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Preparation, Crystal Structure, and Absolute Configuration of $\Delta(-)_{546}$ -Di- μ -hydroxo-(*S,S,S,S*)-tetrakis(L-prolinato)dichromium(III) Tetrahydrate

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Pale purple crystals of $\Delta(-)_{546}$ -di- μ -hydroxo-(*S,S,S,S*)-tetrakis(L-prolinato)dichromium(III) tetrahydrate, $[\text{Cr}(\text{L-pro})_2\text{OH}]_2 \cdot 4\text{H}_2\text{O}$, were prepared. This complex is the first example for the noncharged di- μ -hydroxo dimer complex that is soluble in methanol or dimethyl sulfoxide. The absorption and CD spectra were measured in methanol or dimethyl sulfoxide. The crystal structure and absolute configuration of this complex have been determined from three-dimensional single-crystal X-ray data obtained on an automatic four-circle diffractometer using Mo $K\alpha$ radiation. The compound crystallizes in space group $P2_12_12_1$ of the orthorhombic system with $a = 12.071$ (7) Å, $b = 12.248$ (7) Å, $c = 19.715$ (10) Å, and $Z = 4$. Measured and calculated densities are 1.51 and 1.52 g cm⁻³, respectively. The structure has been refined by full-matrix least-squares techniques to a final residual $R = 0.067$ for 2427 independent nonzero reflections. The structure consists of a well-separated dimeric pair of octahedrally coordinated chromium(III) atoms linked by two hydroxo bridges. Each prolinato ligand is coordinated through nitrogen and oxygen. Though both octahedral units of this complex have the same composition $[\text{Cr}(\text{L-pro})_2(\text{OH})_2]$, their configurations are different; the two nitrogen atoms are mutually trans in one octahedron and are mutually cis in the other one, complexing the Δ -trans(N), Δ -trans(O) structure. Important bond distances are as follows: mean Cr-N = 2.085 (10), Cr-O(carboxyl) = 1.980 (10), Cr-O(hydroxo) = 1.947 (20) Å. The structure presented here appears to be the most stable isomer from consideration of steric hindrance between prolinato ligands and of intramolecular hydrogen bonds between amino hydrogen and carboxyl oxygen atoms.

Introduction

The ordinary methods for the preparation of (amino acidato)chromium(III) complexes have invariably led to facial tris(amino acidato) complexes and/or dihydroxo-bridged dimers. This behavior contrasts with the cobalt(III) chemistry, for which facial and meridional tris(amino acidato) complexes as well as dihydroxo dimers are all reported. While Israili claimed the preparation of the purple meridional isomer of $[\text{Cr}(\text{gly})_3]$,² Gillard et al. showed this complex to be a dihydroxo-bridged dimer, $[\text{Cr}(\text{gly})_2\text{OH}]_2 \cdot 6\text{H}_2\text{O}$.³ Oki et al. reported a number of facial and dihydroxo-bridged dimeric (amino acidato)chromium(III) complexes, but their attempt at the preparation of meridional tris(amino acidato)chromium(III) complexes was not successful.⁴ Thus, no tris(amino acidato)chromium(III) complexes with a meridional configuration are known up to now.

In this work, we have prepared by the reaction of hexaamminechromium(III) nitrate and L-proline, a purple (L-prolinato)chromium(III) complex, for which elemental analysis is consistent with the formulations $[\text{Cr}(\text{L-pro})_3] \cdot 6\text{H}_2\text{O}$ and $[\text{Cr}(\text{L-pro})_2\text{OH}]_2 \cdot 4\text{H}_2\text{O}$. Since all facial isomers of tris(amino acidato)chromium(III) complexes are reported to be pink to red in color, the purple color of the present complex pointed to two possibilities, namely the meridional isomer or the dihydroxo dimer. Also, the compound obtained here is soluble in MeOH and Me₂SO unlike the di- μ -hydroxo chromium(III) dimers reported so far, all of which are insoluble in usual solvents. Though these characteristics suggested the *mer* structure for this compound, the electronic absorption spectrum did not support this postulate. The spectrum of the present complex showed the first and second absorption bands with nearly equal intensities whereas in *mer*- $[\text{Co}(\text{L-pro})_3]$ the second absorption band exhibits a higher intensity than the first one.⁵ Thus, none of these data seemed definitive in assigning the structure and we have undertaken the crystal structure analysis of this compound.

Experimental Section

Preparation of the Compound. Hexaamminechromium(III) nitrate (3.45 g) and L-proline (3.45 g) were dissolved in water (100 mL), and the mixture was heated on a water bath until it became half of the original volume and then was kept standing at room temperature for 3 weeks. $[\text{Cr}(\text{L-pro})_2\text{OH}]_2 \cdot 4\text{H}_2\text{O}$ was gradually deposited as pale purple powder contaminated with $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$. For purification, the pale purple powder was dissolved in methanol, whereupon $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ could be excluded. The methanolic solution was kept standing at room temperature until completely dried. The needlelike crystals obtained were $[\text{Cr}(\text{L-pro})_2\text{OH}]_2 \cdot 4\text{H}_2\text{O}$. Anal. Calcd for C₂₀H₄₂O₁₄Cr₂: C, 36.04; H, 6.35; N, 8.41. Found: C, 35.87; H, 6.54; N, 8.30.

Absorption and CD Measurements. The electronic absorption spectra were taken on a Shimadzu UV-200 double-beam spectrophotometer, and the CD measurements were made on a JASCO J-40CS spectropolarimeter.

X-ray Data Collection. From the systematic absences for $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$), the space group is $P2_12_12_1$. The crystal size used for the cell constant and intensity measurements was 0.10 × 0.15 × 0.35 mm. The cell constants were determined by least-squares treatment of the setting of 15 reflections measured on a Syntex R3 computer-controlled four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Intensity data were collected by the ω - 2θ scan technique to a maximum 2θ value of 55° at a scan rate of 3° min⁻¹. The intensities of 3742 independent reflections were collected. Reflections for which the intensities were less than 3 times their standard deviations were regarded as "unobserved" and were not included in subsequent calculations. Thus, 2427 independent reflections were used for the structure determination. Their intensities were corrected for Lorentz and polarization factors, but no absorption corrections were made since μ (8.5 cm⁻¹) was low.

Determination and Refinement of Crystal Structure

A three-dimensional Patterson map revealed the positions of two chromium atoms. The remaining nonhydrogen atoms were located by the application of the Fourier method. Several cycles of block-diagonal least-squares refinement using isotropic thermal parameters reduced the R_1 value (defined as $\sum ||F_o| - |F_c|| / \sum F_o$) to 0.108. Further refinement using both positional and anisotropic thermal parameters for nonhydrogen atoms reduced the R_1 value to 0.080. At this stage, idealized coordinates of 36 hydrogen atoms excluding those of the water molecules were calculated (C-H, 1.05; N-H, 1.00 Å) with the assumption of tetrahedral angles at carbon and nitrogen atoms. The peaks found in the differential map at $R_1 = 0.080$ confirmed the positions of these hydrogen atoms, and subsequent refinement including these hydrogen atoms (fixed positional parameters with $B = 4.0$ Å²) reduced R_1 to 0.072. A difference map at this stage revealed the

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Table I. Positional and Thermal Parameters for $[\text{Cr}(\text{L-pro})_2\text{OH}]_2 \cdot 4\text{H}_2\text{O}^a$

(a) Positions of Nonhydrogen Atoms ^b									
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr1	4995 (1)	7052 (1)	4786 (1)	202 (6)	349 (7)	250 (6)	-27 (9)	-9 (7)	6 (7)
Cr2	4837 (1)	4964 (1)	4013 (1)	222 (6)	339 (7)	262 (7)	-4 (8)	21 (7)	-5 (7)
O1A	3899 (5)	7985 (6)	5253 (3)	391 (37)	387 (42)	312 (37)	91 (37)	-40 (34)	92 (37)
O2B	6225 (5)	8060 (6)	5028 (3)	239 (32)	385 (41)	281 (35)	-13 (33)	-26 (27)	46 (34)
O3C	4885 (6)	4065 (6)	4824 (3)	437 (40)	452 (39)	351 (37)	80 (43)	27 (40)	60 (36)
O4D	4752 (5)	5724 (6)	3132 (3)	318 (39)	431 (42)	324 (37)	-127 (35)	22 (31)	21 (33)
O5	5960 (5)	5960 (6)	4381 (3)	220 (32)	383 (41)	356 (39)	-50 (34)	4 (31)	-63 (34)
O6	3889 (5)	6069 (6)	4403 (3)	201 (31)	395 (41)	311 (37)	58 (34)	17 (29)	-52 (33)
O7A	2905 (6)	8199 (7)	6182 (4)	390 (41)	720 (58)	323 (43)	239 (43)	33 (33)	-86 (42)
O8B	7313 (5)	9382 (6)	4657 (4)	319 (37)	456 (48)	518 (49)	-49 (36)	-194 (36)	131 (40)
O9C	5712 (10)	2695 (11)	5346 (5)	1415 (95)	1337 (105)	547 (62)	737 (89)	263 (66)	423 (71)
O10D	3648 (7)	6226 (7)	2298 (4)	718 (57)	654 (60)	418 (48)	-216 (51)	-205 (45)	196 (45)
N1A	4975 (7)	6227 (6)	5710 (4)	288 (39)	367 (46)	235 (38)	44 (47)	-40 (42)	17 (34)
N2B	5022 (6)	7983 (7)	3896 (4)	198 (35)	459 (47)	410 (44)	29 (46)	-54 (43)	38 (41)
N3C	5964 (7)	3800 (7)	3669 (5)	324 (46)	379 (54)	453 (56)	96 (44)	-2 (43)	-87 (47)
N4D	3486 (6)	4127 (7)	3600 (4)	241 (40)	293 (47)	300 (46)	-47 (39)	-6 (36)	-25 (39)
C1A	6085 (8)	6034 (11)	6031 (6)	272 (52)	749 (88)	493 (72)	145 (61)	-78 (54)	267 (72)
C2A	5974 (10)	6390 (12)	6743 (6)	453 (69)	877 (104)	370 (69)	121 (72)	-100 (58)	38 (72)
C3A	5119 (10)	7282 (10)	6719 (6)	457 (67)	768 (88)	492 (67)	117 (78)	-168 (65)	-154 (65)
C4A	4281 (8)	6848 (9)	6210 (5)	325 (50)	389 (62)	215 (51)	53 (50)	60 (42)	-105 (48)
C5A	3628 (8)	7737 (9)	5865 (5)	270 (48)	440 (68)	331 (57)	13 (50)	23 (45)	-197 (53)
C6B	3900 (8)	8409 (10)	3682 (6)	266 (52)	595 (78)	379 (63)	-126 (54)	-115 (50)	156 (60)
C7B	4032 (11)	9600 (12)	3615 (10)	582 (86)	574 (91)	1428 (157)	47 (78)	-277 (99)	104 (104)
C8B	4982 (10)	9895 (10)	4054 (6)	567 (69)	473 (67)	791 (80)	-54 (85)	-162 (84)	140 (68)
C9B	5757 (8)	8922 (9)	3983 (6)	289 (50)	461 (67)	385 (62)	-90 (51)	-49 (50)	189 (59)
C10B	6506 (7)	8779 (9)	4601 (5)	220 (46)	387 (62)	225 (52)	-1 (46)	-34 (39)	-71 (46)
C11C	6981 (8)	4226 (11)	3320 (6)	276 (54)	755 (89)	342 (63)	-101 (62)	211 (49)	-134 (65)
C12C	7969 (11)	3833 (14)	3692 (8)	387 (70)	1029 (127)	1054 (128)	71 (84)	-42 (81)	413 (112)
C13C	7533 (11)	3571 (15)	4383 (8)	495 (80)	1128 (141)	824 (114)	135 (90)	-222 (80)	124 (104)
C14C	6331 (9)	3139 (11)	4250 (6)	458 (65)	569 (83)	504 (74)	82 (66)	79 (58)	88 (68)
C15C	5600 (9)	3301 (11)	4857 (6)	391 (62)	624 (82)	541 (80)	200 (61)	-78 (59)	95 (71)
C16D	2542 (9)	3840 (9)	4054 (6)	561 (70)	370 (67)	451 (70)	-145 (58)	104 (63)	114 (59)
C17D	1507 (10)	4346 (12)	3739 (8)	416 (71)	783 (107)	954 (115)	-73 (75)	197 (75)	-18 (96)
C18D	1941 (9)	5258 (11)	3290 (7)	270 (54)	594 (85)	812 (94)	108 (62)	-75 (61)	-14 (78)
C19D	3043 (8)	4773 (9)	3014 (5)	325 (52)	423 (70)	396 (62)	-69 (55)	-36 (48)	-28 (55)
C20D	3859 (9)	5642 (8)	2810 (5)	409 (59)	326 (63)	291 (55)	-101 (53)	48 (48)	-145 (50)
OW1	5264 (8)	3392 (9)	6630 (5)	760 (70)	1077 (80)	675 (64)	283 (64)	-147 (56)	38 (59)
OW2	5656 (9)	7422 (8)	2226 (6)	1104 (82)	667 (69)	1118 (87)	-194 (68)	254 (73)	373 (67)
OW3	3093 (8)	4298 (8)	6449 (5)	613 (54)	834 (72)	757 (67)	165 (57)	164 (52)	283 (59)
OW4	2754 (9)	8307 (12)	7606 (5)	804 (73)	1837 (131)	648 (71)	406 (84)	182 (59)	195 (84)

(b) Positions of Hydrogen Atoms^c

atom	x	y	z	atom	x	y	z	atom	x	y	z
H1N1	466	548	561	H15C8	536	1061	390	H29C17	108	377	345
H2C1	670	647	578	H16C9	628	901	356	H30C18	207	597	357
H3C1	631	521	600	H17N3	596	322	330	H31C18	139	545	290
H4C2	672	666	693	H18C11	698	507	333	H32C19	296	427	258
H5C2	568	576	704	H19C11	700	398	282	H33O5	663	620	404
H6C3	550	801	654	H20C12	862	438	366	H34O6	313	613	465
H7C3	480	745	718	H21C12	828	310	345	H35OW1	525	325	615
H8C4	369	635	644	H22C13	751	433	466	H36OW1	500	400	667
H9N2	531	746	353	H23C13	805	307	465	H37OW2	538	688	240
H10C6	331	822	404	H24C14	632	230	416	H38OW2	613	700	188
H11C6	365	805	323	H25N4	378	338	347	H39OW3	260	387	625
H12C7	329	1000	376	H26C16	270	416	453	H40OW3	313	488	615
H13C7	415	982	310	H27C16	248	300	410	H41OW4	283	813	712
H14C8	474	998	455	H28C17	96	463	410	H42OW4	313	887	760

^a Weighting factor for the atoms is 1.0 throughout. ^b The positions and thermal parameters of nonhydrogen atoms are multiplied by 10^4 . ^c The positions of hydrogen atoms are multiplied by 10^3 .

remaining eight hydrogen atoms. The anomalous dispersion effects for the chromium atoms ($\Delta f' = 0.28$ and $\Delta f'' = 0.62$) were included.⁶ The absolute configuration of the present molecule was determined from the comparison with that of the L-prolinato ligand as an internal reference. The final refinement using the anisotropic temperature factors for all nonhydrogen atoms and with $B = 4.0 \text{ \AA}^2$ for all the hydrogen atom contributions converged to $R_1 = 0.067$ and $R_2 = 0.069$, where $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. A final difference map showed no peaks greater than 0.5 e \AA^{-3} . The weighting scheme used was $w = (\sigma|F_o|^2 + (a|F_o|)^2 + b|F_o|)^{-1}$, where $\sigma|F_o|$ is the standard

deviation obtained from the counting statistics for each reflection and the values of a and b used in the final refinement are 0.03 and 0.2, respectively. The atomic scattering factors from ref 6 were used. All the computations were carried out by a HITAC-8700 computer at the Hiroshima University Computer Center. The computer programs used were FOUR-MMM (Fourier synthesis)⁷ and HBL5-IV (least-squares calculation),⁸ with a slight modification. The final atomic parameters and the temperature factors (with their estimated standard deviations)

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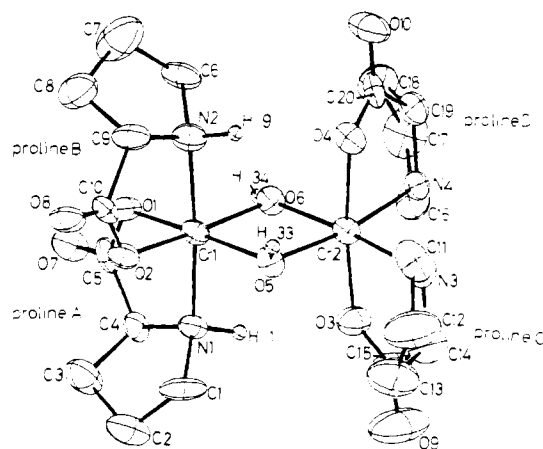


Figure 1. View of the [Cr(L-pro)₂OH]₂ molecule. Hydrogen atoms are omitted for clarity, except for hydrogen atoms in the bridging part. Thermal ellipsoids are shown at the 50% probability.

Table II. Selected Intramolecular Distances and Angles in [Cr(L-pro)₂OH]₂·4H₂O

Distances (Å)			
Cr1-Cr2	2.983 (2)	Cr1-N1	2.081 (9)
Cr1-O1	1.975 (7)	Cr1-N2	2.092 (8)
Cr1-O2	1.988 (7)	Cr2-N3	2.084 (9)
Cr2-O3	1.942 (8)	Cr2-N4	2.092 (8)
Cr2-O4	1.973 (7)	O3-N1	3.175 (11)
Cr1-O5	1.946 (7)	O4-N2	3.166 (11)
Cr1-O6	1.949 (7)	O3...H1	2.339 (7)
Cr2-O5	1.962 (8)	O4...H9	2.366 (7)
Cr2-O6	1.933 (7)		
Angles (Deg)			
Cr1-O5-Cr2	99.5 (3)	O6-Cr2-N3	174.5 (3)
Cr1-O6-Cr2	100.4 (3)	O5-Cr2-N3	95.4 (3)
O1-Cr1-O2	91.7 (3)	O6-Cr2-N4	92.1 (3)
N1-Cr1-N2	176.0 (3)	N1-Cr1-O5	91.9 (3)
O3-Cr2-O4	173.5 (3)	N2-Cr1-O6	89.3 (3)
N3-Cr2-N4	92.7 (3)	N1-Cr1-O6	91.8 (3)
O1-Cr1-O5	171.9 (3)	N2-Cr1-O5	91.1 (3)
O1-Cr1-O6	94.5 (3)	O3-Cr2-O5	91.6 (3)
O2-Cr1-O5	94.5 (3)	O3-Cr2-O6	95.1 (3)
O2-Cr1-O6	170.8 (3)	O4-Cr2-O5	93.9 (3)
O5-Cr2-N4	170.9 (3)	O4-Cr2-O6	89.3 (3)
O3...H1-N1	139.3 (10)	O4...H9-N2	134.4 (10)

are listed in Table I. Complete lists of the $10|F_o|$ and $10|F_c|$ values have been preserved in the supplementary material.

Results and Discussion

Description of the Structure. The structure consists of well-separated dimeric units, [Cr(L-pro)₂OH]₂, as shown in Figure 1. The bond distances and angles in this complex are summarized in Table II. The geometry around each chromium atom is roughly octahedral with two cis hydroxo groups and two coordinated prolinato ligands. The bridging part Cr1, O5, O6, and Cr2 is nearly planar. The Cr1-Cr2 and O5-O6 separations in the bridging part are 2.983 (2) and 2.505 (10) Å, respectively, and the essential similarity of four independent bridging Cr-O bond lengths of 1.946 (7) (Cr1-O5), 1.949 (7) (Cr1-O6), 1.962 (8) (Cr2-O5), and 1.933 (8) Å (Cr2-O6) demonstrates that the bridging oxygen atoms are symmetrically bound to two Cr atoms. The Cr-O-Cr angles in the bridging part are 99.5 (3) (Cr1-O5-Cr2) and 100.4 (3)° (Cr1-O6-Cr2), while the O-Cr-O angles are 80.0 (3) (O5-Cr1-O6) and 80.0 (3)° (O5-Cr2-O6). The metal-metal separation and the geometry of the bridging unit are similar to those found in [Cr(gly)₂OH]₂,⁹ in which the Cr-Cr sepa-

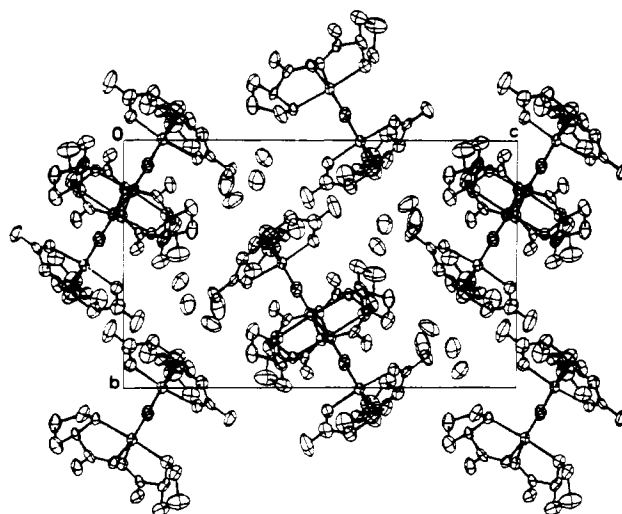


Figure 2. View of the crystals of [Cr(L-pro)₂OH]₂·4H₂O seen in projection down the *b* axis.

ration is 2.974 (2) Å, the Cr-O-Cr angle is 98.2 (2)°, and the O-Cr-O angle is 81.8 (2)°.

The Cr-N distances of 2.081 (9) (Cr1-N1), 2.092 (8) (Cr1-N2), 2.084 (9) (Cr2-N3), and 2.092 (8) Å (Cr2-N4) are slightly longer than the values of 2.061 (5) and 2.067 (5) Å reported for [Cr(gly)₂OH]₂⁹ and the value of 2.068 (1) Å found in *fac*-[Cr(gly)₃].¹⁰ The Cr-O bond lengths of 1.975 (7) (Cr1-O1), 1.988 (7) (Cr1-O2), 1.942 (8) (Cr2-O3), and 1.973 (7) Å (Cr-O4) compare nicely with the values of 1.970-1.977 Å in [Cr(gly)₂OH]₂⁹ and 1.962-1.967 Å in *fac*-[Cr(gly)₃].¹⁰

There is evidence for intramolecular hydrogen bonding in [Cr(L-pro)₂OH]₂. In this complex, the two mutually trans nitrogen atoms on the Cr1 side are directed so as to face the two mutually trans carboxyl oxygens on the Cr2 side; further, the N-H hydrogen of each pyrrolidine ring (N1-H1 and N2-H9) is directed to the carboxyl oxygen atom (O3 and O4), shown in Figure 1, forming the hydrogen bonds O3...H1-N1 and O4...H9-N2. The bond distances of O3...H1, O4...H9, O3...N1, and O4...N2 are 2.339 (7), 2.366 (7), 3.175 (11), and 3.166 (11) Å, respectively. The criterion for the hydrogen bond is that the O...H separation must be less than the sum of the van der Waals radii of oxygen (1.5 Å) and hydrogen (1.2 Å) atoms and the N...O distance must be between 2.57 and 3.24 Å.¹¹ The actual bond distances satisfy this criterion. The bond angles of O3...H1-N1 and O4...H9-N2 are 139.3 (10) and 134.4 (10)°, respectively. The hydrogen bonds found in [Cr(L-pro)₂OH]₂ are somewhat stronger than those found in [Cr(gly)₂OH]₂ in which the corresponding bond distances of O...H and O...N are 2.59 and 3.22 Å, respectively.¹² The dimeric structure of these complexes is probably stabilized by the formation of two such intramolecular multiple hydrogen bonds, which are parallel to their bridging unit.

The bond lengths and angles found in the four independent L-prolinato ligands are given in Table III. As found in other amino acidato complexes,¹³ the five-membered chelate ring exhibits only a small degree of puckering. The maximum deviations (0.100 Å) from the mean plane for the proline A chelate ring are found for N1 and C5 (0.09 and 0.09 Å in

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(12) The intramolecular distances, O...H-N and O...N, were calculated by following the positional table for [Cr(gly)₂OH]₂ in ref 9. This paper has some errors.

(13) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 342.

Table III. Intramolecular Distances and Angles in the L-Prolinato Ligands of $[\text{Cr}(\text{L-pro})_2\text{OH}]_2$

Bond Distances (Å)							
proline ring							
A		B		C		D	
N1-C1	1.501 (16)	N2-C6	1.513 (14)	N3-C11	1.500 (16)	N4-C16	1.489 (14)
N1-C4	1.500 (14)	N2-C9	1.465 (14)	N3-C14	1.470 (16)	N4-C19	1.498 (14)
C1-C2	1.476 (20)	C6-C7	1.472 (22)	C11-C12	1.482 (22)	C16-C17	1.523 (19)
C2-C3	1.504 (19)	C7-C8	1.482 (23)	C12-C13	1.493 (25)	C17-C18	1.520 (21)
C3-C4	1.521 (17)	C8-C9	1.521 (17)	C13-C14	1.569 (22)	C18-C19	1.558 (18)
C4-C5	1.504 (14)	C9-C10	1.526 (16)	C14-C15	1.499 (18)	C19-C20	1.508 (15)
C5-O1	1.288 (13)	C10-O2	1.264 (13)	C15-O3	1.276 (15)	C20-O4	1.252 (13)
C5-O7	1.214 (14)	C10-O8	1.229 (13)	C15-O9	1.225 (18)	C20-O10	1.264 (14)
Bond Angles (Deg)							
proline ring							
A		B		C		D	
O1-Cr1-N1	82.3 (3)	O2-Cr1-N2	81.4 (3)	O3-Cr2-N3	82.0 (3)	O4-Cr2-N4	81.2 (3)
N1-C1-C2	105.9 (8)	N2-C6-C7	105.8 (11)	N3-C11-C12	108.5 (11)	N4-C16-C17	106.8 (10)
C1-N1-C2	107.5 (8)	C6-N2-C9	107.5 (8)	C11-N3-C14	107.6 (9)	C16-N4-C19	108.2 (8)
C1-C2-C3	104.3 (11)	C6-C7-C8	105.8 (14)	C11-C12-C13	103.7 (14)	C16-C17-C18	104.8 (12)
C2-C3-C4	102.9 (10)	C7-C8-C9	103.3 (11)	C12-C13-C14	104.1 (13)	C17-C18-C19	102.4 (11)
N1-C4-C3	103.9 (9)	N2-C9-C8	104.8 (9)	N3-C14-C15	102.8 (11)	N4-C19-C18	103.8 (9)
C3-C4-C5	113.2 (9)	C8-C9-C10	112.3 (10)	C13-C14-C15	111.5 (12)	C18-C19-C20	112.4 (11)
O1-C5-O7	123.6 (10)	O2-C10-O8	124.8 (10)	O3-C15-O9	123.8 (13)	O4-C20-O10	122.4 (10)

opposite sense). The deviations in other chelate rings (L-proline B, C, and D) are similar to those in the proline A chelate ring.

Each pyrrolidine ring is nonplanar. In the proline A ring, the deviation of the C_γ atom (C2) from the mean plane formed by N1, C1, C3, and C4 is 0.48 Å. The corresponding deviations in other pyrrolidine rings (proline B, C, and D) are all nearly equal to the deviation found in the proline A ring and are also similar to those in $[\text{Co}(\text{trien})(\text{L-pro})]_2 \cdot 2\text{H}_2\text{O}$.¹⁴ The average values of bond angles within each pyrrolidine ring are all about $104 (1)^\circ$ in the present structure. This value is quite close to the value 104° found in $[\text{Co}(\text{trien})(\text{L-pro})]_2 \cdot 2\text{H}_2\text{O}$,¹⁴ indicating a significant ring strain within the five-membered ring.

The ORTEP drawing of the unit cell viewed along the b axis is given in Figure 2. The distances of intermolecular hydrogen bonds are listed in Table IV. The asymmetric unit includes four water molecules of crystallization (OW1-OW4). These four water molecules form independent hydrogen bonds with the carbonyl oxygen atoms (O7, O8, O9, and O10) of the prolinato ligands: O7...HW41-OW4, O8...HW40-OW3, O9...HW35-OW1, and O10...HW37-OW2. Two nitrogen atoms (N3 and N4) occupy cis positions in the Cr2 octahedron. These nitrogen atoms are also linked to the oxygen atom of one crystal water (OW2) by two N-H...O-type hydrogen bonds. The water molecules are also linked together by O-H...O-type hydrogen bonds.

Consideration of the Structure of the Di- μ -hydroxo Dimer Complex. The only established example of a binuclear (amino acidato)chromium(III) complex is $[\text{Cr}(\text{gly})_2\text{OH}]_2$.⁹ There has been known, to date, no X-ray crystal structure of a binuclear chromium(III) complex that contains optically active amino acidato ligands.

Though the geometry of the bridging part for $[\text{Cr}(\text{L-pro})_2\text{OH}]_2$ is similar to that in $[\text{Cr}(\text{gly})_2\text{OH}]_2$, the coordination geometry around the central chromium is quite different in both complexes. The glycinato dimer complex has a cis structure with respect to the coordinating nitrogen atoms in both octahedrons, and the overall structure has an inversion center in the middle point of the dimeric unit; that is, the structure is a meso form. On the other hand, the structure of the present prolinato dimer complex consists of a trans(N)

octahedron (Cr1) and a cis(N) octahedron (Cr2) with respect to the coordinating nitrogen atoms, and the structure is described as the Δ -trans(N), Δ -trans(O) form. This complex has an approximate C_2 axis through the Cr1 and Cr2 atoms.

As described in the previous section, the structure of the di- μ -hydroxo dimer complex with amino acid is stabilized by the formation of the two intramolecular N-H...O hydrogen bonds. The number of possible isomers of dihydroxo-bridging dimer complexes with four L-prolinato ligands is 43. Among these 43 isomers, the seven isomers that contain a pair of two mutually facing oxygen and nitrogen atoms are picked out by using the Dreiding model and are illustrated in Figure 3. Here, only the hydrogen atom bonded to the pyrrolidine nitrogen atom is depicted. The reason why the di- μ -hydroxo-prolinato dimer complex takes the Δ -trans(N), Δ -trans(O) configuration (Figure 3a) is considered as follows. The structure of the pyrrolidine ring is considerably rigid. Denning and Piper noted that the steric interaction between the cis-coordinated L-prolinato ligands, implied in the Δ -trans(O) configuration, appears prohibitively large.⁵ The possibility of the isomers b and c in Figure 3 is thus excluded. Two intramolecular N-H...O hydrogen bonds can not be formed in models d, f, and g, because at least one of the two hydrogen atoms on the nitrogen atom is not directed toward the carboxylate oxygen. In model e, two intramolecular hydrogen bonds are possible, but the steric hindrance between the bulky pyrrolidine rings is larger than in model a in Figure 3. From these considerations, it is concluded that the Δ -trans(N), Δ -trans(O) form is the most stable structure.

In the di- μ -hydroxo-glycinato dimer complex, all isomers in Figure 3 can form two intramolecular hydrogen bonds. All the tris-type chromium(III) complexes with amino acids that have been reported so far are of cis,cis structure (*fac*). Thus, if the chromium(III) complex with amino acids has no steric hindrance between amino acidato ligands, it is natural to infer that the cis,cis structure around the central chromium atom is preferred. Indeed the preparation of *cis,cis*- $[\text{Cr}(\text{gly})_2\text{OH}]_2$ is always contaminated by racemic *cis,cis*- $[\text{Cr}(\text{gly})_3] \cdot \text{H}_2\text{O}$.¹⁵ Therefore, if we postulate *cis*- $[\text{Cr}(\text{gly})_2(\text{OH})_2]$ as the precursor of $[\text{Cr}(\text{gly})_3]$, the structure of $[\text{Cr}(\text{gly})_2\text{OH}]_2$ would most probably be the meso *cis,cis* form (Figure 3f), and this

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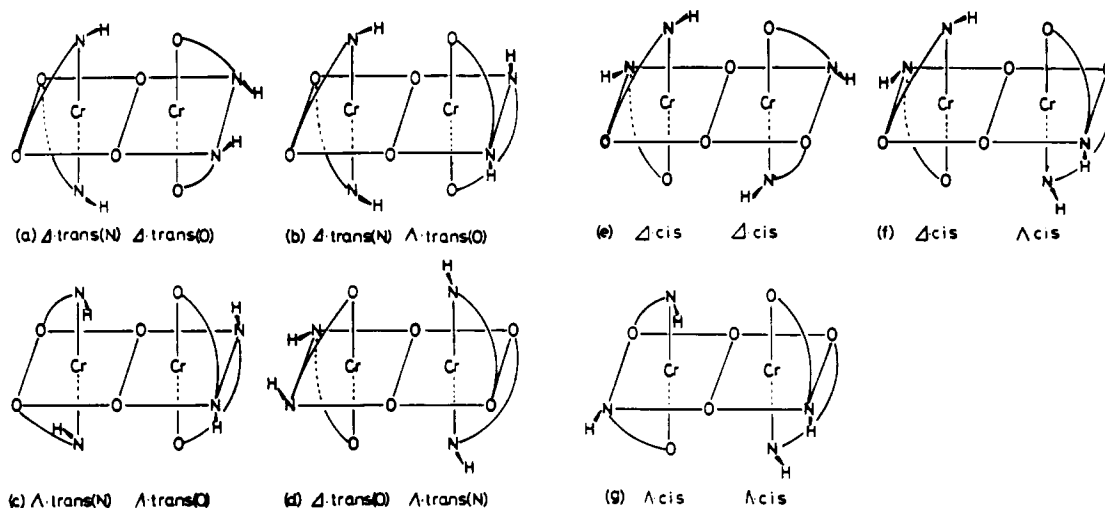


Figure 3. Possible structures of a di- μ -hydroxo dimer in which the two nitrogen atoms are directed to the two carboxyl oxygen atoms. Only the positions of hydrogen atoms on the nitrogen atoms in the pyrrolidine ring are shown.

Table IV. Intermolecular Distances and Angles

X-H...Y	X...Y, Å	H...Y, Å	X-H...Y, deg
OW1-HW35...O9	2.73	1.82	157
OW2-HW37...O10	2.84	2.24	129
OW3-HW40...O8	2.87	2.08	144
OW4-HW41...O7	2.82	1.84	164
N4-H25...OW2	2.84	1.92	149
N3-H17...OW2	3.13	2.41	126
OW1-HW36...OW3	2.87	2.37	120
OW2-HW38...OW4	2.71	2.24	107
OW4-HW42...OW1	2.83	2.54	102
OW3-HW39...O10	2.76	2.56	94

inference is supported by the X-ray analysis.⁹

Absorption and CD Spectra. The absorption and CD spectra of the di- μ -hydroxo-prolinato dimer complex in MeOH and Me₂SO are shown in Figure 4. The absorption and CD curves are not affected by the solvents MeOH and Me₂SO, except the two CD peaks in the spin-forbidden region. The absorption coefficient of the first absorption band (545 nm, $\log \epsilon = 2.08$ in MeOH; 545 nm, $\log \epsilon = 2.08$ in Me₂SO) is nearly equal to that of the second absorption band (393 nm, $\log \epsilon = 2.11$ in MeOH; 394 nm, $\log \epsilon = 2.07$ in Me₂SO). For the whole series of the [Co^{III}(O)_n(N)_{6-n}] complexes, the predicted shifts of the first and second absorption bands have been discussed by Matuoka et al.¹⁶ Their discussion is now applied to [Cr^{III}(O)₄(N)₂] units. Two nitrogen atoms are mutually cis in one unit and are mutually trans in the other. Therefore, the first absorption band should be split into three components. The broadening of the first absorption band reflects the splitting.

The CD curves in the visible transition region are similar to those of (-)₅₈₉-[Cr(dip)₂OH]₂⁴⁺ and (-)₅₈₉-[Cr(phen)₂OH]₂⁴⁺ reported by Mason¹⁷ and (-)₅₈₉-[Cr₂(dip)₂(phen)₂(OH)₂]⁴⁺ reported by Kaizaki et al.¹⁸ However, in the spin-forbidden region, they observed three CD peaks, (-), (-), and (+), from the longer wavelength side, while the present complex shows four separate bands: 717 nm ($\Delta\epsilon = +2.16$), 700 nm ($\Delta\epsilon = -18.0$), 675 nm ($\Delta\epsilon = +33.9$), and 632 nm ($\Delta\epsilon = +85.2$) in MeOH and 727 nm ($\Delta\epsilon = +1.3$), 701 nm ($\Delta\epsilon = -13.0$), 675 nm ($\Delta\epsilon = +34.0$), and 619 nm ($\Delta\epsilon = +187.0$) in Me₂SO, all the CD intensities in this region being

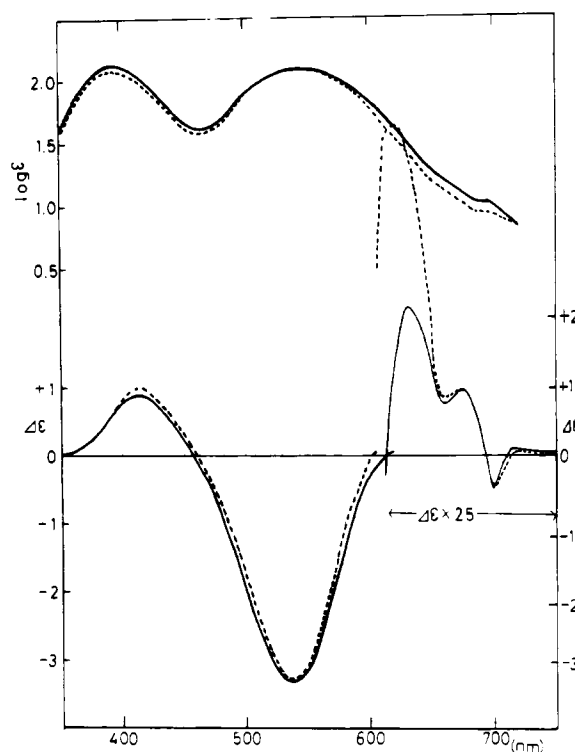


Figure 4. Absorption and CD spectra of [Cr(L-pro)₂OH]₂·4H₂O in MeOH (—) and in Me₂SO (---).

multiplied by 10³. The absorption spectrum in the spin-forbidden region has a shoulder at 690 nm in both solvents. The sign of the CD peak corresponding to this shoulder is negative, which is the same as the sign of the major CD band in the first spin-allowed region. As noted above, the solvent effect is observed for the two peaks in the spin-forbidden region. The peaks of 717 and 632 nm in MeOH are shifted to 727 and 619 nm in Me₂SO. The intensity of the peak at 727 nm in Me₂SO is half of that of the corresponding peak at 717 nm in MeOH, and the peak at 619 nm in Me₂SO is about 2 times larger than that of the corresponding peak at 632 nm in MeOH. The reason for this observation is not clear as yet.

Registry No. [Cr(L-pro)₂OH]₂·4H₂O, 78804-48-5; [Cr(NH₃)₆](NO₃)₃, 15363-28-7.

Supplementary Material Available: Listings of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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