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SOLID-PHASE THERMAL SYNTHESES OF CIS- AND TRANS-$[CrBrIen_2]Z$ (Z = I AND ClO_4)

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The mixture of cis- and trans-$[CrBrIen_2]I$ was prepared via the solid-phase deaquation-anation of cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$. Both the isomers were purely isolated from the mixture by using aqueous $NaClO_4$ solution (trans-$[CrBrIen_2]ClO_4$) and methanol (cis-$[CrBrIen_2]I$).

The syntheses of mixed-dihalogeno bisdiamine chromium(III) complexes having a general formula of cis- and trans-$[CrXY(a\text{-}a)_2]Z$ (X, Y and Z are different unidentate anions and a-a is diamine) are increasingly required to extend more advanced investigations on kinetic behaviors in solution and thermal reactions in solid-phase. However, many troubles are usually required in the preparation of the complexes.[1,2] Ordinary methods for preparing such complexes are primarily based on the idea that halogenoaqua complexes $[CrX(H_2O)(a\text{-}a)_2]Z_2$ are treated with any suitable hydrohalogenic acid (HY) in liquid media to obtain the desired mixed-dihalogeno complexes $[CrXY(a\text{-}a)_2]Z$.[3,4] However, according to the methods, undesired complexes such as [Cr X_2 or $Y_2(a\text{-}a)_2]Z$ or other uncertain mixtures are frequently obtained without success in preparing the disired complexes. Moreover, the application of these methods is limited to only the case X = F and Y = Cl or Br.[5,6]

Anyone who has been concerned with the chromium(III) chemistry knows with bitter experiences that multiple steps and severely controlled conditions are necessary for obtaining the trans-dihalogeno chromium(III) complexes, differing from the corresponding cobalt(III) complexes.7) Thus, it seems almost impossible to synthesize the complexes of $[CrXY(a\text{-}a)_2]Z$ (especially trans-isomer), where X = Br and Y = I.

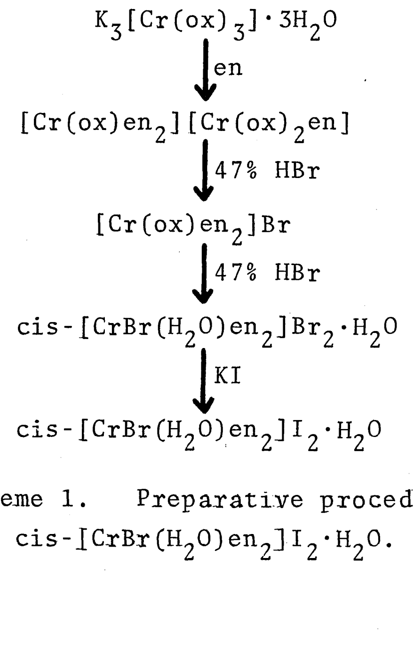
However, such difficulties would be overcome if the following solid-phase thermal deaquation-anation could be employed in preparing the mixed-dihalogeno complexes:

$$[CrX(H_2O)(a\text{-}a)_2]Y_2 \xrightarrow[\Delta]{-\ H_2O} [CrXY(a\text{-}a)_2]Y$$

Additionally, the combination of the cis-to-trans isomerization involved in the above anation has one more merit that trans-mixed-dihalogeno complexes could be prepared from cis-halogenoaqua complexes.

Fee et al. attempted to synthesize some mixed-dihalogeno complexes through thermal dehydration, but the desired complexes were not obtained in a pure form.8) We have now succeeded in preparing pure cis- and trans-$[CrBrIen_2]Z$ (Z = I and ClO_4) from cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$ through the combination of thermal deaquation-anation and cis-to-trans isomerization. We believe that the success in isolating such mixed-dihalogeno complexes based on the above idea (utilization of thermal deaquation-anation and cis-to-trans isomerization), in near future, leads to an extension of the preparation of other new chromium(III) complexes.

Preparation of cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$ as the Starting Material. The compound was prepared via the steps as shown in scheme 1. $K_3[Cr(ox)_3]\cdot 3H_2O$ was reacted at 60—70°C with 95% ethylenediamine in equimolar ratios to obtain red-violet $[Cr(ox)en_2][Cr(ox)en_2]$.9) The red-violet product was treated at 40—50°C with 47% hydrobromic acid to get orange $[Cr(ox)en_2]Br$,9) which was treated at 60—70°C with 47% hydrobromic acid. Red-violet cis-$[CrBr(H_2O)en_2]Br_2\cdot H_2O$10) was thus obtained, which was finally double-decomposed with KI to obtain cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$ (red-violet). Recrystallization was carried out from methanol. About 3 g of the desired complex was yielded



Scheme 1. Preparative procedures for cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$.

from 25 g of $K_3[Cr(ox)_3]\cdot 3H_2O$.

Found: C, 10.71; H, 4.59; N, 12.31%. Calcd for $[CrBr(H_2O)en_2]Br_2\cdot H_2O$: C, 10.71; H, 4.46; N, 12.50%.

Found: C, 9.17; H, 3.76; N, 10.20%. Calcd for $[CrBr(H_2O)en_2]I_2\cdot H_2O$: C, 8.94; H, 3.72; N, 10.36%.

Derivatographic Measurement. The thermal behavior of the starting complex cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$ was observed by means of derivatography in a nitrogen stream at the heating rate of 1°C/min. Five tenth grams of the complex was used. The TG curve in Fig. 1 shows that the complex evolves 2 moles of water in one step at 90—145°C. The complex turned in color from initial red-violet to grayish green at the end of the water evolution step. Then the complex remained unchanged up to 250°C. The grayish green product was, as will be discussed in the later section, in the mixed form of cis(90%)- and trans-(10%)-$[CrBrIen_2]I$. A sharp exothermic DTA peak can be seen in the region of 185°C, but details concerned are now under investigation. At any rate, the information obtained here implies that the deaquation-anation of the complex cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$ is applicable to prepare cis- and trans-$[CrBrIen_2]I$ without any severely controlled condition.

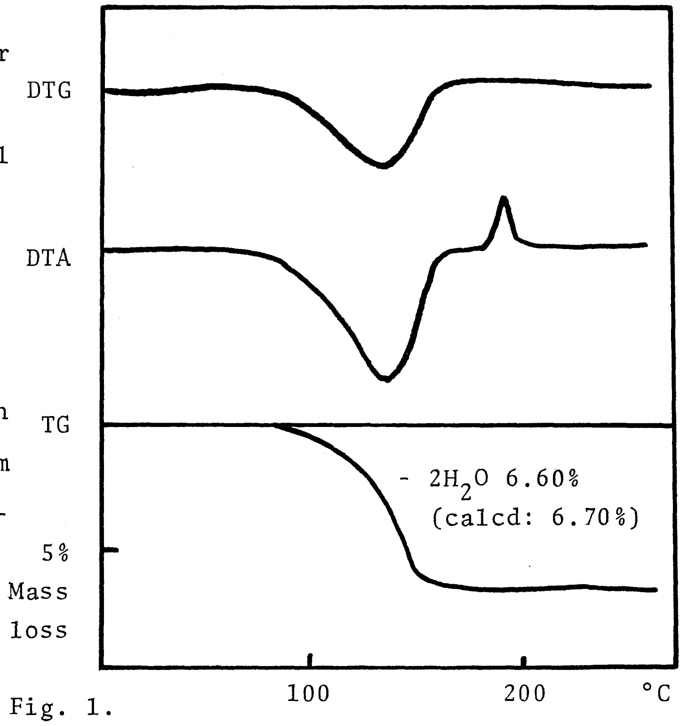
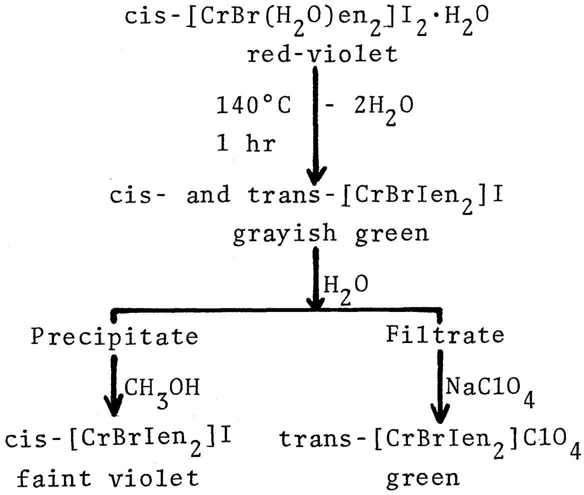


Fig. 1. Derivatogram of cis-$[CrBr(H_2O)en_2]I_2H_2O$.

Thermal Syntheses and Isolation of cis- and trans-$[CrBrIen_2]Z$ (Z = I and ClO_4). Various preparative conditions were preliminarily examined on the basis of the above results. Scheme 2 shows the preparative procedures for cis-$[CrBrIen_2]I$ and trans-$[CrBrIen_2]ClO_4$.

I. Thermal Syntheses of the Mixture of cis- and trans-$[CrBrIen_2]I$. Fifteen grams of cis-$[CrBr(H_2O)en_2]I_2\cdot H_2O$ was spread in a thin layer on a watch glass of diameter 12 cm, and heated at 140°C for one hour in an air bath. Careful control of the temperature is unnecessary, and so any temperature may be selected within the range of 135—190°C. The color of the complex turned grayish green from red-violet. The product was quantitatively obtained and confirmed to consist of $[CrBrIen_2]I$ from elementary analyses.

Found: C, 9.53; H, 3.22; N, 10.89%. Calcd for $[CrBrIen_2]I$: C, 9.50; H, 3.16; N, 11.08%.



Scheme 2. Preparative procedures for cis- and trans-$[CrBrIen_2]Z$ (Z = I and ClO_4).

II. Isolation of trans-$[CrBrIen_2]ClO_4$. Ten grams of the grayish green product was suspended in 100 ml of water and continuously stirred for a few minutes to dissolve the trans-isomer. After the precipitate (about 6.5 g) was filtered off, 8 g of $NaClO_4$ was added to the filtrate and the mixture was allowed to stand in a refrigerator for 2—3 hr. Green product was obtained. The product was washed with ethanol and ether, and air-dried. Yield 0.9 g. The complex was recrystallized from small amounts of water.

Found: C, 11.01; H, 3.64; N, 12.70%. Calcd for $[CrBrIen_2]ClO_4$: C, 10.04; H, 3.37; N, 11.71%.

The analytical data were slightly deviated from those calculated. We have experienced, however, that the compounds of perchlorate often give slightly unsatisfactory analytical data. The composition of the complex is conceivable to be given as above from other evidences such as electronic spectra. We are now attempting to obtain the complex with another counter anions.

III. Isolation of cis-$[CrBrIen_2]I$. The above precipitate was dissolved as much as possible in 300 ml of methanol. After the mixture was filtered, the filtrate was concentrated to about 100 ml of its volume at 10—15°C. Faint violet product was obtained, which was collected by filtration and dried at about 100°C for 30 min. Yield 0.5 g. Crystallization was induced by the addition of small amounts of ether to the above concentrated filtrate.

Found: C, 9.65; H, 3.37; N, 11.19%. Calcd for $[CrBrIen_2]I$: C, 9.50; H, 3.16; N, 11.08%.

Electronic Spectra. Table 1 lists up the absorption maxima due to d-d transition for the complexes obtained in the present study and the reference complexes. The first bands of trans-$[CrBrIen_2]ClO_4$ (16.3×10^3 cm^{-1}) and cis-$[CrBrIen_2]I$

Table 1. Absorption maxima due to d-d transition.

Complex	$\tilde{\nu}_1$ [a] (log ε)	$\tilde{\nu}_2$ (log ε)
cis-$[CrBr(H_2O)en_2]I_2 \cdot H_2O$	19.2 (1.90)	25.5 (1.84)
grayish green product	18.0 (1.94), 20.8sh [d]	b)
trans-$[CrBrIen_2]ClO_4$ isolated	16.3 (1.60), 21.0sh	b)
cis-$[CrBrIen_2]I$ isolated	18.0 (1.97)	b)
trans-$[CrBr_2en_2]Br$	16.5 (1.56), 21.0sh	24.5 (1.50)
trans-$[CrI_2en_2]I$ [c]	16.2 (1.62), 21.0sh	b)
cis-$[CrBr_2en_2]Br$	18.2 (1.82)	24.0 (1.89)

All the spectra were measured in DMSO solution. a) 10^3 cm^{-1}. b) These maxima could not be clearly detected because of the overlap with the subsequent CT band due to the coordinated I^- ion. c) Data cited from Ref. 11. d) sh denotes shoulder.

(18.0 X 10^3 cm^{-1}) appear at slightly smaller wave number regions as compared with those of trans-$[CrBr_2en_2]Br$ (16.5 X 10^3 cm^{-1}) and cis-$[CrBr_2en_2]Br$ (18.2 X 10^3 cm^{-1}). The slight shifts are possibly due to the coordination of I^- ion as a consequence of the deaquation-anation. The second bands of trans-$[CrBrIen_2]ClO_4$, cis-$[CrBrIen_2]I$ and the grayish green product could not be clearly detected because of the overlap with the subsequent CT bands due to the coordination of I^- ion.

The grayish green product has the first band at 18.0 X 10^3 cm^{-1}, which coincides with that of cis-$[CrBrIen_2]I$. The shoulder at 20.8 X 10^3 cm^{-1} probably comes from a split component of the first band of the trans-isomer. The results suggest that the product is in the mixed form of cis- and trans-$[CrBrIen_2]I$. Then, the ratio of cis- to trans-isomers in the product was determined spectrophotometrically according to the following equation:

$$\varepsilon_{554} = 94.5x + 9.6(1 - x)$$

where ε_{554} is the molar extinction of the grayish green product at 554 nm, x is the fraction of the cis-isomer, and 94.5 and 9.6 are the molar extinctions of the cis- and trans-isomers at 554 nm, respectively. It was found from the determination that the product contains 90% cis- and 10% trans-isomers. The ratio was almost unchanged even when the heating temperatures were varied (135, 155 and 190°C) and the heating periods were prolonged (2—4 hr). Therefore, the 10% cis-to-trans isomerization probably takes place simultaneously in the process of the deaquation-anation of cis-$[CrBr(H_2O)en_2]I_2 \cdot H_2O$.

As mentioned above, although cis- and trans-$[CrBrIen_2]^+$ species had previously been considered to be hardly prepared, we succeeded in obtaining them by the use of the deaquation-anation in combination with the cis-to-trans isomerization of cis-$[CrBr(H_2O)en_2]I_2 \cdot H_2O$. The preparative method based on the present idea will shortly lead to proliferous production of other new chromium(III) complexes of the series $[Cr\ XY\ N_4]Z$ and $[Cr\ XYZ\ N_3]$,[12] where N_4 is $(NH_3)_4$, (diamine)$_2$ or tetramine; N_3, $(NH_3)_3$ or triamine; and X, Y and Z denote different unidentate anions.

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