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The Synthesis and X-Ray Structure of (L- or D-Alanine-*N*-acetato)(L-histidinato)chromium(III)

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The (L-alanine-*N*-acetato)(L-histidinato)chromium(III) monohydrate complex, $C_{11}H_{14}N_4O_6Cr$, has been synthesized and its crystal structure has been determined from three dimensional X-ray-diffractometer data. The crystals are orthorhombic, of the space group $P2_12_12_1$, with 4 molecules in a cell with these dimensions: a=11.052(1), b=13.959(3), and c=9.616(2) Å. Block-diagonal least-squares refinements using 1318 independent nonzero reflections have yielded a conventional R factor of 0.033. The structure consists of monomeric [Cr(L-alama)(L-his)] units and water molecules. The L-alama ligand coordinates to the metal as of dianion, with Cr–O(acetyl), Cr–N, and Cr–O(alanine) bond lengths of 1.960(3), 2.078(5), and 1.946(4) Å respectively. The histidinate monoanion coordinates through Cr–N(amino), Cr–N(imidazole), and Cr–O bonds 2.062(4), 2.036(5), and 1.957(4) Å long respectively. The geometry at chromium is a distorted octahedron, with *cis* bond angles in the range from 80.1(2) to 99.3(2)°. Among the six possible isomers of the [Cr(L-alama)(L-his)] complex, only one isomer was prepared and crystallized; its geometry was R-L-*trans*(*O*)*cis*(*N*).

Chromium has been shown to be an essential trace element, and the hypothetical chromium(III) complex occurring in brewers yeast has been found to have outstanding biological activity.[2] Efforts to purify this factor have led to the detection of chromium, nicotinic acid, glycine, glutamic acid, and cysteine in the purified fraction.[3] Several chromium(III) complexes containing amino carboxylate have been studied.[4–6] In these reports, the monomeric tris(aminocarboxylato)complexes have been reported to have only a facial configuration. While Israily claimed the preparation of the purple meridional isomer of $[Cr(gly)_3]$ (gly=glycinate ion), Gillard *et al.* showed this complex to be a dinuclear complex, $[Cr(OH)_2(gly)_2]_2\ 6H_2O$.[5] Oki *et al.* reported a number of facial and dihydroxo-bridged dimeric (amino carboxylato)chromium(III) complexes, but their attempt at the preparation of meridional tris(amino carboxylato)chromium(III) was unsuccessful.[6] We ourselves reported the preparation of a mixed (tridentate-aminocarboxylato)chromium(III) complex[7] in the form of the [Cr(L- or D-asp)(L-his)] complex, where asp=aspartate ion and his=histidinate ion. These isomers were tentatively assigned meridional and facial structures by using the resemblance of the CD spectra and high-speed liquid chromatograms of [Cr(L- or D-asp)(L-his)] to those of [Co(L- or D-asp)(L-his)]. However, some ambiguity remains in this structural assignment because of the lack of X-ray crystallographic data. Attempts to grow crystals suitable for X-ray structural analysis were unsuccessful for the [Cr(L- or D-asp)(L-his)] complexes. This report will deal with the preparation and the assignment of [Cr(L- or D-alama)(L-his)], where alama=alanine-*N*-acetate dianion, which belongs to the same $[Cr(N)_3(O)_3]$ type as that of [Cr(L- or D-asp)(L-his)]. As is shown in Fig. 1, this complex has six possible isomers for each L- or D-alama series because of two factors: the (S) or (R) chirality concerning the asymmetric imino nitrogen atom of alama, which occurs after coordination,[8] and the distribution of coordinated atoms (two meridional isomers and one facial isomer).

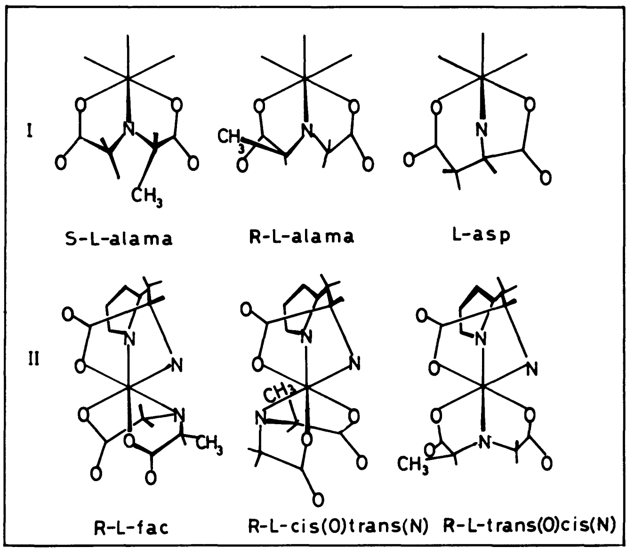

Fig. 1. I; (S) and (R) chirality of L-alama, and L-asp coordinated. II; Three possible R-type geometrical isomers of [Cr(L-alama)(L-his)]. Those of S-type are abbriviated.

Experimental

Isomers of [Cr(L- or D-alama)(L-his)]. To a concentrated ammonia solution (7 cm³) we added $K_2Cr_2(SO_4)_4 \cdot 24H_2O$ (10 g, 0.01 mol). The precipitate was centrifuged and then suspended in 50 cm³ of water. To this suspension we then added L-histidine (0.01 mol) and L-alanine-*N*-acetic acid (0.01 mol). After the suspension had been stirred and heated (*ca.* 80 °C) for 1 h, it was centrifuged and cooled to room temperature. One fourth of this solution was placed in a column (5X50 cm) of SP-Sephadex A-25, a strong-anion exchange resin, which was on the chloride form. The complexes in the column were eluted with water slowly. Three bands descended; the last one contained the neutral species, which was, after having been concentrated and crystallized under room temperature, named *L*. The complex containing D-alanine-*N*-acetate was prepared in a similar way but using D-alanine-*N*-acetic acid instead of L-alanine-*N*-acetic acid; it was named *D*. Anal. Calcd for $[CrC_{11}H_{14}N_4O_6]\cdot H_2O$: C, 35.78; H, 4.64; N, 15.17%, Found (*L*): C, 35.44; H, 4.69; N, 15.24%, Found (*D*): C, 35.32; H, 4.55; N, 14.90%.

Measurements. The visible and ultraviolet absorption spectra were measured with a JASCO UVIDEC-505 spectrometer in an aqueous solution.

Data Collection. The specimens are well-developed orange-yellow prismatic crystals. A crystal with approximate dimensions of 0.20×0.23×0.33 mm was mounted on a Rigaku four-circle automatic diffractometer, AFC-6B, with its elongated axis roughly parallel to the machine axis. Automatic centering and the indexing of 23 low-angle reflections gave the preliminary conditions for data collection. Peak refinement, by which the precise cell parameters was obtained, was performed by the least-squares treatment of the 2θ values of 25 reflections measured with graphite-monochromated Mo $K\alpha_1$ radiation (λ=0.70926 Å). At this point it was clear that the crystal had an orthorhombic symmetry, with a=11.052(1) Å, b=13.959(3) Å, c=9.616(2) Å, and Z=4. Additionally, subsequent measurements of several reflections in order to examine the systematic absences suggested that the crystal belongs to the $P2_12_12_1$ space group. This result was confirmed after the data collection. With Z=4 and the molecular weight of this complex, the calculated density is 1.65 g cm^{-3}, compared with the measured density of 1.64 g cm^{-3} obtained by flotation in a 1,2-dibromoethane-carbontetrachloride mixture. The ω ($2\theta<30°$) and $2\theta-\omega$ ($2\theta>30°$) scan methods were employed with a scanning rate of 1°/min. A unique data set (hkl) was first collected in the range of $5<2\theta<55$. In order to examine the absolute configuration of the ligands, the Bijvoet-pair data set ($\bar{h}\bar{k}\bar{l}$), with 2θ values between 17° and 27°, was then collected under the same conditions. Three standard reflections were monitored every 50 reflections; they showed only a 1—2% random variation in intensity, for which no correction was made. A total of 1472 reflections was measured, and the standard Lorentz and polarization corrections were applied. The final data set, consisting of 1472 reflections, indicated the systematic extentions of (h00) for h odd, (0k0) for k odd, and (00l) for l odd. Since the compound is optically active, the space group of the crystal was defined as $P2_12_12_1$. Of the 1472 reflections collected, 1318 had $F_o>10[\sigma(F_o)]$ and were used in the subsequent analysis. No absorption correction was made, since the μ value (7.9 cm^{-1}) was low.

Solution and Refinement of the Structure. The structure was solved by a standard heavy-atom method and refined by the block-diagonal least-squares method by the use of the Rigaku RASA SAP-2 system. An unsharpened three-dimensional Patterson function revealed the position of the chromium atom. The positions of the remaining nonhydrogen atoms were determined by successive structure-factor and electron-density-map calculations. Isotropic refinement reduced R=0.135 and R'=0.163, where $R=\Sigma||F_o|-|F_c||/|F_o|$ and $R'=(\Sigma(|F_o|-|F_c|)^2/|F_o|^2)^{1/2}$. The absolute configuration of the ligands in the complex ion was taken to be the *L* isomer. Next, the effects of the anomalous dispersion were introduced into F_c, the values of f' and f'' for Cr, O, N, and C being taken from Ref. 9. The anisotropic refinement of all the nonhydrogen atoms was performed, allowing the hydrogen atoms to vibrate isotropically. The final agreement factors, R and R', are 0.033 and 0.040 respectively. A final difference Fourier synthesis showed no significant electron density with a peak higher than 0.2 e Å.$^{-3}$ In this case, the absorption-edge technique was not sufficient to confirm the absolute configuration of the ligands; rather, the Hamilton test described above was useful.11) The final positional parameters, along with their standard deviations, are listed in Table 1. Compilations of the anisotropic thermal parameters and of the observed and calculated structure factors are available.

Results and Discussion

Description of the Molecular Structure. The geometry of the complex is shown in Fig. 2. The coordination around the chromium(III) center is approximately octahedral, the ligand binding as the histidinate monoanion and the L-alanine-*N*-acetate dianion. The geometry of this complex was determined to be R-L-*trans*(*O*)*cis*(*N*), where R means that the chirality of the asymmetric nitrogen atom of alama is R, where L means that this complex contains L-alama, and where *trans*(*O*)*cis*(*N*) means that the coordinated oxygen atom of L-his and that of the $-CH_2COO-$ of L-alama are trans to each other (as is shown in Fig. 1, the $-CH_2COO-$ ring of L-alama corresponds to the amino acid moiety of L-asp), and the nitrogen atom of $NH_2CH(COO^-)R$ of L-his and that of L-alama are *cis* to each other. Each conformation of the four chelate rings is also presented in Fig. 3. References to chromium(III) complexes with histidine are scant, consisting of one preliminary report,12) and one doctoral dissertation by Grouhi-Witte.13) The histidinate ion coordinates to metal through the imidazole [N(1)] and amine [N(3)] nitrogen atoms and through a carboxyl oxygen atom [O(1)] with bond lengths of 2.036(5), 2.062(4), and 1.957(4) Å respectively. It is noted that the bond lengths of the Cr-N(amino) and Cr-O of this complex are comparable to those of $[Cr(gly)_3]$ (2.068 Å for Cr-N-(amino), 1.965 Å for Cr-O)14) and that the bond lengths of Cr-N(imidazole) (2.036(5) Å) and Cr-N-(amino) (2.062(4) Å) of the histidinate ligand in the present complex are longer than the corresponding bond lengths of [Co(L-his)(L-pen)],15) where pen represents the penicilaminate ion, 1.933(3) and 1.925(3) Å respectively. The bond angles subtended the histidinate ligand at chromium N(3)-Cr-O(1)= 80.1(2)°, N(1)-Cr-N(3)=87.2(2)° and O(1)-Cr-N(1)= 89.5(2)°; the smallest angle corresponds to the smallest five-membered ring. The N(3)-Cr-O(1) bond angle, 80.1(2)°, is comparable to that of $[Cr(gly)_3]$, which has an average value of 81.8°.14) The L-alama ion, which is deprotonated at the two carboxyl ends, is coordinated to the metal through the oxygen

Table 1. Final positional parameters and their estimated standard deviations (in parentheses)[a]

Atom	X	Y	Z	Atom	X	Y	Z
Cr	2935.8(7)	2345.2(5)	2294.2(10)	C (9)	3504(6)	2125(5)	−1475(7)
O (1)	3946(3)	1309(2)	1565(4)	C (10)	2695(5)	4166(4)	859(7)
O (2)	5484(4)	355(3)	2030(5)	C (11)	2030(5)	4220(3)	2213(7)
O (3)	1542(3)	1934(3)	1208(4)	O (7)	1647(4)	6427(3)	678(5)
O (4)	816(3)	1794(3)	−931(5)	H (1)	502(4)	297(3)	294(6)
O (5)	2106(3)	3477(2)	3031(4)	H (2)	440(5)	297(4)	426(6)
O (6)	1474(4)	4941(3)	2523(5)	H (3)	401(5)	329(4)	41(6)
N (1)	2462(4)	1494(3)	3924(5)	H (4)	565(6)	367(5)	622(7)
N (2)	1344(5)	549(3)	5214(6)	H (5)	294(6)	2(4)	634(6)
N (3)	4523(3)	2621(3)	3346(5)	H (6)	3(8)	464(6)	497(10)
N (4)	3210(3)	3205(3)	556(5)	H (7)	484(7)	91(5)	508(9)
C (1)	1343(5)	1182(4)	4155(7)	H (8)	577(4)	166(3)	380(6)
C (2)	2538(6)	429(4)	5605(7)	H (9)	739(10)	144(7)	146(12)
C (3)	3216(5)	1035(3)	4839(6)	H (10)	174(8)	534(6)	524(9)
C (4)	4559(5)	1226(4)	4903(8)	H (11)	354(6)	449(5)	105(8)
C (5)	5079(4)	1677(4)	3591(7)	H (12)	424(7)	240(5)	−185(8)
C (6)	4853(4)	1050(3)	2305(7)	H (13)	312(6)	179(4)	−223(7)
C (7)	2610(5)	2739(4)	−652(6)	H (14)	422(8)	153(6)	−101(10)
C (8)	1568(4)	2112(3)	−107(7)				

a) The values have been multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms.

Final thermal parameters ($\times 10^4$) and their estimated standard deviations (in parentheses)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	32.8(4)	26.3(3)	58.4(14)	−1.4(4)	−2.0(9)	3.0(6)
O (1)	48(3)	33(2)	61(7)	1(2)	−1(4)	−9(3)
O (2)	74(4)	52(2)	93(8)	28(2)	−3(5)	−2(3)
O (3)	46(3)	45(2)	60(7)	−9(2)	−8(4)	11(3)
O (4)	55(3)	69(3)	77(8)	−13(3)	−26(5)	−1(4)
O (5)	61(3)	37(2)	64(7)	8(2)	16(4)	10(3)
O (6)	113(4)	44(2)	123(8)	31(3)	48(6)	17(4)
N (1)	47(3)	33(2)	62(9)	3(2)	16(5)	6(3)
N (2)	76(4)	37(2)	83(9)	−7(3)	10(6)	18(4)
N (3)	38(3)	35(2)	71(8)	−4(2)	−2(4)	−11(4)
N (4)	42(3)	34(2)	24(8)	−2(2)	−2(4)	0(3)
C (1)	48(4)	40(3)	81(11)	−3(3)	6(6)	7(5)
C (2)	85(6)	40(3)	58(11)	2(4)	−2(7)	10(5)
C (3)	65(5)	29(2)	39(10)	9(3)	5(6)	1(4)
C (4)	57(5)	52(3)	73(11)	12(3)	0(6)	14(5)
C (5)	32(3)	45(3)	58(11)	6(3)	−11(5)	−7(4)
C (6)	41(4)	34(2)	74(10)	2(2)	10(6)	−5(4)
C (7)	57(4)	38(3)	34(9)	2(3)	−15(5)	0(4)
C (8)	36(4)	33(3)	86(11)	4(3)	−9(6)	−6(4)
C (9)	73(5)	63(4)	54(11)	−4(4)	11(7)	−15(5)
C (10)	84(6)	27(2)	79(11)	−5(3)	28(7)	4(4)
C (11)	52(4)	33(2)	77(10)	−1(3)	9(7)	6(4)
O (7)	101(4)	48(2)	92(8)	20(3)	−7(5)	14(3)

a) Parameters have the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

of the alaninate moiety (*O*-ala), the oxygen of the acetate moiety (*O*-ace), and imino nitrogen (*N*-imino) atoms, with bond lengths of 1.960(3), 1.947(4), and 2.078(5) Å respectively. These distances can be compared to the average (Cr–O) distance of 1.965 Å and the average (Cr–N) distance of 2.086 Å found in $[Cr(gly)_3]$.[14] The bond angles of L-alama at chromium are 81.6(2)° for O(3)–Cr–N(4), 83.9(2)° for O(5)–Cr–N(4), and 93.5(2)° for O(3)–Cr–O(5). The bond angles of five-membered chelate rings can also be compared to those of $[Cr(gly)_3]$, 81.8° on the average.[14] The intramolecular bond distances and angles are

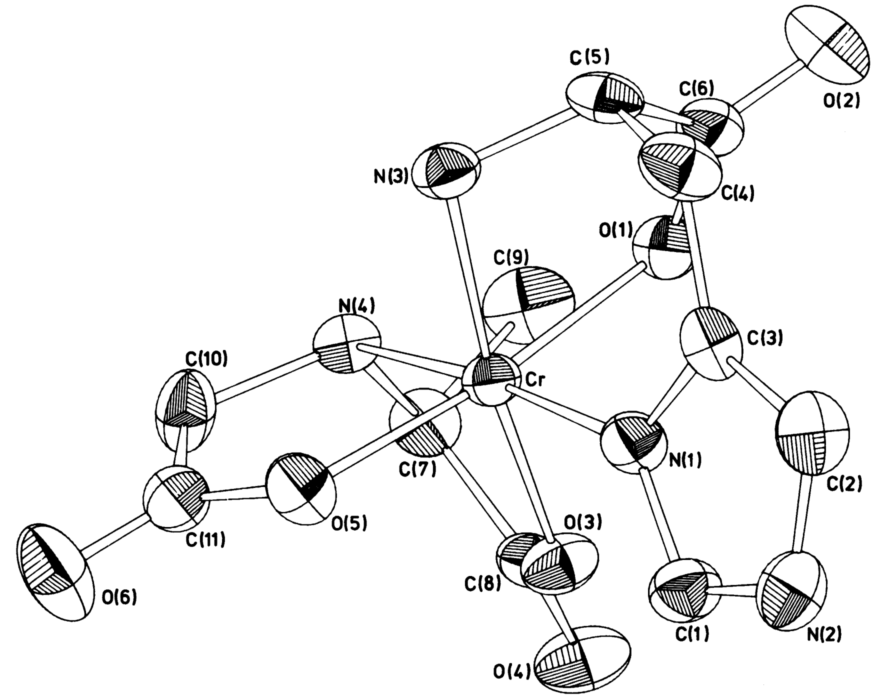

Fig. 2. Perspective drawing of the complex molecule [Cr(L-alama)(L-his)] and the numbering scheme for the atoms.

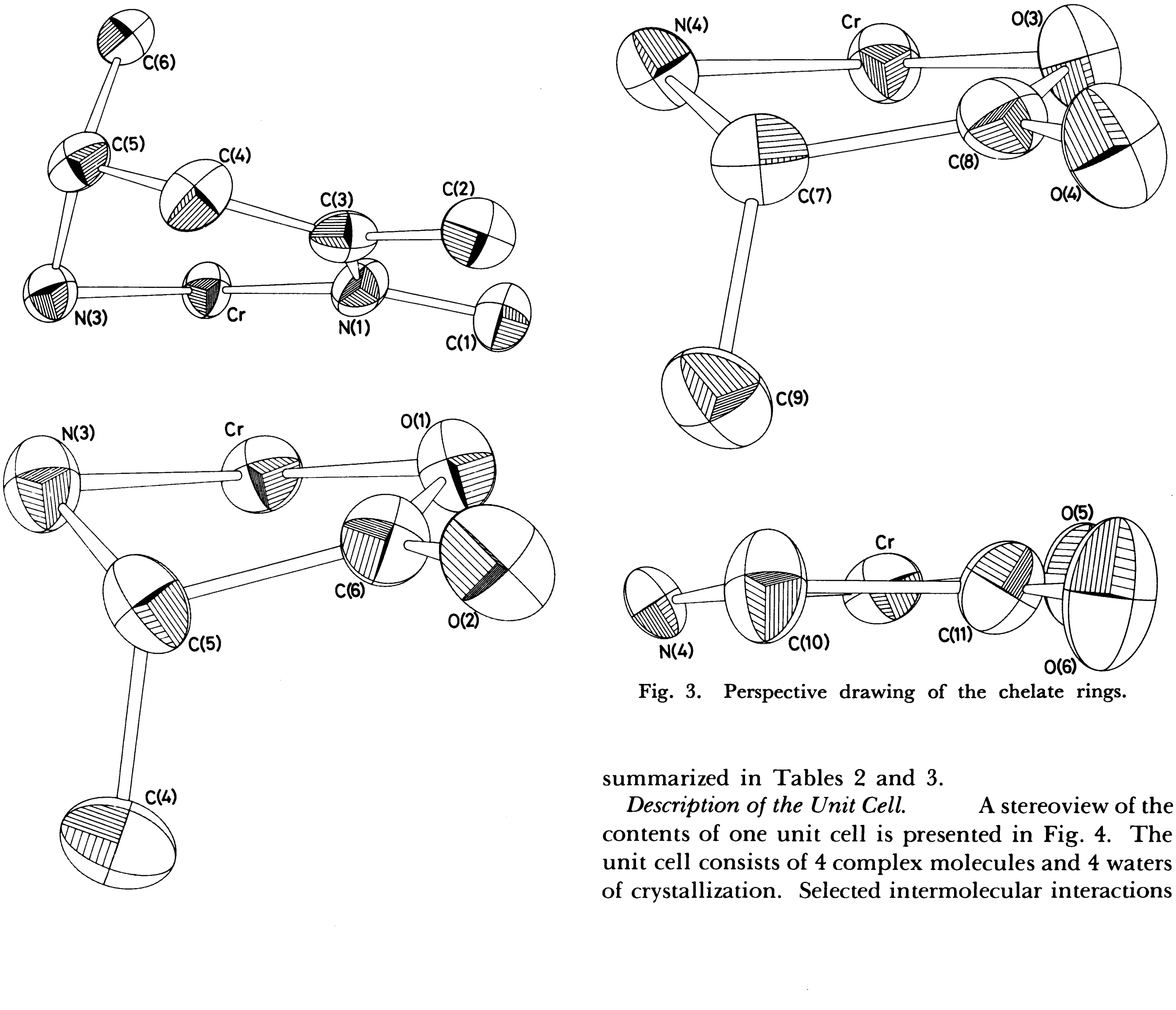

Fig. 3. Perspective drawing of the chelate rings.

summarized in Tables 2 and 3.

Description of the Unit Cell. A stereoview of the contents of one unit cell is presented in Fig. 4. The unit cell consists of 4 complex molecules and 4 waters of crystallization. Selected intermolecular interactions

TABLE 2. BOND DISTANCES (l/Å) AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

Cr-O (1)	1.957 (4)	C (2) - C (3)	1.349 (8)
Cr-O (3)	1.947 (4)	C (3) - C (4)	1.509 (8)
Cr-O (5)	1.960 (3)	C (4) - C (5)	1.523 (9)
Cr-N (1)	2.036 (5)	C (5) - C (6)	1.535 (9)
Cr-N (3)	2.062 (4)		
Cr-N (4)	2.078 (5)	C (7) - C (8)	1.538 (7)
		C (7) - C (9)	1.528 (8)
N (1) - C (1)	1.329 (7)		
N (1) - C (3)	1.371 (7)	C (10) - C (11)	1.497 (9)
N (2) - C (1)	1.348 (8)		
N (2) - C (2)	1.383 (8)		
N (3) - C (5)	1.474 (7)		
N (4) - C (7)	1.488 (7)		
N (4) - C (10)	1.486 (7)		
O (1) - C (6)	1.281 (7)		
O (2) - C (6)	1.223 (6)		
O (3) - C (8)	1.289 (8)		
O (4) - C (8)	1.231 (7)		
O (5) - C (11)	1.304 (6)		
O (6) - C (11)	2.217 (6)		

TABLE 3. BOND ANGLES (ϕ/°) AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

O(1)-Cr-O(3)	92.4(2)	Cr-O(1)-C(6)	117.1(4)
O(1)-Cr-O(5)	173.0(2)	O(1)-C(6)-O(2)	123.3(6)
O(1)-Cr-N(1)	89.5(2)	O(1)-C(6)-C(5)	114.5(4)
O(1)-Cr-N(3)	80.1(2)	O(2)-C(6)-C(5)	122.2(5)
O(1)-Cr-N(4)	93.2(2)		
O(3)-Cr-O(5)	93.5(2)	Cr-N(3)-C(5)	105.4(3)
O(3)-Cr-N(1)	92.2(2)	N(3)-C(5)-C(4)	110.2(5)
O(3)-Cr-N(3)	172.5(2)	N(3)-C(5)-C(6)	108.3(5)
O(3)-Cr-N(4)	81.6(2)		
O(5)-Cr-N(1)	94.1(2)	Cr-O(3)-C(8)	116.9(3)
O(5)-Cr-N(3)	94.0(2)	O(3)-C(8)-O(4)	123.2(5)
O(5)-Cr-N(4)	83.9(2)	O(3)-C(8)-C(7)	117.4(5)
N(1)-Cr-N(3)	87.2(2)	O(4)-C(8)-C(7)	119.4(6)
N(1)-Cr-N(4)	173.3(2)		
N(3)-Cr-N(4)	99.3(2)	Cr-O(5)-C(11)	117.0(4)
		O(5)-C(11)-O(6)	122.9(6)
Cr-N(1)-C(1)	124.0(4)	O(5)-C(11)-C(10)	117.0(4)
Cr-N(1)-C(3)	127.6(3)	O(6)-C(11)-C(10)	120.2(5)
N(1)-C(1)-N(2)	109.9(5)		
N(1)-C(3)-C(2)	107.8(5)	Cr-N(4)-C(7)	108.1(3)
N(1)-C(3)-C(4)	122.8(5)	Cr-N(4)-C(10)	108.0(3)
C(1)-N(1)-C(3)	107.8(5)	N(4)-C(7)-C(8)	108.4(5)
N(2)-C(2)-C(3)	107.7(5)	N(4)-C(7)-C(9)	111.2(4)
C(1)-N(2)-C(2)	106.6(5)	N(4)-C(10)-C(11)	113.8(4)
C(2)-C(3)-C(4)	129.4(6)	C(7)-N(4)-C(10)	112.1(4)
C(3)-C(4)-C(5)	114.3(5)	C(8)-C(7)-C(9)	109.9(4)
C(4)-C(5)-C(6)	111.7(4)		

TABLE 4. SELECTED INTERMOLECULAR INTERACTIONS

A	B	Distance/Å	Position of B
O (1)	N (3)	2.92	1/2−x, −y, −1/2+z
O (2)	N (3)	2.95	1/2−x, −y, −1/2+z
O (3)	O (7)	2.90	1/2−x, 1−y, 1/2+z
O (4)	N (2)	2.85	−1/2+x, 1/2−y, −z
O (4)	N (4)	2.90	−1/2+x, 1/2−y, −z
O (6)	O (7)	2.74	x, y, z

are listed in Table 4. The hydrogen bond of the O-H···O type probably exists between the O(3) atom of L-alama and the water O(7) atom, the O-O distance being 2.90 Å. In the same manner, the O(6) atom of L-alama is also linked to the water O(7) atom at a distance of 2.74 Å. The N(3) atom of the L-histidine residue is associated with the O(1) and O(2) atoms of the other molecule by an N-H···O hydrogen bond at distances of 2.92 and 2.95 Å respectively. The O(4) atom of L-alama is linked to the N(2) atom of the neighboring imidazole ring and the coordinated N(4) atom in the same manner, the O-N distances being 2.85 and 2.90 Å respectively. These interactions probably assist in the formation of the stable crystal structure.

Absorption Spectra. The absorption spectra of [Cr(L- or D-alama)(L-his)] are shown in Fig. 5, along with the spectra of [Cr(L- or D-asp)(L-his)]. As for [Cr(L-alama)(L-his)], the two major peaks in the visible region are identified as $^4A_{2g}{\rightarrow}^4T_{2g}(F)$ for the 580-nm transition and $^4A_{2g}{\rightarrow}^4T_{1g}$ for the 370-nm transition. For the whole series of $[Co(O)_n(N)_{6-n}]^{3-n}$ complexes, the predicted shifts of the first and second absorption bands have been discussed by Matsuoka *et al.*[16] Their discussion is also applicable to $[Cr(O)_3(N)_3]$. The first absorption band of the third eluate isomer of [Cr(L-asp)(L-his)] and the third eluate isomer of [Co(D-asp)(L-his)] showed no splitting or only a small splitting as was predicted by the above discussion that the first absorption band of a facial isomer should not have three components. Compared with these fac isomers, the L- and D-isomers of [Cr(L- or D-alama)(L-his)], along with the first eluate isomer of [Co(L-asp)(L-his)], and the first eluate isomer of the [Co(D-asp)(L-his)] isomer, have a broad peak because of their splitting into three components. The UV spectra of the L- or D-isomers of [Cr(L- or D-alama)-(L-his)] are found to be more similar to those of the first eluate mer isomers than to those of the fac isomers of [Cr(L- or D-asp)(L-his)] by inspecting the width and peak maxma of the first-absorption band region.

Distribution of the Isomers. Though three geometrical isomers, *cis(N)*, *trans(N)(a)*, and *trans(N)(b)* (Fig. 6), are possible in the bis(iminodiacetato)chromate(III) complex, only the *cis(N)* isomer has been prepared.[17] Both the *cis(N)* and the *trans(N)(a)* isomers of $[Cr(ida)_2]^-$ seem to have no steric hindrance between two ligands. In the tris(glycinato)chromium(III) complex, two geometrical isomers, mer and

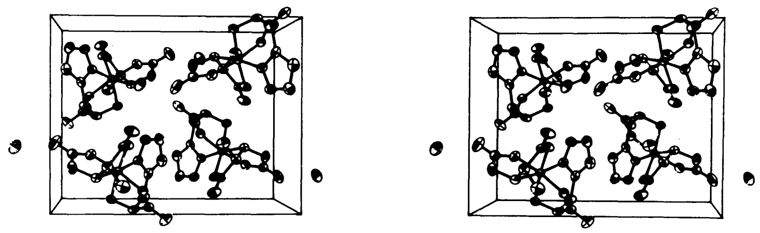

Fig. 4. Stereoscopic illustration of the unit cell contents.

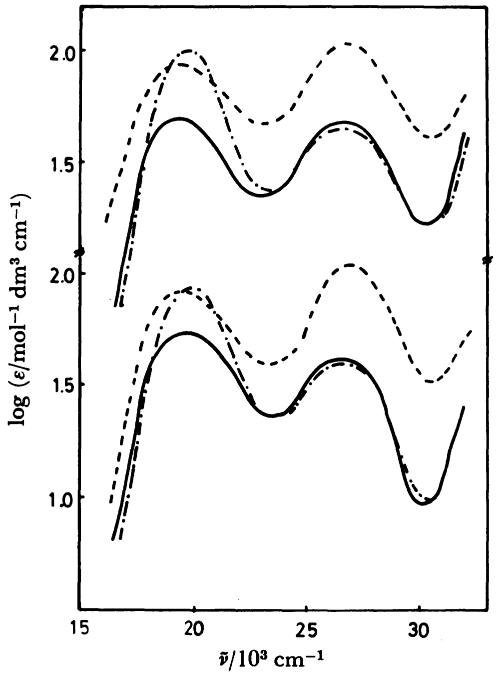

Fig. 5. Visible absorption spectra of [Cr(L- or D-alama)(L-his)] and [Cr(L- or D-asp)(L-his)]. Upper, *L* isomer (----) of [Cr(L-alama)(L-his)]. The first (——) and the third eluates (—•—•) of [Co(L-alama)(L-his)]. Lower, *D* isomer (----) of [Cr(D-alama)(L-his)]. The first (——) and the third eluates (—•—•) of [Co(D-asp)(L-his)].

fac (Fig. 6), are possible, but only the fac isomer has been prepared. We have previously reported that, in the cobalt(III) complex having both L- or D-aspartate and L-histidinate ions the *trans(N)* isomers are less stable than the other isomers.[18] This suggests that the two nitrogen atoms of a five-membered chelate ring avoid the *trans* position around the chromium(III) and cobalt(III) ions. While the two isomers (one mer and one fac isomers) of [Co(L- or D-asp)(L-his)] were prepared in nearly equal amounts, only one mer isomer of [Cr(L- or D-alama)(L-his)] was prepared for each L- or D-series. This stereoselectivity is interesting because it shows the difference in coordination power between asp and alama ligands. When an asp ligand coordinates to a metal ion, it has a rigid skeleton composed of five- and six-membered chelate rings. On the other hand, an alama has two forms in chirality around the coordinated nitrogen atom ((R) and (S) configurations), in which the (R) form has less steric repulsion between methyl protons and methylene protons than does the (S) form, so that the (R) configuration may be preferable to the (S) configuration. Beside the above steric hindrance, a coordinated alama has two five-membered chelate rings which can move around the Cr–N axis. In both the R-L-*cis(O)trans(N)* and R-L-*fac* isomers, the methyl group of alama strikes the imidazole 2-proton or amino protons of the coordinated L-his, while the R-L-*trans(O)cis(N)* isomer has no such repulsion. The steric flexibility seems to be larger in the chromium(III) complex than in the cobalt(III) complex, since we could prepare both a meridional and a facial isomers of the [Co(L- or D-alama)(L-his)] complexes for each L- or D-series.[19]

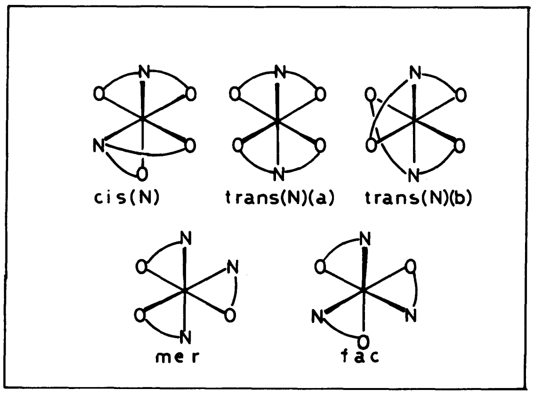

Fig. 6. Geometrical isomers of $[Cr(ida)_2]^-$ (upper) and $[Cr(gly)_3]$ (lower).

References

1) Department of Engineering, National Science Museum, Ueno Park, Tokyo 110, Japan.

2) W. Y. Mertz, *Fed. Proc.*, **33**, 659 (1974).

3) W. Y. Mertz, E. W. Toepfer, E. E. Roginski, and M. M. Polansky, *Fed. Proc.*, **33**, 2275 (1974).

4) N. Israily and *C. R. Hebd. Seances. Acad. Sci.*, **C 262**, 1426 (1966).

5) R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, and C. F. Weick, *J. Chem. Soc., Dalton Trans.*, **1974**, 1385.

6) a) H. Oki and K. Otuka, *Bull. Chem. Soc. Jpn.*, **49**, 1841 (1976); b) H. Oki and Y. Takahashi, *Bull. Chem. Soc. Jpn.*, **50**, 680 (1977); c) H. Oki and Y. Takahashi, *Bull. Chem. Soc. Jpn.*, **50**, 2288 (1977); d) H. Oki and H. Yoneda, *Inorg.*

Chem., **20**, 3875 (1981).

7) M. Watabe, H. Yano, Y. Odaka, and H. Kobayashi, *Inorg. Chem.*, **20**, 3623 (1981).

8) K. Okamoto, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **44**, 1601 (1971).

9) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

10) J. M. Bijvoet, A. F. Peerdeman, and A. J. Van Bommel, *Nature (London)*, **168**, 271 (1951).

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

12) P. E. Hoggard, *Inorg. Chem.*, **20**, 415 (1981).

13) G. Grouhi-Witte, Dissertation, Universitat, Hamburg, 1975.

14) R. F. Bryan, D. T. Greene, D. F. Stokely, Jr., and E. Wilson, *Inorg. Chem.*, **10**,1469 (1971).

15) P. D. Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, **99**, 101 (1977).

16) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **40**, 1868 (1976).

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

18) a) M. Watabe, S. Kawaai, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1845 (1976); b) M. Watabe, M. Zama, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **51**, 1354 (1978); c) M. Watabe, H. Yano, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **52**, 61 (1979).

19) M. Watabe, Unpublished Data.