ACTA CHEMICA SCANDINAVICA 24 (1970) 3362–3372

# Preparation of Bis- and Tris(diamine)chromium(III) Complexes *via* Dimethyl Sulfoxide and Dimethylformamide Complexes. The Novel Series of *cis*-Bis(trimethylenediamine)- and *cis*-Bis[(—)*trans*-1,2-cyclohexanediamine]chromium(III) Complexes

ERIK PEDERSEN

*Chemistry Department I (Inorganic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*

A general and easy procedure for preparing bis- and tris(diamine)-chromium(III) complexes, most of them in high yields, is described. It is based on the reaction between the stoichiometric amount of the diamine and a solution of green chromium(III) chloride in dimethyl sulfoxide or dimethylformamide from which water has been distilled off. Preparation of salts of the following complexes is described: $[Cren_3]^{3+}$ (en=ethylenediamine), $[Crtn_3]^{3+}$ (tn=trimethylenediamine), $[Cr(-)chxn_3]^{3+}$[(—)chxn=(—)*trans*-1,2-cyclohexanediamine], *cis*-$[Cren_2Cl_2]^+$, *cis*-$[Cren_2(DMS)Cl]^{2+}$ (DMS=dimethyl sulfoxide), *cis*-$[Crtn_2Cl_2]^+$, $(-)_D$*cis*-$[Crtn_2Cl_2]^+$, *trans*-$[Crtn_2Cl_2]^+$, *cis*-$[Cr(-)chxn_2(DMS)Cl]^{2+}$, and *cis*-$[Cr(-)chxn_2Cl_2]^+$. The compounds are characterized by their absorption and circular dichroism spectra. The novel series of complexes *cis*-$[Crtn_2X_2]^+$ and *cis*-$[Cr(-)chxn_2X_2]^+$ are described.

In the chemical literature several procedures for preparing tris(diamine)-chromium(III) complexes are mentioned. Bis(diamine)chromium(III) complexes are most often prepared by thermal decomposition of the corresponding tris-complexes.

A general problem in the preparation of amine and ammine complexes of chromium(III) in aqueous solution is the very strong competition from the hydroxide ion which tends to form polynuclear as well as mononuclear species.[1]

In the preparation of the tris(diamine)chromium(III) complexes three important ways of avoiding or partially avoiding this difficulty have been: (a) Oxidation of the tris(ethylenediamine)chromium(II) complex, existing under equilibrium conditions in aqueous solution.[2–4] (b) Exchange of mono-

dentate ligands with diamine as in the reaction of trichlorotris(pyridine)-chromium(III) with ethylenediamine hydrate,[5,6] with propylenediamine hydrate,[7] and with *trans*-1,2-cyclohexanediamine.[8] (c) Reaction between anhydrous chromium(III) chloride and the diamine, either free or in ether solution,[9–11] or between dehydrated chromium alum and ethylenediamine hydrate.[12–14] In addition to these methods the tris(ethylenediamine) complex has also been prepared from hydrated chromium(III) chloride and ethylenediamine in toluene,[15] hot dimethylformamide,[16] water in the presence of activated charcoal,[17] and methanol in the presence of zinc.[18] Homogeneous reaction between trichlorotris(dimethylformamide)chromium(III) in dimethylformamide and ethylenediamine in anhydrous benzene is reported by White [19] to give the tris-complex quantitatively. Recently Woldbye [20] described the reaction between diamines and anhydrous chromium(III) chloride dissolved in dimethyl sulfoxide after addition of a small amount of reductor.

Common disadvantages of the methods (a) are: Procedures are tedious, the yields are not very high due to side reactions, and only a rather small amount of complexes can be prepared in one run. The inhomogeneous reactions (b) and (c) are rather unreliable. The yields vary much and are very sensitive to small amounts of water and the products can be difficult to purify. Common to all these methods is the requirement of an often large excess of diamine. White's method was found useful in the case of the tris(ethylenediamine) complex, but failed to give more than a few per cent of the corresponding trimethylenediamine complex. Woldbye does not give any details of the preparation, but the yields are probably comparable to those obtained here as the reaction conditions are almost equal.

The *cis*-dichlorobis(ethylenediamine)chromium(III) complex has been prepared by treating dihydroxodiaquabis(pyridine)chromium(III) chloride with an aqueous solution of ethylenediamine [6] and by heating of the tris-complex in concentrated hydrochloric acid,[14,21,6] or in tetraline.[22] None of these reactions are useful for a preparative purpose. By far the most popular procedure seems to be Rollinson and Bailar's method of heating the chloride of the tris-complex, containing a little ammonium chloride.[23] After a little training this method can be useful for small scale preparations, but the products can sometimes be difficult to recrystallize due to impurities. Wendlandt and coworkers prepared the complex by the so called "thermal matrix method",[24,25] a tedious procedure involving heating of the tris-complex, heterogeneously mixed with large quantities of ammonium chloride, followed by sublimation of the excess ammonium chloride. White [19] also prepared this complex in dimethylformamide by a procedure similar to that mentioned for the tris-complex.

The preparation of *cis*-dichlorobis(trimethylenediamine)chromium(III) chloride has been described by Wendlandt and Sveum,[26] but as discussed later on their results could not be verified.

In the present paper a general method is described for synthesizing bis- and tris(diamine)chromium(III) complexes in high boiling solvents from which water from the initial material, hydrated chromium(III) chloride, is easily removed by distillation. The principle is that the solvent molecules are so loosely bound to chromium(III) that they are easily substituted by the amines which are strongly bound to chromium(III) under these circumstances. The

chloride ions behave in an intermediate way and in most cases occupy all the coordination positions not already occupied by the amines.

The preparation of tris(ethylenediamine)- and tris(trimethylenediamine)-chromium(III) chloride in this way has been briefly mentioned previously.[27]

As solvent dimethyl sulfoxide, and in a single case dimethylformamide, is used.

## RESULTS

*Initial materials.* Hydrated chromium(III) chloride dissolves very easily in dimethyl sulfoxide with evolution of heat. The species present in the solution after removal of water by distillation has been investigated by Schläfer and Opitz.[28] They found a temperature dependent equilibrium between the green violet *cis*-dichlorotetrakis(dimethyl sulfoxide)chromium(III) and the red-violet trichlorotris(dimethyl sulfoxide)chromium(III) with the dichloro-complex as the main constituent at room temperature, and the trichloro-complex as so above *ca.* 150°C. This agrees well with the observations made here under similar conditions but with much higher complex concentrations.

If the violet solution, containing mainly trichlorotris(dimethyl sulfoxide)-chromium(III) (preparation No. 1) is cooled below *ca.* 100°C it solidifies to a glass or a crystalline mass, dependent on the rate of cooling. The minimum amount of dimethyl sulfoxide has been used here, and it is very important not to distill off the much of it, as the complex solution may then be solid at the temperatures suitable for the reaction with the amines.

The crystalline mass obtained by slow cooling was found to contain 5 moles of dimethyl sulfoxide per mole of chromium, and is probably identical to the compound *cis*-$[Cr(DMS)_4Cl_2]Cl,DMS$ described previously.[29,30] It is "earth brown" in daylight and pure green in electric light. Large quantities of this complex have been stored for years in closed desiccators for future preparations of chromium complexes.

*The preparative reactions.* Trichlorotris(dimethyl sulfoxide)chromium(III) in dimethyl sulfoxide reacts with a series of amines under precipitation of complexes containing coordinated amine and chloride ions, and in a few cases also dimethyl sulfoxide. The desired complexes are prepared by adding equivalent amounts or 10 % excess of the amine. The reactions proceed during a few minutes at 120°C and during hours or days at room temperature.

A similar method of preparing the corresponding bromo-complex bromides or tris-complex bromides cannot be used. During the preparation of the initial solution from hydrated chromium(III) bromide (prepared from the nitrate by adding equivalent amounts of formalin and 65 % hydrobromic acid), hexakis(dimethyl sulfoxide)chromium(III) bromide separates quantitatively and persists reaction with most amines, even at elevated temperatures. (With liquid ammonia at 100°C the hexammine is formed during a few hours [31].)

The reaction with diamines and polyamines has been investigated, but details are given for the bis- and tris(diamine) complexes, only.

*Ethylenediamine* forms the tris-complex smoothly and almost quantitatively. By the addition of two moles of amine per mole of chromium a solution is formed, apparently containing about equal amounts of *cis*-$[Cren_2Cl_2]^+$ and

*cis*-[$Cren_2$(DMS)Cl]$^{2+}$. The dichloro-complex precipitates slowly after the addition of seeding crystals, and the chloro(dimethyl sulfoxide)-complex by the addition of ethanol. In the special case of this dichloro-complex it was found more convenient to do the preparation in dimethylformamide from which it is more easily crystallized. Palmer and Watts [32] found that for lower concentrations in dimethylformamide solution about 75 % of the chromium exists as the dichloro-complex, unless the chloride concentation is very low. This agrees well with the yield obtained here. By adding one mole of amine per mole of chromium and excess of tetraethylamonium chloride to the initial solution a blue compound was precipitated during a few days after addition of ethanol. This was shown to be a mixture containing bis-complex as well as ($Et_4N$)[$CrenCl_4$]. From the absorption spectrum this compound was shown to be equivalent to the cesium salt, previously prepared by cleaving of rhodoso chromium [33] in concentrated hydrochloric acid.[39]

*Trimethylenediamine* forms the tris-complex smoothly but less completely than does the ethylenediamine. The yield of this preparation has been found to vary slightly with the amine product used. Therefore the yield mentioned previously [27] may be a little too optimistic as an average. With two moles of amine per mole of chromium a mixture of the *cis*- and *trans*-bis(diamine) complexes is formed, but the products obtained depend very much on the experimental conditions, especially the temperature of the reaction mixture. Lower temperatures favour the formation of *cis*-[$Crtn_2Cl_2$]$^+$. At temperatures above *ca.* 150°C mainly *trans*-[$Crtn_2Cl_2$]$^+$ is formed. The *cis*-complex is very soluble in dimethyl sulfoxide at elevated temperatures and crystallizes difficultly at lower temperatures. The *trans*-complex is not very soluble and crystallizes easily. These properties complicate the preparation of the *cis*-complex considerably. The formation of the *cis-trans*-mixture appears to be mainly kinetically controlled. In order to favour the *cis*-complex the temperature must be kept low. By addition of seeding crystals the yield is increased considerably. Several experiments were performed to optimize the conditions. *Ca.* 120° was found suitable. At this temperature and with the use of seeding crystals nearly all of the *trans*- and part of the *cis*-complex precipitates. The two isomers are easily separated by extraction with a hot mixture of ethanol and dimethyl sulfoxide in which the *trans*-complex is sparingly soluble. For unknown reasons old mixtures could not be separated easily in this way.

*Propylenediamine* reacts just like ethylenediamine. Only the formation of a tris-complex with the racemic amine was investigated. The similar reaction with (−)-propylenediamine has been described.[35]

(−)-trans-*1,2-Cyclohexanediamine* does not immediately form the tris-complex by the addition of three moles of amine per mole of chromium, but *cis*-[Cr(−)chx$n_2$(DMS)Cl]$Cl_2$ precipitates quickly. After prolonged heating it is converted to a solution of the tris-complex.

trans-*1,2-Cyclopentanediamine* reacts just like ethylenediamine, but with lower yield, about 60 %.

*Diethylenetriamine*, (bis(2-aminoethyl)amine), easily forms the bis-complex ($N_6$-chromophore).

*Triethylenetetramine* 1,4,7,10-tetraazadecane (trien) forms *cis*-[Cr(trien)$Cl_2$]$^+$. By an analogous reaction *cis*-[Cr(entnen)$Cl_2$]$^+$ is formed [36] (entnen = 1,4,8,11-

tetraazaundecane). Due to the very high solubility in dimethyl sulfoxide these complexes are more conveniently prepared as the perchlorates by reacting the difluoro perchlorates [37] with a mixture of hydrochloric acid and perchloric acid.

*Tris(2-aminoethyl)amine* reacts just like triethylenetetramine and is also most conveniently prepared as the perchlorate *via* the difluoro-complex.[37]

*Tetraethylenepentamine* (1,4,7,10,13-pentaazatridecane), (tetren) reacts rather slowly under formation of $[Cr(tetren)Cl]^{2+}$. From the colour changes during the reaction one can almost see the garland amine being wound around the chromium.

## EXPERIMENTAL

*Materials.* Green chromium(III) chloride, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$: Riedel De Haën, "rein". Dimethyl sulfoxide: Fluka, "purum", b.p.$_{10}$: 66–69°C. Dimethylformamide: Riedel De Haën, non specified purity. Ethylenediamine: Riedel De Haën, 98 %. Trimethylenediamine: Fluka, "purum", ≥98 %, b.p. 134–136°C. (−)*trans*-1,2-Cyclohexanediamine was isolated as (−)chxnH$_2$(+)tart (H$_2$tart=tartaric acid) from *cis-trans*-cyclohexanediamine, Fluka, "pract.", by direct precipitation.

***Physical measurements.*** Absorption spectra in the range 300–700 nm were measured on a Cary 14 spectrophotometer. The spectra are characterized by their maxima and minima, $(\varepsilon,\lambda)$, where the molar extinction coefficient, $\varepsilon$, in $l \cdot mol^{-1} \cdot cm^{-1}$ and $\lambda$ is in nm.

Circular dichroism was measured on a Roussel-Juan Dichrographe I. The extremum values of the spectra are given by $(\varepsilon_l - \varepsilon_r,\lambda)$.

Thermogravimetric measurements were performed on the thermobalance described previously.[37]

## Preparations

1. *Chlorodimethylsulfoxidechromium(III) complex as initial material.* 100 g of $[Cr(H_2O)_4Cl_2]Cl,2H_2O$ (0.375 mol) was dissolved by heating in 200 ml of dimethyl sulfoxide (2.8 mol), and the water was distilled off until a vapour temperature of *ca.* 190°C was reached. For dimethyl sulfoxide b.p. ~190°C. For the amounts given here *ca.* 90 ml of liquid was distilled off. After cooling to 110°C a violet liquid with rather high viscosity was obtained. This was used as initial material for most of the following preparations.

2. *Tris(ethylenediamine)chromium(III) chloride,* $[Cren_3]Cl_3$,aq. The violet liquid was poured into 83 ml of ethylenediamine (1.24 mol) under rapid precipitation of the tris-complex. The reaction mixture was subsequently placed at 150°C for 1 h for completion of the reaction. After cooling the yellow mass was stirred with 200 ml of ethanol, filtered, and washed with ethanol. The crude product contains a little dimethyl sulfoxide which was completely removed by one recrystallization. The product (*ca.* 180 g) was dissolved in a mixture of 185 ml of water, and 30 ml of 12 M hydrochloric acid at 65°C, quickly filtered, and heated to 65°C again. Further 40 ml of 12 M hydrochloric acid was added. After cooling to 0°C the product was filtered, washed with 70 % ethanol, and air dried. A second crop of crystals (*ca.* 6 g) may be obtained from the mother liquor by saturation with ether. Total yield 106 g corresponding to 70 % based on chromium. (Found: Cr 13.12; C 18.13; H 7.82; N 21.0; Cl 27.0. Calc. for $[Cr(C_6H_{24}N_6)]Cl_3$,3.2 $H_2O$: Cr 13.11; C 18.17; H 7.73; N 21.20; Cl 26.80.) The water content varies with the relative humidity and the temperature. It was determined by thermogravimetry under equilibrium conditions at 23°C, 35 % relative humidity. Weighings for analyses and spectra were performed under the same conditions. 5.155 mg had constant weight under the specified conditions. By heating 2°C $min^{-1}$ 0.752 mg was lost up to 110°C, followed by weight constancy up to 170°C. The weight loss corresponds to 3.22 moles of water per mole of chromium. $(\varepsilon,\lambda)_{max}$: (74.4, 457.6); (60.2, 350.6). $(\varepsilon,\lambda)_{min}$: (14.2, 395.0); (1.5, 287). Medium: water.

3. *Tris(trimethylenediamine)chromium(III) chloride,* $[Crtn_3]Cl_3$,aq. The preparation and recrystallization was performed as for the corresponding ethylenediamine complex.

104 ml of trimethylenediamine (1.24 mol), and less solvent for the recrystallization was used. Yield of almost pure crude product 128 g, corresponding to 90 %. Yield of recrystallized product 101 g, corresponding to 60 % based on chromium. (Found: Cr 11.40; C 23.80; H 8.53; N 18.47; Cl 23.37. Calc. for $[Cr(C_9H_{30}N_6)]Cl_3,4.1\ H_2O$: Cr 11.43; C 23.78; H 8.47; N 18.49; Cl 23.39.) The water content depends very much on the relative humidity and the temperature. It was determined by thermogravimetry as for the tris(ethylenediamine) complex at 48 % relative humidity, 23°C. 4.928 mg had constant weight under these conditions. 0.802 mg was lost up to 110°C, followed by weight constancy up to 200°C. This corresponds to 4.11 moles of water per mole of chromium. $(\varepsilon,\lambda)_{max}$: (55.3, 464.4); (47.6, 354.7). $(\varepsilon,\lambda)_{min}$: (11.5, 400.0); (4.4, 295). Medium: water.

4. *Tris*[(−)trans-*1,2-cyclohexanediamine*]*chromium(III) chloride*, $[Cr(-)chxn_3]Cl_3$, aq. 7.8 g of $[Cr(H_2O)_4Cl_2]Cl,2H_2O$ (29 mmol) in 25 ml dimethyl sulfoxide was distilled as in preparation No. 1, and poured into a solution of 10 g of (−)-cyclohexanediamine (87 mmol) in 10 ml of dimethyl sulfoxide at 100°C. A red silky compound, *cis*-$[Cr(-)chxn_2(DMS)Cl]Cl_2$ (see preparation No. 11), precipitated at once. At 150°C this dissolved again, and the solution turned yellow brown after 15 min. Only a small amount of tris-complex separated on cooling and addition of 50 ml of ethanol. Dropwise addition of 100 ml of ether gave a yellow crystalline precipitate. Yield of crude product 13.2 g, corresponding to 91 %. The compound was recrystallized from water with a temperature change from 70 to 0°C. (Found: Cr 9.61; C 40.00; H 8.65; N 15.30; Cl 19.60. Calc. for $[Cr(C_{18}H_{42}N_6)]Cl_3,2.3H_2O$: Cr 9.59; C 40.00; H 8.66; N 15.46; Cl 19.59). Thermogravimetry failed to show the water content. In the range 45−120°C a weight loss was observed, corresponding to 0.98 moles of water per mole of chromium (based on the composition mentioned above). This was followed by weight constancy up to 160°C from where further decomposition took place. No ranges with constant weight was observed at higher temperatures. $(\varepsilon,\lambda)_{max}$: (89.0, 460.6); (69.7, 351.7). $(\varepsilon,\lambda)_{min}$: (16.6, 395.7); (2.2, 275.0). $(\varepsilon_l-\varepsilon_r,\lambda)_{extremum}$: (−2.49, 472); (+0.050, 409); (−0.0098, 366); (−0.0084, 353); (−0.0098, 340). Medium: water.

5. cis-*Dichlorobis(ethylenediamine)chromium(III) chloride*, *cis*-$[Cren_2Cl_2]Cl$,aq. 100 g of $[Cr(H_2O)_4Cl_2]Cl,2\ H_2O$ (0.375 mol) was dissolved in 300 ml of dimethylformamide. 150 ml of liquid was distilled off until a vapour temperature of 148°C was reached ($b.p._{DMF}$: 153°C). The violet liquid obtained was transferred to a beaker and allowed to cool to 100°C with stirring. 50 ml of ethylenediamine (0.75 mol) was added dropwise with stirring at a rate of 2 drops/sec. In this way the temperature was kept just below 135°C. (Be careful! The evolution of heat is considerable.) If larger amounts are used cooling may be necessary. The reaction mixture was placed at 150°C for 1 h and slowly cooled to room temperature. (In single cases it may happen that the complex separates as a heavy oil. Then just heat and cool it again in the same way, or scratch with a glass spatula.) The product was filtered, washed with ethanol, and dried in air. Yield 78 g, corresponding to *ca.* 75 %. For the crude product was found $(\varepsilon,\lambda)_{max}$: (75, 528) in 12 M hydrochloric acid. Recrystallization was performed by dissolving on the filter in the minimum amount of water at 60°C and filtering quickly into ice cold 12 M hydrochloric acid. Yield 60 % from the crude product. (Found: Cr 17.28; C 16.07; H 6.12; N 19.06; Cl 35.71. Calc. for $[Cr(C_4H_{16}N_4)Cl_2]Cl,1.15H_2O$: Cr 17.38; C 16.07; H 6.16; N 18.72; Cl 35.61.) The water content was determined by thermogravimetry. 8.215 mg was heated 5°C $min^{-1}$ in air (45 % relative humidity, 23°C). Weight constancy was observed up to 105°C. 0.547 mg was lost from 105 to 125°C, followed by weight constancy. This corresponds to 1.15 moles of water per mole of chromium. $(\varepsilon,\lambda)_{max}$: (79.6, 530.0); (75.9, 401.8). $(\varepsilon,\lambda)_{min}$: (23.8, 456.2); (5.5, 320). Medium: 12 M hydrochloric acid.

6. cis-*Dichlorobis(trimethylenediamine)chromium(III) chloride*, *cis*-$[Crtn_2Cl_2]Cl$,aq. To the violet liquid (preparation No. 1) was added under stirring 63 ml of trimethylenediamine (0.75 mol) during 10 min in portions of 10 ml. The temperature was kept below 130°C. (After addition of 50 ml of amine 1 g of the complex may be added as seeding crystals, otherwise it may happen that the yield is decreased to half the amount, mentioned below.) After half an hour at 100°C the crystalline mush was filtered and washed with 150 ml of ethanol in 5 portions while the precipitate was still hot. The washed product contains considerable amounts of *trans*-complex. The content of *cis*-complex was extracted with 80 ml of a 50 % v/v mixture of ethanol and dimethyl sulfoxide at 100°C. The green *trans*-complex which is almost insoluble under these conditions was filtered off and washed with 100 ml of ethanol. All the filtrates and washing liquids were combined and kept

in the refrigerator at −18°C overnight. After washing with ethanol the yield of the precipitated violet *cis*-complex varied about 40 g, corresponding to 35 %. The crude product contains a little dimethyl sulfoxide. It was recrystallized by dissolving 10 g in 5 ml of 0.5 M hydrochloric acid at room temperature. After a few seconds most of the complex precipitates as the monohydrate. The violet-red powder was washed with a small amount of ice-water and dried in air. Yield about 60 %. A visibly crystalline product may be obtained after a recrystallization as in preparation No. 5, but the yield is low. (Found: Cr 16.23; C 22.59; H 6.71; N 17.63; Cl 33.40. Calc. for $[Cr(C_6H_{20}N_4)Cl,0.75\ H_2O$: Cr 16.25; C 22.50; H 6.77; N 17.50; Cl 33.23.) The water content was determined by thermogravimetry. 16.37 mg was heated 5°C $min^{-1}$ in air (45 % relative humidity, 23°C). 0.68 mg was lost between 40 and 170°C, followed by almost constant weight up to 190°C. This corresponds to 0.75 mole of water per mole of chromium. $(\varepsilon,\lambda)_{max}$: (47.9, 526.5); (47.6, 397.6). $(\varepsilon,\lambda)_{min}$: (13.8, 453.5); (4.0, 315.0). Medium: 12 M hydrochloric acid.

7. cis-*Dichlorobis(trimethylenediamine)chromium(III) perchlorate, cis*-$[Crtn_2Cl_2]ClO_4$. 10 g of the crude chloride was dissolved in 5 ml of 30 % perchloric acid at 60°C. After cooling in ice the violet crystalline perchlorate was washed with ice-water and dried in air. Yield 2 g. (Found: Cr 13.58; C 19.00; H 5.45; N 14.69; Cl 27.80. Calc. for $[Cr(C_6H_{20}N_4)Cl_2]ClO_4,\frac{1}{2}H_2O$: Cr 13.70; C 18.98; H 5.57; N 14.75; Cl 28.00.)

8. $(+)_D$cis-*Dichlorobis(trimethylenediamine)chromium(III) α-bromo*-d-*camphor-π-sulfonate*, $(+)_D$cis-$[Crtn_2Cl_2]$ (α-bromo-*d*-camphor-π-sulfonate). 1.00 g of the crude chloride (3.26 mmol) in 5 ml of water, weakly acidified with nitric acid, was treated with 1.36 g of silver α-bromo-*d*-camphor-π-sulfonate (3.26 mmol) in a mortar. The silver chloride precipitated was filtered off quickly, and 4 ml of ethanol was added dropwise. The violet precipitate was filtered, washed with ethanol and dried in air. Yield 0.2 g. (Found: Cr 8.21; C 30.05; H 6.20; N 8.89; Cl 11.05; Br 12.65. Calc. for $[Cr(C_6H_{20}N_4)Cl_2](C_{10}H_{14}O_4SBr),3\ H_2O$: Cr 8.19; C 30.15; H 6.35; N 8.81; Cl 11.18; Br 12.59.) $(\varepsilon,\lambda)_{max}$: (47.5, 526.2); (48.4, 397.6). $(\varepsilon,\lambda)_{min}$: (14.7, 453.5); (9.2, 340.0). $(\varepsilon_l-\varepsilon_r,\lambda)_{extremum}$: (−0.36, 590); (+0.33, 511); (+0.10, 419); (−0.01, 370). Medium: 12 M hydrochloric acid.

9. $(+)_D$cis-*Dichlorobis(trimethylenediamine)chromium(III) perchlorate*, $(+)_D$*cis*-$[Crtn_2Cl_2]ClO_4$. 0.4 g of the α-bromo-*d*-camphor-π-sulfonate was dissolved in 40 drops of 70 % perchloric acid. The solution was cooled in ice and 15 drops of water was added. The precipitate was filtered, washed, first with a small amount of ice-water, then with ethanol, and dried in air. Yield 0.2 g. (Found: Cr 12.46; C 17.40; H 5.95; N 13.53; Cl 25.85. Calc. for $[Cr(C_6H_{20}N_4)Cl_2]ClO_4,2.5\ H_2O$: Cr 12.49; C 17.32; H 6.07; N 13.48; Cl 25.63.) Medium: 12 M hydrochloric acid.

10. trans-*Dichlorobis(trimethylenediamine)chromium(III) chloride, trans*-$[Crtn_2Cl_2]Cl$. To the violet liquid (preparation No. 1) was added 63 ml of trimethylenediamine (0.75 mol). The reaction mixture was allowed to stand at 150°C for 2 h. After cooling to about 100°C the green precipitate was filtered, washed with ethanol and dried in air. Yield 60 g of *trans*-complex, corresponding to 52 %. From the combined filtrate and washing liquids 10 g of *cis*-complex precipitated after a few hours at 0°C. The crude *trans*-complex, containing a little dimethyl sulfoxide, was dissolved in 340 ml of water at room temperature and filtered. 170 ml of 12 M hydrochloric acid was added under ice-cooling and stirring. The product was washed with ethanol and dried in air. Yield 30 g. (Found: Cr 16.93; C 23.41; H 6.52; N 18.27; Cl 34.71. Calc. for $[Cr(C_6H_{20}N_4)Cl_2]Cl$: Cr 16.96; C 23.50; H 6.57; N 18.26; Cl 34.70.) $(\varepsilon,\lambda)_{max}$: (25.9, 592.5); (23.7, 455.0); (41.9, 398.2). $(\varepsilon,\lambda)_{min}$: (5.9, 522.0); (23.5, 448.0); (1.2, 310.0). Medium: 12 M hydrochloric acid.

11. cis-*Chloro(dimethylsulfoxide)bis(ethylenediamine)chromium(III) chloride, cis*-$[Cren_2(DMS)Cl]Cl_2$. To the violet liquid (preparation No. 1) 50 ml of ethylenediamine (0.75 mol) was added dropwise with stirring. After 1 h at 150°C 250 ml of ethanol was added dropwise with stirring, and the mixture was allowed to stand overnight for precipitation of the red violet product. This was filtered, washed with ethanol, and dried in air. Yield 75 g. Further 33 g could be obtained by adding a mixture of 250 ml ether and 250 ml ethanol to the filtrate. This last fraction contained a little of the dichloro-complex. The total yield corresponds to 81 %. The crude product is contaminated with dimethyl sulfoxide. This chloride is very soluble in water. No solvent suitable for recrystallization was found. The complex was converted to the perchlorate for characterization.

12. cis-*Chloro(dimethylsulfoxide)bis(ethylenediamine)chromium(III) perchlorate, cis*-$[Cren_2(DMS)Cl](ClO_4)_2$. 5 g of the first fraction of the chloride was dissolved in 5 ml of water and 5 ml of 70 % perchloric acid was added. The solution was left for crystalliza-

tion in ice. The red crystals were filtered, washed, first with 10 ml of ice-cold 35 % perchloric acid then with ethanol and dried in air. Yield 3.2 g. (Found: Cr 10.65; C 14.64; H 4.54; N 11.71; Cl 21.93. Calc. for $[Cr(C_4H_{16}N_4)(C_2H_6SO)Cl](ClO_4)_2$: Cr 10.72; C 14.87; H 4.58; N 11.57; Cl 21.94.) The analysis for sulfur failed to be reproducible. $(\varepsilon,\lambda)_{max}$: (73.0, 513.8); (56.4, 392.9). $(\varepsilon,\lambda)_{min}$: (27.3, 442.4); (5.7, 310.0). Medium: 2 M hydrochloric acid.

13. cis-*Chloro(dimethylsulfoxide)bis*[(−)trans-*1,2-cyclohexanediamine*]*chromium(III) chloride, cis*-[Cr(−)chxn$_2$(DMS)Cl]Cl$_2$. 23.4 g of $[Cr(H_2O)_4Cl_2]Cl,2H_2O$ (88 mmol) in 50 ml of dimethylsulfoxide was distilled as in preparation No 1. After cooling to 100°C a solution of 20.0 g of (−)*trans*-1,2-cyclohexanediamine (176 mmol) in 50 ml of dimethyl sulfoxide was added. After a few minutes a pink violet precipitate was formed. The reaction mixture was placed in an oven at 100°C for 1 h and precipitated with 200 ml of ethanol after cooling. The crude product was filtered, washed with ethanol and dried in air. Yield 35 g, corresponding to 81 %. (Found: Cr 10.75; C 35.8; H 7.34; N 11.34; Cl 22.1. Calc. for $[Cr(C_{12}H_{28}N_4)(C_2H_6SO)Cl]Cl_2$: Cr 11.19; C 36.20; H 7.38; N 12.05; Cl 22.88.) This corresponds to 0.24 mole of dimethyl sulfoxide per mole of chromium. For further characterization the chloride was converted to the perchlorate.

14. cis-*Chloro(dimethyl sulfoxide)bis*[(−)trans-*1,2-cyclohexanediamine*]*chromium(III) perchlorate, cis*-[Cr(−)chxn$_2$ (DMS)Cl])$ClO_4)_2$. The perchlorate was precipitated almost quantitatively from an aqueous solution of the chloride by dropwise addition of 70 % perchloric acid. (Found: Cr 8.37; C 27.47; H 5.61; N 9.20; Cl 17.62. Calc. for $[Cr(C_{12}H_{28}N_4)(C_2H_6SO)Cl](ClO_4)_2,H_2O$: Cr 8.51; C 27.55; H 5.95; N 9.17; Cl 17.43.) The analytical results can not be expected to be very accurate as the compound explodes at heating. The water content was determined by thermogravimetry. 7.602 mg was heated 5°C min$^{-1}$ in air (40 % relative humidity, 23°C). 0.223 mg was lost between 35 and 80°C, followed by weight constancy. This corresponds to 1.00 mole of water per mole of chromium. $(\varepsilon,\lambda)_{max}$: (75.5, 515.6); (62.6, 393.5). $(\varepsilon.\lambda)_{min}$: (22.2, 445.0); (1.8, 310.0). $(\varepsilon_l-\varepsilon_r,\lambda)_{extremum}$: (0.147, 584); (−0.626, 507); (−0.216, 415). Medium: 2 M hydrochloric acid.

15. cis-*Dichlorobis*[(−)trans-*1,2-cyclohexanediamine*]*chromium(III) chloride, cis*-[Cr(−)chxn$_2$Cl$_2$]Cl. 3 g of *cis*-[Cr(−)chxn$_2$ (DMS)Cl]Cl$_2$ was dissolved in 10 ml of 12 M hydrochloric acid. The flask was closed and heated to 60°C for 3 h. After icecooling and filtration the violet needle-shaped crystals (containing hydrogen chloride) were dissolved in 5 ml of water at 60°C, from which the hydrate precipitated quickly. After cooling in ice it was washed with a small amount of ice-cold water. Yield 1.0 g. From the filtrate the perchlorate can be precipitated with 70 % perchloric acid. Large crystals can be obtained from the hydrochloric acid filtrate, in which the perchlorate is soluble, by the addition of 3 ml of 70 % perchloric acid and partial evaporations of hydrogen chloride at room temperature. (Found: Cr 12.19; C 34.17; H 7.62; N 13.30; Cl 25.46. Calc. for $[Cr(C_{12}H_{28}N_4)Cl_2]Cl,2\ H_2O$: Cr 12.31; C 34.15; H 7.64; N 13.25; Cl 25.20.) The water content was determined by thermogravimetry. 7.660 mg was heated 5°C min$^{-1}$ in air (40 % relative humidity, 23°C). 0.650 mg was lost between 30 and 125°C followed by weight constancy. This corresponds to 1.99 moles of water per mole of chromium. $(\varepsilon,\lambda)_{max}$: (84.4, 529.4); (76.7, 402.9). $(\varepsilon,\lambda)_{min}$: (24.4, 456.5); (1.6, 315.0). $(\varepsilon_l-\varepsilon_r,\lambda)_{extremum}$: (+0.630, 587); (−0.563, 519); (−0.355, 480); (−0.142, 430); (+0.150, 384). Medium: 12 M hydrochloric acid.

## DISCUSSION

The preparation of *cis*-dichlorobis(trimethylenediamine)chromium(III) chloride was described by Wendlandt and Sveum.[26] They heated a mixture of the tris-complex and a large amount of ammonium chloride to 160°C. The reflectance spectrum of their product showed reflectance minima at about 617 and 425 nm. The elemental analysis agreed well with the formulation given above. We found the reflectance spectrum very suspicious-looking. The position of the reflectance minima of the solid could not be expected to deviate much from the absorbance maxima of a solution, and the trimethylenediamine-

complex was expected to have spectral properties, not very different from the corresponding ethylenediamine-complex with absorbance maxima at 530 and 402 nm. It was tried several times to repeat their method of preparation, but without any success. The result was always a green product (the *trans*-complex), covered with a very thin layer of a red material.

The thermal decomposition of tris(trimethylenediamine)chromium(III) chloride in air was followed by thermogravimetry; see Fig. 1. The stable composition between 210 and 240°C corresponds very closely to the formation of a bis(diamine)-complex. In this temperature interval the colour was grey-green with a tinge of violet. Under the microscope the material was seen to consist of separated violet and green particles. The same result was obtained by heating of large quantities in an oven. Heating of tris-complexes mixed

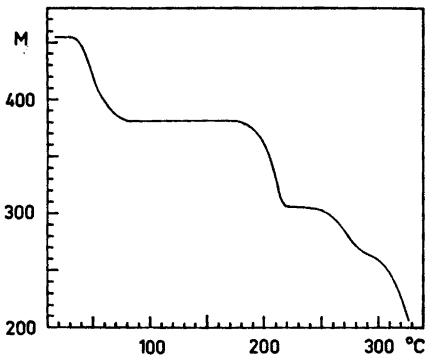


*Fig. 1.* Thermogravimetric analysis of $[Crtn_3]Cl_3$, 4.1 $H_2O$ in air. The ordinate gives a number, proportional to the sample weight, so that the starting value equals the molar weight (corresponding to one chromium atom) of the starting material.

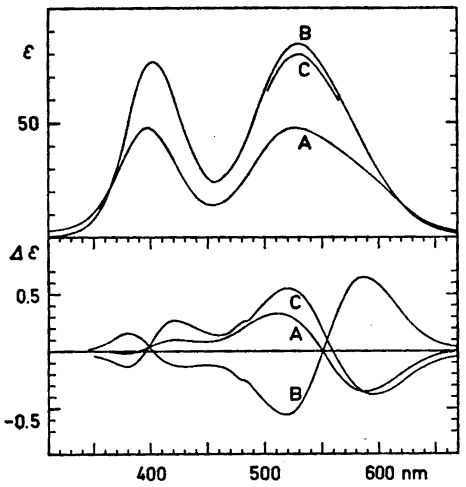


*Fig. 2.* Absorption and CD spectra of A: $(+)_D$*cis*$[Crtn_2Cl_2]^+$; B: *cis*$[Cr(-)chxn_2Cl]^+$; C: $(+)_D$*cis*$[Cren_2Cl_2]^+$.

with, or recrystallized from solutions of ammonium or alkylammonium chlorides, gave the same result. From these products it was possible to obtain small amounts of the pure *cis*-complex by extracting with a little 12 M hydrochloric acid at room temperature. Nearly all of the dissolved *trans*-complex was precipitated by saturation with hydrogen chloride at 0°C. After the addition of ether and cooling to −18°C the pure *cis*-complex crystallized. The best yield obtained was 0.5 %.

The reaction between the tris-complex and a hydrogen chloride atmosphere at elevated temperatures was investigated by thermogravimetry. The results have been published previously.[27] Under these circumstances the pure *trans*-complex was obtained.

The method of preparation of the *cis*-complex given here (preparation No. 6) is not ideal as the yield is not quite reproducible, due to the very delicate dependence of temperature, crystal seeding phenomena, *etc.* A complication is that once the *cis*-complex is formed in solution it is easily converted to the *trans*-complex, especially at higher temperatures. Two dimethyl sulfoxide solutions each containing one of the two isomers had nearly identical absorption spectra after 1 h at 150°C. Although the system is complicated due to the presence of dimethyl sulfoxide complexes, the spectrum showed that more than 80 % was present as the *trans*-dichloro complex. Even at room temperature relatively rapid conversions have been observed. If the *cis*-dichloro chloride is dissolved in 40 % hydrobromic acid, *trans*-dibromo bromide crystallizes, presumably as a hydrobromide, after one or a few hours, dependent of the concentration. Such a fast *cis-trans* conversion is very unusual for a chromium(III) complex.

The resolution of the *cis*-dichlorobis(trimethylenediamine)chromium(III) ion could not be performed with ammonium α-bromo-*d*-camphor-π-sulfonate, but only *via* the silver salt. The manipulations must be performed quickly, and the yield is not quite reproducible. At a pH of 5 it was possible to precipitate an antimony-*d*-tartrate, but without any resolution. The α-bromo-*d*-camphor-π-sulfonate was not recrystallized. If the CD-spectrum is compared with that of the perchlorate of the resolved complex it is seen that the resolution may not be quite complete. It is our impression that the rate of racemization is not fast enough to account for the 5 % lower $(\varepsilon_l - \varepsilon_r)$-values of the perchlorate. The absorption and CD-spectra of $(+)_D$*cis*-$[Cren_2Cl_2]^+$, and $(+)_D$*cis*$[Crtn_2Cl_2]^+$, both resolved as α-bromo-*d*-camphor-π-sulfonates, are qualitatively similar, except for the remarkably low extinction coefficients of the trimethylenediamine-complex (Fig. 2). The $\Delta\varepsilon$-values are comparable, in contrast to what could have been expected from the less strain in the 6-membered rings.

Thermogravimetry showed that *cis*$[Cr(-)chxn_2Cl_2]Cl$ is not a stable intermediate during the thermal decomposition of $[Cr(-)chxn_3]Cl_3$,aq in air. Nevertheless small amounts of the bis-complex could be isolated from such reaction mixtures. The method of preparation given here, *via* $[Cr(-)chxn_2(CMS)Cl]Cl_2$, is much more reliable. The CD- and absorption spectra (Fig. 2) are similar to those of $(+)_D$*cis*-$[Cren_2Cl_2]^+$, except for the apparent difference in absolute configuration. By fractional precipitation no evidence was found for the presence of two isomers. If it is assumed that the *cis* $[Cr(-)chxn_2Cl_2]^+$ ion described here is of the $lel_2$ type, corresponding to $\Delta(\lambda\lambda)$ in the IUPAC nomenclature, it follows that $(+)_D$*cis*-$[Cren_2Cl_2]^+$ and $(+)_D$*cis*$[Crtn_2Cl_2]^+$ has the configuration $\Lambda$.

## REFERENCES

1. Schäffer, C. E. and Andersen, P. In Jeżowska-Trzebiatowska, B. *Theory and Structure of Complex Compounds*, Pergamon, London 1964, p. 571.
2. Balthis, J. H. and Bailer, J. C. *J. Am. Chem. Soc.* **58** (1936) 1474.
3. Berman, D., Bokerman, G. and Perry, R. W. *Inorg. Syn.* **10** (1967) 35.
4. Schäffer, C. E. In Kirschner, S. *Advan. Chem. Coordination Compounds*, MacMillan, New York 1961, p. 628.

5. Pfeiffer, P. *Z. anorg. Chem.* **24** (1900) 279.
6. Pfeiffer, P. *Ber.* **37** (1904) 4255.
7. Pfeiffer, P. and Haiman, M. *Ber.* **36** (1903) 1063.
8. Jaeger, F. M. *Proc. Konikl. Ned. Akad. Wetenschap.* **40** (1937) 108.
9. Schläfer, H. L. and Kling, O. *Z. anorg. allgem. Chem.* **302** (1959) 1.
10. Kling, O. and Woldbye, F. *Acta Chem. Scand.* **15** (1961) 704.
11. Rollinson, C. L. and Bailar, J. C. *J. Am. Chem. Soc.* **65** (1943) 250.
12. Rollinson, C. L. and Bailar, J. C. *Inorg. Syn.* **2** (1946) 196.
13. Linhard, M. *Z. Elektrochem.* **50** (1944) 224.
14. Linhard, M. and Weigel, M. *Z. anorg. allgem. Chem.* **271** (1952) 115.
15. Marchi, L. E. and McReynolds, J. P. *J. Am. Chem. Soc.* **65** (1943) 480.
16. Dwyer, F. P. and Sargeson, A. In Kirschner, S. *Advan. Chem. Coordination Compounds*, MacMillan, New York 1961, p. 21.
17. Bailar, J. C. and Work, J. B. *J. Am. Chem. Soc.* **67** (1945) 176.
18. Gillard, R. D. and Mittchel, P. R. *J. Chem. Soc.* **A 1968** 2129.
19. White, R. C. *Thesis, Univ. of Maryland* **1960**. From *Diss. Abstr.* **21** (1960) 456.
20. Woldbye, F. *Studier over optisk aktivitet*, Thesis, Danmarks Tekniske Højskole 1968, p. 138.
21. Benrath, A. and Steinrath, H. *Z. anorg. allgem. Chem.* **194** (1930) 351.
22. Rock, M. *Thesis, Univ. of Maryland* **1960**. From *Diss. Abstr.* **21** (1960) 2467.
23. Rollinson, C. L. and Bailar, J. C. *Inorg. Syn.* **2** (1946) 200.
24. Wendlandt, W. W. and Stembridge, C. H. *J. Inorg. Nucl. Chem.* **27** (1965) 575.
25. Wendlandt, W. W. and Sveum, L. K. *J. Inorg. Nucl. Chem.* **28** (1966) 393.
26. Wendlandt, W. W. and Sveum, L. K. *J. Inorg. Nucl. Chem.* **29** (1967) 975.
27. Pedersen, E. *J. Sci. Instr. (Journal of Physics E), Ser. 2* **1** (1968) 1013.
28. Schläfer, H. L. and Opitz, H. P. *Z. Chem.* **2** (1962) 216.
29. Schläfer, H. L. and Opitz, H. P. *Z. anorg. allgem. Chem.* **313** (1961) 178.
30. Schläfer, H. L. and Schaffernicht, W. *Angew. Chem.* **72** (1960) 618.
31. Michelsen, K. *Private communication.*
32. Palmer, D. A. and Watts, D. W. *Australian J. Chem.* **20** (1967) 53.
33. Bang, E. *Acta Chem. Scand.* **22** (1968) 2671.
34. Andersen, P. *Private communication.*
35. Andersen, P., Galsbøl, F. and Harnung, S. E. *Acta Chem. Scand. In press.*
36. Bosnich, B., Gillard, R. D., McKenzie, E. D. and Webb, G. A. *J. Chem. Soc.* **A 1966** 1331.
37. Glerup, J., Josephsen, J., Michelsen, K., Pedersen, E. and Schäffer, C. E. *Acta Chem. Scand.* **24** (1970) 247.

Received March 12, 1970.