms in tetraazamacrocyclic complexes has been shown to stabilize the lower oxidation states of transition metal complexes [1–8] and to shift the ligand field bands to longer wavelengths [1, 5, 9]. These effects were attributed to poorer σ-donor strength of the tertiary nitrogen atoms [10], increased cavity size of the N-methylated ligand [6], and/or decreased solvation caused by the hydrophobic nature of the alkyl groups [1, 2, 11].

In extension of a preliminary report [12] we have studied a number of chromium(III) complexes of 1,4,8,11-tetraazacyclodecane (cyclam) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclodecane (tmc) with varying co-ligands. Whereas the structures and spectral properties of the unmethylated chromium cyclam complexes are well documented [13–27], their electrochemistry has drawn less attention. Tetramethylcyclam complexes of chromium(III) have not been prepared before. However, Mani [28] described a chromium(II) complex in accordance with the stabilization of the lower oxidation state in tmc complexes.

*Author to whom correspondence should be addressed.

Experimental

Materials

Cyclam [29], tmc [30], *trans*-[Cr(py)$_4F_2$]BF_4 [31] (py = pyridine) and the ammine complexes that were used in the polarographic measurements were prepared by literature methods. Purities were checked by IR and either NMR or UV–Vis spectroscopy. The *trans*-cyclam chromium(III) complexes were prepared from *trans*-[Cr(cyclam)$(CN)_2]BF_4$ following the method of Kane-Maguire *et al.* [21] as indicated in the reaction scheme (Fig. 1). Caution: HCN is liberated during the synthesis. Evidence that the *trans* isomers were formed is presented in the next section.

Synthesis of trans-[Cr(tmc)F_2]$BF_4 \cdot HBF_4$

A solution of 0.4 g (1.6 mmol) tmc, 0.7 g (1.6 mmol) *trans*-[Cr(py)$_4F_2$]BF_4 and 4 ml anhydrous methylglycol was refluxed for 30 min. After the solution had been cooled down to room temperature, diethyl ether was added, which precipitated a viscous green substance. Repeated treatment with diethyl ether solidified the substance. It was twice reprecipitated by HBF_4 and dried *in vacuo*. Yield 0.23 g (31%). *Anal.* Calc. for

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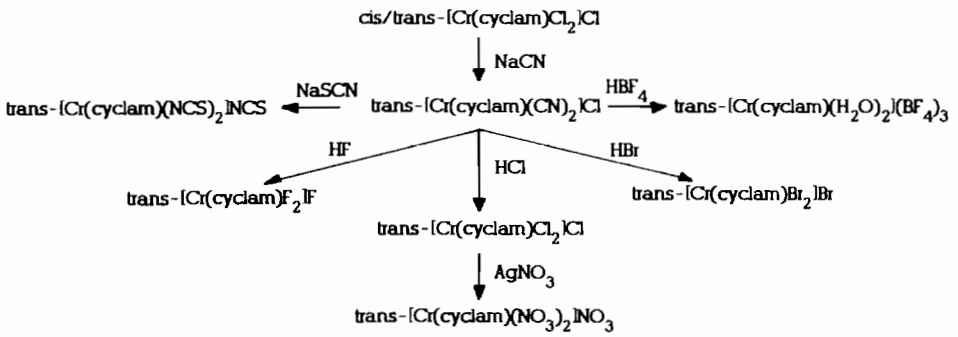

Fig. 1. Reaction scheme for the preparation of the *trans*-Cr(III) cyclam complexes.

$[Cr(tmc)F_2]BF_4 \cdot HBF_4$: C, 33.3; H, 6.3; N, 10.7; Cr, 9.9. Found: C, 34.4; H, 6.8; N, 10.4; Cr, 10.7%.

Synthesis of trans-$[Cr(tmc)(H_2O)_2](BF_4)_3$

1.5 g (5.9 mmol) tmc and 2.9 g (5.9 mmol) *trans*-$[Cr(py)_4F_2]BF_4$ were dissolved in 8 ml methylglycol containing 10% of water (vol./vol.) and refluxed for 30 min. Then 3 drops of HBF_4 were added. After the solution was cooled to room temperature, diethyl ether was added. The precipitated green and viscous substance became solid by treating with diethyl ether. The product was twice reprecipitated by HBF_4 and dried *in vacuo*. It was very hygroscopic. Yield 0.9 g (52%). *Anal.* Calc. for $[Cr(tmc)(H_2O)_2](BF_4)_3 \cdot 4H_2O$: C, 17.6; H, 4.2; N, 5.8; Cr, 5.4. Found: C, 17.9; H, 4.3; N, 5.8; Cr, 5.9%.

Synthesis of trans-$[Cr(tmc)Cl_2]BF_4 \cdot 6HBF_4$

0.1 g (0.2 mmol) *trans*-$[Cr(tmc)F_2]BF_4$ was refluxed for 30 min in 5 ml 6 N HCl. The chloride crystallized when the solution was kept on ice over night. It was converted to the fluoroborate by reprecipitating twice with HBF_4. The green solid was very hygroscopic. Yield 0.03 g (33%). *Anal.* Calc. for $[Cr(tmc)Cl_2]BF_4 \cdot 6HBF_4$: C, 16.9; H, 3.8; N, 5.6; Cr, 5.2. Found: C, 16.8; H, 3.9; N, 5.6; Cr 5.4%.

Synthesis of trans-$[Cr(tmc)Br_2]BF_4 \cdot HBF_4$

0.4 g (0.9 mmol) *trans*-$[Cr(tmc)F_2]BF_4$ was refluxed for 2 h in 20 ml 46% HBr. When the solution had cooled down, the solvent was removed on the rotary evaporator. It was recrystallized twice from HBF_4. The light green complex was less hygroscopic than the other tetramethylcyclam complexes. Yield 0.15 g (29%). *Anal.* Calc. for $[Cr(tmc)Br_2]BF_4 \cdot HBF_4$: C, 18.7; H, 4.9; N, 8.7; Cr, 8.1. Found: C, 18.6; H, 5.2; N, 8.5; Cr, 7.7%.

Analysis

CH and N analyses were obtained on a Haereus CHNO-rapid analyzer. Chromium contents were determined spectrophotometrically at 372 nm ($\epsilon = 4820$ 1 mol^{-1} cm^{-1}) after oxidation to chromate.

Measurements

UV–Vis absorption spectra were recorded on a Cary 14, a Cary 2300 spectrophotometer or a HP 8452 diode array spectrophotometer. IR spectra were recorded on a Perkin-Elmer 457 spectrometer in nujol suspensions. Phosphorescence spectra were obtained with a luminescence spectrometer described elsewhere [32]. pH measurements were performed with a Knick 641 digital pH meter using a Schott glass electrode N 59.

Cyclovoltammograms were recorded on a Bas CV-1B cyclovoltammograph in combination with a Yew type 3086 XY-recorder and a Fluke 8000 A digital multimeter. Polarograms were recorded on a PAR Corporation model 74 polarograph. A three-electrode

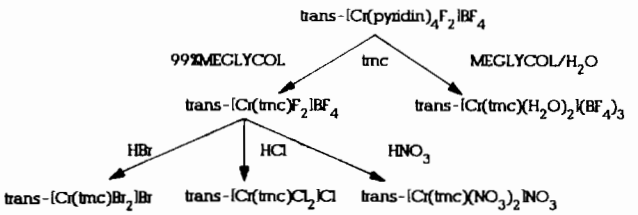

Fig. 2. Reaction scheme for the preparation of the *trans*-Cr(III) tetramethylcyclam complexes.

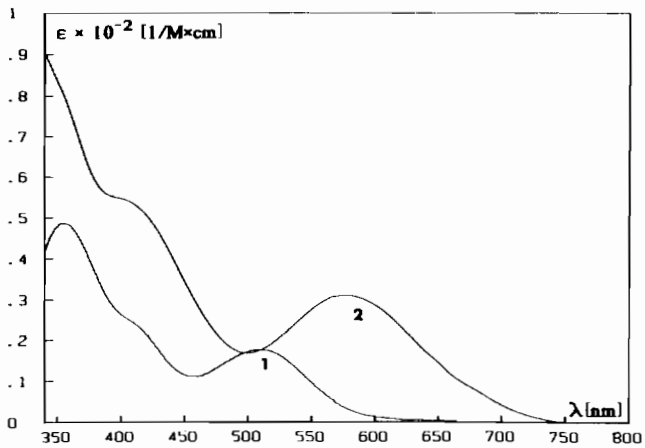

Fig. 3. UV–Vis absorption spectra of: 1, *trans*-diaquo cyclam chromium(III); 2, *trans*-diaquo tetramethylcyclam chromium(III), in aqueous solution (22 °C).

TABLE 1. Spectral data of *trans*-chromium(III) cyclam and *trans*-chromium(III) tmc complexes in the region of the quartet bands (aqueous solutions at 22 °C)

Complex	Reference	cyclam						tmc					
		Q_3		Q_2		Q_1		Q_3		Q_2		Q_1	
		λ_{max}[a]	ϵ[b]	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
trans-$(Br)_2$		362	87	414sh	80	605	43	330	14	440sh	41	656	30
	23	362	87	420sh	79	609	43						
trans-$(Cl)_2$		366	36	407sh	31	569	22	330	85	448sh	30	641	27
	13	365	41	407sh	35	572	20						
trans-$(F)_2$		363	15	410sh	12	504	10	330	80	427sh	28	602	28
trans-$(H_2O)_2$		356	51	405sh	33	510	23	334	92	393sh	54	582	29
	13	350	53	405sh	39	510	24						
trans-$(NO_3)_2$		349	19	402sh	30	518	42	333	160	400sh	30	563	20

[a]λ_{max} in nm. [b]ϵ in l mol^{-1} cm^{-1}.

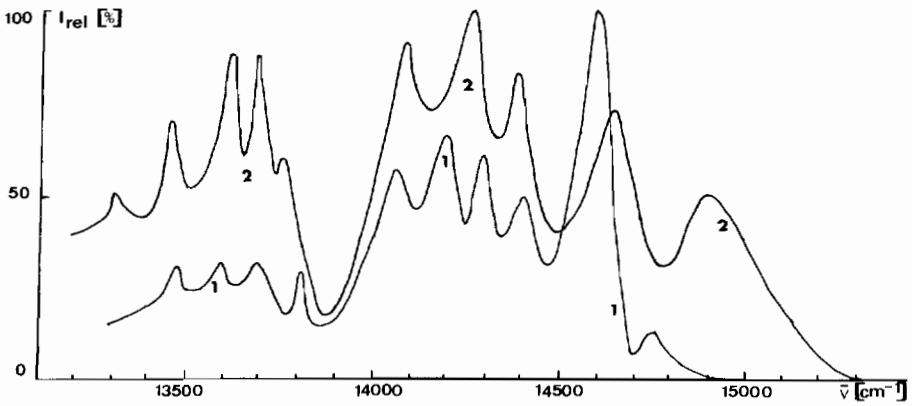

Fig. 4. Phosphorescence spectra of: 1, *trans*-$[Cr(cyclam)(H_2O)_2]^{3+}$; 2, *trans*-$[Cr(tmc)(H_2O)_2]^{3+}$.

cell was used. Working electrodes were a dropping mercury electrode (DME) for polarograms and the Metrohm E 410 hanging-mercury-drop electrode (HMDE) for CV measurements. The auxiliary electrode was a Pt wire and a SCE was used as a reference electrode. All potentials are given versus SCE. Supporting electrolytes were 0.5 N KCl or 0.5 N $NaClO_4$. For all electrochemical measurements the solutions were deaerated by N_2, previously bubbled through a VSO_4 solution in dilute H_2SO_4 over Zn amalgam. The temperature dependence of the redox potentials was determined in a non-isothermal cell as described by Weaver and co-workers [33].

Results and discussion

Preparation

Chromium can be inserted into tetramethyl cyclam by the method of Glerup *et al.* [31], which yielded the *trans*-difluoro complex in anhydrous methylglycol ($\leq 1\%$ H_2O), whereas in methylglycol containing 10% water (vol./vol.) the diaquo complex was formed. The fluoride ligands in the difluoro complex could be easily exchanged by other ligands such as Cl^-, Br^- or NO_3^- by reaction with the corresponding acids as outlined in the reaction scheme of Fig. 2. All tmc complexes are very hygroscopic and have to be kept in a dry atmosphere.

The assignments to the *trans* configuration were based on the fact that the IR band at 800 cm^{-1} (methylene frequency of the ring skeleton) was not split (*cis*-diacidocyclam complexes usually have this band split [34]) and that the UV–Vis spectra (Fig. 3) showed the features that are typical for *trans*-tetraammine complexes, i.e. the rather low absorptivity of the bands in the visible region ($\epsilon \leq 30$ l mol^{-1} cm^{-1}) and the splitting of the $^4T_{2g}(O_h)$ band [35].

Rigorous drying of those *trans*-chromium tmc compounds that had coordinating counterions such as Br^-, Cl^- or F^- produced a colour change from green to purple. The absorption spectra of the purple compound could be recorded in anhydrous solvents (dmso, dmf)

TABLE 2. UV spectral data of *trans*-chromium(III) cyclam and *trans*-chromium(III) tmc complexes (aqueous solutions at room temperature (22 °C))

Complex	cyclam				tmc			
	λ_{max}[a]	ϵ[b]	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
trans-$(Br)_2$	242	11900	284	1275	211	7400	292	1200
trans-$(Cl)_2$	212	10000	236sh	3900			243	1900
trans-$(F)_2$	210	6400			210	5600	255	2500
trans-$(H_2O)_2$	208	6200	269sh	180	211	2700	253	2000
trans-$(CN)_2$	214	4900	253	680				
trans-$(NCS)_2$	226	12800	307	2700				
trans-$(NO_3)_2$	220	20000					234	900

[a]λ_{max} in nm. [b]ϵ in l mol^{-1} cm^{-1}.

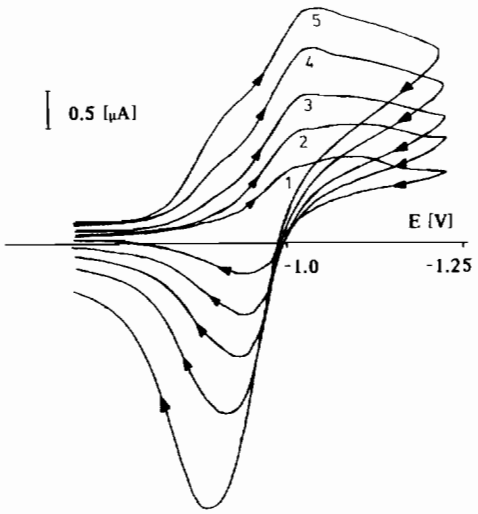

Fig. 5. Cyclovoltammograms of 1.8×10^{-3} M *trans*-[Cr(cyclam)$(H_2O)_2]^{3+}$ in 0.5 M $NaClO_4$ at pH 2.9 at HMDE vs. SCE; at room temperature; scan rates: curves 1 to 5: 10, 20, 40, 80, 160 mV s^{-1}.

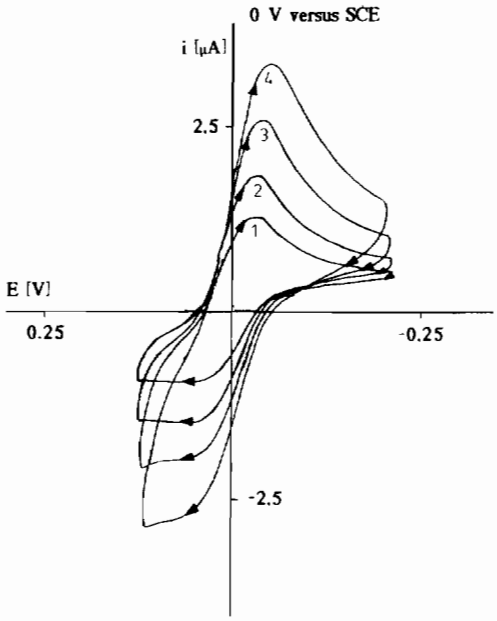

Fig. 6. Cyclovoltammograms of 1.5×10^{-3} M *trans*-[Cr(tmc)$(OH)_2]^{+}$ in 0.5 M $NaClO_4$ at pH 7.9 at HMDE vs. SCE at room temperature; scan rates: curves 1 to 4: 20, 40, 80, 160 mV s^{-1}.

They showed the features typical for *cis*-diacido tetraammine Cr(III) complexes, i.e. two ligand field bands with higher absorptivities. The dichloro tmc complex showed maxima at 570 and 410 nm. Its long wavelength band was shifted 41 nm to the red with respect to *cis*-[Cr(cyclam)$Cl_2]^{+}$ [13]. Traces of water brought back the *trans* complexes.

Spectral characterisation

The typical NH vibrations at 3200, 1600, 1200 and 860–890 cm^{-1} were absent in the spectra of all tmc complexes. The UV–Vis absorption spectra showed a large bathochromic shift on methylation (Fig. 3, Table 1). The energy separation between the low frequency bands of the *trans* tmc and the corresponding cyclam complexes increased with increasing ligand field strength of the axial ligands. We interpret this effect as evidence for the weakening of the axial bonds. Since all studied tmc complexes had axial ligands lower in ligand field strength than tmc, the lowest spin allowed ligand field bands have to be assigned to the $^4B_{1g}$–$^4E_g(D_{4h})$ transition and the following bands to the $^4B_{1g}$–$^4B_{2g}(D_{4h})$ transition. According to theory [36, 37], the position of the latter bands should remain constant, if the axial ligands are changed. The maximum variation within the tmc series of Table 1 is 2.7×10^3 cm^{-1}, whereas the analogous cyclam complexes did not vary by more than 0.7×10^3 cm^{-1}. It seems the axial ligands affect the ring geometry via interaction with the methyl groups.

The luminescence intensity of the tmc complexes is similar to that of the unsubstituted cyclam complexes (Fig. 4). However, the intensity pattern is different. The 0–0 band is the most intense band in *trans*-[Cr(cyclam)$(H_2O)_2]^{3+}$. This fact agrees with the results of Forster and Mønsted [25], but is not in accord with

TABLE 3. Redox potentials for *trans*-chromium(III) cyclam and *trans*-chromium(III) tmc complexes (vs. SCE at room temperature)

X	*trans*-[Cr(cyclam)(X)$_2$]$^{n+}$			*trans*-[Cr(tmc)(X)$_2$]$^{n+}$		
	E_{redox} (V)	$E_{ox}-E_{red}$[c] (V)	i_{ox}/i_{red}	E_{redox} (V)	$E_{ox}-E_{red}$[c] (V)	i_{ox}/i_{red}
$-(H_2O)_2$	−0.900[a]	0.110	0.78	+0.250[a,d]	0.080	0.98
$-(H_2O)(OH)$	−0.960[a]	0.150	0.63	+0.115[a]	0.080	0.97
$-(F)_2$	−0.970[b]	0.250	0.5	+0.045[a]	0.080	0.97
$-(Br)_2$	−0.975[b]	0.090	0.68			
$-(Cl)_2$	−0.985[b]	0.090	0.69	+0.020[a,e]	0.080	0.95
$-(OH)_2$	−1.048[a]	0.170	0.48	+0.020[a]	0.080	0.95
$-(CN)_2$	−1.360[b]	0.230	0.33			

[a]0.5 N sodium perchlorate. [b]0.5 N potassium perchlorate. [c]Scan rate 20 mV/s. [d]Determined at a gold electrode. [e]Corresponds to *trans*-[Cr(tmc)(OH)$_2$]$^+$.

TABLE 4. Polarographic data for chromium(III) amine complexes in 0.5 N KCl vs. SCE at room temperature

Complex[a]	E_{red} (V)[a]	c (M)×10^{-3}	i (A)×10^{-6}	i/c (A/M)
$(NH_3)_6^{3+}$	−1.02	3.1	5.3	1.7
$(en)_3^{3+}$	−1.27	2.6	4.65	1.8
$(tn)_3^{3+}$	−1.10	1.5	2.4	1.7
$(pn)_3^{3+}$	−1.29	1.6	3.02	1.9
$(chxn)_3^{3+}$	−1.27	2.1	4.2	2.0
$(ditn)_2^{3+}$	−1.22	1.7	2.8	1.7
$(en)_2(NH_3)_2^{3+}$	−1.24	2.1	4.04	1.9
$(en)_2(meam)_2^{3+}$	−1.24	1.9	3.36	1.8
$(en)_2(CN)_2^{+}$	−1.46	3.2	6.1	1.9
$(en)_2(NCS)_2^{+}$	−1.14	1.7	3.14	1.8
$(tn)_2(NH_3)_2^{3+}$	−1.15	0.9	1.58	1.8
$(tn)_2(meam)_2^{3+}$	−1.15	1.1	2.02	1.8
$(tn)_2(en)^{3+}$	−1.17	1.7	2.82	1.7
$(pn)_2(en)^{3+}$	−1.24	1.6	3.2	2.0

[a]Abbreviations: en: 1,2-diaminoethane, tn: 1,3-diaminopropane; pn: 1,2-diaminopropane; chxn: diaminocyclohexane; ditn: bis(3-aminopropylamine); meam: methylamine.

expectations for D_{4h} symmetry. Forster [38] assumed that skeletal distortions caused by hydrogen bonding between coordinated water and the solvent are responsible for the discrepancy. On the other hand, the analogous tmc complex has the vibronic sidebands more intense than the 0–0 band. The tmc complex has the interactions with the solvent reduced due to the shielding by the methyl groups; its spectrum agrees with D_{4h} symmetry. In this case the axial water molecules must occupy equivalent positions. If all four methyl groups were situated on the same side of the metal nitrogen plane, the water molecules would not be equivalent. We therefore assume a structure with two methyl groups on each side of the equatorial plane, i.e. *trans*(III) stereochemistry according to Bosnich *et al.* [39].

Table 2 presents the UV band maxima of the tmc complexes. We also included those of the cyclam complexes that we studied electrochemically, because their bands have not been reported before. The short wave bands have to be assigned to charge transfer transitions on account of their intensities. They are almost not shifted by methylation. The bands at longer wavelength could be assigned to the third ligand field bands ($^4A_{2g}$–$^4T_{1g}$[b] in O_h) on account of their lower intensities. However, they do not follow the spectrochemical series. Therefore, it is more reasonable to assign them to the weak πe_u–$b_{2g}(D_{4h})$ transitions [36] or to outer sphere charge transfer bands.

Electrochemistry

Cyclovoltammograms (CV) at different scan rates (Figs. 5 and 6) showed that the electrode reaction was diffusion controlled for the tmc complexes. The peak to peak differences and the ratio between the cathodic and anodic peak currents (Table 3) proved the tmc complexes to be reversible. The cyclam complexes with exception of the fluoro and the cyano complexes may be regarded as quasireversible ($\Delta E \leqslant 0.17$ V).

The number of transferred electrons was determined by comparing the cathodic peak currents with that of *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane nickel(II), where one electron reduction had been established [1]. The chromium peak currents were identical within 10% experimental error with that of a Ni(II) complex solution of the same concentration. Thus, one electron is transferred to Cr(III) in the electrode reaction.

The most striking effect of N-methylation is the shift of the redox potential to more positive values by more than 1 V. The CV data also indicate a correlation with the ligand field strength of the chromium(III) complexes. Since Cr(II) complexes with open chain polyamines or monodentate ligands are labile yielding Cr^{2+}_{aq} within one voltammetric cycle, we used the polarographic half

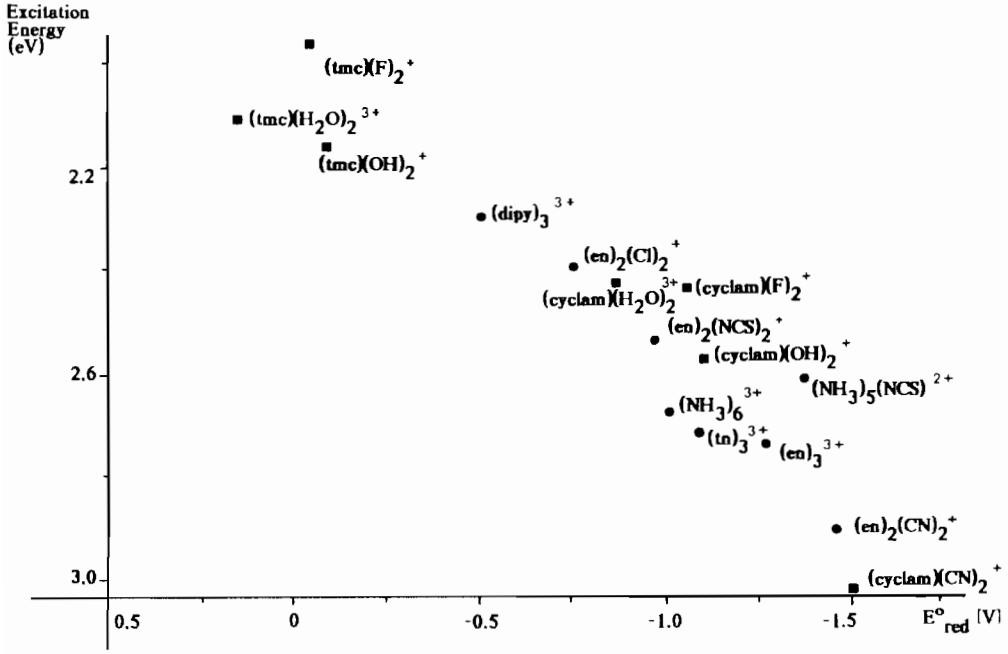

Fig. 7. Reduction potentials (vs. SCE) of various chromium amine complexes as function of the energies of the lowest quartet transitions: ■, redox potentials determined by cyclovoltammetry; ●, polarographic half wave potentials (for abbreviations see Table 4).

TABLE 5. Temperature dependence of the redox potentials and thermodynamic parameters of the reduction processes

trans-[Cr(cyclam)$(H_2O)_2$]$^{3+}$		*trans*-[Cr(cyclam)$(OH)_2$]$^{+}$		*trans*-[Cr(tmc)$(OH)_2$]$^{+}$	
Temperature (K)	E_{redox} (mV)	Temperature (K)	E_{redox} (mV)	Temperature (K)	E_{redox} (mV)
290	−850	299	−1030	285	10
296	−855	307	−1035	291	5
309	−865	314	−1060	296	5
313	−870	320	−1080	304	0
317	−875	324	−1100	311	−5
323	−880	328	−1110		
ΔS (J K^{-1} mol^{-1})	88±18		201±42		53±8
ΔG (kJ mol^{-1})	110±22		124±25		21±4
ΔH (kJ mol^{-1})	136±27		184±37		37±7

wave potentials to study the relation between the electrochemical reduction and the spectroscopic parameters. The obtained data are presented in Table 4 and compared with the energy of the first ligand field bands in Fig. 7. They span a potential range >1.5 V. Within this range the reduction potentials correlate with the excitation energy. When only a few complexes were studied, such correlations have been observed before [40, 41]. However, an extended series of cobalt(III) and rhodium(III) ammine complexes did not correlate [42, 43]. A linear correlation between the polarographic half wave potentials and the energies of the first ligand field bands may not necessarily be expected, because any effect that changes all orbitals equally will not affect the optical transitions but may well affect the electrochemical parameters. For instance, Fig. 7 also shows that the higher charged complexes are more easily reduced, whereas the ligand field strength does not depend upon the complex charge.

The fact that a correlation is observed in the chromium amine series indicates that ligand field stabilization effects are operative. The observed correlation may be understood, if the reduction fills the vacant e_g orbitals, which increase in energy with increasing ligand field strength. However, the same argument would also hold for the Co(III) series, where no correlation exists. On the other hand Cr(III) can further fill up its t_{2g} orbitals, as Vlček suggested [44]. This mechanism, however,

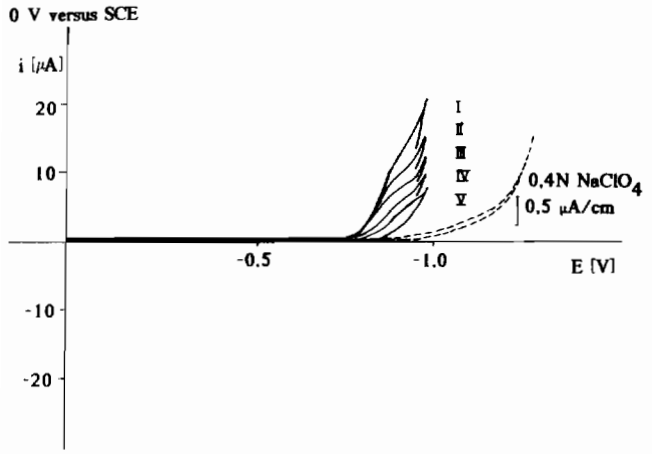

Fig. 8. Cyclovoltammograms of 11.5×10^{-3} M *trans*-$[Cr(cyclam)(H_2O)_2]^{3+}$ on addition of nitrate in 0.5 M $NaClO_4$ at HMDE vs. SCE at room temperature; scan rate 20 mV s^{-1}; curves I to V: 5×10^{-2}, 4×10^{-2}, 3×10^{-2}, 2×10^{-2}, 1×10^{-2} M NO_3^-.

implies that the t_{2g} orbitals are raised in energy with increasing ligand field strength.

Table 3 further shows that for a given ligand L the aquo complexes are the ones that are most easily reduced. They are also not affected by axial substitutions in aqueous solution (except by solvent exchange). We decided to study these two complexes and their conjugate bases in more detail. Potentiometric pH-titration of $[Cr(tmc)(H_2O)_2]^{3+}$ yielded pK_a values of 3.3 and 6.8. They are somewhat higher than the corresponding values of the cyclam complex [13] (3.05 and 6.6). At pH 4.2 the predominate species are the monoaquo–monohydroxo complexes, of which the redox potentials could be measured.

The temperature dependence of the redox potential was determined for *trans*-$[Cr(cyclam)(OH)_2]^+$, *trans*-$[Cr(tmc)(OH)_2]^+$ and *trans*-$[Cr(cyclam)(H_2O)_2]^{3+}$. The aquo tmc complex could not be reduced at the mercury electrode on account of its too positive reduction potential. The data are shown in Table 5 together with the thermodynamic parameters. The lower reaction entropy of the N-methylated cyclam is in accord with the difference in solvation. The hydrophobic alkyl groups reduce the degree of solvation. The decrease in charge that occurs when the complex is reduced cannot liberate so many water molecules as from the stronger solvated cyclam complexes. The effect has been used to explain the stabilization of the lower oxidation state in tmc complexes [1, 2, 11]. However, the more positive reaction entropy favours the reduction of the cyclam complexes. It is the smaller ΔH value of the tmc complexes that compensates the entropy effect.

Electrocatalysis of nitrate reduction

Despite the technical importance of nitrate, there are only rather few compounds that can act as electrocatalysts for the reduction [45] of NO_3^-. Among those cyclam complexes of Co(III) and Ni(II) have been found useful [46]. Therefore it seemed reasonable to check whether chromium cyclam complexes may be active. Figure 8 shows cyclovoltammograms of solutions containing varying concentrations of nitrate in the presence of *trans*-$[Cr(cyclam)(H_2O)_2]^{3+}$. The reduction current of the chromium complex increases with increasing nitrate concentrations and the reoxidation wave of the chromium(II) complex is completely suppressed. Nitrate itself could not be reduced electrolytically at potentials more positive than -1.3 V, where the supporting electrolyte started to be reduced. A solution containing 1×10^{-2} M NO_3^- produced a current of only 0.02 μA at -0.80 V in the absence of the chromium complex, whereas in the presence of 1.15×10^{-3} M *trans*$[Cr(cyclam)(H_2O)_2]$ perchlorate the current was 7.5 μA. The reduction current of the chromium complex in the absence of nitrate was 0.25 μA. The fact that the catalytic activity coincided with the reduction peak of the chromium complex and that the reoxidation peak disappeared on addition of nitrate shows that the *trans*-$[Cr(cyclam)(H_2O)_2]^{3+}$ ion was the electrocatalytic species. The first reduction product of nitrate is probably NO_2^- as with Co and Ni cyclams as catalysts [46].

Conclusions

The data showed that chromium(II) is thermodynamically stabilized on N-methylation. The hydrophobic alkyl groups shield the central ion, so that the chromium tmc complexes are not demetalated in aqueous solution. This group of compounds seems promising for use as redox catalysts.

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