Preparation of (L-Cysteinato)(L- or D-histidinato)chromium(III) Complex

Yoshio ODAKA, Yuichi HASEGAWA, and Masatoshi WATABE*
General Education Department, Kogakuin University, Hachioji, Tokyo 192
(Received March 29, 1985)

Synopsis. Mixed-ligand chromium(III) complexes of the form [Cr(L-cys)(L-or D-his)] (L-cys=L-cysteinate and L-his=L-histidinate anions) were prepared. Isolated isomers of each complex were assigned structures on the basis of their high-speed liquid chromatograms and the distribution of the isomers.

Recently we have reported the preparation and stereochemistry of L- or D-aspartato(L-histidinato)-chromium(III) and bis(aspartato)chromate(III) complexes.[1] Hoggard prepared two of three isomers of the bis(L-histidinato)chromium(III) complex,[2] and Meester *et al.* prepared only one of three isomers of the bis(L-cysteinato)chromate(III) complex, the structure of which was determined as a trans sulfur isomer by X-ray crystallography.[3] Here, we report the preparation, chromatography, and absorption spectra of the chromium(III) complexes containing D- or L-his and L-cys.

Experimental

Preparations of [Cr(L-cys)(L- or D-his)] L-histidine (0.01 mol) and L-cysteine(0.01 mol) were dissolved in 80 cm^3 of water heated on a steam bath. The solution was added to an aqueous solution (60 cm^3) containing $Cr(NO_3)_3 \cdot 9H_2O$ (0.01 mol 4.00 g). After the mixture was heated for 10 min on the steam bath, the pH of the solution was adjusted to 7 with a 1-mol dm^{-3} NaOH solution. The solution was heated for 30 min, evaporated to 30—40 cm^3 and then loaded onto a column (50×500 mm) of QAE Sephadex A-25 anion resin in a chloride form. The column was kept at about 0 °C by circulating ethylene glycol-water. Three bands descended, the first was cations and the second and the third were neutral species corresponding to two isomers of the desired complex which were called A1 and A2, respecively. These two eluates were frozen as quickly as possible and evaporated at 0 °C. Two isomers of [Cr(L-cys)(D-his)] were obtaind by a similar method using D-histidine instead of L-histidine and were called B1 and B2 in the order of the elution in chromatography. As the two isomers in each D- and L-his complex easily isomerize to each other, they should be dissolved in ice-water. Anal. Calcd for $CrC_9H_{13}N_4O_4S \cdot H_2O$: C, 31.52; H, 4.40; N, 16.33%. Found (A1): C,31.01 H,3.95; N, 15.99%. Found (B1): C,31.32; H, 4.21; N, 16.15%. Calcd for $CrC_9H_{13}N_4O_4S \cdot 2H_2O$: C, 29.94; H, 4.74; N, 15.52%. Found (A2): C, 29.44; H, 4.94; N, 14.93%. Found (B2): C, 29.84; H, 5.12; N, 15.21%.

Measurements. The electronic absorption spectra were measured with a JASCO 505 spectrophotometer. The complexes were dissolved in water at 0 °C. The cell was treated with ethyleneglycol to prevent it from becoming wet with dew. The chromium content was determined with an atomic absorption photometer(Nippon Jarrel-Ash AA-845). Chromatographic separation was carried out with a JASCO-LCP-350. A 300×4 mm column containing a QAE Sephadex A-25 anion resin in a chloride form was used. The complexes were eluted with water at a flow rate of 0.1 $cm^3\ min^{-1}$ at a pressure of 40 kg cm^{-2}.

Results and Discussion

Figure 1 shows the six possible isomers of [Cr(L-cys)(L- or D-his)]. These isomers are denoted as L- or D-series with respect to the his ligand used and called L(or D)-*trans*(NNi), L(or D)-*trans*(NN), and L(or D)-*trans*(NO), where the left side N in parenthesis indicates that the nitrogen of cysteine and the following Ni, N, and O stand for the imidazole nitrogen, the nitrogen, and the oxygen atoms of coordinated histidine. Figure 2 shows high-speed liquid chromatograms of A1 and A2 together with that for [Cr(L-asp)(L-his)][1a](isomers CL1 and CL2) since the tridentate cysteinate coordinates with N,O,S atoms and the aspartate with N,O,O atoms so that the geometry and spectral behavior are expected to be similar in both complexes. The "a" in Fig. 2 represents a marker. Since all isomers of [Cr(L-cys)(L- or D-his)] isomerize in water at room temperature, the chromatograms in Fig. 2 show two peaks. Peak b corresponds to isomer A1 and peak c to isomer A2. These were determined by observing the time dependence of the peak heights. The same situation occurs in the chromatogram of [Cr(L-cys)(D-his)]. The peak of A1 appears a little later than that of CL1 and A2 elutes a little faster than CL3 of [Cr(L-asp)-(L-his)].

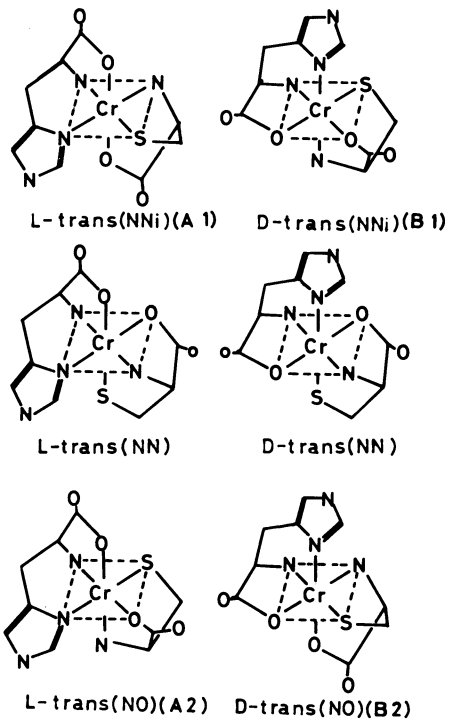

Fig. 1. The six possible isomers of [Cr(L-cys)(L- or D-his)], The isomers obtained are shown in parenthesis.

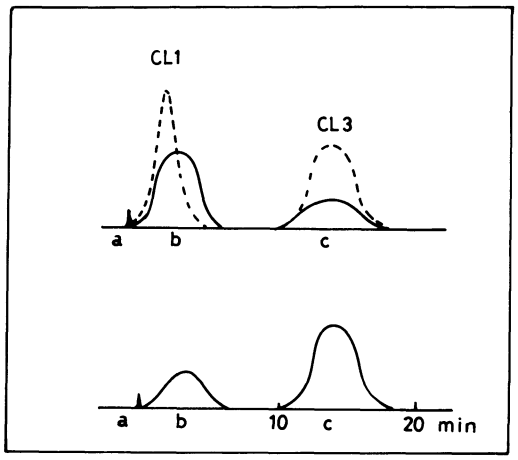

Fig. 2. High-speed liquid chromatograms indicating a mixture of [Cr(L-cys)(L- or D-his)] together with that of [Cr(L-asp)(L-his)]. Upper; from Al, lower; from A2. CL1 (*trans* (NNi)), CL2 (*trans* (NN)), and CL3 (*trans* (NO)) are the prepared isomers of [Cr (L-asp) (L-his)] in the order of elution.

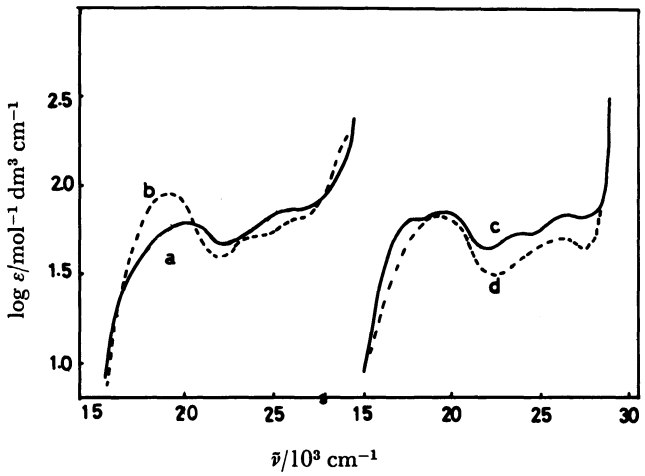

Fig. 3. Visible absorption spectra of [Cr(L-cys)(L- or D-his)]: Left a: Al and b: A2; right c: B1 and d: B2.

Though there are small differences in the peak positions, isomer Al can be assigned as L-*trans*(NNi) or L-*trans*(NN) and isomer A2 as L-*trans*(NO) by taking into consideration that the value of the dipole moment of the [Cr(L-cys)(L-his)] complex may be similar to that of [Cr(L- or D-asp)(L-his)]. In the same way, isomer Bl can be assigned as D-*trans*(NNi) or D-*trans*(NN) and isomer B2 as D-*trans*(NO). Figure 3 shows the visible absorption spectra of [Cr(L-cys)(L-or D-his)]. There are some peaks in the visible absorption spectra of [Cr(L-cys)(L-or D-his)] in both the first and second absorption band regions. Thioether complexes did not show any charge-transfer absorption[4] in the first and second absorption band regions. We tried to change the thiolate complex to a thioether complex by adding dimethyl sulfate. However, it was uncertain whether they were due to a d-d transition or a sulfite charge transfer since the thiolate complex could not be changed quantitatively to a thioether complex by adding dimethyl sulfate. Some infomation was, nevertheless, obtained; the band widths of isomers A2 and B2 in the first absorption band region were narrower than those of isomers Al and Bl, which indicates that A2 and B2 have a *trans*(NO) configuration (facial geometry when CrN_3O_3 type).

It is necessary to assign the first eluted isomers (Al and Bl). We have prepared mixed-ligand type, $[Co(N)_3(O)_3]$ and $[Cr(N)_3(O)_3]$, complexes containing two different tridentate ligands, such as [Co(L- or D-asp)(L-his)] and [Cr(L- or D-asp)(L-his)]. In all cases, the yields of the *trans*(NN) isomers were the lowest of all the possible isomers. In general, yields of isomers are dependent on the steric repulsion between ligands and on the electronic effect, such as the trans effect of a sulfur atom in chromium(III) complexes. We tentatively assigned Al as L-*trans*(NNi), A2 L-*trans*(NO), Bl D-*trans*(NNi) and B2 D-*trans*(NO). Though the isomerization of the complexes in solution could not be studied, it is interesting to note that the isomers of [Cr(L-cys)(L-or D-his)] isomerize in water at temperatures greater than 5 °C, when we consider the role of chromium(III) complexes containing cysteine in biological reactions.[6,7]

References

1) a) M. Watabe, H. Yano, Y. Odaka, and, H. Kobayashi, *Inorg. Chem.*, **20**, 3623 (1981); b) M. Sato, M. Kosaka, and M. Watabe, *Bull. Chem. Soc. Jpn.*, **58**, 874 (1985).
2) P. E. Hoggard, *Inorg. Chem.*, **20**, 415 (1981).
3) P. D. Meester, D. J. Hodgson, H. S. Freeman, and, C. J. Moore, *Inorg. Chem.*, **16**, 1494 (1976).
4) K. Okamoto, K. Wakayama, H. Einaga, S. Yamada, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 165 (1983).
5) M. Watabe, H. Yano, and, S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **52**, 61 (1979).
6) W. Y. Mertz, *Fed. Proc.*, **33**, 659 (1974).
7) W. Y. Mertz, E. W. Toepfer, E. E. Roginski, and M. M. Polansky, *Fed. Proc.*, **33**, 2275 (1974).