the soluble compex into the previously described[3] insoluble $[Pd_2(bmp)Cl_4]_n$ and free ligand.

In conclusion, although it has previously been found that in many cases open-chain tetradentate ligands coordinated to square-planar palladium(II) and platinum(II) prefer to bridge between metal atoms rather than form monomers with all ligand sites coordinated, we have shown that in the absence of halide ligands a large series of open-chain tetrathioether ligands with varying backbones form monomeric $[M(S_4)]^{2+}$ species. The spectroscopic properties of these species support the premise that the 2-3-2 sequence of backbone size in open-chain tetradentates coordinated around a square plane gives the minimum of strain.

Registry No. $[Pd(2,2,2)](ClO_4)_2$, 69501-98-0; $[Pd(2,3,2)](ClO_4)_2$, 69502-00-7; $[Pd(3,2,3)](ClO_4)_2$, 69502-02-9; $[Pd(3,3,3)](ClO_4)_2$, 69502-04-1; $[Pd(bme)](ClO_4)_2$, 69502-06-3; $[Pd(bmp)](ClO_4)_2$, 57407-95-1; $[Pd(bmb)](ClO_4)_2$, 69502-08-5; $[Pt(2,2,2)](ClO_4)_2$, 69502-10-9; $[Pt(2,3,2)](ClO_4)_2$, 69502-12-1; $[Pt(3,2,3)](ClO_4)_2$, 69502-14-3; $[Pt(3,3,3)](ClO_4)_2$, 69501-84-4; $[Pt(bme)](ClO_4)_2$, 69501-86-6; $[Pt(bmp)](ClO_4)_2$, 69501-88-8; $[Pt(bmb)](ClO_4)_2$, 69501-90-2; $Pd(CH_3CN)_2Cl_2$, 14592-56-4; $Pt(CH_3CN)_2Cl_2$, 13869-38-0.

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Deamination of Tris(ethylenediamine)chromium(III) Thiocyanate

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The loss of ethylenediamine (en) from heated $[Cr(en)_3](NCS)_3$ offers the usual method of preparing *trans*-$[Cr(en)_2(NCS)_2]NCS$.[2] Rollinson and Bailar showed that the solid-state process is catalyzed by NH_4SCN.[3] The acid catalyst apparently protonates one end of a coordinated ethylenediamine molecule breaking it loose from the metal ion in the rate-determining step. Bear and Wendlandt studied this process by using thermogravimetric analysis and reported that the activation energies are 34 and 18 kcal/mol, respectively, when no catalyst is used and when NH_4SCN is present.[4] These workers reported that the presence of NH_4Br or NH_4I had no effect on the activation energy for deamination.

Considerable study has been devoted to determining kinetic information about this reaction. From isothermal weight loss studies, activation energies of about 47.4 and 33.1 kcal/mol, respectively, were determined for the uncatalyzed and catalyzed reactions.[5] An unusual feature is that deamination of $[Cr(en)_3](NCS)_3$ produces *trans*-$[Cr(en)_2(NCS)_2](NCS)$ while deamination of $[Cr(en)_3]Cl_3$ produces a cis product.[6] However, Wendlandt and Svenum have shown that heating the tris(ethylenediamine) complexes with a large excess of NH_4SCN leads to *cis*-$[Cr(en)_2(NCS)_2](NCS)$.[7] The products of these thermal matrix reactions were identified by using reflectance spectroscopy.

More recently, Akabori and Kushi[8] studied the deamination of $(+)_{589}$-$[Cr(en)_3](NCS)_3$ and $(\pm)$-$[Cr(en)_3](NCS)_3$ as catalyzed by "minute traces" of NH_4SCN. It was shown by elution chromatography that the product is *trans*-$[Cr(en)_2(NCS)_2]NCS$. Thus, the deamination reaction leads to a trans product when carried out in the presence of "small" amounts of catalyst but leads to a cis product when "large" amounts of catalyst are used.

As a part of our study of deamination reactions, it was noted that deamination of $[Cr(en)_3](NCS)_3$ in the presence of NH_4SCN or NH_4Cl lowered the activation energy but gave a different ΔH value from that when no catalyst is present.[9] We have sought to clarify this situation by using differential scanning calorimetry and thermogravimetric analysis, and this report presents results of these studies.

Experimental Section

The thiocyanate complex was prepared from $[Cr(en)_3]_2(SO_4)_3$ which was prepared by the method of Rollinson and Bailar.[10] The $[Cr(en)_3](NCS)_3$ was obtained by dissolving 100 g of the sulfate in 275 mL of warm water and adding 147 g of solid NH_4SCN. After the solution was cooled, the solid product was removed by filtration. The product was recrystallized from water, washed with alcohol and ether, and air-dried. Anal. Calcd for $[Cr(en)_3](NCS)_3 \cdot H_2O$: Cr, 12.27; C, 25.50; H, 6.13; N, 29.65; S, 22.68. Found: Cr, 12.73; C, 25.43; H, 6.13; N, 29.66; S, 22.85.

Thermal studies on the deamination of $[Cr(en)_3](NCS)_3$ were carried out by using a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. Procedures used were similar to those previously described.[11] A heating rate of 10 °C/min and a nitrogen flow rate of 30 cm^3/min were used with samples in the range of 4–6 mg. Activation energies were determined by the method of Thomas and Clarke.[12] This procedure was used to study the initial 50–60% of the reaction, and good linear plots were obtained. Heats of reaction were obtained by comparing peak areas with those of standards using the fusion of tin.

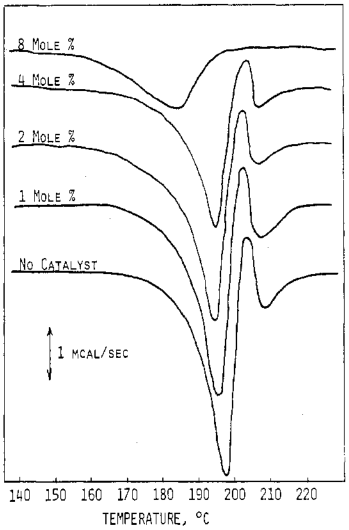

Figure 1. DSC curves for deamination of $[Cr(en)_3](NCS)_3$ containing various amounts of NH_4SCN.

Thermogravimetric curves were taken on a Perkin-Elmer thermal gravimetric system, Model TGS-2. A heating rate of 10 °C/min was used with the samples maintained in a nitrogen atmosphere.

In order to study the effect of varying the amount of catalyst, we introduced NH_4SCN by adding the desired volume of a standard solution of NH_4SCN in acetone to a weighed sample of the complex. The acetone was then evaporated under reduced pressure. Several samples of the complex containing each concentration of catalyst were studied.

Results and Discussion

Samples of $[Cr(en)_3](NCS)_3$ containing no catalyst and those containing 1.0, 2.0, 4.0 and 8.0 mol % NH_4SCN were studied by using DSC and TGA. Samples containing no NH_4SCN were actually the monohydrate, $[Cr(en)_3](NCS)_3{\cdot}H_2O$, originally, and a broad endotherm due to loss of water was seen in the range 40–90 °C. The samples containing NH_4SCN were anhydrous owing to the dehydration during catalyst addition. All samples showed an endotherm in the range 170–200 °C, corresponding to the loss of ethylenediamine. The DSC curves for the deamination are shown in Figure 1. As can be seen from the DSC curves, the large endothermic peak corresponding to deamination is followed in order by small exothermic and endothermic peaks. These smaller peaks were not previously recorded.[9]

For the loss of 1 mol of ethylenediamine/mol of complex, the expected mass loss is about 14.7%. Mass loss curves obtained by using TGA show that the first endothermic transition is accompanied by a mass loss of about 8.8% (equivalent to about two-thirds of a mole of en per mole of complex). The transition giving rise to the smaller endothermic peak is accompanied by a mass loss of about 4.2% (equivalent to about one-third of a mole of ethylenediamine per mole of complex). The curves shown in Figure 1 confirm that the smaller exothermic and endothermic peaks are totally absent when the catalyst level is 8.0 mol %. When this amount of catalyst is present, only a single large endothermic peak is seen and the mass loss corresponds very closely to that expected for the loss of 1 mol of ethylenediamine/mol of complex. The TGA curves shown in Figure 2 confirm that there is no mass loss during the exothermic transition which may correspond to some rearrangement in the solid phase. A similar sharp exotherm is apparent in the DTA curve of Akabori and Kushi when no catalyst was used.

The DSC curves were used to obtain the ΔH values and activation energies for the deamination shown in Table I.

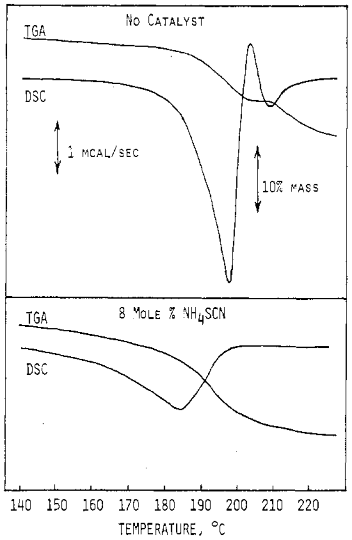

Figure 2. DSC and TGA curves for deamination of $[Cr(en)_3](NCS)_3$ with no catalyst present and with 8 mol % NH_4SCN present.

Table I. Reaction Parameters for the Deamination of $[Cr(en)_3](NCS)_3$

mol % NH_4SCN	initn temp, °C	% wt loss[a]	E_{act},[b] kcal/mol	ΔH,[b] kcal/mol
0	170	13.9	66.9 ± 3.6	20.5 ± 1.0
1.0	165	14.8	59.3 ± 4.7	19.6 ± 1.9
2.0	155	14.7	48.7 ± 2.3	20.4 ± 2.8
4.0	155	14.9	45.3 ± 3.3	15.1 ± 1.2
8.0	145	14.9	38.3 ± 0.5	12.9 ± 1.2

[a] For loss of one molecule of ethylenediamine per molecule of complex, the expected loss is 14.7%. [b] Shown as mean value ± average deviation from the mean.

For a reaction which leads to a given product, ΔH should be the same whether or not a catalyst is present. However, the data shown in Table I indicate that ΔH decreases more or less regularly as the amount of NH_4SCN present increases. Previously, the catalyzed reaction was studied at 5.0 mol % NH_4SCN.[9] The data obtained in this work indicate that there is a general decrease in ΔH as the amount of catalyst increases. Accordingly, it must be concluded that at higher catalyst levels the product is predominantly *cis*-$[Cr(en)_2(NCS)_2]NCS$. When a large amount of NH_4SCN is present, deamination produces *cis*-$[Cr(en)_2(NCS)_2]NCS$ by the thermal matrix process.[7] Also, the ΔH value obtained when no catalyst is present is about 20.5 kcal/mol. However, when 8.0 mol % catalyst is used, the ΔH value is 12.9 kcal/mol. These results and the nature of the DSC curves clearly indicate that the catalyzed and uncatalyzed reactions lead to different products. The fact that ΔH depends on the amount of catalyst used is indicative that the ratio of cis/trans isomers in the product depends on the amount of catalyst used. Akabori and Kushi have shown that the trans product results when "minute traces" of catalyst are present.[8] The NH_4SCN catalyst was added by recrystallization of the complex from a 1% NH_4SCN solution, and no attempt was made to determine the amount of catalyst present.

For a reaction following the usual rate law for an acid-catalyzed reaction,[13] increasing the amount of catalyst increases the fraction of the reaction proceeding by the catalyzed pathway. In this case, the large decrease in activation energy as the amount of catalyst is increased probably indicates that a different product is obtained as well.[5] Since the catalyzed reaction can be carried out isothermally at 110–130 °C, the reaction occurring in the DSC at 170–210 °C may be quite different. Thus, the usual synthetic reaction at lower temperature with trace amounts of catalyst present produces *trans*-$[Cr(en)_2(NCS)_2]NCS$ as reported.[3,8]

From the DSC and TGA curves, it appears that the deamination at low catalyst levels is a two-step process. The first step of this process involves the loss of two molecules of en for each three molecules of complex. The intermediate is stable over about a 10 °C range of temperature. The second step involves the loss of one molecule of en for each three molecules of complex to give the final product. At the high catalyst levels, the deamination occurs in one step corresponding to loss of one molecule of en per molecule of complex, and in these higher temperature nonisothermal studies the thermal data are consistent with a cis product.

Registry No. $[Cr(en)_3](NCS)_3$, 14176-00-2; NH_4SCN, 1762-95-4.

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Kinetics and Mechanism of the Reduction of Iodo- and Bromopentaammineruthenium(III) by Titanium(III)

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The redox reactions of the halopentaammine complexes of cobalt(III) and ruthenium(III) with reductants such as chromium(II),[1] vanadium(II),[2-4] uranium(III),[5,6] europium(II),[2,3] tris(bipyridyl)chromium(II),[3] hexaammineruthenium(II),[7] aquapentaammineruthenium(II),[8] and titanium(III)[9,10] have been investigated extensively. The reactivity order has come to be known as "normal" or "inverse", depending on whether rate increases or decreases with increasing atomic number of the halogen. The normal reactivity order ($I > Br > Cl$) is observed for the reactions of chromium(II), vanadium(II), hexaammineruthenium(II), and tris(bipyridyl)chromium(II) with halopentaamminecobalt(III),[1,3] and for the reactions of uranium(III) and aquapentaammineruthenium(II) with halopentaammineruthenium(III).[6,8a] The inverse order ($I < Br < Cl$) is observed for the reactions of europium(II), iron(II), and uranium(III) with halopentaamminecobalt(III)[3-5] and for the reactions of chromium(II) and europium(II) with halopentaammineruthenium(III).[2] An unusual order ($Cl > I > Br$)[9,10] is observed for the reactions of titanium(III) with the halopentaamminecobalt(III) complexes, and Thompson and Sykes[10] have been able to assign an outer-sphere mechanism to the reactions by using modified Marcus theory plots.

Reactivity trends listed above are not diagnostic of mechanism since both inner-sphere and outer-sphere mechanisms apply to some of the reactions of normal and inverse orders. Haim[11] pointed out that the normal reactivity trend observed in the chromium(II)–halopentaamminecobalt(III) reactions is indicative of the relative stabilities of the halogen-containing transition states.

Chalilpoyil, Davies, and Earley[12] recently investigated the reactions of titanium(III) with chloropentaammineruthenium(III) and assigned[13] an outer-sphere mechanism to these, using linear free-energy plots. We here report studies of the reduction of iodo- and bromopentaammineruthenium(III) complexes by titanium(III). A reactivity trend is obtained and the ambiguous reactivity trend[8] criterion is avoided in assigning a mechanism to these reactions.

Experimental Section

Reagents were prepared and purified by standard procedures.[14,15] The spectra of the complexes $Ru(NH_3)_5Br^{2+}$ and $Ru(NH_3)_5I^{2+}$ agreed with those in the literature.[15] Pure titanium(III) chloride (Koch-Light Laboratories, Ltd.) was used as previously described.[16]

The reactions were monitored on an SP 500 spectrophotometer by following decreasing absorbances of the oxidants at the wavelength[6] of maximum absorption: $Ru(NH_3)_5Br^{2+}$, λ 398 nm, $\epsilon = 1.85 \times 10^3$ $dm^3\ mol^{-1}\ cm^{-1}$; $Ru(NH_3)_5I^{2+}$ λ 545 nm, $\epsilon = 2.11 \times 10^3$ $dm^3\ mol^{-1}\ cm^{-1}$. All runs were performed at 25.0 ± 0.1 °C under pseudo-first-order conditions in chloride and trifluoromethanesulfonate media, with $I = 1.0$ mol dm^{-3}. The reduction potentials of the chloro- and bromopentaammineruthenium(III) complexes are available in literature,[17,18] but that of the iodo complex is not available. It was therefore measured by using the method of Kallen and Earley,[19] in trifluoroacetate buffers.

Results

The observed rate constants are presented as functions of acid in Table I. The reactions are free of complications as judged from the linear pseudo-first-order plots. Rate constants obtained with chloride and trifluoromethanesulfonate as ionic strength media agree very well (Table I). Where the effects of anions (Cl^-, N^{3-}, SCN^-) were investigated, it was convenient therefore to use trifluoromethanesulfonate to maintain the ionic strength at 1.0 mol dm^{-3}.

In the acid concentration range 0.01–1.00 mol dm^{-3}, the observed second-order rate constant is inversely proportional to $[H^+]$. The data obtained therefore fit eq 1. This implies

$$k_{obsd} = a/[H^+] \tag{1}$$

that $TiOH^{2+}$, rather than Ti^{3+}, is the predominant reducing species,[12] with $a = k_2K_a$, where K_a is the acidity constant of Ti^{3+} and k_2, the electron-transfer rate constant for $TiOH^{2+}$. Application of eq 1 to the data gave a as 0.28 ± 0.03 s^{-1} for the $Ti(III)/Ru(NH_3)_5Br^{2+}$ reaction and 0.56 ± 0.03 s^{-1} for the $Ti(III)/Ru(NH_3)_5I^{2+}$ reaction. Some measurements of k_{obsd} as a function of acid concentration at $[H^+] < 0.01$ mol dm^{-3} indicate that $K_a \approx 5 \times 10^{-3}$ mol dm^{-3}, in agreement with the value of K_a employed by Chalilpoyil, Davies, and Earley[12] to calculate k_2. When this value for the acidity constant K_a is employed for Ti^{3+}, k_2 for the $Ti(III)/Ru(NH_3)_5Br^{2+}$ and $Ti(III)/Ru(NH_3)_5I^{2+}$ reactions are 56.0 ± 5.3 $dm^3\ mol^{-1}\ s^{-1}$ and 112.0 ± 6.2 $dm^3\ mol^{-1}\ s^{-1}$, respectively.

The effects of added anions (Cl^-, N_3^-, SCN^-) on the reactions of Ti(III) with bromopentaammineruthenium(III) were investigated. The anions catalyze the reaction in the order $SCN^- >> N_3^- > Cl^-$ (Table II). The reduction potential ($\mathcal{E}°$, mV vs. NHE) of the iodopentaammineruthenium(III) complex (which was measured as the average of the cathodic and anodic peak potentials in ~1 mol dm^{-3} $CF_3COOH/LiCF_3COO$ solutions, pH 2–3, sweep rate ~20 V/s) is −21.

Discussion

These results further testify to the characteristic hydrolytic[12,16] behavior of Ti(III), in which $TiOH^{2+}$ is the predominant reactive component. Since the value of k_2 obtained by Chalilpoyil, Davies, and Earley for the $Ti(III)/Ru(NH_3)_5Cl^{2+}$ reaction[12] is 12.0 $dm^3\ mol^{-1}\ s^{-1}$ and those obtained for the $Ti(III)/Ru(NH_3)_5Br^{2+}$ and Ti(III)/Ru-

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