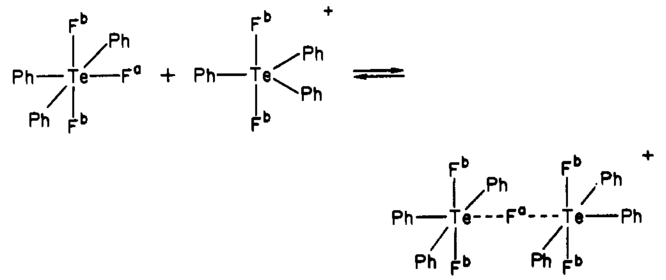
Inorg. Chem. **1986**, *25*, 2129–2134



The stereoselective exchange of F^a ligands is opposed by statistical factors (2 F^b vs. 1 F^a) but must be favored by the significantly longer Te–F^a bond length (1.960 Å) compared to the Te–F^b bond lengths (1.923 and 1.924 Å) in the solid-state structure. In addition, an intermediate with F^a in the bridging position minimizes the steric interactions among the six phenyl substituents.

It was also found that "ion selective" fluorine exchange can be carried out; i.e., fluorine exchange in either the tellurium cation or phosphorus anion can be initiated without affecting intermolecular exchange in the other ion. Exchange in the *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ system does not involve the anion PF_6^- as the ^{19}F signal of PF_6^- remains a sharp doublet throughout the exchange process. When excess PF_5 is added to $Ph_3TeF_2^+PF_6^-$, however, a single line is observed in the phosphorus–fluoride region, due to rapid fluorine exchange in the PF_5–PF_6^- system,[25] but the tellurium species remain unaffected, as confirmed by fluorine NMR.

All intermolecular fluorine exchange in the *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ system is stopped by adding NaF or R_4NCl because any five-coordinate Te(VI) species is converted to a six-coordinate Te(VI) species. This observation was applied to the purification of *mer*-Ph_3TeF_3 and other phenyltellurium(VI) fluorides: washing samples with NaF was sufficient to convert line-broadened NMR spectra to spectra characteristic of "rigid" compounds.

Acknowledgment. The financial assistance of the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The purchase of the AM300 spectrometer was made possible by grants from the NSERC and the Manitoba Health Research Council. We also thank the University of Manitoba Earth Sciences Department for use of the X-ray diffraction facilities and the Computer Services Department for assistance.

Registry No. *mer*-Ph_3TeF_3, 99893-86-4; PF_5, 7647-19-0; $Ph_3TeF_2^+$-PF_6^-, 102109-26-2; $Ph_3TeF_2^+$, 102109-25-1; $[Ph_3TeF_2$–F–$TeF_2Ph_3]^+$, 102109-27-3; PF_6^-, 16919-18-9; $Ph_3Te^+BF_4^-$, 26202-89-1; Ph_3TeF, 34814-96-5; Ph_3TeCl, 31426-14-9; ^{125}Te, 14390-73-9; F_2, 7782-41-4.

Supplementary Material Available: Tables of hydrogen coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles involving phenyl carbons and hydrogens and complete lists of torsion angles (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Program in Biochemistry and Biophysics,
Washington State University, Pullman, Washington 99164-4630, and Department of Chemistry,
Faculty of Science, Nara Women's University, Nara 630, Japan

Synthesis and Characterization of the Three Geometrical Isomers of Difluoro(1,3-propanediamine-*N*,*N*′-diacetato)chromate(III). Crystal Structure of *trans*-Li[CrF_2(1,3-pdda)]·$2H_2O$

Robert J. Bianchini,[1a] Urs Geiser,[1a] Helen Place,[1a] Sumio Kaizaki,[1b] Yasuyo Morita,[1b]
and J. Ivan Legg*[1a]

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The synthesis and isolation of chromium(III) complexes of the linear tetradentate ligand 1,3-propanediamine-*N*,*N*′-diacetate (1,3-pdda) with monodentate (F^-) and bidentate (malonate, oxalate) ligands are reported. The three geometrical isomers (sym-cis, unsym-cis, trans) of $[CrF_2(1,3\text{-pdda})]^-$ and the unsym-cis isomer of the corresponding malonate and oxalate complexes were isolated. Characterization was accomplished with UV/visible spectroscopy, ^2H NMR spectroscopy, and single-crystal X-ray diffraction analysis. The complex *trans*-Li[CrF_2(1,3-pdda)]·$2H_2O$ ($LiCrF_2O_4N_2C_7H_{12}$·$2H_2O$) crystallizes in the space group *Pnma* of the orthorhombic crystal system with a = 12.137 (6) Å, b = 15.450 (6) Å, c = 7.050 (3) Å, $\alpha = \beta = \gamma = 90°$, and Z = 4. A residual of 0.053 was obtained for 1985 independent "observed" reflections collected at ambient temperature with use of a full-matrix least-squares refinement procedure. The complex has distorted-octahedral geometry around the chromium, with two fluorines trans to one another and a F–Cr–F angle of 176.67 (9)°. The Cr–F distances are 1.878 (2) and 1.901 (2) Å. The independent Cr–O and Cr–N distances are 1.992 (2) and 2.060 (2) Å, respectively. The stability of *trans*-$[CrF_2(1,3\text{-pdda})]^-$ was established by ^2H NMR and is attributed in part to the chair conformation of the ligand diamine hydrocarbon "backbone". A new synthetic scheme for incorporating deuterons into polyamino poly(carboxylic acid) ligands is also reported.

Introduction

The study of geometrical isomerism in substitution-inert transition-metal complexes has been an area of intense activity and has provided much of the basic structural information for the study of transition-metal chemistry in general. Most of the classical stereochemical work has been done with more easily made and characterized Co(III) complexes. Investigation of isomerism for Cr(III) complexes has been hampered by the lack of an NMR technique due to the extreme broadening of most nuclei brought about by the paramagnetic Cr(III) center. Recently, deuteron nuclear magnetic resonance (^2H NMR) spectroscopy was shown to be a powerful technique for studying chromium(III) complexes in solution.[2-5] In order to determine whether ^2H NMR could

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(1) (a) Washington State University. (b) Nara Women's University.

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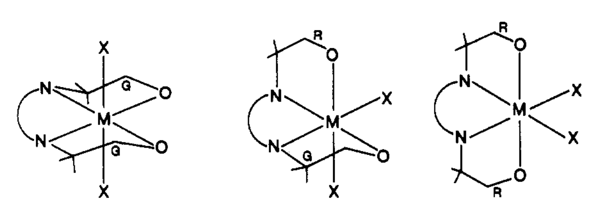

Figure 1. The possible geometric isomers for an $[MX_2(\text{linear tetradentate})]^n$ complex (sym-cis = symmetrical-cis or α-cis, unsym-cis = unsymmetrical-cis or β-cis, R = out-of-plane or "relaxed" ring, G = in-plane or "girdling" ring[9]).

be used to distinguish geometric isomers in solution, a new series of linear tetradentate polyamino polycarboxylate chromium(III) complexes was prepared for which a variety of geometric arrangements are possible as shown in Figure 1.

For chromium(III), only the symmetrical-cis (sym-cis) and unsymmetrical-cis (unsym-cis) configurations have been obtained with linear polyamino poly(carboxylic acid) ligands. To our knowledge, the only trans edda-type[6] transition-metal complexes reported are with platinum(IV)[7] and recently with cobalt(III).[8] The trans isomer is seldom found due to the greater ring strain associated with chelation about the equatorial plane. This strain is evident in the different torsional angles exhibited by the "girdling" (G) in-plane and "relaxed" (R) out-of-plane glycinate rings (Figure 1) as first observed in the crystal structure of $[Co(edta)]^-$.[9] By introducing an additional methylene group into the ligand diamine hydrocarbon backbone, the ring strain should be alleviated somewhat and the trans isomer might be expected to form. A preliminary study indicated the presence of three isomers for $[CrF_2(1,3\text{-pdda})]^-$.[10]

In this study we report the synthesis and isolation of chromium(III) complexes of 1,3-pdda with monodentate (F^-) and bidentate ligands (mal, ox). Characterization of the geometrical isomers is accomplished through a combination of UV/visible spectroscopy, ^2H NMR spectroscopy, and single-crystal X-ray diffraction analysis. A new synthetic scheme for incorporating deuterons into polyamino poly(carboxylic acid) ligands is also described.

Experimental Section

Materials. Reagent grade sodium malonate and oxalic acid were purchased from Sigma Chemical Co., St. Louis, MO. Deuterium oxide was purchased from Aldrich Chemical Co., Milwaukee, WI, and was at least 99.8 atom % ^2H. Other materials were of reagent grade quality and were used without further purification.

Synthesis. 1,3-Propanediamine-*N*,*N'*-diacetonitrile Dihydrochloride (1,3-pddacn·2HCl). *In a well ventilated area*, 29.4 g (0.2 mol) of 1,3-propanediamine dihydrochloride was suspended in 200 mL of diethyl ether in a 600-mL graduated beaker at 2–5 °C. A solution of 26.0 g (0.4 mol) of KCN in 40 mL of water was added dropwise with stirring. After the mixture was stirred for 10 min, 38.0 g (0.4 mol) of formalin (37%) was added dropwise over a 30-min period at 10 °C. The reaction mixture was stirred for 2 h at room temperature, 200 mL of methanol was added, and the solution was kept at 5 °C overnight. The resulting precipitate (KCl) was collected on a glass fritted funnel and washed with methanol until the filtrate was clear. The pale yellow filtrate was transferred to a three-neck 1-L round-bottom flask and was saturated with hydrogen chloride gas for 2 h while the temperture was kept below 10 °C. After an additional 1 h of stirring at room temperature, the precipitate was collected on a glass fritted funnel, washed with methanol and ether, and dried in a vacuum desiccator. An additional crop of the desired material was obtained by further saturating the filtrate with hydrogen chloride gas; yield 40 g (88%).

1,3-Propanediamine-*N*,*N'*-diacetic Acid Dihydrochloride (H_2-1,3-pdda·2HCl). Although the preparation of this ligand has been reported previously,[11] we have found the following synthetic method more useful with respect to ease of ligand synthesis and deuterium incorporation. Freshly prepared 1,3-pddacn·2HCl (9.1 g, 0.04 mol) was added to 50 mL of a stirred solution of 20% potassium hydroxide. An air stream was passed through the reaction mixture while it was heated at 80 °C for 2 h. After the mixture was cooled to room temperature, 50 mL of methanol was added and the solution was stored at 0 °C overnight. The salt that precipitated was collected on a glass fritted funnel and washed with 10-mL portions of methanol until the filtrate was clear. The filtrate was acidified with 6 N HCl, the volume was reduced to half of the original volume, 100 mL of acetone was added, and the solution was stored at 0 °C overnight. The precipitate that formed was collected on a glass fritted funnel, washed with acetone and anhydrous ether, and vacuum-dried overnight. Several additional crops of material were obtained by treating the filtrate in a similar manner. Recrystallization was carried out by dissolving the product in a minimum amount of water, adjusting the pH to 1.0 with 6 N HCl, adding acetone until just cloudy, scraping the beaker with a glass rod, and storing at 0 °C overnight. The product was collected by filtration and washed with acetone and ether; yield 6.2 g (56%).

Deuterated 1,3-Propanediamine-*N*,*N'*-diacetic Acid Dihydrochloride (H_2-1,3-pdda-α-d_4·2HCl). The deuterated ligand was prepared by the same method as described above for H_2-1,3-pdda·2HCl, except potassium deuteroxide (10 g of KOH in 40 g of ^2H_2O) was substituted in the hydrolysis step. Proton NMR indicated that at least 50% deuterium incorporation was achieved.

Synthesis and Separation of the Isomers of Lithium Difluoro(1,3-propanediamine-*N*,*N'*-diacetato)chromate(III), Li[CrF$_2$(1,3-pdda-α-d_n)] (n = 0, 4). In a 400-mL graduated beaker, 1.06 g (0.004 mol) of H_2-1,3-pdda-α-d_n·2HCl (n = 0, 4) was dissolved in 100 mL of water. The pH was adjusted to 8.0 with a solution of potassium carbonate (1.1 g in 10 mL of water). To this solution was added with stirring 2.0 g of crystalline *trans*-$[CrF_2(py)_4]NO_3$.[12] The solution was diluted to 200 mL and placed on a steam bath for 2 h. The solution changed from purple to dark red-violet, while the odor of pyridine became less noticeable as the reaction proceeded. The reaction solution was filtered and then poured onto a 5 cm × 60 cm column of QAE-Sephadex (A-25, Cl^- form). Unreacted starting material was eluted with water, leaving a light violet band bound at the top of the column. The adsorbed band was then eluted in the dark at room temperature with 0.05 M LiCl with a flow rate of ca. 1.0 mL/min. Three bands separated within 8 h, pale violet (B-I), violet (B-II), and orange violet (B-III). The first band eluted much faster than the second and third bands, and a small yellow band remained bound to the top of the column. The eluates from the first band (B-I) were collected and reduced to 10 mL at 25 °C on a rotoevaporator in the dark. The bound third band (B-III) was removed from the top of the column, reintroduced onto a small column of QAE-Sephadex, and quickly eluted with 3 M LiCl in the dark at room temperature. The concentrated eluate was rotary evaporated to 10 mL at 25 °C in the dark. The remaining band, B-II, was eluted off the column with 0.05 M lithium chloride and concentrated in the dark by lyophilization to 20 mL. To each concentrated solution was added 20 mL of acetone, followed by 50 mL of anhydrous ether. A dark violet oil formed at the bottom of each beaker. The ether was decanted, and the extraction process was repeated three more times. Ten milliliters of methanol was then added to each concentrated band, followed by 100 mL of acetone. Refrigeration at 0 °C overnight yielded violet and red-violet powders, which were collected on fine glass fritted funnels, immediately washed with anhydrous ether, and vacuum dried. Recrystallization was carried out by dissolving each isomer in a small amount (ca. 10 mL) of methanol/water (1:1) and then adding acetone until cloudy. The third band (B-III) was isolated as red-violet crystals, whereas the first and second bands (B-I and B-II) were obtained as violet powders. Yields for each isomer were typically 0.10 g (8%) and did not change significantly by varying the reaction time by ±1 h.

Preparation of Lithium *unsym-cis*-(Malonato)(1,3-propanediamine-*N*,*N'*-diacetato)chromate(III), *unsym-cis*-Li[Cr(mal-α-d_n)(1,3-pdda-α-d_n)] (m = 0, 2, n = 0, 4). In a beaker 1.3 g (0.005 mol) of H_2-1,3-

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(6) Abbreviations: mal = malonate; ox = oxalate; edda = ethylenediamine-*N*,*N'*-diacetate or 2,5-diazahexanedionate; 1,3-pdda = 1,3-propanediamine-*N*,*N'*-diacetate or 2,6-diazaheptanedionate; 1,3-pdda-α-d_4 = 2,6-diazaheptanedionate-1,1,7,7-d_4. An alternate nomenclature for 1,3-pdda, tmdda (trimethylenediamine-*N*,*N'*-diacetate), has appeared in the literature.

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Table I. Elemental Analyses

complex[a]	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	C:N calcd	C:N found
H_2-1,3-pdda·2HCl·0.5H_2O	30.8	31.0	6.3	6.2	10.3	10.3	3.5	3.5
trans-Li[CrF_2(1,3-pdda)]·2H_2O	26.1	26.1	5.0	4.9	8.7	9.2	3.5	3.3
trans-Li[CrF_2(1,3-pdda-α-d_4)]·2H_2O	26.0	25.8			8.6	8.3	3.5	3.8
unsym-cis-Li[CrF_2(1,3-pdda)]·H_2O	27.7	27.4	4.6	4.7	9.2	9.0	3.5	3.5
unsym-cis-Li[CrF_2(1,3-pdda-α-d_4)]·6H_2O	21.2	21.5			7.0	6.6	3.5	3.7
unsym-cis-Li[Cr(mal)(1,3-pdda)]·3H_2O	29.7	29.8	5.0	4.6	6.9	6.6	5.0	5.2
unsym-cis-Li[Cr(mal)(1,3-pdda-α-d_4)]·6H_2O	26.1	26.1			6.1	5.7	5.0	5.3
unsym-cis-Li[Cr(ox)(1,3-pdda)]·2H_2O	29.1	29.3	4.3	4.3	7.5	7.5	4.5	4.5
unsym-cis-Li[Cr(ox)(1,3-pdda-α-d_4)]·2H_2O	28.9	29.1			7.5	7.5	4.5	4.5
sym-cis-Li[CrF_2(1,3-pdda)]·2H_2O	26.1	26.4	5.0	5.1	8.7	8.4	3.5	3.6
sym-cis-Li[CrF_2(1,3-pdda-α-d_4)]·2H_2O·14LiCl	9.0	9.1			3.0	2.9	3.5	3.6

[a] Molecular weights of the deuterated complexes were calculated by assuming 50% deuterium incorporation (see Experimental Section).

pdda-α-d_n·2HCl ($n = 0, 4$) was dissolved in 25 mL of water and the pH adjusted to 8.0 with a solution of potassium carbonate (1.1 g in 10 mL of water). This solution was then added dropwise to a stirred solution of 1.2 g (0.004 mol) of $CrCl_3\cdot 6H_2O$ in 25 mL of water. The resulting blue-gray solution (pH 3.9) was heated on a steam bath until it turned deep violet (~2 h). After the mixture was cooled to room temperature, 0.85 g (0.005 mol) of sodium malonate hydrate was added in portions with stirring. The reaction mixture was heated at 45 °C for 4 h, cooled to room temperature, and loaded onto a 5 cm × 45 cm column containing QAE-Sephadex (A-25, Cl^- form). After the column was washed with water, the adsorbed band was eluted with 0.05 M LiCl. Only one violet band was separated with a light blue band of $Cr(mal)_3^{3-}$ remaining bound to the top of the column. The middle portion of the eluted band was collected and concentrated at 25 °C on a rotary evaporator to 10 mL. To this was added 50 mL of acetone followed by 50 mL of anhydrous ether. The acetone/ether layer was decanted from the deep red-violet oil, and the process was repeated. A red-violet powder was obtained by adding 15 mL of methanol, followed by 100 mL of acetone, and then storing at 0 °C overnight. The powder was collected on a fine glass fritted funnel, washed with acetone and ether, and vacuum-dried overnight; yield 0.5 g (31%). Deuteration of the malonate was accomplished by dissolving 0.3 g of the title compound in 5.0 mL of deuterium oxide. Three drops of pyridine was added, and the solution was allowed to stand overnight in a sealed vial at room temperature. The next day acetone was added to the solution until it just turned cloudy, and then it was cooled to 0 °C. The red-violet powder was collected on a fine glass fritted funnel and washed with acetone. Isotopic exchange was confirmed by IR spectroscopy.

Preparation of Lithium *unsym-cis*-(Oxalato)(1,3-propanediamine-*N,N'*-diacetato)chromate(III), *unsym-cis*-Li[Cr(ox)(1,3-pdda-α-d_n)] (n = 0, 4). The procedure used is similar to the synthesis of the corresponding malonato complex described above. A solution of 1.30 g (0.005 mol) of H_2-1,3-pdda-α-d_n·2HCl ($n = 0, 4$) in 25 mL of water was adjusted to pH 8.0 with potassium carbonate. This was added dropwise to a stirred solution of 1.20 g (0.004 mol) of $CrCl_3\cdot 6H_2O$ in 25 mL of water. The mixture was heated on a steam bath for 2 h and then cooled to room temperature. A pH 7 solution of 0.63 g (0.005 mol) of oxalic acid dihydrate in 10 mL of water was then added dropwise with stirring, and the reaction mixture was heated for an additional 2 h at 45 °C. The deep violet solution was cooled, filtered, and introduced onto a 5 cm × 45 cm column of QAE-Sephadex (A-25, Cl^- form). The column was washed with water, and the bound band was eluted with 0.05 M LiCl. Only one band was eluted, which was reloaded onto a smaller column containing QAE-Sephadex and eluted with 3 M LiCl. The middle portion of the eluted band was then added to a large quantity of acetone (~300 mL), whereupon a deep red-violet oil formed. A red-violet powder was obtained by decanting the acetone, adding 30 mL of methanol, followed by adding just enough acetone until cloudiness persisted, and cooling. The powder was collected on a fine glass fritted funnel, washed with acetone and ether, and then vacuum-dried. Recrystallization was carried out from water, methanol, and acetone (1:1:2); yield 0.3 g (19%).

Physical Measurements. Analysis. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, or the C, H & N Analytical Facility, Department of Chemistry, University of Idaho, Moscow, ID. The results, along with the C:N ratios, are reported in Table I. The C:N ratios are reported since accurate hydrogen analysis cannot be obtained for deuterated complexes.

UV/Visible Spectra. UV/visible spectra were recorded on a Varian/Cary 219 spectrophotometer and are given in Table II and Figure 2.

Table II. Electronic Spectral Data

complex[b]	band position[a] I	band position[a] II
trans-[CrF_2(1,3-pdda)]$^-$ [c]	571 (sh), 493 (73)	375 (19)
unsym-cis-[CrF_2(1,3-pdda)]$^-$	537 (81)	392 (65)
sym-cis-[CrF_2(1,3-pdda)]$^-$	533 (74)	387 (49)
unsym-cis-[Cr(mal)(1,3-pdda)]$^-$	518 (87)	389 (64)
unsym-cis-[Cr(ox)(1,3-pdda)]$^-$	519 (110)	391 (93)

[a] In nm with ε (in parentheses) in M^{-1} cm^{-1}; sh = shoulder. [b] Data obtained in H_2O. Spectra were not pH-dependent. [c] The solid-state spectrum showed absorbance maxima at 579 (sh), 495, and 364 nm.

Table III. Deuteron NMR Spectral Data

complex	δ (ω)[a]	rel integration
trans-[CrF_2(1,3-pdda-α-d_4)]$^-$ [b]	−14 (120), −50 (185)	1:1
unsym-cis-[CrF_2(1,3-pdda-α-d_4)]$^-$ [b]	−8 (300), −30 (215), −41 (300), −65 (310)	1:1:1:1
unsym-cis-[Cr(mal)(1,3-pdda-α-d_4)]$^-$ [c]	−12 (185), −34 (185), −52 (280), −84 (500)	1:1:1:1
unsym-cis-[Cr(mal-d_2)(1,3-pdda)]$^-$ [c]	+56 (300), −1 (60)	1:1
unsym-cis-[Cr(ox)(1,3-pdda-α-d_4)]$^-$ [b]	−15 (250), −30 (215), −69 (400), −87 (590)	1:1:1:1
sym-cis-[CrF_2(1,3-pdda-α-d_4)]$^-$ [b]	−13 (430), −35 (530)	1:1

[a] Legend: δ = chemical shift with respect to C^2HCl_3 at +7.26 ppm (downfield shifts given positive values); ω = width at half-height in Hz. [b] Data obtained in H_2O. [c] Data obtained in 1 mM $HClO_4$.

Table IV. Angular Overlap Model Predictions for the First Absorption Band of [CrF_2(1,3-pdda)]$^-$ Complexes[a]

isomer	positions predicted[b]	positions obsd
trans-[CrF_2(1,3-pdda)]$^-$	19.50	20.31
	17.76	17.50 (sh)
	17.76	
sym-cis-[CrF_2(1,3-pdda)]$^-$	18.50	18.69
	18.28	
	18.28	
unsym-cis-[CrF_2(1,3-pdda)]$^-$	19.01	18.64
	18.28	
	17.76	

[a] In units of 10^3 cm^{-1}. [b] Calculations were carried out by using the following parameters: $\Delta(O) = 18.05 \times 10^3$ cm^{-1}, $\Delta(N) = 21.00 \times 10^3$ cm^{-1}, $\Delta(F) = 16.00 \times 10^3$ cm^{-1}.

NMR Spectra. The 30.7-MHz ^2H NMR spectra were recorded at 18 °C on a Nicolet NT-200WB spectrometer operating at a field of 4.7 T. Five milliliters of 30–100 mM solutions in 12-mm tubes were used in data collection. Spectra were obtained by employing a sweep width of 12000 Hz (8K data block) and a quadrature detection system. An acquisition time of 0.338 s, a pulse repetition rate of 0.438 s, and a flip angle of 30° were used. Scanning time was 0.5–12 h depending on sample concentration. For most samples the free induction decay (FID) was multiplied by a line broadening factor of 5 Hz before transformation to improve the signal to noise ratio. All signals were observed to fall in the ±100 ppm region with respect to an external standard of C^2HCl_3 (7.26 ppm). The upfield shifts are defined as negative values. Proton NMR spectra were

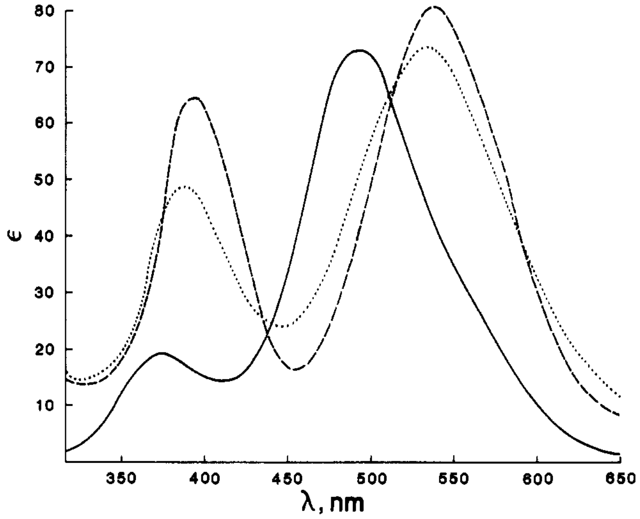

Figure 2. UV/visible spectra of the three isomers of $[CrF_2(1,3\text{-pdda})]^-$ (ϵ in units of M^{-1} cm^{-1}): (---) unsym-cis (B-I); (···) sym-cis (B-II) ; (—) trans (B-III).

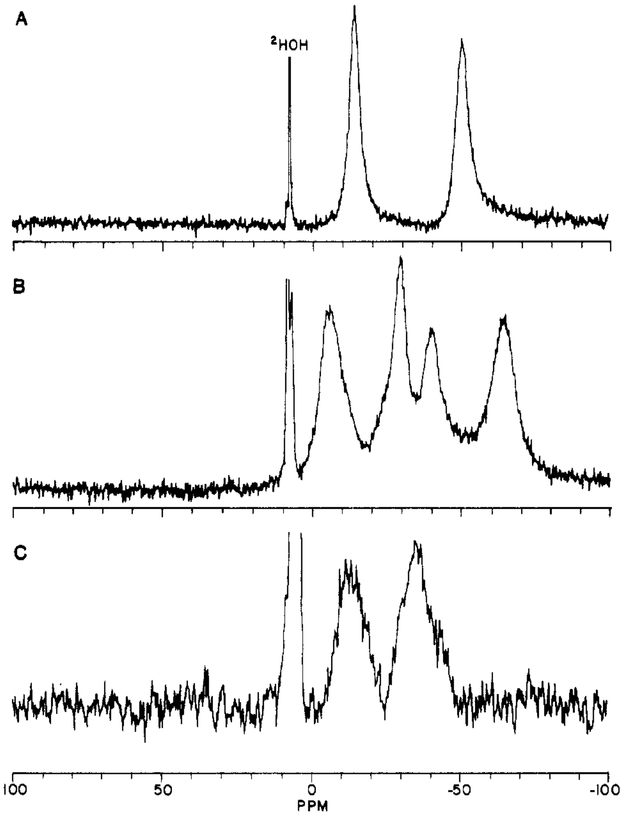

Figure 3. Deuteron NMR spectra of the three isomers of $[CrF_2(1,3\text{-pdda-}\alpha\text{-}d_4)]^-$: (A) trans (B-III); (B) unsym-cis (B-I); (C) sym-cis (B-II).

Table V. Positional and Equivalent Isotropic Thermal Parameters of Lithium *trans*-Difluoro(1,3-propanediamine-*N*,*N′*-diacetato)chromate(III) Dihydrate

atom	x/a	y/b	z/c	$1000U_{eq}$, Å^2
Cr	0.36139 (4)	0.2500	0.14663 (7)	22.3 (3)
Li	0.1518 (4)	0.2500	0.4978 (8)	30 (3)
F(1)	0.5045 (2)	0.2500	0.0454 (3)	39 (1)
F(2)	0.2202 (2)	0.2500	0.2634 (3)	36 (1)
N	0.4040 (2)	0.3484 (1)	0.3297 (3)	33 (1)
O(1)	0.3159 (1)	0.3483 (1)	−0.0188 (2)	31.3 (8)
O(2)	0.3214 (2)	0.4915 (1)	−0.0492 (3)	55 (1)
O(3)	0.2093 (2)	0.1481 (1)	0.6263 (3)	44 (1)
C(1)	0.3443 (2)	0.4246 (1)	0.0371 (3)	33 (1)
C(2)	0.4126 (2)	0.4294 (2)	0.2176 (4)	41 (1)
C(3)	0.5004 (2)	0.3335 (2)	0.4572 (4)	45 (2)
C(4)	0.4916 (4)	0.2500	0.5688 (6)	53 (2)
H(N)	0.338 (4)	0.352 (3)	0.416 (7)	63
H(1,C2)	0.381 (4)	0.481 (3)	0.290 (7)	63
H(2,C2)	0.496 (4)	0.438 (3)	0.185 (6)	63
H(1,C3)	0.571 (4)	0.330 (3)	0.360 (6)	63
H(2,C3)	0.505 (3)	0.381 (3)	0.547 (6)	63
H(1,C4)	0.546 (5)	0.2500	0.657 (9)	63
H(2,C4)	0.423 (6)	0.2500	0.649 (9)	63
H(1,O3)	0.194 (4)	0.108 (3)	0.573 (7)	63
H(2,O3)	0.233 (4)	0.147 (3)	0.735 (8)	63

Table VI. Interatomic Bond Distances (Å) and Angles (deg) in Lithium *trans*-Difluoro(1,3-propanediamine-*N*,*N′*-diacetato)chromate(III) Dihydrate[a]

Cr–F(1)	1.878 (2)	N–C(3)	1.493 (3)
Cr–F(2)	1.901 (2)	C(3)–C(4)	1.514 (4)
Cr–O(1)	1.992 (2)	Li–F(1^{i})	1.813 (6)
Cr–N	2.060 (2)	Li–F(2)	1.849 (6)
O(1)–C(1)	1.291 (3)	Li–O(3)	1.946 (4)
C(1)–O(2)	1.231 (3)	Cr–H(1,C2)	3.71 (5)
C(1)–C(2)	1.521 (4)	Cr–H(2,C2)	3.34 (4)
C(2)–N	1.484 (3)		

F(1)–Cr–F(2)	176.7 (1)	C(2)–N–C(3)	113.3 (2)
F(1)–Cr–O(1)	91.97 (7)	C(3)–N–Cr	117.4 (2)
F(2)–Cr–O(1)	90.19 (7)	N–C(3)–C(4)	112.9 (3)
O(1)–Cr–N	82.77 (8)	C(3)–C(4)–C(3^{ii})	116.7 (4)
F(1)–Cr–N	90.31 (8)	F(1^{i})–Li–F(2)	107.0 (3)
F(2)–Cr–N	87.44 (8)	F(1^{i})–Li–O(3)	115.6 (2)
O(1)–Cr–O(1^{ii})	99.28 (9)	F(2)–Li–O(3)	104.8 (2)
O(1)–Cr–N^{ii}	176.88 (8)	O(3)–Li–O(3^{ii})	108.0 (3)
N–Cr–N^{ii}	95.09 (11)	Li^{iii}–F(1)–Cr	167.3 (2)
Cr–O(1)–C(1)	116.3 (1)	Li–F(2)–Cr	142.3 (2)
O(1)–C(1)–O(2)	123.8 (2)	H(1,C2)–C(2)–H(2,C2)	112 (3)
O(2)–C(1)–C(2)	119.7 (2)	H(1,C2)–C(2)–N	111 (3)
O(1)–C(1)–C(2)	116.5 (2)	H(1,C2)–C(2)–C(1)	105 (2)
C(1)–C(2)–N	111.5 (2)	H(2,C2)–C(2)–N	107 (2)
C(2)–N–Cr	107.9 (1)	H(2,C2)–C(2)–C(1)	110 (2)

[a] Symmetry operations: (i) $-{}^1/_2 + x$, ${}^1/_2 - y$, ${}^1/_2 - z$; (ii) x, ${}^1/_2 - y$, z; (iii) ${}^1/_2 + x$, ${}^1/_2 - y$, ${}^1/_2 - z$.

recorded on a JEOL MH-100 spectrometer. The data are summarized in Table III and Figure 3.

Crystal Structure Determination. Crystals of complex B-III suitable for X-ray analysis were grown from a 0.1 M LiOAc solution by slow evaporation at room temperature in the dark. A red-violet crystal of size 0.2 × 0.5 × 0.3 mm with limiting faces {210} and {201} was selected. Data were collected on an automated Picker four-circle diffractometer equipped with a Zr-filtered Mo Kα X-ray source (λ = 0.7107 Å). Twelve high-angle reflections were accurately centered, and the lattice parameters (a = 12.137 (6) Å, b = 15.450 (6) Å, c = 7.050 (3) Å, $\alpha = \beta = \gamma$ = 90°) as well as the crystal orientation were optimized by a least-squares procedure. One octant (h, k, and l all positive) of data with $2\theta < 63°$ was collected at ambient temperature with use of θ–2θ scans (bisecting mode) yielding 2536 reflections (2274 unique). Of these, 1985 were deemed observed ($F > 2\sigma(F)$) and used in the analysis. Absorption corrections were made based on crystal size and shape (μ = 8.9 cm^{-1}, transmission factors 0.79–0.84). Lorentz and polarization corrections were then applied. The space group *Pnma* was determined from systematic absences and intensity distribution and confirmed by the successful refinement.

The structure was solved by direct methods yielding one Cr, two F, one O, one N, and two C atoms. The remaining non-hydrogen atoms were found on a ΔF map. Positional, isotropic, and, at a later stage, anisotropic thermal parameters were refined to R = 8%. All hydrogen atoms could be located on a ΔF map. They were included and their positional parameters refined on the last two cycles. A full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - F_c|)^2$ was used. Final agreement factors[13] were R = 0.061 and R_w = 0.057. Scattering factors for Cr (corrected for the real part of anomalous scattering), F, O, N, and C were taken from ref 14 and for H from ref 15. There was no evidence

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(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_c^{\,2}]^{1/2}$.

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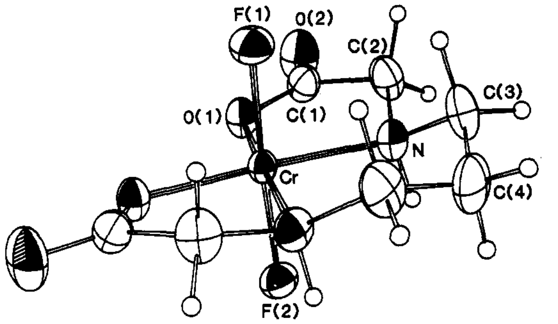

Figure 4. ORTEP drawing and labeling scheme for *trans*-$Li[CrF_2(1,3\text{-pdda})]\cdot 2H_2O$. All atoms, except hydrogen, are drawn at the 50% probability level.

for extinction; thus, no corrections were made. The local computer program library has been summarized elsewhere,[16] except for the new direct-methods program MITHRIL.[17] Atomic positions are given in Table V, and bond distances and angles are found in Table VI. A view of the *trans*-$[CrF_2(1,3\text{-pdda})]^-$ ion is shown in Figure 4. Anisotropic thermal parameters and structure factors are available as supplementary material.

Results and Discussion

Methods of Deuteration. Deuteration of malonate was accomplished by performing the isotopic substitution directly on chromium in basic solution as previously reported.[2] Isotopic exchange was confirmed by comparing the infrared spectra of the deuterated and undeuterated complexes. This method has also been used to deuterate malonate on cobalt(III) complexes.[23] Unfortunately, many chromium complexes are hydrolytically unstable in basic solution and tend to olate or decompose. Indeed, in the ^2H NMR spectra of the malonato complexes it was observed that some $[Cr(mal\text{-}\alpha\text{-}d_2)_3]^{3-}$ ($\delta = 29$)[2] had formed when deuteration was performed on the complex.

The ligand H_2-1,3-pdda was deuterated by incorporating the isotopic label directly into the ligand synthetic scheme. This proved useful for making large quantities of H_2-1,3-pdda-α-d_4. The method involves synthesis of the acetonitrile intermediate (1,3-pddacn) via the cyanomethylation reaction, followed by hydrolysis under basic conditions in the presence of ^2H_2O. A similar procedure has been used successfully by Kawato et al. to make H_2edda.[24] Isotopic exchange was confirmed by observing the decrease of the acetate proton resonance ($\delta = 4.1$ from Me_4Si) in the ^1H NMR spectrum.

Stereochemistry. Three geometric isomers are theoretically possible for an $[MX_2(\text{linear tetradentate})]^n$ type complex (Figure 1). For all previously reported chromium(III) and cobalt(III) complexes, where the linear tetradentate group is a polyamino polycarboxylate group and X is a monodentate ligand, a maximum of only two well-characterized isomers has been obtained.[18-21] In the present study, when *trans*-$[CrF_2(py)_4]NO_3$ was reacted with 1,3-pdda in aqueous solution, three distinct bands with −1 charge were separated from the reaction mixture by chromatography on anion-exchange Sephadex. Each isolated band gave an elemental analysis consistent with the formulated structure $Li[CrF_2(1,3\text{-pdda})]\cdot xH_2O$ (Table I). When X_2 is a bidentate ligand, only two isomers are theoretically possible since the trans isomer (Figure 1) is not expected to form for the chelated ligand. When the bidentate ligands oxalate and malonate were employed in conjunction with 1,3-pdda to complete the coordination sphere around the chromium(III), only one isomer predominated. This behavior is similar to the results obtained by Gailey et al. with cobalt(III).[22] The physical and structural characterization of these new complexes is described below.

UV/Visible Spectra. The spectral data are reported in Table II and Figure 2. The angular overlap model (AOM)[25] was used to calculate the expected first absorption band positions for the three isomers of $[CrF_2(1,3\text{-pdda})]^-$. The results are summarized in Table IV. It can be seen that the AOM predicts a large splitting of the low-energy band when there is a trans arrangement of fluorides. Since complex B-III exhibits this behavior (Figure 2), this suggested that it was the trans isomer. Splitting of the first absorption band has also been observed in the ligand field analogue *trans*-$[CrF_2(en)(mal)]$.[26] The band maxima for the unsym-cis and sym-cis configurations are too close for assignment of each by the AOM method. The remaining complexes, $[Cr(mal)(1,3\text{-pdda})]^-$ and $[Cr(ox)(1,3\text{-pdda})]^-$, show absorbance maxima (Table II) in the region expected for a *cis*-$[Cr(N_2O_4)]$ complex.[18]

Deuteron Nuclear Magnetic Resonance Spectra. The use of ^2H NMR as a stereochemical probe of paramagnetic chromium(III) complexes has recently been demonstrated in this laboratory.[2-5] The initial study showed that chemically distinct geminal deuterons could be resolved.[2] This has been further documented in studies with edta and edta-like complexes.[4,5] These studies also demonstrated that, due to the small homonuclear coupling constant, each chemically distinct deuteron, or set of deuterons, gives rise to one resonance, and a zero-order spectrum is observed, as expected.[27,28]

The geminal acetate deuterons in the three isomers of $[CrF_2(1,3\text{-pdda-}\alpha\text{-}d_4)]^-$ are expected to give rise to two, four, and two signals in the ^2H NMR spectrum, respectively, for the trans (C_s, vide infra), unsym-cis (C_1), and sym-cis (C_2) isomers (Figure 1). Figure 3 shows the spectra for the three isomers of $[CrF_2(1,3\text{-pdda-}\alpha\text{-}d_4)]^-$. It is evident from figure 3B and Table III that band B-I is unequivocally the unsym-cis isomer since it gives rise to four peaks having equal integration values. The spectrum of B-I also compares well with the four peaks obtained for the *unsym-cis*-$[Cr(mal)(1,3\text{-pdda-}\alpha\text{-}d_4)]^-$ and *unsym-cis*-$[Cr(ox)(1,3\text{-pdda-}\alpha\text{-}d_4)]^-$ complexes (Table III). In addition, the unsym-cis configuration for the malonato complex was confirmed by deuteration of the coordinated malonate on the complex as previously described.[2] Two peaks of equal integration were obtained (Table III), independently confirming the unsymmetrical environment.

The spectra of bands III and II are shown in parts A and C, respectively, of Figure 3. Two peaks of equal integration were obtained for both complexes, as expected. The poor signal to noise ratio of the B-II spectrum was due to the low isomer concentration. We had hoped to distinguish between the sym-cis and trans isomers by comparing their ^2H NMR spectra with complexes for which the trans isomer is precluded by the presence of a bidentate ligand (mal, ox) in the remaining two positions. Unfortunately, no sym-cis isomer was obtained for these complexes, and comparison of NMR data with those of *sym-cis*-$[Cr(edda)X_2, \text{bidentate})]^n$ complexes[2,29] did not lead to any obvious conclusions.

When isomer B-II was allowed to stand for 24 h at room temperature in aqueous solution, the intensity of the ^2H NMR peaks diminished and several new peaks, which corresponded to the positions of the unsym-cis isomer and a neutral decomposition product, were observed. Bands B-I and B-III were shown to be stable at room temperature for several days by ^2H NMR, and both bands withstood mild heating at ca. 45 °C for several hours under basic conditions (pH 9.5) before decomposing. Solutions

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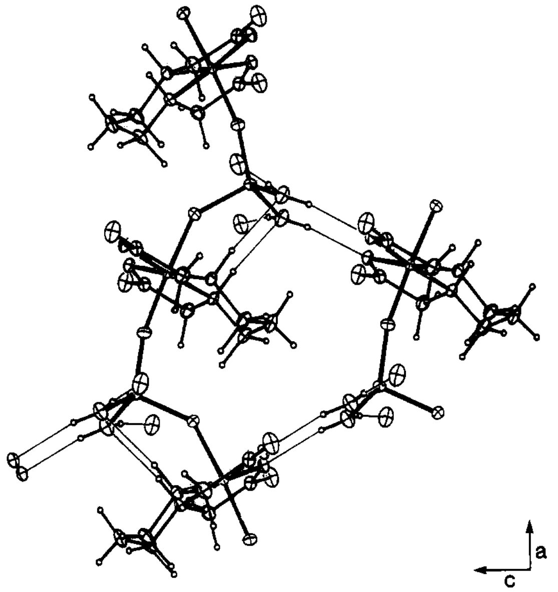

Figure 5. Packing diagram for the complex *trans*-Li[CrF$_2$(1,3-pdda)]·2H$_2$O.

of all three isomers were shown to be photolytically unstable, and upon standing in the light at room temperature, red-violet insoluble crystals eventually formed. These are most likely the neutral fluoro/aqua species since chromium fluoride complexes are known to be photoactivated.[30]

Description of the Crystal Structure of *trans*-Li[CrF$_2$(1,3-pdda)]·2H$_2$O. The crystal structure confirmed the trans structure for isomer B-III as predicted by the AOM analysis. Therefore, isomer B-II must be the sym-cis isomer. The six ligated atoms describe a distorted-octahedral geometry around the chromium in *trans*-[CrF$_2$(1,3-pdda)]$^-$ (Figure 4). A mirror plane, described by the chromium, two fluorines, and the central carbon (C(4)) of the bridging diamine backbone, dissects the complex. The trans fluorides are not linear with respect to the chromium but are bent toward the diamine backbone to give a F–Cr–F angle of 176.7° (Table VI). The six-membered ring is in the chair conformation, and the five-membered rings are significantly nonplanar (largest deviation from least-squares plane 0.152 (2) Å). The chromium to acetate hydrogen distances were initially calculated by assuming tetrahedral geometry around the acetate carbons. The refined chromium to acetate distances are included in Table VI because this information is pertinent to future consideration of the effect of the paramagnetic Cr(III) on deuteron line widths and chemical shifts.

The crystal packing consists of the complex units linked by lithium counterions (Figure 5). Each lithium is coordinated in a distorted-tetrahedral geometry to two fluorines from different complex units within the *ac* plane and to two water molecules, thus forming lithium-bridged F–Cr chains along the *a* direction (Figure 5). The Li$^+$ ion is apparently of optimum size for the stabilization of a strongly interacting three-dimensional network. This network may account (in part) for the distortion of the F–Cr–F bond angle from 180°. Counterions such as Na$^+$, K$^+$, and Ba^{2+} did not yield a crystalline complex. The Li$^+$ ion has been used successfully to produce other crystalline Cr(III) salts.[31] Hydrogen bonds from H(2,O3) to O(1) and from H(1,O3) to O(2), connect the chains along the *c* and *b* directions, respectively. Additional hydrogen bonds are found between H(N) and O(3), thus reinforcing the chair conformation of the six-membered chelate ring.

Summary. The three geometric isomers of [CrF$_2$(1,3-pdda)]$^-$ have been synthesized and separated by chromatography. Electronic absorption spectroscopy was used to tentatively assign complex B-III as the trans isomer but could not distinguish between the sym-cis and unsym-cis configurations. Deuteron NMR spectroscopy was used to conclusively assign isomer B-I as the unsym-cis isomer. Single-crystal X-ray diffraction analysis confirmed the trans structure for complex B-III. Thus, isomer B-II must be the sym-cis isomer. The deuteron NMR spectra of B-II and B-III are consistent with these assignments. It had been anticipated that if a bidentate ligand (mal, ox) was employed in place of the fluorides, isomers B-II and B-III could be distinguished by ^{2}H NMR since isomer B-III is precluded for a bidentate ligand. However, only the unsym-cis isomer (B-I for the difluoride complex) was found for [Cr(mal)(1,3-pdda)]$^-$ and [Cr(ox)(1,3-pdda)]$^-$, necessitating the crystal structure determination to complete the assignments.

The larger 1,3-pdda ligand was selected for this study to enhance the probability of forming the trans isomer and, consequently, the likelihood of obtaining all three isomers expected for a linear diamine dicarboxylate ligand. The trans isomer is rarely obtained for the smaller edda analogue due to the appreciable strain imposed on the chelate in this configuration. Not only was a stable trans isomer obtained with the 1,3-pdda ligand but also the sym-cis isomer (the predominant isomer for most edda complexes) was only obtained in small quantities and proved to be unstable. These results are consistent with the relative stabilities predicted for six-membered diamine chelates.[32] Molecular models show that the diamine chelate ring can adopt the more stable chair conformation in the trans and unsym-cis isomers but must adopt the less stable skew-boat conformation in the sym-cis isomer.

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Supplementary Material Available: A listing of positional and anisotropic thermal parameters for *trans*-Li[CrF$_2$(1,3-pdda)]·2H$_2$O (1 page). Ordering information is given on any current masthead page.

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