arsenic "anion" separations within the layers are fixed in position. Improved nesting of the sheets and polarization of the arsenic atoms may be involved.

Relationship with Li_3NaSi_6. We have very recently become aware of the existence of a remarkably similar layered anion structure in Li_3NaSi_6.[20] The isoelectric layers there contain the same columns or tubes of shared, five-membered rings, but their interconnection is slightly different. The relative positions of half of the exocyclic bridges are altered in Li_3NaSi_6 as would be accomplished by inverting alternate columns. Thus, the central ring system seen in Figure 2 becomes related to those on both sides by a horizontal screw axis or glide plane centered on the Si(3)–Si(3) connection rather than by the normal twofold axis found at that point with KSi_3As_3. The altered arrangement appears to generate much better cavities along the chain for lithium.

Relationship with SiAs. The structure determined by Wadsten[3] for SiAs in space group $C2/m$ is closely and logically related to that of KSi_3As_3. The former is shown in Figure 4 in the [010] projection. The tricyclic units can be derived from Si_3As_2As rings in KSi_3As_3 by joining these in pairs at the exocyclic As(1) atoms. This generates a pair of puckered five-member rings condensed onto a central six-membered ring at the disilicon edges in the latter. Such a member is centered about a screw axis at $^1/_4$, y, 0 in Figure 4. These ring systems are then linked into strings in the plane of the figure through Si(3)–Si(3) bonds and condensed along $\vec{b}$ to form layers as before. Twofold axes are again found normal to the centers of the Si(3)–Si(3) bonds.

The chemical and structural conversion

$$6SiAs + 2K \rightarrow 2KSi_3As_3 \qquad (2)$$

within one layer of SiAs can be achieved by (1) cleavage of opposite As(1)–Si(2) edges of the six-membered rings to form chains of dibonded As(1) atoms, Figures 1 and 2, and (2), displacement of half of the result by $b/2$ with respect to the other and rotation to allow formation of the Si(2)–Si(2) bonds in KSi_3As_3. The change is depicted symbolically on the same tricyclic unit around $^1/_4$, $^1/_2$, 0 in Figure 4. The direction of opening of these six-membered rings in the conversion to KSi_3As_3 alternates between layers in order to provide good interlayer bonding sites for potassium. It is not obvious, however, that such a reduction (or oxidation) process could actually be achieved in a truly concerted manner. Not surprisingly, KSi_3As_3 and SiAs exhibit very comparable distances as well as similar distributions of angles about equivalent atoms, the latter suggesting somewhat similar strain problems in both structures. The same may pertain to the closely related $GeAs_2$[4] as well.

Further reduction of the anion layers in KSi_3As_3 leads to the chain structure noted before in $Sr_3Si_2As_4$ where the connectivity is $^1_\infty[Si_2(As_2)As_{4/2}]$ via four-membered Si_2As_2 rings. It is interesting that in the related $Sr_3Ge_2As_4$, five-membered $Ge_{1/2}$–Ge–(As_2)–As–$Ge_{1/2}$–As– rings analogous to those found condensed in KSi_3As_3 occur in chains, but with one germanium now common to two rings. The anion structure of KSi_3As_3 was presumably not found during earlier studies with alkaline-earth-metal cations because half as many cations of higher field would not support a stable layered structure.

Acknowledgment. The authors are indebted to Drs. K.-H. Lii and R. Haushalter for early communication of their structural results on KSnAs and KSnSb and to H.-G. von Schnering and R. Nesper for unpublished information on Li_3NaSi_6.

Supplementary Material Available: A listing of anisotropic thermal parameters (1 page); a table of observed and calculated structure factors for KSi_3As_3 (2 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of the Three Geometrical Isomers of (1,3-Propanediamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionato)chromate(III). Crystal Structure of *trans*(O_6)-K[Cr(1,3-pddda)]·$3H_2O$

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Received December 30, 1986

Chromium(III) complexes with the sexidentate ligand 1,3-propanediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate (1,3-pddda) were prepared, chromatographically separated into the three geometrical isomers with respect to the N–O chelate ring size (trans(O_5), trans(O_5O_6), and trans(O_6), where O_5 and O_6 refer to the five- and six-membered N–O rings, respectively), and isolated. The X-ray analysis of a crystal from the last-eluted isomer showed the isomer to be *trans*(O_6)-K[Cr(1,3-pddda)]·$3H_2O$, in which the six-membered 3-propionate rings occupy trans-axial sites while the acetate rings lie in the equatorial plane with the two nitrogen atoms. This result confirms the assignment made on the basis of the magnetic circular dichroism and deuteron NMR spectroscopy for the complexes with the 1,3-pddda deuteriated on the methylenes of either the acetate or 3-propionate arms. *trans*(O_6)-K[Cr(1,3-pddda)]·$3H_2O$ ($KCrC_{13}H_{18}N_2O_8\cdot3H_2O$) crystallizes in the monoclinic space group $P2_1/a$ with unit cell parameters a = 16.815 (6) Å, b = 11.862 (3) Å, c = 9.449 (3) Å, β = 91.20 (7)°, and Z = 4. The structure converged to R = 0.037 for 2038 reflections.

Introduction

The edta-like ligands (diamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionato)chromate(III) might be expected to yield a maximum of three geometric isomers when coordinated as sexidentate chelating agents (Figure 1). Both the trans(O_5) and trans(O_5O_6) isomers have been characterized for cobalt(III) and rhodium(III) complexes of ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate (eddda).[2,3] For the eddda–chromium(III) complex, however, only the trans(O_5) isomer has been isolated and identified.[4,5] The favored isomers are those in which the larger six-membered β-alaninate chelate rings are found in the more strained girdling

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[1] (a) Nara Women's University. (b) Washington State University. (c) Osaka City University.

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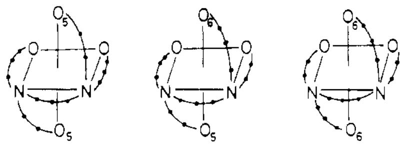

trans(O5) trans(O5O6) trans(O6)

Figure 1. Possible geometrical structures of 1,3-pddda complexes.

(G) in-plane positions. In-plane five-membered glycinate chelate rings are considerably more strained than in-plane six-membered β-alaninate rings as evidenced in the crystal structures of $(-)_D$-*trans*(O_5)-Li[Cr(eddda)]$\cdot 5H_2O$[5] and K[Cr(edta)]$\cdot 2H_2O$[6] or Na[Cr(*rac*-cydta)]$\cdot 4.5H_2O$[7] (edta = ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate; cydta = 1,2-cyclohexanediamine-*N*,*N*,*N′*,*N′*-tetracetate). The in-plane strain may be eased when the five-membered diamine chelate backbone is enlarged to a six-membered diamine chelate ring as found in the structure analysis of Na[Cr(1,3-pdta)]$\cdot H_2O$[8] (1,3-pdta = 1,3-propanediamine-*N*,*N*,*N′*,*N′*-tetraacetate); i.e., the substitution of 1,3-propanediamine for ethylenediamine in eddda to give 1,3-propanediamine-*N*,*N′*-diacetate-*N*,*N′*-di-3-propionate(1,3-pddda) might make it possible to form all geometrical isomers (Figure 1).

This paper deals with the preparation, chromatographic separation, and isolation of the three geometrical isomers of [Cr(1,3-pddda)]$^-$. The isomers are characterized through a combined use of ^{2}H NMR spectroscopy, magnetic circular dichroism, and single-crystal X-ray diffraction analysis. Deuteron NMR spectroscopy has proved particularly useful in the characterization of Cr^{III} complexes.[9-12] The novel intensity behavior of the first absorption band associated with the $^4T_4 \leftarrow {}^4A_2$ transition is found and discussed for these complexes.

Experimental Section

Preparation of the Ligands. 1,3-Propanediamine-*N*,*N′*-diacetic-*N*,*N′*-di-3-propionic acid (H_4-1,3-pddda) was prepared by alkylation of 1,3-propanediamine-*N*,*N′*-diacetic acid (H_2-1,3-pdda) with 3-chloropropionic acid and directly used in the syntheses of the desired complexes as described subsequently. The corresponding ligand with deuteriated acetate arms was obtained with the use of deuteriated 1,3-pdda-d_4[12c,13] by the same method. 3-Propionate deuteriated on the 2-position was prepared by base hydrolysis of 1,3-propanediamine-*N*,*N′*-di-3-propionitrile in D_2O. The di-3-propionitrile was obtained from the reaction of 1,3-propanediamine with acrylonitrile by the method used to synthesize ethylenediamine-*N*,*N′*-di-3-propionitrile.[14] Anal. Calcd for H_2-1,3-pddp$\cdot$2HCl: C, 37.11; H, 6.93; N, 9.62. Found: C, 36.93; H, 7.04; N, 9.65. The deuteriation of the ligands was confirmed by NMR. About 75% of the desired protons in the ligands were found to be deuteriated. These sexidentate ligands were also used for the preparation of the complexes without isolation. The abbreviations are 1,3-pddda-5-*d* and 1,3-pddda-6-*d* for the 1,3-pddda ligands with the deuteriated acetate and the deuteriated 3-propionate arms, respectively.

1,3-Propanediaminetetraacetic acid with deuteriated acetate methylenes was obtained by the reaction of 1,3-pdda-d_4 with chloroacetate by the method described for 1,3-pddda. Ethylenediamine-*N*,*N′*-diacetic-*N*,*N′*-di-3-propionic acid (eddda) with deuteriated acetate methylenes (eddda-5-*d*) and deuteriated 2-methylenes (eddda-6-*d*) of the 3-propionates were prepared with ethylenediamine by the same method.

Table I. Crystallographic Data for *trans*(O_6)-K[Cr(1,3-pddda)]$\cdot 3H_2O$

formula	$C_{13}H_{24}N_2O_{11}KCr$
space group	$P2_1/a$
cell constants	
a, Å	16.815 (6)
b, Å	11.862 (3)
c, Å	9.449 (3)
β, deg	91.20 (7)
V, Å^3	1884 (1)
Z	4
d_{measd}, g cm^{-3}	1.67
d_{calcd}, g cm^{-3}	1.676
cryst size, mm	0.35 × 0.30 × 0.18
cryst color	red
cryst faces	(010), (001), (100), (011), $(01\bar{1})$, $(0\bar{1}0)$, $(00\bar{1})$, $(\bar{1}00)$, $(0\bar{1}\bar{1})$, $(0\bar{1}1)$
μ(Mo Kα), cm^{-1}	8.71
scan method	ω
scan speed, deg s^{-1}	0.05
scan width, deg	$1.0 + 0.4 \tan \theta$
data collcn range (2θ), deg	4–46
no. of unique data, $F_o^2 > 3\sigma(F_o^2)$	2038
R_F[a]	0.037
R_{wF}[b]	0.050

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Preparation of the Complexes. H_2-1,3-pdda$\cdot$2HCl (2 g, 0.0075 mol) was suspended in 2 mL of water. To this mixture was added 1.98 g (0.03 mol) of potassium hydroxide in 5 mL of water. A cooled mixture of 1.8 g (0.0165 mol) of 3-chloropropionic acid in 5 mL of water and 1.1 g (0.0165 mol) of KOH in 3 mL of water was added. The solution was heated to 75–80 °C, and an additional 1.1 g of KOH in 3 mL of water was added to keep the pH near 9–10. The reaction solution was further heated at 85–90 °C for 2 h. Two grams of $CrCl_3\cdot 6H_2O$ in 3 mL of water was added dropwise to the solution. The mixture was heated at 85–90 °C for 14–18 h with stirring. The color of the reaction solution changed from green to red-violet. After the red-violet solution was diluted 30 times with water, the half-volume of it was poured onto a column (i.d. 30 × 900 mm) of a QAE-Sephadex anion exchanger in the chloride form. After the column was washed with water, the charged complexes were eluted with a 0.02 M NaCl solution at a rate of 1–1.5 mL/min at 5 °C. Six bands for the non-deuteriated complexes, five for the 1,3-pddda-5-*d* complexes, and four for the 1,3-pddda-6-*d* complexes developed. A red-violet band on the top of the column was not eluted with a 0.02 M NaCl solution. Due to its apparent higher negative charge, this complex was not considered further. The remaining bands were red (B-I), reddish purple (B-II), purplish red (B-III), red (B-IV), and dull red-purple (B-V) in elution order. Each of these eluates was condensed by a vacuum rotary evaporator to as small a volume as possible at 30–35 °C. The complexes were extracted with methanol so that sodium chloride was removed from the solution. Powders of each complex were obtained by adding acetone to the methanol solution. Purification was performed by repeating the same procedure. The elemental analyses showed contamination by sodium chloride. The sodium salts were converted to the lithium salts for the second and third (B-II and B-III) bands and to the potassium salt for the fourth (B-IV) band by using a cation-exchange resin. Anal. Calcd for $C_{13}H_{25}N_2O_{11.5}CrLi$ (B-II): C, 34.52; H, 5.57; N, 6.20. Found: C, 34.42; H, 5.36; N, 6.10. Calcd for $C_{13}H_{24}N_2O_{11}CrLi$ (B-III): C, 35.22; H, 5.45; N, 6.32. Found: C, 35.85; H, 5.54; N, 6.23. Calcd for $C_{13}H_{24}N_2O_{11}CrK$ (B-IV): C, 32.86; H, 5.07; N, 5.89. Found: C, 32.58; H, 5.07; N, 5.82. Calcd for $C_{14}H_{28}N_2O_{12}CrNa_{2.5}Cl_{1.5}$ (B-I): C, 28.32; H, 4.76; N, 4.72. Found: C, 28.45; H, 4.71; N, 4.67. Calcd for $C_{13}H_{26}N_2O_{12}CrNa_{6.5}Cl_{5.5}$ (B-V): C, 19.54; H, 3.29; N, 3.51. Found: C, 19.14; H, 3.29; N, 3.54. The corresponding deuteriated complexes were synthesized by the same methods as the all-protic compounds and characterized by the absorption spectra. The 1,3-pdta-d_4 and *trans*-(O_5)-eddda-5-*d* and -6-*d* complexes were prepared by the literature methods, and their identities were confirmed by their absorption spectra.[4,15]

X-ray Analysis of *trans*(O_6)-K[Cr(1,3-pddda)]$\cdot 3H_2O$ (B-IV). Crystals of this complex suitable for X-ray analysis were grown from a concen-

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Table II. Fractional Coordinates and Temperature Factors for *trans*(O_6)-K[Cr(1,3-pddda)]·3H_2O (B-IV)[a]

atom	*x*	*y*	*z*	*U*(eq) or *U*, Å^2
Cr	0.7820 (6)	0.0674 (6)	0.2931 (6)	0.0193 (2)
K	0.523 (1)	−0.028 (1)	0.7900 (9)	0.0350 (3)
O(1)	0.682 (3)	0.035 (3)	0.190 (2)	0.026 (1)
O(2)	0.597 (3)	0.075 (3)	0.018 (3)	0.033 (1)
O(3)	0.881 (3)	0.108 (3)	0.396 (3)	0.030 (1)
O(4)	0.949 (3)	0.150 (4)	0.589 (3)	0.052 (1)
O(5)	0.791 (3)	0.213 (3)	0.195 (3)	0.029 (1)
O(6)	0.872 (3)	0.308 (3)	0.054 (3)	0.049 (1)
O(7)	0.717 (3)	0.115 (3)	0.452 (3)	0.028 (1)
O(8)	0.626 (3)	0.051 (3)	0.599 (3)	0.043 (1)
O(W1)	0.947 (3)	0.324 (3)	0.790 (4)	0.054 (1)
O(W2)	0.485 (4)	−0.180 (4)	−0.420 (4)	0.059 (1)
O(W3)	0.569 (4)	0.290 (4)	0.174 (4)	0.070 (2)
N(1)	0.847 (3)	0.010 (3)	0.122 (3)	0.021 (1)
N(2)	0.778 (3)	−0.087 (3)	0.398 (3)	0.021 (1)
C(1)	0.799 (4)	−0.032 (4)	−0.003 (4)	0.026 (1)
C(2)	0.731 (4)	0.047 (4)	−0.047 (4)	0.030 (1)
C(3)	0.664 (4)	0.053 (4)	0.059 (4)	0.024 (1)
C(4)	0.842 (4)	−0.106 (4)	0.509 (4)	0.031 (1)
C(5)	0.860 (4)	−0.005 (5)	0.603 (4)	0.034 (2)
C(6)	0.899 (4)	0.091 (4)	0.527 (4)	0.030 (1)
C(7)	0.894 (4)	0.111 (4)	0.082 (4)	0.030 (1)
C(8)	0.850 (4)	0.219 (4)	0.110 (4)	0.030 (1)
C(9)	0.699 (4)	−0.084 (4)	0.467 (4)	0.026 (1)
C(10)	0.678 (4)	0.035 (4)	0.513 (4)	0.027 (1)
C(11)	0.901 (4)	−0.084 (4)	0.169 (4)	0.028 (1)
C(12)	0.859 (4)	−0.191 (4)	0.215 (4)	0.030 (1)
C(13)	0.780 (4)	−0.181 (4)	0.293 (4)	0.027 (1)

[a] Standard deviations in the least significant figures are given in parentheses.

trated aqueous solution in a refrigerator for a few days. The crystal data and experimental details are shown in Table I. Weissenberg photography was used for the determination of the space group. Unit-cell parameters were derived by a least-squares analysis of 19 θ values of higher angle reflections (θ = 7–14°), measured on a Philips PW1100 diffractometer by use of Mo Kα radiation (λ = 0.7107 Å).

Intensity data were collected on the diffractometer by using graphite-monochromated Mo Kα radiation at room temperature. The intensities of three standard reflections (20$\bar{1}$, 080, 003) monitored every 4 h showed no appreciable decay during the data collection. Of the 2484 unique reflections measured in the $h,k,\pm l$ region, 2038 with $F_o^2 > 3\sigma(F_o^2)$ were used for the structural analysis. No correction was made for absorption.

The crystal structure was solved by direct methods (MULTAN).[16] The positional and thermal parameters were refined by the block-diagonal-matrix least-squares method. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma(F_o)^{-2}$. Hydrogen atoms were introduced in the calculated positions (C–H = 0.97 Å), but those of the water molecules were located from the difference synthesis. These H atoms were included in the least-squares calculation, but their parameters were not refined. Each H atom was assigned an isotropic temperature factor equal to that of the atom to which it is bonded. The convergence was attained with R_F and R_{wF} listed in Table I. All the parameter shifts in the final cycle of the refinement were <0.2σ. The final difference synthesis showed no significant features.

The atomic scattering factors, with correction for the real part of the anomalous dispersion effect for Cr and K$^+$, were taken from ref 17. Tables of observed and calculated structure factors, thermal parameters, and hydrogen atom coordinates are available as supplementary material. Computational work was carried out by using standard programs.[18] The atomic coordinates are given in Table II.

Measurements. Absorption spectra were obtained with a Shimadzu UV-240 spectrophotometer. Magnetic circular dichroism spectra were recorded on a Jasco MOE-1 spectropolarimeter at a magnetic field of 1.5 T (1 T = 10 000 G) and room temperature. Deuteron nuclear magnetic resonance spectra (30.7 MHz) were measured on a Nicolet NT-200WB spectrometer operating at a field of 4.7 T at room temperature as described in detail previously.[9-12] Proton NMR spectra were obtained on a Hitachi FT-NMR R-600 spectrometer operating at a magnetic field of 1.41 T at room temperature. DSS (sodium 4,4-dimethyl-4-sila-1-pentanesulfonate) was used as an internal reference. Infrared spectra were measured with a Jasco DS-402G spectrophotometer.

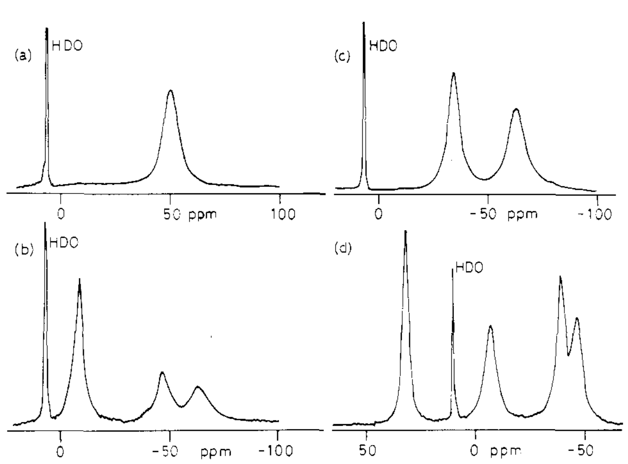

Figure 2. Deuteron NMR spectra of the (a) trans(O_5) (B-II) and (b) trans(O_5O_6) (B-III) isomers of (1,3-pddda-5-*d*)Cr^{III} complexes, (c) *trans*(O_5)-[Cr(eddda-5-*d*)]$^-$, and (d) [Cr(1,3-pdta-d_4)]$^-$ in water.

Results and Discussion

Syntheses of the Ligands. 1,3-Propanediamine-*N*,*N'*-diacetic-*N*,*N'*-di-3-propionic acid was synthesized by two routes: from 1,3-propanediamine-*N*,*N'*-diacetic acid and from 1,3-propanediamine-*N*,*N'*-di-3-propionic acid for 1,3-pddda-5-*d* and 1,3-pddda-6-*d*, respectively. The methods involve syntheses of the acetonitrile and the 3-propionitrile intermediates, followed by the base hydrolyses in ^2H_2O solutions. Isotopic substitution was confirmed by observing the decrease in the integrated intensity of the acetate methylenes and the 2-methylenes of 3-propionates (δ = ca. 4 and 2.7 from DSS, respectively) in the ^{1}H NMR spectra. The extent of deuteriation was found to be 60–80%.

Characterization of the Complexes. From five bands separated on chromatography of [Cr(1,3-pddda)]$^-$, solids were isolated for each band with elemental analyses consistent with the formulated structure, but in some cases it was not possible to remove all the methanol and NaCl present during the isolation. The complexes show only one asymmetric carboxyl stretching band at about 1620 cm^{-1} in the infrared absorption spectra. Moreover, no frequency shift to lower energy of the first d–d band is observed with increasing pH (ca. 10) for each isomer. These observations indicate that there are no free carboxylate groups and no coordinated water for the five isolated isomers.

Three geometrical isomers are predicted for [Cr(1,3-pddda)]$^-$ as shown in Figure 1; hence, the isolation of apparently five isomers needs explanation. The comparison with the ^{2}H NMR spectra of the 1,3-pddda-5-*d* and -6-*d* complexes suggests that the B-II, B-III, and B-IV bands correspond to the three expected geometrical isomers but that the B-I and B-V isomers can not be characterized yet. Only three normal geometrical isomers will hereinafter be described and discussed.

The ^{2}H NMR spectra of the B-II and B-III complexes are shown in Figure 2. The B-II complex with 1,3-pddda-5-*d* gives only one resonance for the deuteriated acetate methylenes at −50 ppm, whereas three resonances are observed for B-III with the integrated intensity ratio of 2:1:1 at −8.78, −46.4, and −63.0 ppm, respectively. This fact leads exclusively to the assignment of the B-III isomer to the trans(O_5O_6) isomer, but B-II may be either the trans(O_5) or trans(O_6) isomer, because the former has four inequivalent deuterons in contrast to the latter with a C_2 axis as seen from Figure 1. In comparison to the ^{2}H NMR spectra observed for the deuteriated acetate methylenes of [Cr(1,3-pdta)]$^-$ and *trans*(O_5)-[Cr(eddda)]$^-$ (Figure 2c,d), it has been shown that

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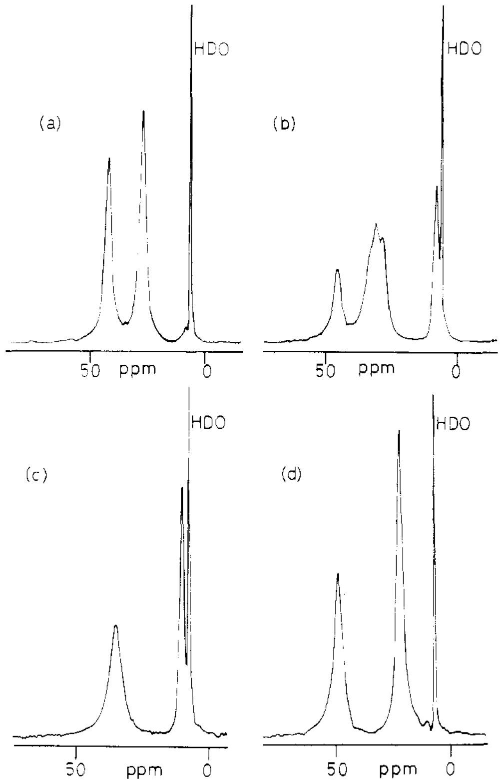

Figure 3. Deuteron NMR spectra of the (a) trans(O_5) (B-II), (b) trans(O_5O_6) (B-III), and (c) trans(O_6) (B-IV) isomers of (1,3-pddda-6-*d*)Cr^{III} complexes and (d) *trans*(O_5)-[Cr(eddda-6-*d*)]$^-$ in water.

the acetate ^2H NMR resonances in the out-of-plane (R) rings are always located at higher fields than those in the in-plane girdle (G) rings. This NMR behavior agrees with the results of the edta and cydta complexes as reported by Wheeler et al.[10] On this basis, it is likely that the −50 ppm resonance observed for the B-II complex is due to four acetate deuterons in the two R rings but two expected resonances due to two inequivalent deuterons happen to be coincident with each other as in Figure 2a.

Therefore, the B-II complex may be assigned to the trans(O_5) isomer.

This assignment is supported by the observation of the highest frequency positive magnetic circular dichroism (MCD) peak at 21 370 cm^{-1} due to the $^2T_2 \leftarrow {}^4A_2$ spin-forbidden d-d transition in accordance with the MCD position for the edta-type complexes having six-membered β-alaninate chelates in the G-ring positions as previously shown.[19] The B-IV complex is most likely the trans(O_6) isomer, because the corresponding MCD peak at 22 170 cm^{-1} is located at the highest frequency among the three complexes, indicating the coordination of the five-membered chelate rings in the G-ring position. As predicted from the above consideration for the trans(O_5O_6) isomer, the highest frequency positive MCD peak of the B-III isomer observed at 21 930 cm^{-1} is intermediate to those obtained for the B-II and B-IV isomers.

This assignment is confirmed by the ^2H NMR spectra observed for the 1,3-pddda-6-*d* complexes as shown in Figure 3. That is, the B-III complex gives four downfield resonances for the 2-methylenes of the propionates. This is consistent with a trans(O_5O_6) geometrical structure for the B-III isomer with four inequivalent deuterons. Since two NMR resonances are observed for the B-II and B-IV isomers, these complexes should have a C_2 symmetry axis. Inspection of the ^2H NMR resonances of the trans(O_5O_6) 1,3-pddda-6-*d* and trans(O_5) eddda-6-*d* complexes (Figure 3c,d) shows two resonances between +48 and +45 ppm and between +28 and +20 ppm that are ascribed to the 2-methylenes of the 3-propionate arms in the G rings. Thus, the two remaining resonances at +30 and +8 ppm observed for the trans(O_5O_6) isomer are due to the deuterons in the R rings. Consistent with these assignments, the B-II complex giving resonances at +41.8 and +26.0 ppm has the propionate chelate rings in the G-ring position, whereas the B-IV isomer with resonances at +31.5 and +8.9 ppm has the chelate rings in the R-ring position. This assignment is the same as that obtained for the 1,3-pddda-5-*d* complexes on the basis of the NMR and MCD data. In conclusion, the B-II, B-III, and B-IV complexes have been determined to be the trans(O_5), trans(O_5O_6), and trans(O_6) isomers, respectively.

Table III. Bond Distances (Å) and Bond Angles (deg)

Cr–O(1)	1.958 (3)	N(1)–C(1)	1.503 (5)
Cr–O(3)	1.963 (3)	N(1)–C(7)	1.488 (5)
Cr–O(5)	1.970 (3)	N(1)–C(11)	1.493 (5)
Cr–O(7)	1.962 (3)	N(2)–C(4)	1.501 (5)
Cr–N(1)	2.086 (3)	N(2)–C(9)	1.495 (5)
Cr–N(2)	2.084 (3)	N(2)–C(13)	1.499 (5)
O(1)–C(3)	1.283 (5)	C(1)–C(2)	1.518 (6)
O(2)–C(3)	1.222 (5)	C(2)–C(3)	1.524 (6)
O(3)–C(6)	1.287 (5)	C(4)–C(5)	1.512 (6)
O(4)–C(6)	1.228 (5)	C(5)–C(6)	1.508 (6)
O(5)–C(8)	1.287 (5)	C(7)–C(8)	1.519 (6)
O(6)–C(8)	1.234 (5)	C(9)–C(10)	1.516 (6)
O(7)–C(10)	1.294 (5)	C(11)–C(12)	1.521 (6)
O(8)–C(10)	1.220 (5)	C(12)–C(13)	1.537 (6)
O(1)–Cr–O(3)	177.0 (1)	Cr–N(2)–C(9)	103.0 (2)
O(1)–Cr–O(5)	90.7 (1)	Cr–N(2)–C(13)	109.6 (2)
O(1)–Cr–O(7)	87.1 (1)	C(4)–N(2)–C(9)	109.6 (3)
O(1)–Cr–N(1)	90.6 (1)	C(4)–N(2)–C(13)	108.8 (3)
O(1)–Cr–N(2)	91.8 (1)	C(9)–N(2)–C(13)	109.9 (3)
O(3)–Cr–O(5)	86.8 (1)	N(1)–C(1)–C(2)	113.9 (3)
O(3)–Cr–O(7)	91.7 (1)	C(1)–C(2)–C(3)	114.0 (3)
O(3)–Cr–N(1)	90.6 (1)	O(1)–C(3)–O(2)	122.8 (4)
O(3)–Cr–N(2)	90.7 (1)	O(1)–C(3)–C(2)	117.7 (3)
O(5)–Cr–O(7)	99.1 (1)	O(2)–C(3)–C(2)	119.5 (3)
O(5)–Cr–N(1)	82.9 (1)	N(2)–C(4)–C(5)	114.7 (3)
O(5)–Cr–N(2)	177.2 (1)	C(4)–C(5)–C(6)	113.6 (3)
O(7)–Cr–N(1)	177.0 (1)	O(3)–C(6)–O(4)	121.4 (4)
O(7)–Cr–N(2)	82.1 (1)	O(3)–C(6)–C(5)	118.3 (4)
N(1)–Cr–N(2)	96.0 (1)	O(4)–C(6)–C(5)	120.3 (4)
Cr–O(1)–C(3)	128.8 (3)	N(1)–C(7)–C(8)	111.9(3)
Cr–O(3)–C(6)	128.8 (3)	O(5)–C(8)–O(6)	124.0 (4)
Cr–O(5)–C(8)	114.3 (3)	O(5)–C(8)–C(7)	116.5 (4)
Cr–O(7)–C(10)	115.1 (3)	O(6)–C(8)–C(7)	119.5 (4)
Cr–N(1)–C(1)	115.4 (2)	N(2)–C(9)–C(10)	111.1 (3)
Cr–N(1)–C(7)	102.9 (2)	O(7)–C(10)–O(8)	123.8 (4)
Cr–N(1)–C(11)	109.9 (2)	O(7)–C(10)–C(9)	115.7 (3)
C(1)–N(1)–C(7)	110.2 (3)	O(8)–C(10)–C(9)	120.5 (4)
C(1)–N(1)–C(11)	108.0 (3)	N(1)–C(11)–C(12)	114.7 (3)
C(7)–N(1)–C(11)	110.3 (3)	C(11)–C(12)–C(13)	119.1 (3)
Cr–N(2)–C(4)	115.7 (2)	N(2)–C(13)–C(12)	114.1 (3)

Description of the Crystal Structure of *trans*(O_6)-K[Cr(1,3-pddda)]·3H_2O. The perspective drawing of *trans*(O_6)-[Cr(1,3-pddda)]$^-$ is shown in Figure 4. The bond lengths and angles are summarized in Table III. The coordination geometry is approximately octahedral. The average Cr–N and Cr–O bond lengths are nearly equal to those found in [Cr(1,3-pdta)]$^-$[8] and [Cr(cydta)]$^-$.[7] The crystal structure analysis confirmed the trans(O_6) structure for the isomer B-IV as predicted by the ^2H NMR and MCD spectra. Therefore, the isomer B-II must take the trans(O_5) structure. The conformations of the chelate rings are found to be the envelope for the acetates and the skew boat for the propionates and 1,3-propanediamine rings.

There is a remarkable difference between the formation behavior of the trans(O_6) isomer of the eddda complex and that of the 1,3-pddda complex; the former has never been observed before, but the latter was obtained in the present study. For these complexes, this difference might arise from strain in the G-ring chelates. The ring strain may be evaluated in terms of the bond angles for the five-membered rings.[20] The sum of the G-ring bond angles in the trans(O_6) 1,3-pddda complex (average 527.75°) is larger than that in the *rac*-cydta complex[7] (average 524.0°), almost

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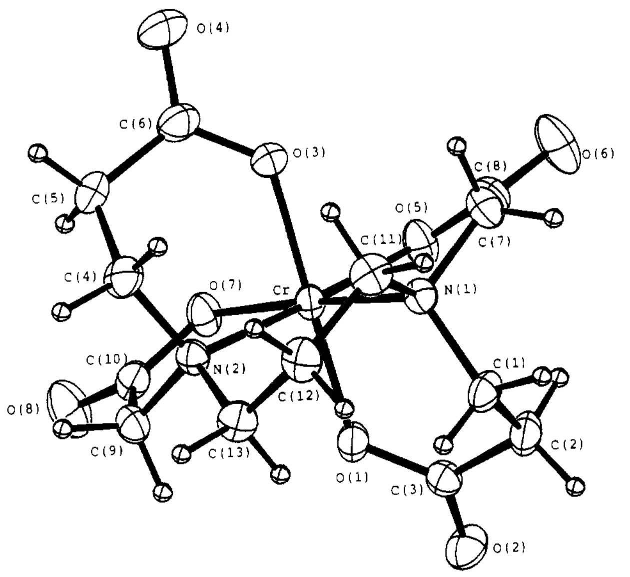

Figure 4. Molecular structure of *trans*(O_6)-[Cr(1,3-pddda)]$^-$ ion as the potassium trihydrate salt. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented as spheres of arbitrary radius.

Table IV. Absorption Data for [Cr(1,3-pddda)]$^-$ in H_2O

complex	band positions^a	
	I	II
trans(O_5) (B-II)	18.50 (126.9)	24.80 (81.0)
trans(O_5O_6) (B-III)	18.90 (118.4)	25.60 (69.8)
trans(O_6) (B-IV)	19.60 (90.6)	26.10 (44.7)

^{a} In units of 10^3 cm^{-1} for the absorption maxima and mol^{-1} dm^3 cm^{-1} for ϵ, the molar absorbance, in parentheses.

equal to that in the 1,3-pdta complex[8] (average 528.35°), and smaller than that in the $(ida)_2$ complex (average 533.82°),[21] suggesting less strained five-membered G-rings in the 1,3-pddda complex. In view of this fact, it is plausible that the trans(O_6) isomer can be formed more easily than the corresponding eddda complex, in which the sum of the G-ring bond angles is predicted to be nearly equal to that of the edta or cydta complex. For these complexes an in-plane ring is easily dissociated to form a less strained pentadentate chelate with an aqua ligand in the sixth position.[9,10,22] A similar situation is found for the tetradentate 1,3-pdda complex. The recent X-ray structure analysis of *trans*(*F*)-Li[CrF_2(1,3-pdda)]·$2H_2O$ shows that the sum of the acetate G-ring bond angles in the complexes (534.97°) is much larger than those found for any other complexes.[11] This observation agrees with the expected stability of this type of isomer, although the chair conformation of the 1,3-propanediamine backbone in the latter 1,3-pdda complex is different from the skew-boat conformation for the 1,3-pddda complexes.

Absorption Spectra. The visible absorption spectra of three isomers of the 1,3-pddda complexes are different from each other; especially the low-energy first band of the trans(O_6) isomer is shifted to higher energy relative to those of the other isomers as shown in Table IV. The position of the first band observed at 19 600 cm^{-1} for the trans(O_6) isomer is close to that for the 1,3-pdta complex,[23] whereas the positions observed at 18 500 cm^{-1} for the trans(O_5) and trans(O_5O_6) isomers resemble those for the trans(O_5) eddda and edta or cydta complexes. These observed positions correspond to either of two predicted components in the $^4T_2 \leftarrow {}^4A_2$ transition of *cis*-$[Cr(O)_4(N)_2]$ type complexes with holohedralized D_{4h} symmetry in terms of the angular overlap model or Yamatera's rule;[24] i.e., the degenerate and nondegenerate components are estimated to be at 18 790 and 19 520 cm^{-1}, respectively, by using the parameter values $\Delta(N) = 21\,000$ cm^{-1} for $[Cr(en)_3]^{3+}$ and $\Delta(O) = 18\,050$ cm^{-1} for $[Cr(ox)_3]^{3-}$. The lower energy degenerate component is due to the $t_{2g} \rightarrow e_g$ ($^4E \leftarrow {}^4B_1$) transition within the "CrN_3O" plane, whereas the higher energy nondegenerate component is due to the $t_{2g} \rightarrow e_g$ ($^4B_2 \leftarrow {}^4B_1$) transition within the "CrN_2O_2" plane. Thus, this spectral behavior seems to result from the relative difference in intensity of the two components between the former and the latter group of complexes. Similar intensity behavior is also observed for *trans*(*F*)-$[CrF_2(N_2O_2)]$ type complexes. For *trans*(*F*)-[CrF_2(1,3-pdda)]$^-$, the intensity of the nondegenerate $^4B_2 \leftarrow {}^4B_1$ transition within the "CrN_2O_2" plane is stronger than that of the degenerate $^4E \leftarrow {}^4B_1$ transition within the "CrF_2NO" plane.[11] In the case of *trans*(*F*)-[CrF_2(mal)(en)]$^-$ with the same chromophore as the 1,3-pdda complex, the opposite intensity behavior is observed; the degenerate transition is more intense than the nondegenerate one.[25] Such an intensity difference may arise from the structural characteristics between the chelate rings in these complexes; i.e., the former group of complexes has a six-membered diamine ring and two five-membered acetate rings, whereas the latter contains a different combination of the chelate ring members in the "CrN_2O_2" plane. In other words, the intensity associated with the nondegenerate transition within the "CrN_2O_2" plane consisting of 5–6–5-ring members may be enhanced more remarkably than the degenerate one within the "$CrNO_3$" or "CrF_2NO" plane, despite the fact that the ligand field transition to the degenerate excited state is usually more intense than that to the nondegenerate one. This kind of anomalous intensity behavior has also been observed for *cis*-$[Cr(N)_4X_2]$ type complexes with *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (cycb).[26] For these complexes, it has been claimed that the intensification of the lower energy nondegenerate component can be ascribed to the pronounced tetrahedral distortion of the "CrN_2X_2" plane as found by the X-ray analyses.[27] In the trans(O_6) 1,3-pddda or 1,3-pdta and 1,3-pdda complexes, however, no significant distortion of the "CrN_2O_2" plane in comparison with the case of the trans(O_5) eddda and cydta complexes has been found by the X-ray analyses.[7,8,11] Therefore, it appears that the 5–6–5-membered chelate ring backbone in the "CrN_2O_2" plane causes more remarkable enhancement of the nondegenerate transition intensity than that of the degenerate one.

Acknowledgment. We wish to express our thanks to Drs. Robert J. Bianchini, Charles A. Green, and Norio Koine of Washington State University for obtaining the ^2H NMR spectra. We also thank Professor Yoichi Shimura of Osaka University for making the MCD spectra available.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and the derived hydrogen positions, and Figure S1, labeling the hydrogen atoms, for *trans*(O_6)-[Cr(1,3-pddda)]·$3H_2O$ (4 pages); a table of structure factors for this compound (2 pages). Ordering information is given on any current masthead page.

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