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**Inorganica
Chimica Acta**

Inorganica Chimica Acta 228 (1995) 153–158

Mercury(II)-promoted formation and aquation of linkage isomers of *trans*-dicyanotetraamminechromium(III). A polarographic and spectral study

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Received 30 March 1994; revised 6 June 1994

Abstract

Polarography and spectrophotometry reveal various interactions between *trans*-Cr(NH₃)₄(CN)₂⁺ and Hg²⁺ in acidic aqueous solution. There is evidence for formation of two trinuclear adducts with Cr:Hg proportions of 2:1 and 1:2, accompanied by linkage isomerization (Cr–NC–Hg) of the cyanide bridging groups. These processes are followed by Hg²⁺-induced aquation of CN⁻. The six Cr(III) species occurring in the reaction sequence are identified by their half-wave reduction potentials. The *trans* configuration of the final aquation product, Cr(NH₃)₄(H₂O)₂³⁺, indicates complete stereoretention during all the reactions, consistent with the observed stoichiometry of Cr–Hg association which differs from that of a *cis*-dicyano analogue. The linkage isomerization of *trans*-Cr(NH₃)₄(CN)₂⁺ is much faster than that of *trans*-Cr(NH₃)₄(H₂O)(CN)₂²⁺, while the rates of the respective Hg²⁺-promoted aquation reactions are the same, denoting *trans* effects of CN⁻ in the former process but not in the latter.

Keywords: Polarography; Aquation; Chromium complexes; Ammine complexes; Cyano complexes

1. Introduction

Formation of adducts between chromium cyano complexes and either Ag⁺ or Hg²⁺ ions is known to be accompanied by linkage isomerization of the cyanide bridging groups [1]. The phenomenon has been extensively investigated with various monocyano species: Cr(H₂O)₅(CN)₂²⁺ [2–4], Cr(H₂O)₄(NO)(CN)⁺ [5–8] and, more recently, Cr(NH₃)₅(CN)₂²⁺ [9]. Analogous studies have been performed on dicyano species such as *cis*-Cr(H₂O)₄(CN)₂²⁺ [4], *cis*-Cr(H₂O)₃(NO)(CN)₂ [10] and *cis*-Cr(en)₂(CN)₂⁺ [11–13]; these systems, however, are somewhat entangled by the larger variety of oligonuclear compounds potentially obtainable. An additional difficulty arising with *cis*-type complexes is that the two metals may associate through either single [12] or double [4,11] bridges. The latter circumstance is not incurred with *trans*-dicyano complexes. In view of this difference, and following previous work where polarography proved successful in characterizing the various Cr moieties involved [6,7,9], we have obtained elec-

trochemical as well as spectrophotometric information on the multiple interactions of *trans*-Cr(NH₃)₄(CN)₂⁺ with mercuric ion in aqueous solution.

2. Experimental

Trans-[Cr(NH₃)₄(CN)₂]ClO₄ and *trans*-[Cr(NH₃)₄(H₂O)(CN)](ClO₄)₂ were synthesized by published methods [14]: their purity was confirmed by analysis of Cr and CN⁻ and by the UV–Vis absorption spectra which agreed with previously reported data [15]. Solutions of Hg(ClO₄)₂ were prepared by treating mercuric oxide with a small excess of perchloric acid. All other reagents were of analytical grade. Triply-distilled water was employed for the electrochemical measurements. Chromium and cyanide were determined by spectrophotometry and polarography, respectively, as already described [9].

Potentiometry made use of an OP-205 potentiometer (Radelkis, Budapest) and a hanging mercury drop electrode, with a saturated calomel electrode (SCE) as reference, connected by a 1 M NaNO₃ salt bridge.

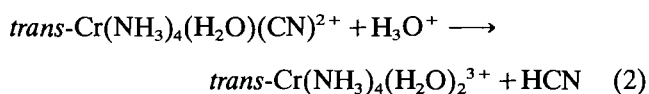
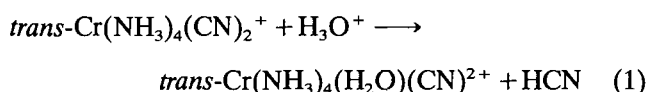
* Corresponding author.

Polarographic measurements were carried out on a PA 4 polarograph (Laboratorní přístroje, Praha); the dropping mercury electrode had a flow rate of 1.65 mg s^{-1} and a drop time of 4.3 s at a reservoir height of 64 cm and in a short circuit with a SCE. Rapid-scan spectra were recorded by a Hewlett-Packard 8452A diode-array instrument. Rate constants were evaluated by computerized non-linear regressions on at least 50 absorption data points.

3. Results and discussion

3.1. Polarography of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ and its aquation products

In acid solution, *trans*-dicyanotetraamminechromium(III) is known [15] to undergo stepwise, acid-assisted aquation of the CN^- ligands with complete stereo-retention.



Step (1) is faster than step (2) by 3 orders of magnitude [16], so that polarographic characterization of the dicyano, cyanoaqua and diaqua complexes is possible at suitable reaction times. In moderately acidic medium ($[\text{H}_3\text{O}^+] = 0.01 \text{ M}$; $\mu = 1.0 \text{ M Na}^+, \text{H}_3\text{O}^+, \text{ClO}_4^-$), reduction of the three species appears as three distinct, diffusion-controlled, irreversible waves. The irreversibility is deduced from logarithmic analysis of the wave shapes [17]. The limiting currents denote exchange of one electron, being comparable with that for the one-electron polarographic reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The values of the half-wave potentials, $E_{1/2}$ versus SCE, are reported in Table 1 (waves 1, 4 and 6, respectively). In conformity with a trend recognizable when simple ligands are coordinated, the reducibility of Cr(III) decreases with increasing number of CN^- groups, i.e. with increasing ligand-field stabilization [18,19].

Table 1

Polarographic half-wave potentials of the Cr(III) species occurring in aqueous solutions of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ in the presence of Hg^{2+} *

Wave	Parent species	Electroactive species	$E_{1/2}$ (V vs. SCE)
1		$\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$	-1.15
2	$[(\text{NC})\text{Cr}(\text{NH}_3)_4(\text{NC})]_2\text{Hg}^{4+}$	$\text{trans-Cr}(\text{NH}_3)_4(\text{CN})(\text{NC})^+$	-0.80
3	$\text{Hg}(\text{CN})\text{Cr}(\text{NH}_3)_4(\text{NC})\text{Hg}^{5+}$	$\text{trans-Cr}(\text{NH}_3)_4(\text{NC})_2^+$	-0.65
4		$\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$	-0.98
5	$\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})\text{Hg}^{4+}$	$\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})^{2+}$	-0.74
6		$\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	-0.82

* $[\text{H}_3\text{O}^+] = 0.01$; ionic strength: 1.00 M ($\text{ClO}_4^-, \text{Na}^+, \text{H}_3\text{O}^+, \text{Hg}^{2+}$); $t = 25^\circ \text{C}$.

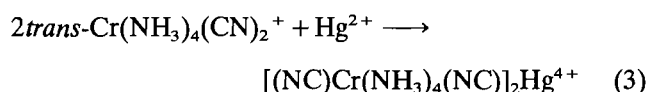
3.2. Interaction of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ with Hg^{2+}

Under the above-mentioned conditions, addition of mercuric ion to the dicyano complex brings about considerably rapid changes. Electrochemistry provides information as to the stoichiometry of such an interaction.

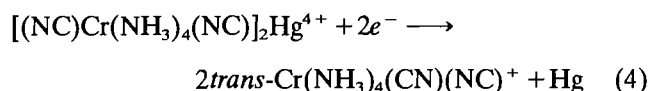
The potentiometric titration curve exhibits its inflection at a molar ratio of Hg^{2+} to $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ equal to 0.5. As noted in similar instances [4,5,9], the reaction is not instantaneous: in the present case, steady potential readings were reached 15–20 s after Hg^{2+} mixing at room temperature. Interference of the subsequent, slower aquation of the Cr–Hg adduct ultimately leading to $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ (vide infra), was avoided by separately obtaining each titration point from fresh reactants.

Polarograms show that wave 1 of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ (Fig. 1, curve a) gradually drops on adding Hg^{2+} , to completely disappear when $[\text{Hg}^{2+}]:[\text{Cr}] = 0.5$.

These results indicate formation of a stable trinuclear compound with a Cr:Hg ratio of 2:1. In the light of previous experience with $\text{Cr}(\text{H}_2\text{O})_5(\text{CN})^{2+}$ [4] and $\text{Cr}(\text{NH}_3)_5(\text{CN})^{2+}$ [9], the reaction is envisaged in terms of immediate Cr–Hg association, followed by $\text{CN} \rightarrow \text{NC}$ isomerization about Cr: the rearrangement would be responsible for the gradual reaching of equilibrium in the titration reaction:



All over the negative potential region relative to SCE, Hg^{2+} bound in the trinuclear adduct is polarographically reducible:



The two-electron reduction of complexed Hg(II), in fact, occurs around 0 V versus SCE. Owing to distortion by current maxima, no useful indication can be drawn

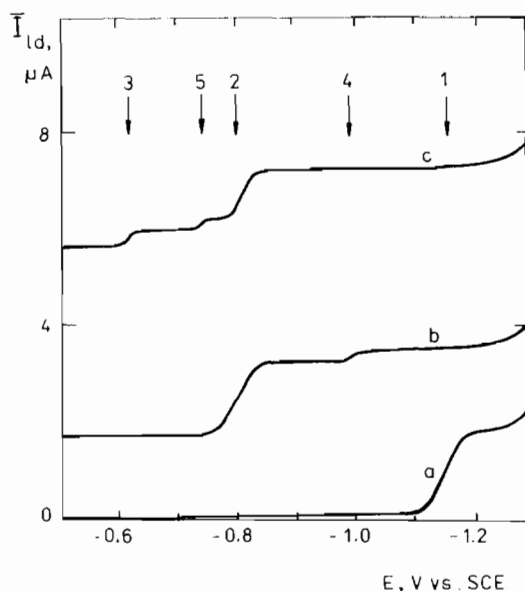
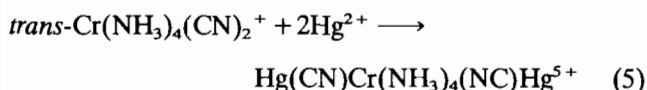


Fig. 1. Schematic representation of the polarographic behavior of aqueous 1.00 mM $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ in 0.01 M HClO_4 ; $\mu = 1.00$ M (ClO_4^- , Na^+ , H_3O^+ , Hg^{2+}); $t = 25$ °C. Waves: a, before Hg^{2+} addition; b, after addition of 0.5 mM Hg^{2+} ; c, after addition of 2.0 mM Hg^{2+} . See Table 1 for the assignment of half-wave reduction potentials 1–5.

from the shape analysis of this wave. Such maxima, however, do not interfere with the limiting currents at potentials more negative than -0.35 V versus SCE: consequently, the cathodic current of $\text{Hg}(\text{II})$ makes up the background for curves b and c (Fig. 1) recorded following addition of mercuric salt. Wave 2 of curve b, developing at a less negative potential while wave 1 of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ disappears, is ascribed to the one-electron reduction of the less stable $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})(\text{NC})^+$ linkage isomer released at the electrode by reaction (4). Up to this stage, the electrochemical behavior is quite similar to that we observed earlier in the $\text{Cr}(\text{NH}_3)_5(\text{CN})^{2+}/\text{Hg}^{2+}$ system [9]. No differences are noticed when $[\text{Hg}^{2+}]:[\text{Cr}]$ is increased from 0.5 to 1.0.

With a two-fold molar excess of Hg^{2+} (Fig. 1, curve c), wave 2 is still present as the major feature, being accompanied by wave 3 at an even less negative $E_{1/2}$; the latter is attributed to reduction of $\text{trans-Cr}(\text{NH}_3)_4(\text{NC})_2^+$ (with both cyanides N-linked to Cr). The simplest explanation for this occurrence is that at higher Hg^{2+} proportions, besides the adduct of Eq. (3), another adduct is partially formed with a Cr:Hg ratio of 1:2.



Formation of the same compound at the expense of $[(\text{NC})\text{Cr}(\text{NH}_3)_4(\text{NC})]_2\text{Hg}^{4+}$ cannot be ruled out in principle.

Polarograms b and c are complicated by two additional waves, 4 and 5, which increase at longer times after full growth of waves 2 and 3. These reductions are assigned to the products of Hg^{2+} -induced aquation of the cyano-isocyano and di-isocyano isomers, respectively: $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$ (4, curve b) and $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})^{2+}$ (5, curve c). The $E_{1/2}$ value of wave 4 is actually the same as that of the first-step product of acid hydrolysis (Eq. (1)). A plausible assignment of wave 5 then follows by exclusion.

All possible combinations of cyano, isocyano and aqua ligands are thus polarographically identified. The half-wave potentials are listed in Table 1. It is seen that the stabilities of the various complexes are related to the sequence: $\text{CN}^- > \text{H}_2\text{O} > \text{NC}^-$. The same order has already been found in the pentaqua [4] and pentaammine systems [9]. Naturally, the isocyano isomers are the less stable when liberated in situ by reduction of $\text{Hg}(\text{II})$ bound in the adducts, that is, upon removal of the soft-acid/soft-base Hg–C interaction that lends stability to the Cr–NC bonding mode.

It is interesting to compare the present stoichiometry with that of analogous interactions of *cis*-dicyano complexes [4,10,11,13]. These were found to form 1:1 Cr–Hg adducts, in contrast with the 2:1 and 1:2 compositions encountered here. The 1:1 proportion was related to formation of double Cr–NC–Hg bridges resulting in six-membered rings. Such a kind of bridging, of course, cannot be expected with a *trans* arrangement of the CN groups about Cr, which only allows formation of linear assemblies like either Cr–NC–Hg–CN–Cr or Hg–CN–Cr–NC–Hg.

The lack of any inflection on the potentiometric titration curve in correspondence of a 1:1 reactant ratio is also in accord with the absence of dinuclear species.

3.3. Absorption spectra

Spectrophotometry validates the formulations inferred from the electrochemical experiments. In the presence of Hg^{2+} , the ligand-field bands of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ are, in general, displaced to the red. For each $[\text{Hg}^{2+}]$, the variations take place in two distinct time domains. An initial fast change, accompanied by an intensification of the long-wavelength band, is observed within the first 15 s, that is the same time lapse required to obtain stable potentials in the titration. The successive, slower evolution, consisting of a further red shift and a progressive decrease in absorption, is complete in 4–5 h at 25 °C.

In the first stage, the band position corresponding to attainment of the highest optical density moves until $[\text{Hg}^{2+}]:[\text{Cr}] = 0.5$; above this proportion, such maxima remain essentially constant. In all cases, isosbestic points persist during this interval. In the course of the second stage, the isosbestic behavior is generally lost, indicating overlap of several processes, as polarography suggests.

It is notable that, regardless of the evolution, the final spectrum for $[\text{Hg}^{2+}]:[\text{Cr}] \geq 0.5$ coincides with that of $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$, which is unmistakably different from its *cis* counterpart [20]: this demonstrates that the *trans* configuration is retained throughout all the reactions considered, as is generally true for Cr(III) substitutions in aqueous media.

The spectrum recorded at the end of the fast process (virtually invariant over the ensuing 30 s) is shown in Fig. 2 (curve 2), and its maxima are given in Table 2. That this absorption identifies the isomerized $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})(\text{NC})^+$ moiety is strongly supported by comparison with the data of $\text{Cr}(\text{NH}_3)_5(\text{CN})^{2+}$ [21] (Table 2): the likeness of the two spectra is indeed congruent with conversion of the initial CrN_4C_2 chromophore to CrN_5C .

No information of this kind was obtainable on the presumed $\text{trans-Cr}(\text{NH}_3)_4(\text{NC})_2^+$ moiety with maxima predictable at still longer wavelengths. This failure is

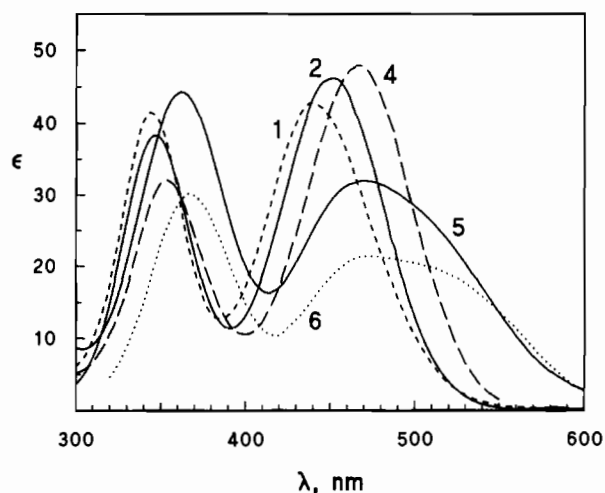


Fig. 2. UV-Vis absorption spectra in acidic aqueous solution. 1, $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$; 2, $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})(\text{NC})^+$ moiety; 4, $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$; 5, $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})^{2+}$ moiety; 6, $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$.

Table 2
Ligand-field absorption spectral data in acidic aqueous solution

Chromophore	Absorption maxima (nm) ^a	Reference
$\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$	440 (42.6) 344 (41.5)	[15]
$\text{trans-Cr}(\text{NH}_3)_4(\text{CN})(\text{NC})^+$ ^b	452 (46) 347 (38)	this work
$\text{Cr}(\text{NH}_3)_5(\text{CN})^{2+}$	451 (42.6) 347 (37.7)	[21]
$\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$	468 (48.0) 354 (32.2)	[15]
$\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})^{2+}$ ^c	475 (32) ^d 360 (44)	this work
$\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	480 (35.1) 359 (30.3)	[22]
$\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	476 (20.6) 368 (29.7)	[20]

^a Extinction coefficients ($\text{M}^{-1} \text{cm}^{-1}$) in parentheses.

^b Solutions with $[\text{Hg}^{2+}]:[\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+] \geq 0.5$, ~15 s from mixing at 25 °C.

^c Calculated (see text).

^d ± 5%.

ascribed to the limited occurrence of $\text{Hg}(\text{CN})\text{Cr}(\text{NH}_3)_4(\text{NC})\text{Hg}^{5+}$ even at $[\text{Hg}^{2+}]:[\text{Cr}] = 6$, coupled with a slower formation of this second adduct (not unlikely in consideration of the 1–2 min timescale for the fast reaction of $\text{Cr}(\text{NH}_3)_5(\text{CN})^{2+}$ [9]), which would make it spectrally indiscernible from the competing, incipient aquation of the principal adduct.

In order to characterize the $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})^{2+}$ isomer, the same types of measurements were made starting from pure $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$. Again, the spectral sequence is suggestive of at least two stages and terminates with $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$. The first stage (associated with a marked growth of the short-wavelength band which successively decreases) is much slower than in the case of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$. The rate constants for sequential linkage isomerization and CN^- aquation were evaluated as described below, allowing an estimate of the time concentrations of the three species involved. The spectrum of the isocyanoaqua intermediate was then obtained from the experimental absorption curves and the (known) spectra of the cyanoaqua and diaqua complexes. Several fittings performed at various early reaction times (when the amounts of the diaqua species are only a few percent) were concordant within ± 1.5 ϵ units. The result is included in Fig. 2 (curve 5) and the maxima are compared in Table 2 with those of the $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ model compound [22]. While the correspondence of the short-wavelength maximum is consistent with CrN_5O coordination, the agreement of the long-wavelength one is apparently less satisfactory. It should be kept in mind, though, that in tetragonal complexes this band is actually split into two components, the different intensities of which may affect the maximum position of the resulting broad absorption. The band in question is, in fact, rather asymmetric. This effect is even more pronounced in $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ (Fig. 2), the long-wavelength feature of which is not in line with the general trend of Table 2.

3.4. Bulk generation and back isomerization of isocyano species

Attempts were made to obtain the 'free' isocyano complexes by bulk-phase electrolysis (coulometry) of the adduct(s). However, steady-state amounts of these isomers were undetectable during the experiment, implying an exceedingly large rate of $\text{NC} \rightarrow \text{CN}$ retroisomerization.

Another way to detach Hg^{2+} from the isomerized complexes is treatment with excess iodide, which binds mercury in the highly stable HgI_4^{2-} ion and yields the maximum concentration of free Cr–NC species within the time of mixing. Also in this instance, conversion

to the stable Cr–CN forms was too fast to be followed polarographically, in spite of its measurability in analogous work with $\text{Cr}(\text{H}_2\text{O})_4(\text{NO})(\text{CN})^+$ [8].

Fast-sequence absorption spectra confirm this conclusion. Addition of I^- to a solution of the adduct ($[\text{Hg}^{2+}]:[\text{Cr}] \geq 0.5$) 15 s after Hg^{2+} mixing (when the band at 452 nm has fully developed), is followed by prompt (< 1 s) restoration of the maximum of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ at 440 nm (the short-wavelength band is hidden by the strong absorption of HgI_4^{2-}).

Similarly, in the $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}/\text{Hg}^{2+}$ system, I^- addition at various times (100–300 s from mixing) immediately brings back the spectrum close to its original shape, showing that the initial evolution is actually caused mainly by linkage isomerization of CN^- .

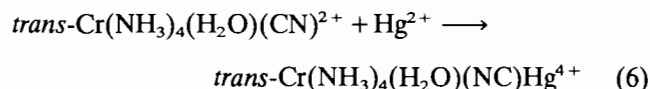
The interaction with iodide was helpful in assigning polarographic waves 2, 3 and 5 (Table 1), believed to pertain to isocyano compounds. In the presence of I^- these waves disappear with total recovery of waves 1 and 4 corresponding to the $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ and $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$ parent complexes.

3.5. Reaction rates

Kinetics was beyond the scope of this work mainly devoted to the polarographic and spectral properties, and a complete study would probably be hampered by the high complexity of the system. Nevertheless, semi-quantitative information could be gathered on some of the processes in 0.01 M acid at 25 °C.

The rate of linkage isomerization of one CN^- group in $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ was estimated spectrophotometrically from the initial growth of the 452 nm band (Fig. 2, curve 2). First-order fittings gave better results than second-order fittings, although the stoichiometry of Eq. (3) would suggest bimolecular involvement of the Cr(III) absorbing species. In any case, the data are taken as no more than empirical indicators of the relative magnitude of this reaction. Several runs for $[\text{Hg}^{2+}]:[\text{Cr}] = 0.5\text{--}2.0$ averaged $k_3 = 0.33 \pm 0.08 \text{ s}^{-1}$, with no apparent trend on varying the Hg:Cr ratio.

The CN^- isomerization rate of $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$ was likewise evaluated from the initial spectral changes (up to ~ 1 half-life) consequent to Hg^{2+} addition to the isolated cyanoaqua complex and assumed to be due to:

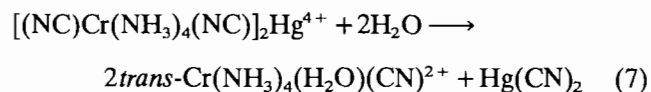


Eq. (6) may represent a stoichiometric oversimplification since bimolecular association cannot be excluded; yet, the variations were reproduced much better by a first-order rate law in this case also. A number of measurements at various wavelengths, among which the crossing point (550 nm) between $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})$ -

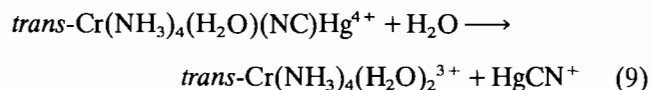
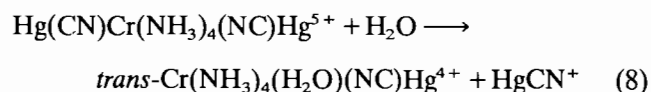
$(\text{NC})^{2+}$ and $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$, gave $k_6 = (5.5 \pm 1.0) \times 10^{-3} \text{ s}^{-1}$.

Though approximate, the k_3 and k_6 values reveal a considerable difference between the proneness to linkage isomerization of $\text{trans-Cr}(\text{NH}_3)_4(\text{CN})_2^+$ and $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$. The higher reactivity (~ 60 -fold) of the trans -dicyano complex clearly denotes a trans labilizing effect of cyanide, which parallels the effect previously noted in the H_3O^+ -assisted aquation of the same compounds (Eqs. (1) and (2)) [16] and, more significantly, in that of the trans/cis -dicyanotetraammine pair [15]. The latter more direct comparison is not possible here because of the lack of rate data on Hg^{2+} -induced isomerization of cis -dicyanochromium(III) species. However, additional evidence for the present trans effect is provided by the slower rearrangement ($k \sim 1.5 \times 10^{-2} \text{ s}^{-1}$) of another monocyano complex, $\text{Cr}(\text{NH}_3)_5(\text{CN})^{2+}$, under the same conditions [9].

Loss of $\text{Hg}(\text{II})$ -bound CN^- may proceed through various reactions. A likely process, implied by the electrochemical findings, is decomposition of the 2:1 adduct:



and may well take place in two steps. Other conceivable reactions are:



The $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NC})\text{Hg}^{4+}$ adduct can also arise from combination of free Hg^{2+} with $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})^{2+}$, generated by either reaction (7) or competition of reaction (1) with reaction (3), although in 0.01 M acid this competition is quite negligible. Formation of the diaqua end product mainly through path (9) is suggested by the fact that aquation is complete in ~ 5 h, whereas the half-life for acid hydrolysis of the cyanoaqua complex at $[\text{H}_3\text{O}^+] = 0.01$ and 25 °C is ~ 55 h [16].

Despite its occurrence in a complicated context, the disappearance of $\text{Hg}(\text{CN})\text{Cr}(\text{NH}_3)_4(\text{NC})\text{Hg}^{5+}$ (Eq. (8)) could be monitored polarographically by the time dependence of the height of wave 3. The electrochemical technique proved especially advantageous in this spectrophotometrically unfavorable situation. The decrease of the wave was found to be consistent with first-order kinetics. In the concentration range $[\text{Hg}^{2+}]:[\text{Cr}] = 2\text{--}4$ and $[\text{H}_3\text{O}^+] = 0.01\text{--}1.0$, the rate constants are independent of both $[\text{Hg}^{2+}]$ and $[\text{H}_3\text{O}^+]$ within error limits,

and the average value is $k_8 = (2.0 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$. The acid independence is in agreement with the behavior of other Cr–NC–Hg systems [5,9,10,13] in which loss of the CN bridging groups is not affected by H_3O^+ catalysis, since proton bonding is inhibited by the more stable mercury bonding. The impossibility of protonation of both coordinated cyanides further supports the assignment of wave 3.

The measurement of the aquation rate of *trans*-Cr(NH₃)₄(H₂O)(NC)Hg⁴⁺ was based on the spectrally plausible hypothesis that reaction (9) follows reaction (6) upon mixing pure *trans*-Cr(NH₃)₄(H₂O)(CN)²⁺ with Hg²⁺, and was carried out as follows. Excess iodide was added to a series of samples at different times after mixing, ranging from 100 to 3600 s. This caused instantaneous reconversion of the isocyanoaqua complex still present to the cyanoaqua form, so that at this point the mixtures consisted of *trans*-Cr(NH₃)₄(H₂O)(CN)²⁺ and *trans*-Cr(NH₃)₄(H₂O)₂³⁺ only. The time concentrations of the diaqua product were then calculated from the absorption spectra, and used in combination with the k_6 parameter to determine k_9 by a treatment of consecutive first-order reactions. Various runs for $[\text{Hg}^{2+}]:[\text{Cr}] \geq 1$, yielded $k_9 = (2.2 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$.

The rates of Hg²⁺-assisted aquation of the dicyano (k_8) and monocyano (k_9) complexes can be compared with the corresponding known rates (k_1 and k_2) of H₃O⁺-assisted aquation. In $[\text{H}_3\text{O}^+] = 0.01 \text{ M}$, these differ by a thousandfold: $k_1 = 4.8 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 3.5 \times 10^{-6} \text{ s}^{-1}$ at 25 °C [16], in contrast with the close values of the order of 10^{-4} s^{-1} for k_8 and k_9 . It must not be fortuitous that the analogous rate constant for Cr(NH₃)₅(NC)Hg⁴⁺ at 25 °C is again of this magnitude: $2.2 \times 10^{-4} \text{ s}^{-1}$ [9]. The indication is that the reactivity of the adducts is leveled off with respect to that of the non-associated chromium(III) species. Binding to Hg(II) evidently causes a great attenuation of the thermodynamic and kinetic *trans* effects that differentiate the rates of acid-catalyzed CN⁻ aquation of the cyanoammine complexes [16,23]: this attests to the

marked alteration of the nature of the cyanide ligand by such an association.

Acknowledgement

This research has been supported in part by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica.

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