

for anomalous dispersion were applied to the Rh, Cl, and P scattering curves.

Throughout the refinement, the phenyl rings were treated as rigid groups constrained with C-C = 1.392 Å, C-H = 1.00 Å, and all bond angles 120°, and with isotropic temperature factors for C varied individually while those for H were held fixed at 3.5 Å². Isotropic refinement omitting all nongroup H atoms approached convergence at $R = 0.080$ and $R_w = 0.088$. Anisotropic refinement was begun at this stage for all nongroup atoms, except the THF atoms which were always treated isotropically. When values of $R = 0.066$ and $R_w = 0.071$ were reached in the anisotropic refinement, unduly high thermal parameters for some of the carbons of the norphos ligand suggested the presence of disorder in this ligand. A difference density map, omitting the three carbons of the 1,2-ethylidene bridge and the methylene bridge of the norbornene ring system, revealed that these three carbons were each occupying two positions, related by a pseudo-two-fold axis approximately bisecting the P-Rh-P angle and approximately normal to the C5-C6 bond. Each of these six positions was described as being occupied by a half-weighted carbon atom, and these were treated isotropically in all subsequent refinement.²⁶

So that the assignment of absolute configuration could be tested, the structure was at this point subjected to two parallel refinements, one for each of the possible enantiomers. With the use of coordinates describing the *S,S* structure, convergence was achieved at $R = 0.052$ and $R_w = 0.056$, while the *R,R* structure could be refined only to $R = 0.054$ and $R_w = 0.059$. A statistical interpretation of the *R* factor ratio using Hamilton's test²⁷ indicated that the *R,R* configuration for (+)-**15** could be rejected in favor of *S,S* at a confidence level far exceeding 99.5%. This result is consistent with the assignment by Brunner.⁵

At this stage, a difference density map contained peaks at all computed hydrogen positions,²⁸ including those of the disordered

carbons. Hydrogens were included at these idealized positions and assigned isotropic temperature factors corresponding to the thermal motion of the carbons to which they were attached. Attempts to refine these hydrogen temperature factors resulted in unreasonable values, so these were held fixed at their initial values while positions were allowed to vary. Hydrogens on the THF molecule were also held fixed in their initial idealized positions. Final convergence of the refinement was obtained with $R = 0.047$ and $R_w = 0.048$. Inclusion of all reflections in a final structure factor calculation gave $R = 0.062$ and $R_w = 0.048$. A final difference density map contained only small peaks ($<0.9 \text{ e } \text{Å}^{-3}$).

Final fractional crystallographic coordinates and anisotropic temperature factors for the nonhydrogen, nongroup atoms appear in Table IV. Rigid group parameters used to describe the phenyl rings are presented in Table V. Bond lengths, angles, and selected dihedral angles are contained in Table VI.

Observed and calculated structure factor amplitudes, final parameters for nongroup hydrogen atoms, and fractional crystallographic coordinates and temperature factors for the rigid group atoms and for the atoms in THF appear in supplementary tables.²⁶

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Registry No. (-)-**2**, 71075-23-5; (-)-**3**, 71042-54-1; **4**, 55065-02-6; (-)-**11**, 78822-58-9; (-)-**12**, 78803-92-6; **13**, 12257-42-0; **14**, 32354-50-6; (-)-**15**-C₄H₈O, 78791-09-0; (+)-**16**, 78803-86-8; **17**, 5429-56-1; **19**, 97-65-4; **21**, 32799-34-1; (+)-**12**, 78803-93-7.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Supplementary Table I), anisotropic thermal parameters (Supplementary Table II), derived fractional coordinates for rigid atom groups (Supplementary Table III), and fractional coordinates and isotropic thermal factors for atoms in the tetrahydrofuran molecule (Supplementary Table IV) (26 pages). Ordering information is given on any current masthead page.

(26) Evrard, G.; Thomas, R.; Davis, B. R.; Bernal, I. J. *Organomet. Chem.* **1977**, *124*, 59-70.

(27) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(28) Idealized hydrogen positions were generated by the use of the local program HIDEAL written by R. C. Collins.

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Preparation and Characterization of Some Chromium(III) Complexes of the Forms [Cr(L- or D-asp)(L-his)] and [Cr(L-asp)₂]⁻ (asp = Aspartate and his = Histidinate Ions)

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Mixed-ligand chromium(III) complexes of the form [Cr(L- or D-asp)(L-his)] and [Cr(L-asp)₂]⁻ were prepared. Isolated isomers of each complex were assigned structures on the basis of their visible spectra and high-speed chromatograms. The CD spectra of the [Cr(L- or D-asp)(L-his)] complexes are similar to those of the [Co(L- or D-asp)(L-his)] complexes, permitting tentative structural assignments for three isomers of the [Cr(L-asp)₂]⁻ complexes. The observed distribution of the isomers suggests that in these complexes, as well as in previously reported [Co(L- or D-asp)(L-his)] complexes, amino groups avoid being trans to each other.

Introduction

Only a few Cr(III) complexes containing bis(tridentate) amino acidate ligands have been prepared.¹⁻³ Though three geometrical isomers (*fac-cis*(N), *fac-trans*(N), and *mer-trans*(N)) are possible for the Cr^{III}N₂O₄ complexes coordinating bis(iminodiacetate) or bis((methylimino)diacetate) ligands, only one each has been prepared for the former complex, which exists as the *cis*(N) isomer, and for the latter

complex, being *trans*(N). While three isomers have been prepared for the [Cr(L-asp)₂]⁻ complexes, their geometrical configurations have not been assigned even tentatively because their UV and CD spectra resemble each other.³

We have reported so far preparations of the [Co(A)(B)] type complexes that take the form of Co^{III}N₃O₃, where A = L- or D-aspartate or iminodiacetate and B = L-histidinate, L-2,4-diaminobutyrate, or L-ornithinate.⁴⁻¹¹ Though every

(1) A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **43**, 1394 (1970).

(2) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

(3) G. Grouhi-Witte and E. Weiss, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **31B**, 1190 (1976).

(4) M. Watabe, K. Onuki, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **48**, 687 (1975).

(5) M. Watabe and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **48**, 2185 (1975).

(6) M. Watabe, S. Kawai, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1848 (1976).

series has three isomers (two meridional and one facial), we could assign each isomer to a certain geometry by using mainly their ^1H NMR, UV, and CD spectra. These assignments were substantiated with an X-ray crystal study of one of the cobalt(III) complexes coordinating L-aspartate and L-ornithinate.¹¹

Here we report the preparation and characterization of the mixed chromium complexes having L- or D-aspartate and L-histidine, along with the refined preparation of the $[\text{Cr}(\text{L-Asp})_2]^-$ complexes and their geometrical assignments. From the distribution of the isomers it becomes clear, in analogy with those for the Co(III) complexes, that amino groups avoid being trans to each other.

Experimental Section

Materials. L-Histidine and L- and D-aspartic acid were purchased from Tokyo-Kasei Co.

Isomers of $[\text{Cr}(\text{L-asp})(\text{L-his})]$. To a concentrated ammonia solution (7 mL) was added $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ (10 g, 0.01 mol). The precipitate was centrifuged and suspended in 50 mL of water. To this suspension were added L-aspartic acid (0.01 mol) and L-histidine (0.01 mol). After the suspension was stirred and heated (ca. 80 °C) for 1 h, it was centrifuged and cooled to room temperature. One-fourth of this solution was loaded on a column (50 × 500 mm) of Sp-Sephadex C-25 strong cation resin which was in the sodium form. The column was eluted with water slowly. Three bands descended and were called C-1, C-2, and C-3. They were concentrated with a vacuum rotary evaporator below 10 °C. They were loaded again on a column (50 × 500 mm) of QAE-Sephadex A-25 anion resin, which was in the chloride form, and eluted with water. From the column containing C-1, a small amount of neutral species descended but was not the isomer desired. From the column loaded with C-2, only one band of neutral species descended and was concentrated to 20 mL with a rotary evaporator at less than 10 °C. After the sample was kept in a refrigerator, a small amount of red-violet precipitate appeared and was called CL1. From the column with C-3, only one band was eluted, which was concentrated to 10 mL below 10 °C and stored in a refrigerator. Red crystals appeared and were called CL3 (the reason that it was not called CL2 is given later).

Isomers of $[\text{Cr}(\text{D-asp})(\text{L-his})]$ were obtained by the method described above using D-aspartic acid instead of L-aspartic acid and were called CD1 and CD3 in order of elution.

Anal. Calcd for $[\text{CrC}_{10}\text{H}_{13}\text{N}_4\text{O}_6] \cdot 4.5\text{H}_2\text{O}$: C, 28.71; H, 5.30; N, 13.39. Found (CL1): C, 28.44; H, 5.10; N, 13.41. Calcd for $[\text{CrC}_{10}\text{H}_{13}\text{N}_4\text{O}_6] \cdot 2\text{H}_2\text{O}$: C, 30.69; H, 4.90; N, 14.30. Found (CL3): C, 30.25; H, 4.53; N, 14.25. Calcd for $[\text{CrC}_{10}\text{H}_{13}\text{N}_4\text{O}_6] \cdot 2.5\text{H}_2\text{O}$: C, 31.42; H, 4.74; N, 14.65. Found (CD1): C, 31.28; H, 4.81; N, 14.88. Calcd for $[\text{CrC}_{10}\text{H}_{13}\text{N}_4\text{O}_6] \cdot 2\text{H}_2\text{O}$: C, 32.18; H, 4.59; N, 15.01. Found (CD3): C, 31.90; H, 4.74; N, 15.21.

Isomers of $[\text{Cr}(\text{L-asp})_2]^-$. While the preparation of the isomers of the $[\text{Cr}(\text{L-asp})_2]^-$ complexes has been reported, we refined the method, because the products were considered to be mixtures of the possible isomers. To a solution of 50 mL containing L-aspartic acid (2.7 g, 0.02 mol) was added a solution of 0.01 mol of chromium trichloride. After the solution was heated at 80 °C for 10 min, the pH of the solution was adjusted to 5.0–5.5. After the solution was heated and stirred for 1 h, it was cooled to room temperature and loaded on a column containing QAE-Sephadex A-25 anion resin in chloride form (50 × 500 mm). Any uncharged or cationic species produced in reaction were washed from the column with 200 mL of water. Separation of the Cr(III) complexes was achieved by eluting with 0.1 M NaCl at rate of 1 drop/5 s. Five colored bands descended, and all were red-violet. Each band was frozen and evaporated by using a freeze-dryer. Each solid containing NaCl was dissolved in 10 mL of water. Each solution was desalted by using a column (50

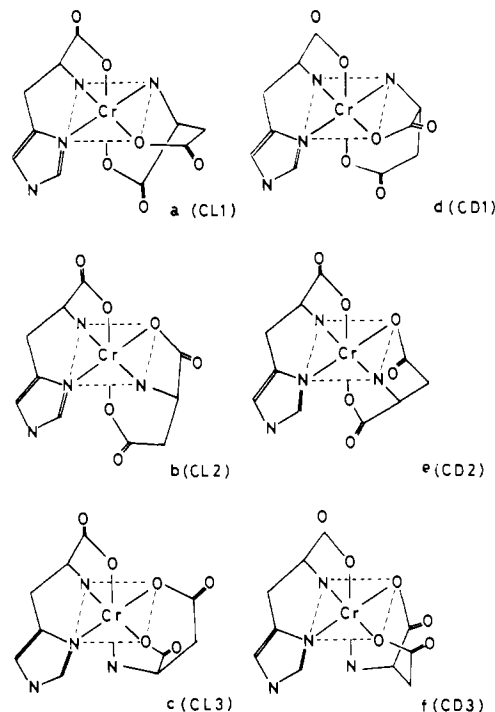


Figure 1. The six possible isomers of $[\text{Cr}(\text{L- or D-asp})(\text{L-his})]$: (a) L-trans(O_5),cis(N_5); (b) L-cis(O_5),trans(N_5); (c) L-fac; (d) D-cis(O_5),cis(N_5); (e) D-trans(O_5),trans(N_5); (f) D-fac. The isomers obtained were tentatively assigned and are shown in parentheses.

× 500 mm) containing Sephadex G-25 Gel resin. These UV spectra and the results of elemental analysis showed that the second, third, and fourth bands were the desired complexes, which were called respectively B, C, and D in order of elution.

Anal. Calcd for $\text{Na}[\text{CrC}_8\text{H}_{10}\text{N}_2\text{O}_8] \cdot 3\text{H}_2\text{O}$: C, 24.56; H, 4.12; N, 7.16. Found (B): C, 23.20; H, 4.40; N, 6.54. Found (D): C, 23.76; H, 3.80; N, 7.02. Calcd for $\text{Na}[\text{CrC}_8\text{H}_{10}\text{N}_2\text{O}_8] \cdot 3.5\text{H}_2\text{O}$: C, 24.00; H, 4.28; N, 7.00. Found (C): C, 23.50; H, 3.80; N, 7.02.

Spectra. Visible and circular dichroism spectra were measured with a Jasco J-20 spectrophotometer in aqueous solution. High-speed liquid chromatograms were obtained by using a column containing a strong cation-exchange resin, TSK LS-212 Toyo Soda Ind., Na form. The separation was achieved by using water as eluant.

Results and Discussion

Figure 1 shows the possible isomers of the $[\text{Cr}(\text{L- or D-asp})(\text{L-his})]$ complexes. They are denoted by L or D series with respect to the asp used. Both series of mixed complexes are composed of two meridional and one facial isomers, $[\text{CrN}_3\text{O}_3]$. The two L-mer isomers are denoted by L-trans(O_5),cis(N_5) (oxygen atoms of the five-membered chelate rings are trans with each other and those of nitrogen atoms are cis with each other) and L-cis(O_5),trans(N_5). The three $[\text{Cr}(\text{L-asp})(\text{L-his})]$ isomers (L-trans(O_5),cis(N_5), L-cis(O_5),trans(N_5), and L-fac) are related by an imaginary twist through 120° of one coordinated ligand relative to the other about an axis passing through the two ligands occupying triangular faces of the chromium(III) coordination octahedron. The same kind of relationship exists for the three isomers containing coordinated D-aspartate ion.

Assignment of the $[\text{Cr}(\text{L- or D-asp})(\text{L-his})]$ Isomers. Since the two neutral complexes for each series exhibit electronic absorption spectra (Figure 2) that agree with the crystal field consideration that the first absorption band of a facial isomer has smaller splitting than that for a meridional isomer, it is possible to assign the mer geometry to CL1 and CD1 and fac geometry to CL3 and CD3. It is of significance to determine to which geometry the two mer isomers (CL1 and CD1) can be assigned. High-speed liquid chromatograms for L or D series are given in Figure 3 together with those for $[\text{Co}(\text{L- or D-}$

- (7) M. Watabe, H. Yano, and S. Yoshikawa, *Nippon Kagaku Kaishi*, 1833 (1977).
- (8) M. Watabe, M. Zama, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **51**, 1354 (1978).
- (9) M. Watabe, Y. Hashimoto, and S. Yoshikawa, *Nippon Kagaku Kaishi*, 903 (1978).
- (10) M. Watabe, H. Yano, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **52**, 61 (1979).
- (11) S. Yano, M. Watabe, and S. Yoshikawa, *Inorg. Nucl. Chem. Lett.*, **14**, 279 (1978).

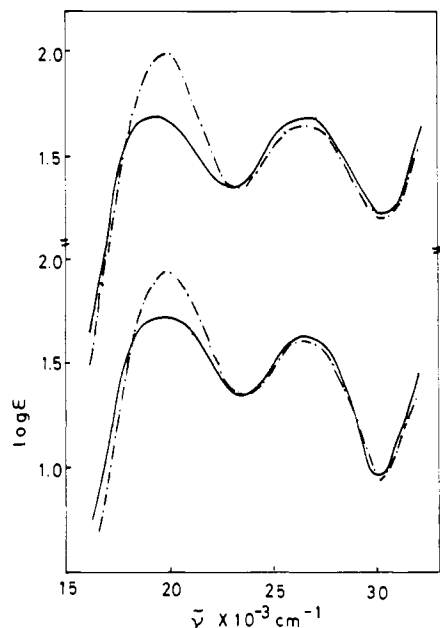


Figure 2. Visible absorption spectra of [Cr(L- or D-asp)(L-his)]: upper, CL1 (—) and CL3 (---); lower, CD1 (—) and CD3 (---).

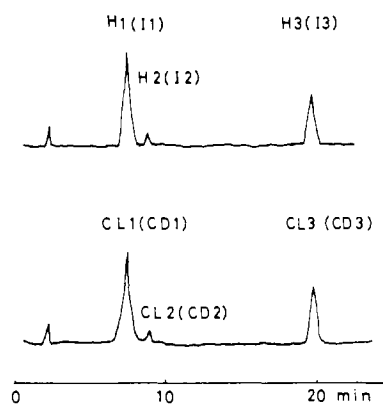


Figure 3. High-speed liquid chromatograms indicating the mixture of [Co(L- or D-asp)(L-his)] (upper) and those of [Cr(L- or D-asp)(L-his)] (lower). The amount of CD2 is traced.

asp)(L-his)]. The chromatograms of the mixed solution containing C-2 and C-3 showed three peaks for each series except for a marker. The first peak corresponded to that for CL1 and the third to that for CL3. The second peak is considered to be the other *mer* isomer desired since it lies at the same position as that for H2 isomer of the [Co(L-asp)(L-his)] complexes. The similarity of the band positions and the relative concentration ratios of the [Cr(L- or D-asp)(L-his)] complexes with those for the [Co(L- or D-asp)(L-his)] complexes is particularly surprising. In our chromatography the elution order of the complexes is considered to correspond to the reverse order of the magnitudes of the dipole moments of these complexes. We therefore tentatively assigned the geometrical configuration to the isomers prepared as below: CL1 to L-*trans*(O₅),*cis*(N₅), CL2 to L-*cis*(O₅),*trans*(N₅), and CL3 to L-*fac*.

By the same consideration, CD1 may be assigned to D-*cis*(O₅),*cis*(N₅), CD2 to D-*trans*(O₅),*trans*(N₅), and CD3 to D-*fac*. There is no discrepancy between the assignments by high-speed chromatograms and UV-visible spectra. Because of the low proportions of the CL2 (CD2) isomer and the difficulty of their isolation from the mixture of two *mer* isomers by Sephadex chromatography, we could not obtain pure CL2 and CD2 isomers. Though the CL1 and CD1 isomers crystallized from the C-1 eluate, the amount of the CL2 (CD2) isomer gradually

decreased owing to isomerization.

Figure 4 shows CD spectra of [Cr(L- or D-asp)(L-his)] compared with those of the corresponding [Co(L- or D-asp)(L-his)] complexes. In Figure 4a, which shows CD spectra of the CL1 and H1 isomers, there seem to be three peaks (ca. 19, 22, and 28 × 10³ cm⁻¹) in the absorption region outside of the charge-transfer band. Two of the three peaks in this region have positive signs (at 22 and 28 × 10³ cm⁻¹) for both CL1 and H1 while the peaks at 19 × 10³ cm⁻¹ for CL1 and H1 have opposite signs. In Figure 4b, which shows CD spectra of the CL3 and H3 isomers, the signs and the shapes of the three peaks outside the charge-transfer band resemble each other though the CD peak intensities of the CL3 isomer are slightly lower than the corresponding peaks of the H3 isomer. In Figure 4c, which shows CD spectra of CD1 and I1 isomers, only two peaks outside the charge-transfer region are recognizable for the CD spectrum of the CD1 isomer of [Cr(D-asp)(L-his)] while three peaks (19, 22, and 29 × 10³ cm⁻¹) are found for that of I1 isomer of [Co(D-asp)(L-his)]. When these two CD spectra are compared, two peaks (ca. 19 and 22 × 10³ cm⁻¹) for each complex have negative and positive signs from the lower energy side in the first absorption band to the second absorption band though these intensities greatly vary. In Figure 4d, which shows CD spectra of CD3 and I3 isomers, the two negative peaks (ca. 21 and 28 × 10³ cm⁻¹) of CD3 are found in the absorption region outside the charge-transfer band region, corresponding to the negative peaks (21 and 28 × 10³ cm⁻¹) of I3 though I3 has one more negative peak at 18 × 10³ cm⁻¹.

In the charge-transfer-band region, two CD peaks appear in all cases of the [Cr(L- or D-asp)(L-his)] complexes, while one peak appears for all the [Co(L- or D-asp)(L-his)] complexes. Accordingly, no similarity in this region is found between the CD spectra of the [Cr(L- or D-asp)(L-his)] complexes and those of the [Co(L- or D-asp)(L-his)] complexes. In conclusion, comparison of the CD spectra for both the Cr(III) and the Co(III) complexes shows their shapes and signs are similar only between the higher energy side of the first-absorption-band region and the second-absorption-band region (ca. (20–30) × 10³ cm⁻¹).

Isomers of [Cr(L-asp)₂]⁻. Generally, the assignment of isomers of the Co(III) complexes containing optically active tridentate amino acids by means of CD spectra is known to be difficult.^{12,13} Yamada et al.¹³ have reported the preparation of the three isomers of the [Co(L-asp)₂]⁻ complexes. Oonishi has reported the X-ray crystal study of one of these three isomers.¹⁴ The three isomers of [Co(L-asp)₂]⁻ have been assigned in order of elution as *trans*(N), *cis*(N₅),*trans*(O₅), and *cis*(N₅),*trans*(O₆) isomers, respectively.

Witte et al.³ have reported the preparation and UV and CD spectra of the corresponding Cr(III) complexes, but they could not assign these isomers to their geometries (Figure 5). According to their results, the CD and UV spectra of the three isomers resembled each other. We also prepared the above complexes with caution, especially with regard to the evaporating temperature and method of desalting. A freeze-dryer was used when the eluates of the isomers were evaporated. Figure 6 shows the absorption spectra of the [Cr(L-asp)₂]⁻ complexes.

Generally, the *trans*(N) isomer of the [M₂N₂O₄] type has greater splitting and the lower intensity in the first absorption band than do the *cis*(N) isomers. The ratio of the peak heights (log ε) of the first absorption bands to those of the second

(12) S. R. Ebner and R. J. Angelici, *Inorg. Chem.*, **19**, 1031 (1980).

(13) S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem.*, **10**, 2187 (1971).

(14) I. Oonishi, M. Shibata, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **B29**, 2448 (1973).

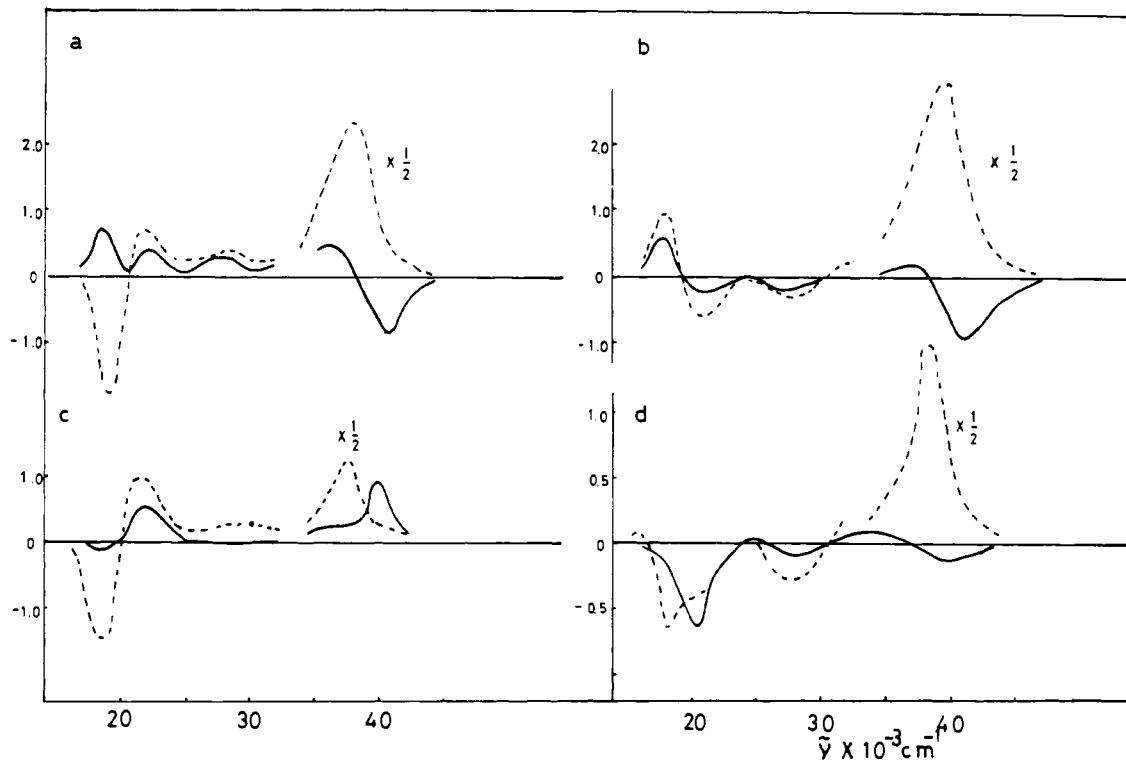


Figure 4. CD spectra of $[\text{Cr}(\text{L- or D-asp})(\text{L-his})]$ (—) and $[\text{Co}(\text{L- or D-asp})(\text{L-his})]$ (---): (a) L-*trans*(O_5),*cis*(N_5) (CL1 and H1); (b) L-*fac* (CL3 and H3); (c) D-*cis*(O_5),*cis*(N_5) (CD1 and I1); (d) D-*fac* (CD3 and I3).

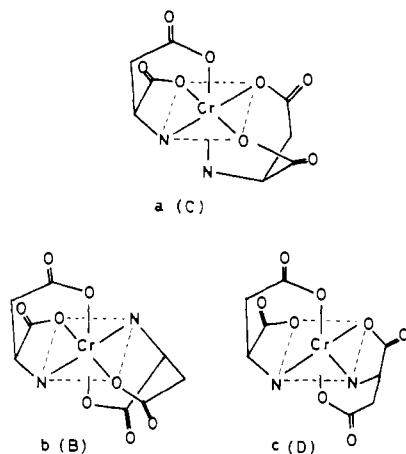


Figure 5. Isomers of $[\text{Cr}(\text{L-asp})_2]^-$: (a) *cis*(N_5),*trans*(O_5); (b) *trans*(N_5); (c) *cis*(N_5),*trans*(O_5). The isomers obtained were tentatively assigned and are shown in parentheses.

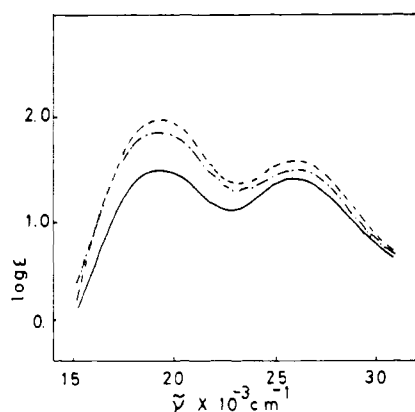


Figure 6. Visible absorption spectra of $[\text{Cr}(\text{L-asp})_2]^-$: B (—); C (---); D (-.-).

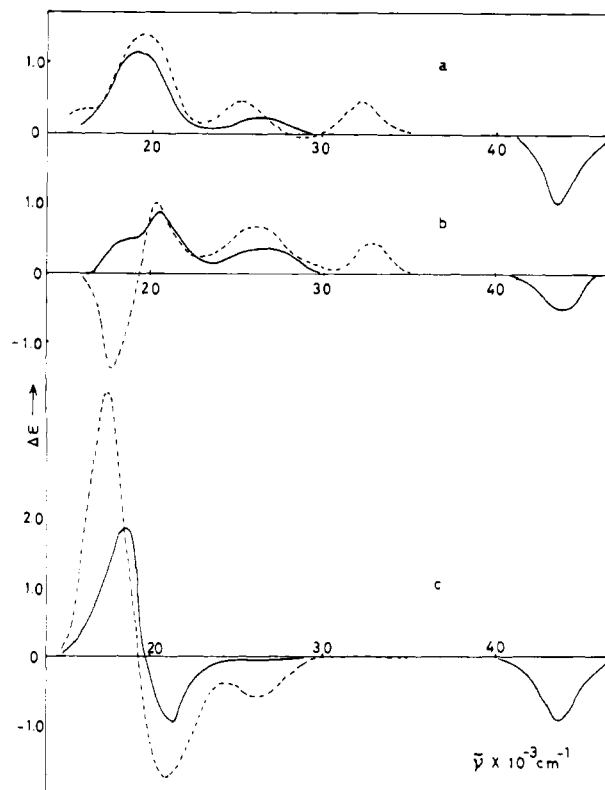


Figure 7. CD spectra of $[\text{Cr}(\text{L-asp})_2]^-$ (—) and those for $[\text{Co}(\text{L-asp})_2]^-$ (---): (a) B and F isomers; (b) C and S isomers; (c) D and T isomers.

bands are 1.14 for B, 1.27 for C, and 1.28 for D. Though the splitting of the peak of B in the first-absorption-band region is not so clearly distinguishable as *trans*(N), since the ratio for B is smallest of the three, B seems to be the *trans*(N) isomer, and C and D appear to be the *cis*(N) isomers. Further evidence for this argument is given by the analogy of the order

Table I. Product Yields in Preparation of [M(L- or D-asp)(L-his)] and [M(L-asp)₂]⁻ (M = Cr, Co)

	[Co(L-asp)- (L-his)]	[Cr(L-asp)- (L-his)]
trans(O ₅),cis(N ₅)	0.53	0.61
cis(O ₅),trans(N ₅)	0.06	0.02
L-fac	0.41	0.37
	[Co(D-asp)- (L-his)]	[Cr(D-asp)- (L-his)]
cis(O ₅),cis(N ₅)	0.48	0.58
trans(O ₅),trans(N ₅)	0.01	trace
D-fac	0.51	0.42
	[Co(L-asp) ₂] ⁻	[Cr(L-asp) ₂] ⁻
trans(N ₅)	0.26	0.33
cis(N ₅),trans(O ₅)	0.47	0.40
cis(N ₅),trans(O ₆)	0.27	0.27

of elution and the elution intervals among Cr(III) complexes with those for Co(III) complexes.

For the case of Cr(III) complexes having these ligands, difficulty of characterization arises since no information is obtainable from their ¹H NMR spectra. By comparing the CD spectra of the [Cr(L- or D-asp)(L-his)] complexes with those of the [Co(L- or D-asp)(L-his)] complexes, we found a similarity in their CD spectra between the second-absorption-band region and the higher energy side of the first-absorption-band region. This similarity must serve for the characterization of the isomers of [Cr(L-asp)₂]⁻. Figure 7a shows that the first eluate (B) of the Cr(III) complexes has one CD peak in the first absorption region and one in the second absorption region, while the first eluate isomer (F) of the Co(III) complexes has two peaks in the first absorption region. In comparison of these two CD spectra between the

higher energy side region of the first absorption and the second absorption region, the sign (positive at 20 and 27 × 10³ cm⁻¹) is found to be the same. As is shown in Figure 7b the second eluate isomer (C) of the Cr(III) complexes has two positive peaks in the first-absorption-band region and one positive in the second-absorption-band region. On the other hand, three peaks (negative, positive, positive in order of energy increase) appear for the second eluate of [Co(L-asp)₂]⁻. Good agreement concerning their signs are obtained between the higher energy side of the first-absorption-band region and the second absorption band. For both of the third eluates (Figure 7c), similarity of those CD spectra seems to exist in the whole region outside the charge-transfer-band region, though the intensity of the CD spectrum of the third eluate D isomer of the [Cr(L-asp)₂]⁻ complexes at the second-absorption-band region is slightly smaller than that for the third isomer of the [Co(L-asp)₂]⁻ complexes. Therefore the similarity of the CD spectra between the higher energy side of the first-absorption-band region and the second-absorption-band region may be used to assign isomer B as trans(N₅),cis(O₅), isomer C as cis(N₅),trans(O₅), and isomer D as cis(N₅),trans(O₆).

In comparison of the CD spectra of the [Cr(L-asp)₂]⁻ complexes with those of the [Co(L-asp)₂]⁻ complexes in the charge-transfer region, surprisingly great differences are seen in their peak maxima and their signs.

Distributions of the isomers obtained here are listed in Table I together with those of the corresponding Co(III) complexes. The distributions of the [Cr(L- or D-asp)(L-his)] complexes are quite similar to those of the [Co(L- or D-asp)(L-his)] complexes and indicate that factors affecting the instabilities of these complexes such as steric hindrance and/or electronic effects are similar for both metal ions.

Registry No. CL1, 78685-02-6; CD1, 78685-03-7; CL3, 78638-59-2; CD3, 78684-38-5; B, 78684-39-6; C, 78656-76-5; D, 78684-40-9.

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Reaction of Metallocene Dichlorides of Titanium(IV) and Zirconium(IV) with Lithium Bis(trimethylsilyl)amide

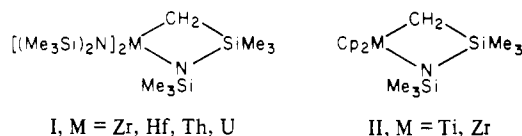
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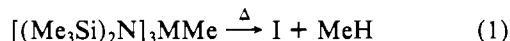
Reaction of Cp₂TiCl₂ with 1 or 2 molar equiv of LiN(SiMe₃)₂ yields the previously described metallacycle

Cp₂TiCH₂SiMe₂NSiMe₃. Mass balance shows that for each mole of metallacycle formed, 1 molar equiv of hydrogen chloride is also formed. The related zirconium metallacycle was prepared from Cp₂Zr(H)(Cl) and LiN(SiMe₃)₂. The bis(silylamide) of zirconium, Cp₂Zr[N(SiMe₃)₂]₂, was prepared from Cp₂ZrCl₂ and 2 molar equiv of LiN(SiMe₃)₂. The Me₃Si groups in the latter compound are magnetically nonequivalent at 27 °C but coalesce at 84 °C on the ¹H NMR time scale.

The four-membered-ring heterocyclic molecules (I) have



been prepared recently by γ elimination of methane from the tris(silylamido) alkyls as shown in eq 1.¹ A related metal-



lacycle II, M = Ti, was isolated some years ago in the reaction

of dicyclopentadienyltitanium dichloride and 2 molar equiv of lithium bis(trimethylsilyl)amide.² It was implicitly suggested that the γ -hydrogen atom of a bis(trimethylsilyl)amido group in hypothetical Cp₂Ti[N(SiMe₃)₂]₂ was eliminated as (Me₃Si)₂NH, since the latter molecule was detected. Later, an explicit mechanism was proposed that suggested lithium bis(trimethylsilyl)amide deprotonates a γ -methyl group of the coordinated silylamide ligand in hypothetical Cp₂Ti[N(SiMe₃)₂](Cl) and (Me₃Si)₂NH, yielding Li[Cp₂Ti[N(SiMe₃)(SiMe₂CH₂)](Cl) and (Me₃Si)₂NH. The former ion pair then eliminates lithium chloride, yielding II, M = Ti.^{3a} To confuse the matter further,

- (1) (a) Simpton, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728. (b) *Inorg. Chem.*, in press. (c) Planalp, R. P.; Simpton, S. J.; Andersen, R. A., unpublished results.
 (2) (a) Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. (b) Unpublished results as quoted in ref 3a.

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