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# Preparation and Solid-Phase Thermal Deamination of the Unitary, Binary, and Ternary Tris(diamine)chromium(III) Complexes

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The unitary, binary, and ternary tris(diamine)chromium(III) complexes $[Cr(aa)_3]X_3{\cdot}nH_2O$, $[Cr(aa)_2(bb)]X_3{\cdot}nH_2O$, and $[Cr(aa)(bb)(cc)]X_3{\cdot}nH_2O$ were prepared and their thermal deamination was investigated both nonisothermally (derivatographically) and isothermally in the solid phase, where aa, bb, and cc are different diamines selected from ethylenediamine (en), *d,l*-1,2-propanediamine (pn), and 1,3-propanediamine (tn), X is chloride or thiocyanate ion, and *n* is a number of 0–3. The complexes obtained by the reaction were isolated and identified by means of IR and visible spectrophotometry and TLC. The diamines evolved by the deamination were captured as the hydrochlorides and identified by IR spectrophotometry. The results showed that all the chlorides evolve 1 mol of diamine to be converted into the *cis*-dichlorobis(diamine) complexes, whereas all the thiocyanates undergo deamination to give the *trans*-bis(diamine)bis(isothiocyanato) complexes. In the deamination of the binary and ternary tris(diamine) complexes, it was found that the diamine which escapes from the complexes is a diamine having the lower boiling point than other diamines contained. *cis*-$[CrCl_2(tn)_2]Cl$ obtained by the deamination of $[Cr(tn)_3]Cl_3{\cdot}H_2O$, $[Cr(en)(tn)_2]Cl_3{\cdot}2H_2O$, and $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$ readily isomerizes to the trans form upon subsequent heating. The order of ease of evolution of diamines in the unitary complexes was pn < en < tn, whereas that in the binary and ternary complexes was tn < pn < en which is consistent with the decreasing order of boiling points of the diamines.

## Introduction

In 1904, Pfeiffer et al. first reported that $[Cr(en)_3]X_3$ (X = $Cl^-$ or $SCN^-$), when heated, deaminate to form *cis*-$[CrCl_2(en)_2]Cl$ or *trans*-$[Cr(NCS)_2(en)_2]SCN$.[2] Rollinson and Bailar found that the deamination[3] is catalyzed by the presence of small amounts of ammonium chloride or ammonium thiocyanate, and the reaction constitutes the best method for preparing a series of *cis*- and *trans*-diacidobis(ethylenediamine)chromium(III) complexes.[4] Until recently, the deamination has been used widely as the standard synthetic procedures for the above series.[5] Thereafter, the reaction has increasingly been approached by means of thermoanalytical techniques, e.g., TG and DTA[6] or DSC.[7] Akabori and Kushi have tried to know the relationships between the reaction and crystal structures.[8]

However, several essential problems still remain to be solved in the deamination, one of which is why the variation of anions ($X^-$) gives rise to the difference in geometries of the final products obtained by the deamination and whether or not the situation is also true for other homologous tris(diamine)chromium(III) complexes. Another question is whether one of three diamines could preferentially or randomly be evolved from the tris(diamine) complexes. The question is not solvable in the unitary tris(diamine) complexes ($[Cr(aa)_3]X_3$) but can be approached in the binary ($[Cr(aa)_2(bb)]X_3$) and ternary tris(diamine) complexes ($[Cr(aa)(bb)(cc)]X_3$).[9]

The present study was therefore undertaken to investigate the details of the solid-phase thermal deamination of a complete series of tris(diamine)chromium(III) complexes. The complexes in the present study are divided into three groups: The first consists of the unitary tris(diamine) complexes $[Cr(aa)_3]X_3$, the second, of the binary tris(diamine) complexes $[Cr(aa)_2(bb)]X_3$, and the third, of the ternary tris(diamine) complexes $[Cr(aa)(bb)(cc)]X_3$, where aa, bb, and cc are different diamines selected from ethylenediamine (en), *d,l*-1,2-propanediamine (pn), and 1,3-propanediamine (tn) and X is the $Cl^-$ or $SCN^-$ ion.

## Experimental Section

**Preparation of Unitary Tris(diamine) Complexes.** $[Cr(en)_3]Cl_3{\cdot}3H_2O$, $[Cr(pn)_3]Cl_3{\cdot}H_2O$, and $[Cr(tn)_3]Cl_3{\cdot}H_2O$ were prepared by the known methods partially modified.[10]

$[Cr(tn)_3]Br_3{\cdot}H_2O$ was prepared by the metathesis of $[Cr(tn)_3]Cl_3{\cdot}H_2O$ with ammonium bromide.

$[Cr(en)_3](SCN)_3{\cdot}H_2O$, $[Cr(pn)_3](SCN)_3$, and $[Cr(tn)_3](SCN)_3$ were obtained by the metatheses of the respective chlorides with ammonium thiocyanate.

**Preparation of Binary Tris(diamine) Complexes.** $[Cr(en)_2(pn)]Cl_3{\cdot}H_2O$, $[Cr(en)(pn)_2]Cl_3{\cdot}H_2O$, $[Cr(en)(tn)_2]Cl_3{\cdot}H_2O$, and $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$ were derived by the reaction of *cis*-$[CrCl_2(aa)_2]Cl$ with the second diamine (bb). In a 50-mL round-bottom flask provided with a reflux condenser, 0.05 mmol of *cis*-$[CrCl_2(aa)_2]Cl$ was suspended in 30 mL of ethanol and thereto 0.1 mmol of the respective second diamine was added. The mixture was heated to the refluxing temperature for about 5 h with continuous stirring. The resulting mixture was then allowed to cool to room temperature. Yellow products thus obtained were collected by filtration and washed with ethanol and then ether. They were recrystallized from water; yield 60%.

$[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$ and $Cr(pn)_2(tn)]Cl_3{\cdot}H_2O$ were not obtained by the reaciton of *cis*-$[CrCl_2(aa)_2]Cl$ with tn but prepared by the reaction of *cis*-$[CrCl_2(aa)(tn)]Cl$ with additional aa, where aa is en or pn. A 0.05-mmol sample of the respective cis complexes and a solution of 0.1 mmol of aa in 30 mL of ethanol were charged in a 50-mL round-bottom flask equipped with a reflux condenser. The mixture was refluxed for 5 h with stirring and then permitted to cool to ambient temperatures. Yellow precipitates were collected by filtration, washed with ethanol and then ether, and air-dried. Recrystallization was carried out from water; yield 60% based on the amounts of the starting materials used.

Anal. Calcd for $[Cr(en)_2(pn)]Cl_3{\cdot}H_2O$: C, 22.67; H, 7.67; N, 22.67. Found: C, 22.56; H, 7.34; N, 22.02. Calcd for $[Cr(en)(pn)_2]Cl_3{\cdot}H_2O$: C, 24.97; H, 7.86; N, 21.84. Found: C, 24.75; H, 7.44; N, 21.76. Calcd for $[Cr(en)(tn)_2]Cl_3{\cdot}H_2O$: C, 24.97; H, 7.86; N, 21.84. Found: C, 24.55; H, 7.63; N, 21.66. Calcd for $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$: C,

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[1] To whom correspondence should be addressed.

[2] Pfeiffer, P.; Koch, P.; Land, G.; Treischmann, A. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 4256, 4269, 4277.

[3] The term "deamination" has already been used to express the evolution of diamines from tris(diamine) complexes in the solid-phase; see for example: (a) Wendlandt, W. W.; Smith, J. P. "The Thermal Properties of Transition-Metal Ammine Complexes"; Elsevier: Amsterdam, 1967; p 1. (b) House, J. E., Jr.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 67.

[4] Rollinson, C. L.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1944**, *66*, 641.

[5] Rollinson, C. L.; Bailar, J. C., Jr. *Inorg. Synth.* **1946**, *2*, 196.

[6] Bear, J. L.; Wendlandt, W. W. *J. Inorg. Nucl. Chem.* **1961**, *17*, 286.

[7] House, J. E., Jr.; Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1791.

[8] Akabori, K.; Kushi, Y. *J. Inorg. Nucl. Chem.* **1978**, *40*, 625; 1317.

[9] Throughout this paper, the terms "unitary tris(diamine)", "binary tris(diamine)", and "ternary tris(diamine)" complexes were employed to express the tris(diamine)chromium(III) complexes containing the same three diamines ($[Cr(aa)_3]X_3$), two different diamines ($[Cr(aa)_2(bb)]X_3$), and three different diamines ($[Cr(aa)(bb)(cc)]X_3$), respectively. In addition, the terms "unitary bis(diamine)" and "binary bis(diamine)" complexes stand for the bis(diamine)chromium(III) complexes containing the same two diamines ($[CrX_2(aa)_2]X$) and two different diamines ($[CrX_2(aa)(bb)]X$).

[10] Pedersen, E. *Acta Chem. Scand.* **1970**, *24*, 3362.

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27.10; H, 8.03; N, 21.08. Found: C, 26.89; H, 7.98; N, 20.23. Calcd for $[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$: C, 22.67; H, 7.67; N, 22.67. Found: C, 22.30; H, 7.71; N, 21.76. Calcd for $[Cr(pn)_2(tn)]Cl_3{\cdot}H_2O$: C, 27.10; H, 8.03; N, 21.08. Found: C, 27.82; H, 8.10; N, 21.51.

The thiocyanates $[Cr(en)_2(pn)](SCN)_3$, $[Cr(en)(pn)_2](SCN)_3{\cdot}0.5H_2O$, $[Cr(en)(tn)_2](SCN)_3{\cdot}0.5H_2O$, $[Cr(pn)(tn)_2](SCN)_3{\cdot}H_2O$, $[Cr(en)_2(tn)(SCN)_3$, and $[Cr(pn)_2(tn)](SCN)_3{\cdot}H_2O$ were obtained by the metatheses from the respective chlorides and $NH_4SCN$.

**Preparation of Ternary Tris(diamine) Complexes.** $[Cr(en)(pn)(tn)]Cl_3{\cdot}2H_2O$ was derived from *cis*-$[CrCl_2(en)(tn)]Cl$ or *cis*-$[CrCl_2(pn)(tn)]Cl$ and the third diamine (pn or en). In a 50-mL round-bottom flask with a condenser, 0.05 mmol of either one of the above cis complexes and 30 mL of ethanol were charged and to this 0.1 mmol of the third diamine was added. The resulting mixture was refluxed for 5 h with stirring and then allowed to cool to room temperatures. Yellow products were obtained, which were collected and recrystallized from water; yield 65%.

Anal. Calcd for $[Cr(en)(pn)(tn)]Cl_3{\cdot}2H_2O$: C, 23.85; H, 7.95; N, 20.87. Found: C, 24.58; H, 7.70; N, 21.47.

The metathesis of the chloride with $NH_4SCN$ gave the thiocyanate $[Cr(en)(pn)(tn)](SCN)_3$.

**Preparation of Unitary Bis(diamine) Complexes.**[9] *cis*-$[CrCl_2(en)_2]Cl{\cdot}H_2O$, *cis*-$[CrCl_2(pn)_2]Cl$, and *cis*-$[CrCl_2(tn)_2]Cl{\cdot}0.75H_2O$ were prepared according to a modification of the known methods.[10,11] *trans*-$[Cr(NCS)_2(en)_2]SCN$, *trans*-$[Cr(NCS)_2(pn)_2]SCN$, and *trans*-$[Cr(NCS)_2(tn)_2]SCN$ were easily obtained from the reaction of the corresponding chlorides with KSCN in a manner similar to that reported previously.[2]

**Preparation of Binary Bis(diamine) Complexes.**[9] *cis*-$[CrCl_2(en)(pn)]Cl$, *cis*-$[CrCl_2(en)(tn)]Cl$, *cis*-$[CrCl_2(pn)(tn)]Cl$, *trans*-$[CrCl_2(en)(pn)]Cl{\cdot}0.75H_2O$, *trans*-$[CrCl_2(pn)(tn)]Cl{\cdot}H_2O$, and *trans*-$[CrCl_2(en)(tn)]Cl{\cdot}HCl{\cdot}2H_2O$ were prepared by a method similar to that described earlier.[12-14] *trans*-$[Cr(NCS)_2(en)(pn)]SCN$, *trans*-$[Cr(NCS)_2(en)(tn)]SCN$, and *trans*-$[Cr(NCS)_2(pn)(tn)]SCN$ were derived from the corresponding chlorides and KSCN according to a literature method.[2]

**Nonisothermal (Derivatographic) Measurements.** The derivatograms of the sample were recorded on a MOM derivatograph Typ-OD-102. All the measurements were carried out at the heating rate of 1 °C min$^{-1}$, with 0.4 g of the samples being used in each run.

**Isothermal Measurements.** For the determination of suitable heating conditions for obtaining the desired products which have lost just 1 mol of diamine, isothermal measurements were carried out by a Chyo 1001 thermobalance in static air at various temperatures.

**Spectral Measurements.** Visible spectra of the samples were measured with a JASCO UVIDEC 505 spectrophotometer. IR spectra were measured in a Nujol mull state or on KBr disks with a JASCO A-3 infrared spectrophotometer.

**TLC.** TLC was mainly employed to identify the binary and ternary tris- or bis(diamine) complexes. The plates used were those of silica gel 60F-254 made by Merck Ltd.

**Purification of Products Obtained by Deamination.** The chlorides and thiocyanates of tris(diamine) complexes were triturated and heated to obtain the deaminated products. The heating was carried out at temperatures and for time periods which were determined from isothermal measurements described above. The complexes thus obtained from the chlorides and thiocyanates were purified by recrystallization from 6 mol dm$^{-3}$ HCl or ethanol and water, respectively. They were identified by means of electronic spectrophotometry and TLC. The product obtained by the deamination of $[Cr(tn)_3]Br_3{\cdot}H_2O$ was recrystallized from 0.5 mol dm$^{-3}$ HBr and characterized by means of electronic spectrophotometry.

On the other hand, gaseous diamines evolved during heating were passed into 6 mol dm$^{-3}$ HCl to crystallize as the hydrochlorides and identified by IR spectrophotometry.

## Results

**TLC of the Starting Tris(diamine) Complexes.** Table I shows the results of TLC for the unitary, binary, and ternary tris(diamine) complexes. The $R_f$ values for the binary complexes fall between those for the unitary complexes: e.g., the $R_f$ values for the $(en)_2(pn)$ (0.55) and $(en)(pn)_2$ (0.59) complexes lie in between those for $(en)_3$ (0.50) and $(pn)_3$ (0.65). The same situation is also valid for the other binary complexes. The ternary (en)(pn)(tn) complex gave a different $R_f$ value (0.55) from those for the $(en)_3$ (0.52), $(pn)_3$ (0.63), and $(tn)_3$ (0.39) complexes. These results indicate that the binary and ternary complexes are not the mixtures of the unitary complexes.

**Table I.** Results of Thin-Layer Chromatography for Tris(diamine)chromium(III) Chlorides[a,b]

|  |  |  |  |  |
|---|---|---|---|---|
|  | $(en)_3$ | $(en)_2(pn)$ | $(en)(pn)_2$ | $(pn)_3$ |
| $R_f$ | 0.50 | 0.55 | 0.59 | 0.65 |
|  | $(tn)_3$ | $(en)(tn)_2$ | $(en)_2(tn)$ | $(en)_3$ |
| $R_f$ | 0.40 | 0.45 | 0.51 | 0.55 |
|  | $(tn)_3$ | $(pn)(tn)_2$ | $(pn)_2(tn)$ | $(pn)_3$ |
| $R_f$ | 0.40 | 0.53 | 0.59 | 0.66 |
|  | $(tn)_3$ | $(en)_3$ | $(pn)_3$ | (en)(pn)(tn) |
| $R_f$ | 0.39 | 0.52 | 0.63 | 0.55 |

[a] The mixture of *n*-butyl alcohol, water, and concentrated hydrochloric acid (7:1:2) was used as the developer. A single plate was employed in each run. [b] $(en)_3$, $(en)_2(pn)$, and $(en)(pn)_2$ designate $[Cr(en)_3]^{3+}$, $[Cr(en)_2(pn)]^{3+}$, and $[Cr(en)(pn)_2]^{3+}$, respectively, and other complexes are abbreviated in the same manner.

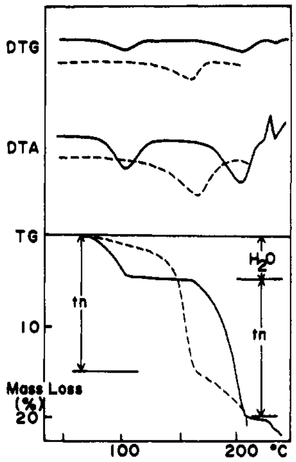

Figure 1. Derivatograms of $[Cr(tn)_3]Cl_3{\cdot}H_2O$ (—) and $[Cr(tn)_3](SCN)_3$ (- - -).

**Thermal Reactions under Nonisothermal Conditions. Unitary Tris(diamine) Complexes.** The thermal decomposition of $[Cr(en)_3]X_3$[4-8] and $[Cr(pn)_3]X_3$[15] has already been reported, but little is known for $[Cr(tn)_3]X_3$ (X = $Cl^-$ or $SCN^-$). The thermal decomposition patterns of $[Cr(en)_3]X_3$ and $[Cr(pn)_3]X_3$ were essentially similar to those reported earlier except that the deamination temperatures are slightly lower than those reported in literature. The difference comes from different heating rates.

Figure 1 shows the derivatograms of $[Cr(tn)_3]Cl_3{\cdot}H_2O$ and $[Cr(tn)_3](SCN)_3$. As seen from the TG curve of the chloride, $[Cr(tn)_3]Cl_3{\cdot}H_2O$ is dehydrated at 70–100 °C followed by the evolution of 90% of 1 mol of tn at 170–210 °C. The complex changed in color from original yellow to violet and then green. The color changes are due to the conversion of $[Cr(tn)_3]Cl_3$ to *cis*- and then *trans*-$[CrCl_2(tn)_2]Cl$. Two endothermic DTA peaks at about 100 and 200 °C are ascribed to the dehydration and the evolution of tn. The sharp exothermic DTA peak near 230 °C is partly due to the cis-to-trans isomerization[19] and partly due to subsequent decomposition. It should be mentioned that $[Cr(tn)_3]Br_3{\cdot}H_2O$ loses 1 mol of lattice water at 50–90 °C and then evolves 95% of 1 mol of tn at 180–220 °C.

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(15) Bear, J. L.; Wendlandt, W. W. *J. Inorg. Nucl. Chem.* **1961**, *17*, 286.

Table II. Results of Deamination under Nonisothermal and Isothermal Conditions

| | nonisothermal condition | | | | isothermal condition | | |
|---|---|---|---|---|---|---|---|
| complexes | dehydration temp, °C | deamination temp, °C | % amine evolved[a] | | temp, °C | time, min | product[b] |
| $[Cr(en)_3]Cl_3{\cdot}3H_2O$ | 50-150 | 190-230 | 90 | en | 205 | 120 | cis |
| $[Cr(en)_3](SCN)_3{\cdot}H_2O$ | 80-110 | 120-160 | 95 | en | 130 | 180 | trans |
| $[Cr(pn)_3]Cl_3{\cdot}H_2O$ | 60-160 | 210-230 | 60 | pn | 210 | 180 | cis |
| $[Cr(pn)_3](SCN)_3$ | | 120-170 | 80 | pn | 135 | 180 | trans |
| $[Cr(tn)_3]Cl_3{\cdot}H_2O$ | 70-100 | 170-210 | 90 | tn | 170 | 60 | cis → trans[c] |
| $[Cr(tn)_3]Br_3{\cdot}H_2O$ | 50-90 | 190-220 | 95 | tn | 195 | 120 | cis ⇒ trans[d] |
| $[Cr(tn)_3](SCN)_3$ | | 120-150 | 90 | tn | 130 | 180 | trans |
| $[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$ | 100-160 | 190-230 | 50 | en | 190 | 60 | cis |
| $[Cr(en)_2(tn)](SCN)_3$ | | 50-135 | 70 | en | 130 | 60 | trans |
| $[Cr(en)(tn)_2]Cl_3{\cdot}H_2O$ | 100-160 | 190-230 | 45 | en | 190 | 60 | cis → trans[c] |
| $[Cr(en)(tn)_2](SCN)_3{\cdot}0.5H_2O$ | 70-90 | 100-150 | 70 | en | 125 | 180 | trans |
| $[Cr(en)_2(pn)]Cl_3{\cdot}H_2O$ | 110-150 | 180-230 | 50 | en | 200 | 180 | cis |
| $[Cr(en)_2(pn)](SCN)_3$ | | 115-145 | 50 | en | 130 | 60 | trans |
| $[Cr(en)(pn)_2]Cl_3{\cdot}H_2O$ | 100-140 | 200-230 | 60 | en | 200 | 180 | cis |
| $[Cr(en)(pn)_2](SCN)_3{\cdot}0.5H_2O$ | 45-110 | 110-150 | 60 | en | 130 | 60 | trans |
| $[Cr(pn)_2(tn)]Cl_3{\cdot}H_2O$ | 95-160 | 200-230 | 60 | pn | 210 | 180 | cis |
| $[Cr(pn)_2(tn)](SCN)_3{\cdot}H_2O$ | 70-110 | 110-160 | 80 | pn | 125 | 180 | trans |
| $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$ | 100-140 | 200-230 | 50 | pn | 210 | 180 | cis → trans[c] |
| $[Cr(pn)(tn)_2](SCN)_3{\cdot}H_2O$ | 70-120 | 120-160 | 55 | pn | 125 | 180 | trans |
| $[Cr(en)(pn)(tn)]Cl_3{\cdot}2H_2O$ | 80-160 | 200-225 | 60 | en | 200 | 60 | cis |
| $[Cr(en)(pn)(tn)](SCN)_3$ | | 120-160 | 70 | en | 130 | 180 | trans |

[a] In the column, for example, 90% en indicates that 90% of 1 mol of en is evolved. [b] cis and trans designate *cis*- and *trans*-$[CrX_2(diamine)_2]X$, respectively. [c] cis → trans means that the cis form isomerizes to the trans form upon subsequent heating. [d] cis ⇒ trans stands for extremely rapid isomerization.

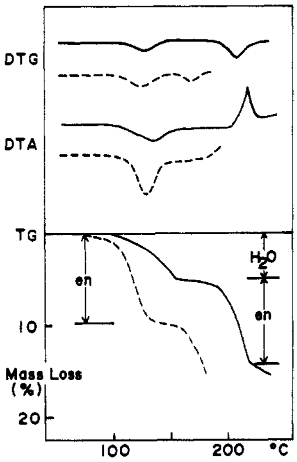

Figure 2. Derivatograms of $[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$ (—) and $[Cr(en)_2(tn)](SCN)_3$ (---).

The color of the complex turns from yellow to extremely transient violet and finally to green. This indicates that the *cis*-$[CrBr_2(tn)_2]Br$ produced by the deamination isomerizes to the trans form much faster than the *cis*-$[CrCl_2(tn)_2]Cl$. On the other hand, $[Cr(tn)_3](SCN)_3$ releases 90% of 1 mol of tn at 120–150 °C accompanied by the color change from yellow to orange and then gradually decomposes.

**Binary Tris(diamine) Complexes.** Figure 2 shows the derivatograms of $[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$ and $[Cr(en)_2(tn)](SCN)_3$, which are the representatives of the binary tris(diamine) complexes. The chloride dehydrates 1 mol of water at 100–160 °C and then evolves 50% of 1 mol of en. In this case, the fact that the diamine evolved is en was confirmed by capturing and identifying the gas evolved during heating as mentioned in Experimental Section. Figure 3 depicts the IR spectra of diamine hydrochlorides captured during the deamination of $[Cr(en)_2(tn)]X_3$ and $[Cr(en)(tn)_2]X_3$ together with those of en•2HCl and tn•2HCl. A glance of the figure readily tells us that the diamines evolved from these complexes are en, not tn. The complex $[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$, after deamination, turned violet (cis form) and then remained unchanged until it began to decompose in a complicated manner at about 230 °C. No isomerization was observed. On the other hand, $[Cr(en)_2(tn)](SCN)_3$ evolves 70% of 1 mol of en at 50–135 °C to change in color from yellow to orange.

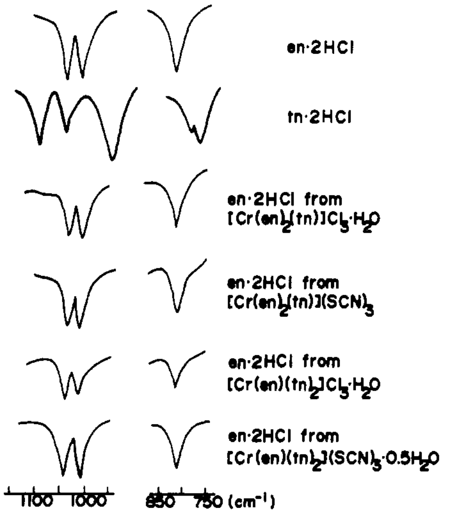

**Figure 3.** IR spectra of en•2HCl, tn•2HCl, and diamine hydrochlorides from $[Cr(en)_2(tn)]X_3$ and $[Cr(en)(tn)_2]X_3$.

It should be noted that all the chlorides of other binary tris(diamine) complexes also deaminate to be converted into cis form and the only *cis*-$[CrCl_2(tn)_2]Cl$ obtained from $[Cr(en)(tn)_2]Cl_3{\cdot}H_2O$ and $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$ readily isomerizes to green trans form upon subsequent heating.

**Ternary Tris(diamine) Complexes.** The derivatograms of $[Cr(en)(pn)(tn)]Cl_3{\cdot}2H_2O$ and $[Cr(en)(pn)(tn)](SCN)_3$ are depicted in Figure 4. The chloride dehydrates at 80–160 °C and then loses 60% of 1 mol of en at 200–225 °C to convert to the cis form. The thiocyanate evolves 70% of 1 mol of en at 120–160 °C.

**Isothermal Heating.** Deamination was frequently overlapped with subsequent complicated decomposition under nonisothermal conditions, but the isothermal heating at a temperature near the initiation temperature of deamination makes it possible to obtain the products which have lost just 1 mol of diamines. Table II summarizes the results of deamination

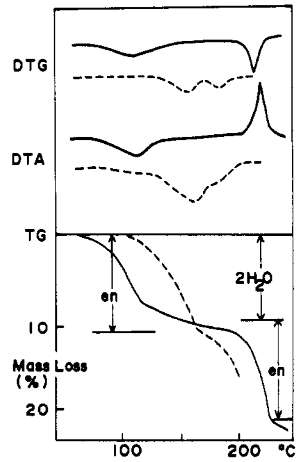

**Figure 4.** Derivatograms of $[Cr(en)(pn)(tn)]Cl_3{\cdot}2H_2O$ (—) and $[Cr(en)(pn)(tn)](SCN)_3$ (---).

**Table III.** Results of Thin-Layer Chromatography for *cis*-$[CrCl_2(aa)_2$ or $(aa)(bb)]Cl$ and the Products Obtained from $[Cr(aa)_2(bb)$ or $(aa)(bb)(cc)]Cl_3$[a]

| | *cis*-$[CrCl_2(aa)_2$ or $(aa)(bb)]Cl$ | | | products from $[Cr(aa)_2(bb)$ or $(aa)(bb)(cc)]Cl_3$ | |
|---|---|---|---|---|---|
| | $(en)_2$ | (en)(pn) | $(pn)_2$ | $(en)_2(pn)$ | $(en)(pn)_2$ |
| $R_f$ | 0.46 | 0.58 | 0.68 | 0.57 | 0.68 |
| | $(tn)_2$ | (pn)(tn) | $(pn)_2$ | $(pn)_2(tn)$ | $(pn)(tn)_2$ |
| $R_f$ | 0.31 | 0.56 | 0.68 | 0.55 | 0.28 |
| | $(en)_2$ | (en)(tn) | $(tn)_2$ | $(en)_2(tn)$ | $(en)(tn)_2$ |
| $R_f$ | 0.45 | 0.39 | 0.30 | 0.40 | 0.31 |
| | (en)(pn) | (en)(tn) | (pn)(tn) | (en)(pn)(tn) | |
| $R_f$ | 0.59 | 0.40 | 0.53 | 0.52 | |

[a] The mixture of methanol and acetic acid (19:1) was used as the developer. A single plate was employed in each run.

under nonisothermal and isothermal conditions.

**Evolved Diamines.** As seen from Table II, the diamine which preferentially evolves from the binary and ternary tris(diamine) complexes is the one which has the lower boiling point than other diamines contained in the complexes. The boiling points of en, pn, and tn are 116.5, 120.5, and 137.7.[16] For instance, en is preferentially deaminated from the en–pn, en–tn, and en–pn–tn series, and pn is evolved from the pn–tn series.

**Complexes Obtained by the Deamination.** The complexes produced by the deamination were recrystallized from 6 mol dm$^{-3}$ HCl or ethanol for the chlorides and from water for the thiocyanates. They were identified by means of spectrophotometry and TLC. The electronic spectra of $[Cr(N)_6]^{3+}$ and $[CrX_2(N)_4]^+$ ions (where N is the nitrogen chromophore and X is halide or pseudohalide ion) have been well-known both theoretically and experimentally,[17] and hence details of the spectra will be omitted to avoid tedious discussion.

The products obtained from the binary and ternary tris(diamine) complexes were also confirmed by TLC; the results are listed up in Table III. As seen from the first row of the table, the $R_f$ values for the products obtained from $[Cr(en)_2(pn)]Cl_3{\cdot}H_2O$ and $[Cr(en)(pn)_2]Cl_3{\cdot}H_2O$ are 0.57 and 0.68 which are quite close to those of *cis*-$[CrCl_2(en)(pn)]Cl$ (0.58) and *cis*-$[CrCl_2(pn)_2]Cl$ (0.68). Similarly, it is conceivable that the final products of $[Cr(pn)_2(tn)]Cl_3{\cdot}H_2O$, $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$, $[Cr(en)_2(tn)]Cl_3{\cdot}H_2O$, and $[Cr(en)(tn)_2]Cl_3{\cdot}H_2O$ are *cis*-$[CrCl_2(pn)(tn)]Cl$, *cis*-$[CrCl_2(tn)_2]Cl$, *cis*-$[CrCl_2(en)(tn)]Cl$, and *cis*-$[CrCl_2(tn)_2]Cl$, respectively. The value of 0.52 for the product which resulted from $[Cr(en)(pn)(tn)]Cl_3{\cdot}2H_2O$ is very close to that of *cis*-$[CrCl_2(pn)(tn)]Cl$ (0.53). The coordination structures (cis or trans) of the final products thus determined are noted in the last column of Table II.

Scheme I

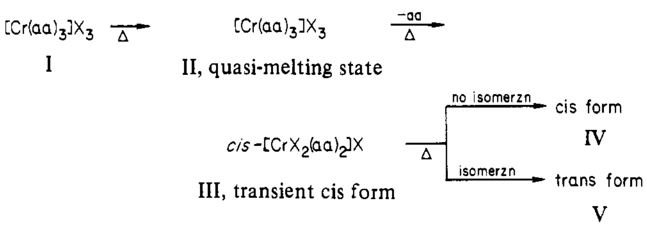

**Table IV.** Relationships between Isomerization of Transient *cis*-$[CrX_2(aa)_2]X$ and Combination of Members in Chelate Rings

| transient cis form | combn of members in chelate rings | isomerzn | final products |
|---|---|---|---|
| $X = Cl^-$ | 5,5 | no | cis |
| | 5,6 | no | cis |
| | 6,6 | yes | cis → trans[a] |
| $X = SCN^-$ | 5,5 | yes | trans |
| | 5,6 | yes | trans |
| | 6,6 | yes | trans |

[a] $[Cr(tn)_3]Br_3{\cdot}H_2O$ is converted into *cis*-$[CrBr_2(tn)_2]Br$, which isomerizes more rapidly to the trans form than *cis*-$[CrCl_2(tn)_2]Cl$.

From the results of TLC, it can also be concluded that en is preferentially evolved from the en–pn, en–tn, and en–pn–tn series, and pn from the pn–tn series.

As mentioned above, $[Cr(tn)_3]Br_3{\cdot}H_2O$ deaminates at 180–220 °C accompanied by the color change from original yellow to transient violet and finally to green. Many attempts to isolate the transient violet product during the deamination failed; instead the green product was always obtained. The green product was spectrophotometrically identified as *trans*-$[CrBr_2(tn)_2]Br$. The deamination temperature (180–200 °C) is very close to the isomerization temperature (200–225 °C) of *cis*-$[CrBr_2(tn)_2]Br$.[18] From these results, the transient violet product is probably *cis*-$[CrBr_2(tn)_2]Br$.

## Discussion

**Features of the Deamination.** Inspection of Table II reveals the following four features in the deamination. First, the products obtained from the chlorides are cis form, whereas those from the thiocyanates are trans form without exception. Second, *cis*-$[CrCl_2(tn)_2]Cl$ obtained from $[Cr(tn)_3]Cl_3{\cdot}H_2O$, $[Cr(en)(tn)_2]Cl_3{\cdot}H_2O$, and $[Cr(pn)(tn)_2]Cl_3{\cdot}H_2O$ readily isomerize to trans form upon subsequent heating. Third, the binary and ternary tris(diamine) complexes evolve a diamine which has the lower boiling points than other diamines contained in the complexes; i.e., the order of ease of evolution of diamines is tn < pn < en. Fourth, the thiocyanates, in all cases, show considerably lower deamination temperatures than the corresponding chlorides.

**Deamination Pathway.** Scheme I is a tentatively proposed pathway for the deamination in the solid phase. The original tris(diamine) complexes (I) are assumed to first become the quasi-melting state (II).[19] The idea may be supported by the facts that (1) the binary and ternary tris(diamine) complexes

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[16] Weast, R. C., Ed. "CRC Handbook of Chemistry and Physics"; CRC Press: Cleveland, OH, 1978.

[17] (a) Garner, C. S.; House, D. A. *Transition Met. Chem.* (N.Y.) **1970**, *6*, 59–294. (b) Forster, L. S. *Ibid.* **1969**, *5*, 1–45.

[18] Mitra, S.; Uehara, A.; Tsuchiya, R. *Thermochim. Acta* **1979**, *34*, 189.

[19] "Quasi-melting state" is a state resembling but not actually being the melting state.

lose selectively a diamine which has the lower boiling point and (2) the thiocyanates deaminate in considerably lower temperature ranges than the corresponding chlorides, which is parallel to the fact that MSCN have much lower melting points as compared with MCl (M is ammonium or alkali-metal ion). In the next stage, the complexes (II) evolve a diamine (aa) to form transient *cis*-$[CrX_2(aa)_2]X$ (III). Whether or not the transient cis form undergoes isomerization upon further heating is largely dependent upon the combination of members in chelate rings of $(aa)_2$ and the size of the anions ($X^-$). Table IV shows the relationships between the isomerization of the transient cis form and the combination of members in chelate rings. In the case of $X = Cl^-$, if the transient cis form has two five-membered or five- and six-membered chelate rings, it does not isomerize, whereas if it contains two six-membered chelate rings, it isomerizes to the trans form, which coincides with the observation that only cis-to-trans isomerization takes place in the bis(diamine) complexes $[CrX_2(tn\text{ or }ptn)_2]X$ in which tn and ptn form a six-membered chelate ring with chromium(III) ion.[20-22] On the other hand, in the case of $X = SCN^-$, the transient cis form is considered to isomerize to the trans form in an indeterminably rapid period of time irrespective of the combination of members in the chelate rings probably because of the greater size of $SCN^-$ (1.95 Å) as compared to $Cl^-$ (1.67 Å). The idea is also supported by the fact that $[Cr(tn)_3]Br_3 \cdot H_2O$, which contains $Br^-$ having an intermediate ionic size (1.87 Å), deaminates to form the unstable cis form which extremely rapidly isomerizes to the trans form. Therefore, it may be reasonable to conclude that the combination of members in chelate rings and anion sizes have important effects on the final geometry of the bis(diamine) complexes obtained by the deamination.

**Registry No.** $[Cr(en)_3]Cl_3$, 14023-00-8; $[Cr(pn)_3]Cl_3$, 14949-95-2; $[Cr(tn)_3]Cl_3$, 17978-78-8; $[Cr(tn)_3]Br_3$, 17631-72-0; $[Cr(en)_3](SCN)_3$, 14176-00-2; $[Cr(pn)_3](SCN)_3$, 22754-50-3; $[Cr(tn)_3](SCN)_3$, 17978-79-9; $[Cr(en)_2(pn)]Cl_3$, 81194-26-5; $[Cr(en)(pn)_2]Cl_3$, 81194-25-4; $[Cr(en)(tn)_2]Cl_3$, 41101-31-9; $[Cr(pn)(tn)_2]Cl_3$, 81194-24-3; $[Cr(en)_2(tn)]Cl_3$, 41101-32-0; $[Cr(pn)_2(tn)]Cl_3$, 81194-23-2; $[Cr(en)_2(pn)](SCN)_3$, 81194-22-1; $[Cr(en)(pn)_2](SCN)_3$, 81194-21-0; $[Cr(en)(tn)_2](SCN)_3$, 81194-20-9; $[Cr(pn)(tn)_2](SCN)_3$, 81194-19-6; $[Cr(en)_2(tn)](SCN)_3$, 81194-09-4; $[Cr(pn)_2(tn)](SCN)_3$, 81194-17-4; $[Cr(en)(pn)(tn)]Cl_3$, 81194-15-2; $[Cr(en)(pn)(tn)](SCN)_3$, 81194-14-1; *cis*-$[CrCl_2(en)_2]Cl$, 14240-29-0; *cis*-$[CrCl_2(pn)_2]Cl$, 18251-59-7; *cis*-$[CrCl_2(tn)_2]Cl$, 17632-36-9; *trans*-$[Cr(NCS)_2(en)_2]SCN$, 15654-67-8; *trans*-$[Cr(NCS)_2(pn)_2]SCN$, 17632-32-5; *trans*-$[Cr(NCS)_2(tn)_2]SCN$, 72982-94-6; *cis*-$[CrCl_2(en)(pn)]Cl$, 71884-67-8; *cis*-$[CrCl_2(en)(tn)]Cl$, 71884-68-9; *cis*-$[CrCl_2(pn)(tn)]Cl$, 81244-80-6; *trans*-$[CrCl_2(en)(pn)]Cl$, 71861-01-3; *trans*-$[CrCl_2(pn)(tn)]Cl$, 71861-02-4; *trans*-$[CrCl_2(en)(tn)]Cl$, 81194-12-9; *trans*-$[Cr(NCS)_2(en)(pn)]SCN$, 81194-11-8; *trans*-$[Cr(NCS)_2(en)(tn)]SCN$, 81205-62-1; *trans*-$[Cr(NCS)_2(pn)(tn)]SCN$, 81255-39-2; *trans*-$[CrCl_2(tn)_2]Cl$, 26186-25-4; *trans*-$[CrBr_2(tn)_2]Br$, 30862-87-4; *cis*-$[CrBr_2(tn)_2]Br$, 18251-60-0; tn·2HCl, 10517-44-9; en·2HCl, 333-18-6.

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# Chemistry of Sputtered Molybdenum Disulfide Films

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Radio-frequency- (rf) sputtered molybdenum disulfide films are being used increasingly as lubricants for spacecraft applications. The stoichiometry of such films has been tied to sputtering parameters; however, the change in stoichiometry and chemistry of these films after preparation has not been examined. In this study the room-temperature oxidation of rf-sputtered molybdenum disulfide has been investigated. Films were stored in various environments such as dry air, 100% relative humidity, and vacuum for a minimum of 2 weeks. The chemical states were examined by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Results of XPS analysis of films stored in 100% relative humidity show complete oxidation of Mo(IV) to Mo(VI) at the molybdenum disulfide surface. Both XPS and AES results show that sulfur is removed from the surface when oxidation occurs. The Auger results indicate that sulfur is removed from samples to a depth of at least 45 Å, which indicates that oxidation has occurred at this depth. XPS analysis shows that the retained sulfur is in the form of sulfide or elemental sulfur. There is no oxidation of sulfur to sulfite or sulfate. Wear-test measurements show that oxidation of films causes substantial degradation of the lubricating properties of the films. Also, Auger analyses reveal a degradation of molybdenum disulfide films as a result of wear even for unoxidized films.

## I. Introduction

Solid-film lubricants such as molybdenum disulfide ($MoS_2$) have received much attention in the past decade for spacecraft applications because they maintain their lubricating properties over extreme temperature ranges, high and low bearing velocities, and unidirectional or oscillatory motion and under various loads. Sputtered $MoS_2$ films ~2000 Å thick have been found to have much longer wear life and better overall performance than films applied by other commonly accepted techniques such as burnishing or electroplating or with the use of binders.[1,2] Although sputtered films offer superior overall lubricating performance compared with that of films prepared by other techniques, the lubricating properties of such films can be greatly altered by varying the sputtering conditions during film preparation.[3-6] Wheeler used photoelectron spectroscopy as a surface diagnostic tool to show that the stoichiometries of films were altered greatly as a result of variation in sputtering conditions.[5] He found that the coefficient of friction increased with a decrease in sulfur in the sputtered films. Much work has been done on the effect of sputtering conditions on the initial chemical and lubricating properties of sputtered $MoS_2$ films, but no work has been reported on the chemical behavior of these films after preparation (i.e., during storage or use as lubricants). In this paper, we present findings on the room-temperature oxidation of $MoS_2$ films stored in various environments and on the effects

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