as well when going from basic to acidic compositions as within the acidic range itself.

(2) In acidic melts, the Np(IV)-Np(III) and U(IV)-U(III) systems exhibit similar behavior with respect to complexation and electron-transfer properties. This is in line with the fact that their ionic radii are very close to each other.

(3) The linearization method of Nugent has been applied to the actinides IV-III potentials measured in acidic melts. The comparison of our results with data in other solvents shows that the +4 oxidation state of actinides is less solvated in the melt than in other room-temperature solvents with respect to the +3 state.

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Registry No. Cs_2NpCl_6, 17030-04-5; $NpCl_6^{2-}$, 20577-81-5; $Cs_2NaNpCl_6$, 35796-99-7; $NpCl_6^{3-}$, 58343-97-8; $AlCl_3$, 7446-70-0; BuPyCl, 1124-64-7; Np, 7439-99-8; C, 7440-44-0; 1-methyl-3-ethylimidazolium chloride, 65039-09-0.

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Fluoro-Containing Complexes of Chromium(III). 13. Preparation and Characterization of Some Ethylenediamine 1,3-Propanediamine Complexes[1]

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The reaction of *trans*-difluorodiaqua(ethylenediamine)chromium(III) chloride, $[Cr(en)F_2(OH_2)_2]Cl$, with 1,3-propanediamine, tn, in refluxing absolute alcohol has been utilized to prepare *trans*-$[Cr(en)(tn)F_2]Cl$. Upon reaction with concentrated perchloric acid *trans*-$[Cr(en)(tn)F_2]Cl$ yields *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2{\cdot}H_2O$. The *trans*-fluoroaqua complex upon reaction with NH_4X ($X = F^-, Cl^-, SCN^-$) in methyl alcohol yields *trans*-$[Cr(en)(tn)FX]^+$. Dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}H_2O$ over magnesium perchlorate at room temperature produces *trans*-$[Cr(en)(tn)FCl]Cl$; however, there is no evidence for the formation of *trans*-$[Cr(en)(tn)FBr]Br$ when the corresponding bromide salt is dehydrated under the same conditions. Heating of *trans*-$[Cr(en)(tn)FCl]Cl$ or *trans*-$[Cr(en)(tn)F(OH_2)]Br_2{\cdot}0.5H_2O$ at elevated temperatures apparently produces a mixture of products, one of which is tentatively identified as *cis*-$[Cr(en)(tn)FX]X$ (X = Cl, Br). Reaction of this mixture of products with NH_4F or NH_4SCN in methyl alcohol produces *cis*-$[Cr(en)(tn)F_2]^+$ or *cis*-$[Cr(en)(tn)FNCS]^+$. The geometry of *cis*-$[Cr(en)(tn)F_2]^+$ was confirmed by the isolation of $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$. By the use of optical rotatory dispersion studies $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$ was assigned the Δ absolute configuration.

Introduction

In 1973 Vaughn and Marzowski[3] reported the first successful preparation of mixed-ligand complexes of the type $[Cr(pn)(aa)F_2]^+$, where pn = 1,2-propanediamine and aa = ethylenediamine (en), 1,3-propanediamine (tn), *trans*-1,2-diaminocyclohexane (dach). Trans isomers were easily isolated when aa = en or tn, but only the cis isomer was formed when aa = dach. Upon acid hydrolysis with concentrated perchloric acid the *trans*-difluoro complexes produced the corresponding *trans*-fluoroaqua cations as insoluble perchlorates. Later Seiler[4] reported the preparation and characterization of *trans*-$[Cr(pn)(en)FCl]ClO_4$ as well as compounds identified as *cis*-$[Cr(pn)(en)FX]X$ and *cis*-$[Cr(pn)(tn)FX]X$, ($X = Br^-, Cl^-$).

The primary objectives of the present investigation were to prepare and characterize mixed-ligand complexes of the general type $[Cr(en)(tn)FX]^{n+}$ ($X = Br^-, Cl^-, F^-, NCS^-, H_2O$) and to determine what the effect of two chelate rings of different sizes would have on the preparative chemistry. In addition, it was desirable to investigate the synthetic utility of some of the cis isomers to prepare presently unknown mixed-ligand complexes that could be useful in kinetic, photochemical, and absolute configuration studies.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive, and care should be exercised when handling these materials. The explosive nature of both transition-metal perchlorates and of perchloric acid solutions of transition-metal complexes has been well documented.[5]

Ethylenediamine (en) was dried by distillation from solid potassium hydroxide pellets, and the fraction that boiled from 116 to 118 °C was collected. 1,3-Propanediamine (tn) was dried in the same fashion, and the fraction that boiled from 138 to 140 °C was collected. Methyl alcohol was dried with use of molecular sieves (4A, 4-8 mesh, Eastman Kodak) that had been previously dried.

Preparation of Starting Materials. (±)-*cis*-$[Cr(en)_2F_2][Cr(en)F_4]{\cdot}H_2O$ was prepared as previously described.[6] *trans*-$[Cr(en)F_2(OH_2)_2]Br$ was prepared and converted to the chloride salt by the literature method.[7] Both the elemental analyses and electronic spectral data for the chloride salt were in agreement with the values quoted in the literature.

Preparation of *trans*-$[Cr(en)(tn)F_2]Cl$. A 5.0-g (23-mmol) sample of *trans*-$[Cr(en)F_2(OH_2)_2]Cl$ was suspended in 250 mL of absolute alcohol contained in a 500-mL flask fitted with a reflux condenser. The rapidly stirred solution was heated to reflux before 4.0 mL (47 mmol) of previously dried tn was added. After 6 h at the reflux temperature the hot reaction mixture was filtered. The crude product was collected, washed with cold absolute alcohol followed by acetone, and finally air-dried; yield 4.1 g (69%). The electronic spectrum of the crude material in 0.1 M perchloric acid exhibited the multibanded pattern expected for tetragonally distorted complexes of Cr(III). Although the *trans*-$[Cr(en)(tn)F_2]Cl$ obtained at this point is not pure, the product is suitable for further synthetic work. This reaction can be scaled up as high as 60.0 g of *trans*-$[Cr(en)F_2(OH_2)_2]Cl$ with good results.

The filtrate from the above reaction was stored at 8 °C overnight. A second fraction (0.54 g) was collected, washed, and dried as described previously. In 0.1 M perchloric acid the electronic spectrum of the second fraction was characterized by λ_{max} 525 nm, λ_{min} 432 nm, and λ_{max} 382 nm.

Preparation of *trans*-$[Cr(en)(tn)F_2]I{\cdot}H_2O$. This complex was isolated from a 0.5-g (1.9-mmol) sample of crude *trans*-$[Cr(en)(tn)F_2]Cl$ by the

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(1) Part 12: Vaughn, J. W. *Inorg. Chem.* **1983**, *22*, 844.

(2) Taken in part from a dissertation submitted by J.S.F. to the Graduate School of Northern Illinois University in partial fulfillment for the Ph.D. degree, Dec 1983.

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Table I. Electronic Spectral Data[a] for Complexes of the Type $[Cr(en)(tn)FX]^{n+}$

complex	$\lambda_{max}{}^{b}$ (ϵ^{c})	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)	
trans-$[Cr(en)(tn)F_2]I$	525[d] (17.1)		468 (25.6)	415 (15.9)	395[d] (16.0)	353 (22.9)
trans-$[Cr(en)(tn)F_2]ClO_4$	520[d] (17.0)		468 (25.0)	410 (14.9)	390[d] (15.8)	354 (22.4)
trans-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$	522 (22.9)	500 (21.9)	458 (29.5)	416 (21.0)	368 (42.8)	
trans-$[Cr(en)(tn)F(OH_2)]I_2$	519 (22.8)	500 (22.3)	458 (29.7)	418 (21.5)	369 (43.5)	
trans-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$[e]	520 (22.4)	500 (21.8)	455 (28.3)	418 (20.9)	368 (41.5)	
trans-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$[f]	522 (22.4)	500 (22.0)	458 (28.5)	418 (19.6)	368 (41.5)	
trans-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$	522 (22.1)	500 (21.3)	455 (28.3)	418 (20.3)	368 (41.7)	
trans-$[Cr(en)(tn)F(OH_2)](SCN)_2$	520 (23.1)	498 (22.7)	452 (29.5)	414 (21.4)	365 (42.8)	
trans-$[Cr(en)(tn)FNCS]SCN$	500 (95.9)		460 (35.1) (sh)	418 (27.2)	360 (36.6)	
trans-$[Cr(en)(tn)FCl]ClO_4$	555 (20.1)	508 (13.6)	458 (26.6)	422 (20.6)	382 (38.6)	
trans-$[Cr(en)(tn)FCl]Cl\cdot 0.5H_2O$	554 (20.8)	508 (14.4)	459 (25.5)	422 (20.9)	382 (37.5)	
trans-$[Cr(en)(tn)FCl]Cl\cdot 0.5H_2O$[g]	554 (20.8)	508 (14.4)	459 (25.5)	422 (20.9)	382 (37.5)	
trans-$[Cr(en)(tn)FBr]Br$	558 (24.0)	508 (18.5)	464[h] (27.2)	428 (23.0)	388 (37.8)	
$[Cr(en)(tn)FBr]Br$[i]	518 (52.0)	442 (20.9)	388 (36.2)			
$[Cr(en)(tn)F(OH_2)]SO_4\cdot H_2O$	506 (61.0)	430 (17.1)	365 (38.7)			
$[Cr(en)(tn)FCl]Cl$[i]	520 (45.1)	440 (19.9)	386 (37.3)			
cis-$[Cr(en)(tn)F_2]Br$	516 (73.3)	430 (9.8)	374 (35.9)			
cis-$[Cr(en)(tn)FNCS]Br$	498 (88.2)	421 (15.7)	370 (45.3)			

[a] All spectra were determined in 0.1 M $HClO_4$ at room temperature unless otherwise noted. [b] Wavelengths in nanometers. [c] Molar absorptivities in M^{-1} cm^{-1}. [d] This band present as a shoulder. [e] Preparative method A; see Experimental Section. [f] Preparative method B; see Experimental Section. [g] Spectrum determined in aqueous solution. [h] This band present as a spike. [i] Compound may be a cis–trans mixture.

literature method[8] except that potassium iodide was used in place of sodium iodide; yield 0.10 g (15%). Anal. Calcd. for *trans*-$[Cr(en)(tn)F_2]I\cdot H_2O$: C, 16.26; H, 5.42; N, 15.18; Cr, 14.10; I, 34.40. Found: C, 16.25; H, 5.24; N, 15.29; Cr, 13.90; I, 35.02. In 0.1 M aqueous perchloric acid the electronic spectrum of this complex was characterized by λ_{sh} 525 nm (ϵ 17.1 M^{-1} cm^{-1}), λ_{max} 468 (ϵ 25.6), λ_{min} 415 (ϵ 15.9), λ_{max} 395 (ϵ 16.0), and λ_{max} 353 (ϵ 22.9).

Preparation of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2\cdot 0.5H_2O$. A 10.0-g (38.5-mmol) sample of *trans*-$[Cr(en)(tn)F_2]Cl$ was slowly added to 50 mL of ice-cold 72% perchloric acid with constant stirring. The red solution was filtered to remove any undissolved material, and the filtrate was allowed to stand at room temperature for 1 h. At the end of this time the solution was cooled in an ice bath for 15 min and 15 mL of ice-cold water was added dropwise with stirring. After 1–2 h of cooling at 8 °C precipitation began and was complete after 10–12 h at this temperature. The red crystals were collected by filtration, and the filtrate was discarded before the product was washed three times with 10-mL portions of absolute alcohol; yield 8.2 g (51%). *Caution*! The alcohol wash was discarded before the product was washed with ether and air-dried. Anal. Calcd for *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2\cdot 0.5H_2O$: C, 13.92; H, 4.87; N, 12.99; Cr, 12.06. Found: C, 14.06; H, 4.81; N, 12.75; Cr, 12.09.

A 1.0-g (2.3-mmol) sample of the above product was dissolved in 1.0 mL of water; the orange solution was filtered and the filtrate cooled in an ice bath for 30 min. The product was collected, washed with acetone, and air-dried before being further dried over magnesium perchlorate for 18 h at room temperature and 0.05–0.1 mmHg; yield 0.30 g (30%). Anal. Calcd for *trans*$[Cr(en)(tn)F(OH_2)](ClO_4)_2$: C, 14.22; H, 4.74; N, 13.27; Cr, 12.32; F, 4.50. Found: C, 14.02; H, 4.73; N, 13.15; Cr, 12.25; F, 4.65. The electronic spectral data for this compound as well as all other compounds prepared in this study are in Table I.

Conversion to the corresponding iodide salt was accomplished in 76% yield with use of the method described in the literature.[4] Anal. Calcd for *trans*-$[Cr(en)(tn)F(OH_2)]I_2$: C, 12.58; H, 4.19; N, 11.74; Cr, 10.90; I, 53.24. Found: C, 12.54; H, 4.26; N, 11.80; Cr, 10.54; I, 53.11.

Preparation of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$. Method A. A filtered solution of 1.0 g (2.4 mmol) of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ in 2.0 mL of water was diluted with a solution of 0.36 g (4.8 mmol) of potassium chloride in 2 mL of water. The reaction mixture was stirred for 15 min at room temperature and cooled in an ice bath for 30 min before the precipitated potassium perchlorate was collected and discarded. The filtrate was acidified with 0.2 mL of concentrated hydrochloric acid and added dropwise to 250 mL of rapidly stirred acetone. The resulting suspension was stirred for 15 min, the acetone decanted, another 250 mL of fresh acetone added, the stirring continued for 30 min, and the product collected, washed with fresh acetone, and finally air-dried; yield 0.68 g (92%). Anal. Calcd for *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$: C, 19.23; H, 7.05; N, 17.95; Cr, 16.67; Cl, 22.72. Found: C, 19.35; H, 7.18; N, 18.18; Cr, 16.46; Cl, 22.62. Prolonged drying over magnesium perchlorate was avoided since this results in loss of the coordinated water.

Method B. The complex *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ (4.0 g, 9.5 mmol) was dissolved in 8 mL of water and the resulting solution passed through an anion-exchange column (Dowex AG-X8, 100–200 mesh, 20.0 cm × 3.5 cm, Cl^- form, elution rate 0.5 mL min^{-1}). The eluate was dripped directly into 1800 mL of rapidly stirring acetone. The column was washed with small portions of water until the red-orange cation had been eluted. The desired product was collected, washed with acetone, and dried in vacuo for 30 min to remove the acetone. The analytical data were in agreement with the expected values.

Preparation of *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$. This compound was prepared from 5.0 g (35.5 mmol) of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ and 8.5 g (71.0 mmol) of potassium bromide by method A used for the preparation of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$; yield 12.0 g (85%). Anal. Calcd for *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$: C, 15.31; H, 5.36; N, 14.29; Cr, 13.27; Br, 40.81; F, 4.84. Found: C, 15.18; H, 5.19; N, 14.17; Cr, 13.21; Br, 40.77; F, 4.85.

Preparation of *trans*-$[Cr(en)(tn)F(OH_2)](SCN)_2$. This compound was prepared from 5.0 g (12 mmol) of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ and 2.3 g (24 mmol) of potassium thiocyanate by modification of method A used for the preparation of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$. After the removal of the potassium perchlorate, 2.0 g (25 mmol) of solid sodium thiocyanate was dissolved in the filtrate; the reaction mixture was cooled in an ice bath for 15 min before the solid product was collected, washed with acetone, and air-dried; yield 1.0 g (26%). Anal. Calcd for *trans*-$[Cr(en)(tn)F(OH_2)](SCN)_2$: C, 24.78; H, 5.90; N, 24.78; Cr, 15.34. Found: C, 24.89; H, 6.04; N, 24.56; Cr, 15.55.

Preparation of Complexes of the Type *trans*-$[Cr(en)(tn)FX]^+$ (X = NCS^-, Cl^-, Br^-, F^-). *trans*-$[Cr(en)(tn)FNCS](SCN)$. A 1.0-g (3.0-mmol) sample of *trans*-$[Cr(en)(tn)F(OH_2)](SCN)_2$ was suspended in 10 mL of dry methyl alcohol in a 25-mL Erlenmeyer flask equipped with a reflux condenser. The suspension was heated to reflux and the red-orange solution refluxed 1 h. The reaction mixture was allowed to cool to room temperature before being added dropwise to 30 mL of rapidly stirred ether. The ether was decanted and the slurrying with fresh ether repeated three times before the finely divided product was collected and dried in vacuo over magnesium perchlorate for 18 h at room temperature; yield 0.91 g (93%). Anal. Calcd for *trans*-$[Cr(en)(tn)FNSC]SCN$: C, 26.17; H, 5.61; N, 26.17; Cr, 16.20; F, 5.92. Found: C, 26.02; H, 5.69; N, 25.89; Cr, 15.97; F, 5.67.

***trans*-$[Cr(en)(tn)FCl]ClO_4$.** A 10.0-g (23.7-mmol) sample of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ was stirred with 300 mL of methyl alcohol for 15 min before the suspension was filtered to remove a small amount of insoluble material. Solid ammonium chloride (5.50 g, 103 mmol) was added; the solution was stirred for 15 min and filtered. The reaction mixture was heated at 55 °C for 1 h and then allowed to stir overnight at room temperature before the pink product was collected, washed with methyl alcohol followed by ether, and dried; yield 4.7 g (58%). Anal. Calcd. for *trans*-$[Cr(en)(tn)FCl]ClO_4$: C, 17.65; H, 5.29; N, 16.47; Cr, 15.29; Cl, 10.44; F, 5.59. Found: C, 17.65; H, 5.39; N, 16.77; Cr, 15.57; Cl, 10.64; F, 5.40.

***trans*-$[Cr(en)(tn)FCl]Cl\cdot 0.5H_2O$.** A 2.3-g (7.4-mmol) sample of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$ was suspended in 20 mL of dry methyl alcohol. The reaction mixture was refluxed for 30 min and allowed to cool to room temperature before the purple solution was slowly

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(8) Vaughn, J. W.; Stvan, O. J., Jr.; Magnuson, V. E. *Inorg. Chem.* **1968**, *7*, 736.

added to 200 mL of rapidly stirring acetone. The suspension was stirred for 15 min, the suspension was allowed to settle, and the acetone was decanted and discarded. The slurrying with acetone was repeated for 15 min and the product collected, washed with fresh acetone, and dried in vacuo over magnesium perchlorate overnight; yield 1.4 g (66%). Anal. Calcd for *trans*-$[Cr(en)(tn)FCl]Cl\cdot 0.5H_2O$: C, 21.05; H, 6.67; N, 19.65; Cr, 18.25. Found: C, 20.93; H, 6.55; N, 19.45; Cr, 18.14.

A filtered solution of a 0.60-g (2.2-mmol) sample of the above product in 1.0 mL of water was treated with 2.0 mL of aqueous sodium perchlorate (1.0 g of sodium perchlorate/mL). The reaction mixture was cooled in an ice bath for 15 min. The product was collected, washed, and dried as described above for *trans*-$[Cr(en)(tn)FCl]ClO_4$; yield 0.42 g (60%). The analytical data and electronic spectral data were in good agreement with the expected values.

***trans*-[Cr(en)(tn)FBr]Br.** This compound was prepared from 2.1 g (5.5 mmol) of *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$ by the method described for *trans*-$[Cr(en)(tn)FCl]Cl\cdot 0.5H_2O$; yield 0.95 g (48%). Anal. Calcd for *trans*-[Cr(en)(tn)FBr]Br: C, 16.44, H, 4.93; N, 15.34; Cr, 14.25; F, 5.21. Found: C, 16.49; H, 5.16; N, 15.15; Cr, 14.02; F, 5.28.

***trans*-$[Cr(en)(tn)F_2]ClO_4$.** A filtered solution of 2.0 g (4.7 mmol) of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ in 100 mL of methyl alcohol was treated with a solution of 0.35 g (9.5 mmol) of ammonium fluoride in 10 mL of methyl alcohol. The reaction mixture was stirred for 2.5 h at room temperature. Precipitation of the product began in 0.5 h and appeared to be complete in 2.5 h. The product was collected, washed first with methyl alcohol and then acetone, and finally dried in vacuo over magnesium perchlorate at room temperature for 18 h; yield 1.2 g (81%). Anal. Calcd for *trans*-$[Cr(en)(tn)F_2]ClO_4$: C, 18.55; H, 5.56; N, 17.31; Cr, 16.07. Found: C, 18.40; H, 5.40; N, 17.20; Cr, 15.91.

Dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$. A finely ground sample of red-orange *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$ (12.4 g, 31.1 mmol) was spread in a thin layer on a watch glass and placed in an oven at 90 °C. The temperature was increased to 140 °C over a period of 15 min, and the solid was heated at this temperature overnight. The red-orange starting material dehydrated completely to a purple product, yield 11.6 g (98%). Anal. Calcd for [Cr(en)(tn)FBr]Br: C, 16.44; H, 4.93; N, 15.34; Cr, 14.25; Br, 43.81: F, 5.21. Found: C, 16.48; H, 5.06; H, 15.07, Cr, 14.21; Br, 43.59; F, 4.95.

A 1.00-g sample of the above dehydration product was dissolved in water and the stoichiometric amount of solid silver sulfate added. The reaction mixture was stirred for 15 min before the precipitated silver bromide was removed by filtration. The filtrate was evaporated to dryness in the dark at room temperature. The solid was slurried with acetone, collected, and washed with more acetone, and dried in vacuo over magnesium perchlorate. Anal. Calcd. for $[Cr(en)(tn)F(OH_2)]SO_4\cdot H_2O$: C, 17.83; H, 6.53; N, 16.62; Cr, 15.43; F, 5.64; SO_4, 28.49. Found: C, 17.71; H, 6.60; N, 16.59; Cr, 15.51; F, 5.39; SO_4, 28.44. Heating of this compound overnight at 110 °C resulted in the loss of 1 mol of water/mol of complex.

Dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$. A 1.0-g (3.4-mmol sample of the chloride salt was dehydrated at 150 °C by essentially the same method used for the bromide except that the chloride salt was ground several times during the dehydration; yield 0.86 g (91%). Anal. Calcd for [Cr(en)(tn)FCl]Cl: C, 20.41; H, 6.80; N, 19.05; Cr, 17.69. Found: C, 20.84; H, 6.61; N, 19.29; Cr, 17.84.

Preparation of (±)-*cis*-$[Cr(en)(tn)F_2]Br$. A 1.0-g (3.3-mmol) sample of crude [Cr(en)(tn)FBr]Br obtained from the dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot H_2O$ was stirred with 30 mL of methyl alcohol for 0.5 h at room temperature before a small amount of undissolved material was removed by filtration. Solid ammonium fluoride (0.20 g, 5.4 mmol) was added to the filtrate, the stirring was continued for 15 min, and the reaction mixture refiltered. The reaction mixture was stirred at room temperature for 3 h before the purple-pink product was collected, washed first with methyl alcohol and then with acetone, and finally air-dried; yield 0.51 g (61%). A 0.30-g (1.0-mmol) sample of the crude product was dissolved in 1.0 mL of water, the solution filtered, and the filtrate acidified with 0.10 mL of concentrated hydrobromic acid. The stirred, acidified solution was diluted 1 mL at a time with 6.0 mL of methyl alcohol. The reaction mixture was cooled in an ice bath for 15 min before the product was collected, washed first with methyl alcohol and then with acetone, air-dried, and finally dried at 120 °C; yield 0.14 g (47%). The electronic spectrum and elemental analyses did not change when the recrystallization was repeated. Anal. Calcd for (±)-*cis*-$[Cr(en)(tn)F_2]Br$: C, 19.32; H, 5.92; N, 18.42; Cr, 17.11; F, 12.50. Found: C, 19.32; H, 6.01; N, 18.26; Cr, 17.00; F, 12.33.

Preparation of (±)-*cis*-[Cr(en)(tn)FNCS]Br. A 1.0-g (3.3-mmol) sample of crude [Cr(en)(tn)FBr]Br was dissolved in methyl alcohol as described in the synthesis of (±)-*cis*-$[Cr(en)(tn)F_2]Br$. Solid ammonium thiocyanate (0.40 g, 5.2 mmol) was added and the reaction mixture stirred for 15 min before being refiltered. After 24 h of stirring at room temperature the reaction mixture had a change in color from purple to orange, but no insoluble product had formed. The orange solution was rotoevaporated to half its volume and allowed to stand at room temperature for 2–3 h. The product was collected, washed with acetone, air-dried, and finally dried at 125 °C overnight: yield 0.62 g (66%). Anal. Calcd for (±)-*cis*-[Cr(en)(tn)FNCS]Br: C, 20.99; H, 5.24; N, 20.40; Cr, 15.16; F, 5.54. Found: C, 20.71; H, 5.32; N, 20.34; Cr, 15.04; F, 5.11.

Preparation of $NH_4((+)\text{-}C_{10}H_{14}O_4BrS)$. The ammonium salt of (+)-α-bromocamphor-π-sulfonic acid was prepared by the method of Kipping and Pope.[9] The crude product was recrystallized from boiling water; yield 41.0 g (29%). The elemental analyses were in agreement with the calculated values. $[\alpha]^{25}{}_D$ was 83.9° (lit.[9] 84.5°).

Preparation of $Ag((+)\text{-}C_{10}H_{14}O_4BrS)\cdot H_2O$. The silver salt was prepared by essentially the method of Halloran, Gillie, and Legg.[10] The analytical data were in agreement with the calculated values.

Resolution of (±)-*cis*-$[Cr(en)(tn)F_2]Br$. A filtered aqueous solution (40 mL) of twice-recrystallized (±)-*cis*-$[Cr(en)(tn)F_2]Br$ (10.0 g, 32.9 mmol) at room temperature was added dropwise to a rapidly stirring solution of 14.4 g (33.0 mmol) of $Ag((+)\text{-}C_{10}H_{14}OBrS)\cdot H_2O$ in 100 mL of water. The reaction mixture was stirred for 0.5 h before the precipitated silver bromide was removed by filtration and discarded. The filtrate was evaporated to dryness under an air stream, in the dark, at room temperature for 2 days. The solid was slurried with acetone, collected, washed with more acetone, and air-dried; yield 15.3 g (82%). Anal. Calcd for (±)-*cis*-$[Cr(en)(tn)F_2]((+)\text{-}C_{10}H_{14}O_4BrS)\cdot H_2O$: C, 31.58; H, 6.32; N, 9.83; Cr, 9.12. Found: C, 31.64; H, 6.38; N, 9.94; Cr, 9.12. The electronic spectrum of the compound in 0.1 M perchloric acid was characterized by λ_{max} 516 nm (ϵ 66.3 M^{-1} cm^{-1}), λ_{min} 433 (ϵ 12.5), and λ_{max} 376 (ϵ 37.7).

The optical rotatory dispersion spectrum of a 0.2% aqueous solution of the complex at room temperature was characterized by $[\alpha]_x$ ($[\alpha]$ = specific rotation; x = wavelength in nm): $[\alpha]_{589}$ 51°; $[\alpha]_{546}$ 62°; $[\alpha]_{500}$ 80°; $[\alpha]_{450}$ 122°.

A 15.0-g (23.6-mmol) sample of the crude product was added in small portions to 13 mL of water, the mixture filtered, and the filtrate cooled in an ice bath for 15 min. The product was collected, washed with acetone, and air-dried; yield 1.96 g (13.1%). The recrystallization was repeated, and the ORD spectrum of a 0.2% aqueous solution of the complex was characterized by $[\alpha]_{589}$ 94°, $[\alpha]_{570}$ 0°, $[\alpha]_{546}$ −239°, $[\alpha]_{530}$ −296°, $[\alpha]_{500}$ 0°, and $[\alpha]_{450}$ 312°. Further recrystallization did not change the specific rotations or the elemental analyses. Anal. Calcd for $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]((+)\text{-}C_{10}H_{14}O_4BrS)\cdot 2H_2O$: C, 31.58; H, 6.32; N, 9.83; Cr, 9.12. Found: C, 31.65; H, 6.23; N, 9.73; Cr, 9.24.

A 500-mg (0.9-mmol) sample of the above material was dissolved in 1.5 mL of water, and the solution was acidified with 0.5 mL of concentrated hydrobromic acid. The solution was slowly diluted with 15 mL of methyl alcohol before the cloudy reaction mixture was cooled in ice for 15 min. The product was collected, washed with acetone, and air-dried; yield 0.20 g. Anal. Calcd for $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$: C, 19.74; H, 5.92; N, 18.42; Cr, 17.10; F, 12.50. Found: C, 19.70; H, 6.10; N, 18.30; Cr, 16.94; F, 12.05. The ORD spectrum determined as described previously was characterized by $[\alpha]_{589}$ 82°, $[\alpha]_{570}$ 0°, $[\alpha]_{546}$ −548°, $[\alpha]_{530}$ −685°, $[\alpha]_{500}$ 0, $[\alpha]_{450}$ 367°, and $[\alpha]_{380}$ 99°. The electronic spectrum in 0.1 M perchloric acid was characterized by λ_{max} 515 nm (ϵ 66.7 λ_{min} 431 (ϵ 10.1), and λ_{max} 375 nm (ϵ 36.5).

Weight Loss and Spectroscopic Studies. Previously tared samples (six each) of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2\cdot H_2O$ and *trans*-$[Cr(en)(tn)F(OH_2)]Br_2\cdot 0.5H_2O$ were placed in a vacuum desiccator over anhydrous magnesium perchlorate and evacuated for 1 week at room temperature and 0.05–0.1 mmHg. The desiccator was protected from light during the dehydration studies. One sample of each compound was removed from the desiccator every 24 h, and both the weight loss and the electronic spectrum of each sample were determined.

Discussion

The primary starting material for the preparation of the mixed-ligand complexes of chromium(III) is the double salt (±)-*cis*-$[Cr(en)_2F_2][Cr(en)F_4]$, which can be readily prepared via the reaction[6]

$$2CrF_3\cdot 3.5H_2O(s) + 3en(l) \rightarrow (\pm)\text{-}cis\text{-}[Cr(en)_2F_2][Cr(en)F_4](s) + 7H_2O(g)$$

Upon reaction with concentrated hydrobromic acid[7] the double salt yields $[Cr(en)F_2(OH_2)_2]Br$, a compound well suited for the syntheses of mixed-ligand complexes since the fluoro ligand is

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already bound to the Cr(III) center and the experimental difficulties of binding the fluoro ligand can be avoided. Recent X-ray structural studies have established that this particular cation that arises from the acid hydrolysis of the $[Cr(en)F_4]^-$ anion of the starting material[6] involves a trans arrangement of the two fluoro ligands.[11]

The reaction of *trans*-$[Cr(en)F_2(OH_2)_2]Cl$ with 1,3-propanediamine, tn, in refluxing absolute alcohol is the basis for the preparation of the new compounds. Earlier studies in this laboratory have demonstrated the utility of a similar complex, $[Cr(pn)F_2(OH_2)Br]Br$, for the preparation of mixed-ligand complexes of the type $[Cr(pn)(aa)F_2]^+$, aa = ethylenediamine, 1,3-propanediamine, *trans*-1,2-diaminocyclohexane, and their derivatives.[3]

Although Cr(III) binds more strongly to oxygen donor ligands than to nitrogen donors, the replacement of the relatively strong $Cr-OH_2$ bond with the relatively weaker Cr–N bond is probably due to the operation of the chelate effect. Hence, the increase in entropy of the system due to the formation of the six-membered chelate ring more than compensates for the reduction in metal–ligand bond strength.

Due to the trans arrangement of the fluoro ligands in the starting material, the reaction with tn produced the anticipated *trans*-$[Cr(en)(tn)F_2]Cl$ complex as the major product. In accord with previous investigations in this laboratory,[4] it was possible to isolate a second product, contaminated with the trans isomer, from the reaction mixture. The electronic spectrum of this impure second fraction (λ_{max} 520 nm, λ_{min} 428 nm, and λ_{max} 369 nm) was not consistent with what would be expected from variable mixtures of *trans*-$[Cr(pn)F_2(OH_2)Br]Br$ with pn in absolute alcohol; the second product was thought to be a mixture of *cis*- and *trans*-$[Cr(pn)_2F_2]Br$.[4] The recent isolation, purification, and characterization of *cis*-$[Cr(pn)_2F_2]ClO_4{\cdot}H_2O$[12] serves to confirm the correctness of this original assignment. Additional support for the second product's being a mixture of *cis*- and *trans*-$[Cr(en)(tn)F_2]Cl$ comes from the fact that, under one carefully controlled set of experimental conditions, it was possible to isolate a fraction whose electronic spectrum was in qualitative agreement with what would be expected for a trans:cis ratio of 3:1.

It is not clear at this time whether the second product arises (1) entirely from a trans → cis isomerization of *trans*-$[Cr(en)(tn)F_2]Cl$, (2) by direct reaction of *trans*-$[Cr(en)F_2(OH_2)_2]Cl$ with tn via a dissociative mechanism as discussed by Basolo,[13] or (3) from a combination of (1) and (2). However, there is good evidence that prolonged reaction times in the reactions of *trans*-$[Cr(py)_4F_2](ClO_4)$ with pn in refluxing 2-methoxyethanol do result in the isomerization of the initially formed *trans*-$[Cr(pn)_2F_2]^+$ to the corresponding cis isomer.[12] Although the preparative method does yield some *cis*-$[Cr(en)(tn)F_2]Cl$, the yields obtained under the specific conditions utilized in the present study are so low that this method does not represent a viable preparative route to obtain this material in quantity.

As in the case of the complex *trans*-$[Cr(en)_2F_2]Cl$,[8] reaction of crude *trans*-$[Cr(en)(tn)F_2]Cl$ with concentrated perchloric acid produced the corresponding *trans*-fluoroaqua perchlorate as the insoluble product.

An examination of the visible electronic spectrum of *trans*-$[Cr(en)(tn)F(OH_2)](ClO_4)_2$ revealed that only the first cubic band (${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ in O_h) was split by the ligand field. The nonobserved splitting of the second cubic band was not unexpected since the low-temperature polarized single-crystal spectrum of the closely related compound *trans*-$[Cr(en)_2F(OH_2)](ClO_4)_2$[14] indicates the splitting of the ${}^4E$ and ${}^4A_2$ states to be 210 cm^{-1}. By treatment of the trans-monodentate ligands as an average ligand pair and assumption of a symmetry of D_{4h} as described in the literature, the *Dq* value for this complex is 2183 cm^{-1}, which is essentially the same as the *Dq* values of 2183 and 2174 cm^{-1} found for *trans*-$[Cr(en)_2F(OH_2)]^{2+}$ and *trans*-$[Cr(tn)_2F(OH_2)]^{2+}$, respectively.[15]

The visible electronic spectrum of the corresponding difluoro complex, *trans*-$[Cr(en)(tn)F_2]ClO_4$, did however exhibit splitting of both the first and second cubic bands in accord with previously reported studies.[8,16] By assumption of a local site symmetry of D_{4h}, the ${}^4B_{1g} \rightarrow {}^4B_{2g}$ transition provides a reliable estimate of the *Dq* values, which are 2136, 2150, and 2146 cm^{-1} for *trans*-$[Cr(en)(tn)F_2]^+$, *trans*-$[Cr(en)_2F_2]^+$, and *trans*-$[Cr(tn)_2F_2]^+$, respectively.

By the use of anation reactions similar to those described previously,[17,18] it was possible to utilize methyl alcohol solutions of the perchlorate or chloride salts of *trans*-$[Cr(en)(tn)F(OH_2)]^{2+}$ to prepare new *trans*-FX compounds. When F^- or Cl^- was the entering ligand, solid products precipitated directly from the reaction mixture or could be easily isolated. In these cases the electronic spectra confirmed that the least soluble fractions were the stereoretentive products. The refluxing of methyl alcohol solutions of *trans*-$[Cr(en)(tn)F(OH_2)]X_2{\cdot}0.5H_2O$ ($X = Cl^-, Br^-, NCS^-$) that did not contain any ammonium salt was utilized to prepare compounds formualted as *trans*-$[Cr(en)(tn)FX]X{\cdot}YH_2O$ ($Y = 0.5$ for $X = Cl^-$; $Y = 0$ for $X = Br^-, NCS^-$). The $^1/_2$ mol of water of hydration found for the *trans*-FCl complex is probably due to incomplete drying of this hygroscopic material rather than the compound's being a mixture of the desired product and unreacted starting material since the electronic spectrum is in agreement with that found for *trans*-$[Cr(en)(tn)FCl]ClO_4$.

In accord with the spectrochemical series, the energies of the first spin-allowed transitions (${}^4B_1 \rightarrow {}^4E$ in D_{4h}) for the series *trans*-$[Cr(en)(tn)FX]^+$ shifted to lower values as X was changed from F to Cl to Br. The energy of the ${}^4B_1 \rightarrow {}^4B_2$ transition, which as been shown by Perumareddi[19] predominately to involve changes in electron density in the *xy* plane, exhibited little change for the *trans*-$[Cr(en)(tn)FX]^+$ ($X = F^-, Cl^-, Br^-$) complexes.

As found by Wirth, Bifano, Walters, and Linck[20] for *trans*-$[Cr(en)_2FBr]Br$, the electronic spectrum of *trans*-$[Cr(en)(tn)FBr]Br$ exhibited a narrow, weak transition superimposed on the second spin-allowed band at 464 nm (21 552 cm^{-1}). The origin of this band is probably due to both spin–orbit coupling effects and the near-degeneracy of the ${}^2T_{2g}(O_h) \rightarrow {}^2E + {}^2B_2$ transition with the ${}^4B_1 \rightarrow {}^4B_2$ transition as discussed by Linck and coworkers.

It has been well established that *trans*-fluoroaquabis(ethylenediamine)chromium(III) complexes that contain coordinating anions undergo loss of the aqua ligand at elevated temperatures. The rupture of the $Cr-OH_2$ bond is accompanied by partial, if not complete, isomerization to the corresponding cis isomers.

In the case of the mixed-en-tn compounds, the products of the dehydrations are hygroscopic, and it was never possible to obtain completely anhydrous materials from the dehydrations. The electronic spectra of acidic solutions of these materials exhibited a band pattern and wavelengths of the absorption maxima consistent with a cis arrangement of the monodentate ligands; however, the molar absorptivities at the absorption maxima were lower than what would be expected for an exclusively cis product.

Detailed weight loss and spectroscopic studies clearly showed, in the case of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$, that dehydration over anhydrous magnesium perchlorate at room temperature resulted in the exclusive formation of *trans*-$[Cr(en)(tn)FCl]Cl$. The electronic spectra data were in excellent agreement with those found for *trans*-$[Cr(en)(tn)FCl]ClO_4$

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prepared by anation of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$ with ammonium chloride in methyl alcohol. Thus the reaction in all probability proceeded through a square-pyramidal intermediate.

Similar studies at elevated temperatures also clearly indicated the first step in the dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$ to be the formation of *trans*-$[Cr(en)(tn)FCl]Cl$. Continued heating of the product resulted in a new material, the electronic spectrum of which indicated that another reaction had taken place. The product could be predominately *cis*-$[Cr(en)(tn)FCl]Cl$ that was formed as the result of a trans → cis isomerization of the original dehydration product. Such a product could arise either via a dissociative type mechanism that involved a trigonal-bipyramidal intermediate or via Cr–N bond rupture and the opening of a chelate ring as described by Mitra.[21] On the basis of the data currently available it is not possible to establish which of these mechanisms is most nearly correct. A coordinating anion is apparently necessary for the second reaction since *trans*-$[Cr(en)(tn)FCl]ClO_4$ is stable under the conditions where *trans*-$[Cr(en)(tn)FCl]Cl$ reacts. If the second product is the result of a trans → cis isomerization, the reaction does not apear to be complete since the molar absorptivities of the final product are lower than expected for a pure cis isomer.

Studies similar to those carried out for *trans*-$[Cr(en)(tn)F(OH_2)]Cl_2{\cdot}0.5H_2O$ indicated that *trans*-$[Cr(en)(tn)F(OH_2)]Br_2$ did not lose any coordinated water when dried for 7 days over magnesium perchlorate. When the dehydration was carried out at elevated temperatures, it was not possible to detect the presence of any *trans*-$[Cr(en)(tn)FBr]Br$. The dehydration reaction, which appears to occur via a different mechanism, is thought to yield *cis*-$[Cr(en)(tn)FBr]Br$ as the major product.

Reaction of an aqueous solution of the dehydration product with silver sulfate appears to yield predominately *cis*-$[Cr(en)(tn)F(OH_2)]^{2+}$. The electronic spectrum of the product is similar to that reported[6] for *cis*-$[Cr(en)_2F(OH_2)]^{2+}$. However, the molar absorptivities appear to be lower than expected for a pure cis isomer.

Reaction of a methyl alcohol solution of the product, obtained by the prolonged dehydration of *trans*-$[Cr(en)(tn)F(OH_2)]Br{\cdot}0.5H_2O$ at 140 °C, with ammonium fluoride or ammonium thiocyanate was the basis for the preparation of (±)-*cis*-$[Cr(en)(tn)F_2]Br$ and (±)-*cis*-$[Cr(en)(tn)FNCS]Br$. The cis geometry of the difluoro complex was confirmed by the isolation of $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$. Since it has been well established that anation reactions of Cr(III) complexes are stereoretentive, the resolution of the product of such a reaction serves to confirm the presence of a cis isomer in the starting material. From a comparison of the optical rotatory dispersion curves of $(-)_{546}$-*cis*-$[Cr(en)_2F_2]^+$,[22] $(-)_{546}$-*cis*-$[Cr(en)_2FNCS]^+$,[6] $(-)_{546}$-*cis*-$[Cr(en)_2F(OH_2)]^{2+}$,[23] and $(-)_{546}$-*cis*-$[Cr(en)_2FNH_3]^{2+}$,[1] the absolute configuration of $(-)_{546}$-*cis*-$[Cr(en)(tn)F_2]Br$ was assigned as Δ. The isolation of one of the chiral forms of *cis*-$[Cr(en)(tn)F_2]^+$ also serves to confirm the trans geometry of those complexes whose cations contain the identical ligands but whose electronic spectra exhibit more than two absorption bands. Apparently *cis*-$[Cr(en)(tn)F_2]^+$ is the first fluoro-containing complex of Cr(III) of its type to be resolved.

Although the geometry of the complex identified as *cis*-$[Cr(en)(tn)FNCS]Br$ was not established via resolution techniques, the assigned geometry is well supported by the electronic spectral data.

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Notes

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Two More Space Group Changes

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$TaCl_2H_2(PMe_3)_4$. The crystal structure of this paramagnetic hydride complex of Ta^{IV} was described[1] in space group *Cc* (monoclinic; $a = 15.127$ (3) Å, $b = 12.005$ (3) Å, $c = 12.410$ (2) Å, $\beta = 92.49$ (1)°, $Z = 4$). It should be described, instead, in space group *C2/c*, with the molecule lying on a site of crystallographic symmetry C_2.

After the coordinates in Table II of ref 1 were adjusted by $\Delta x = 0.0214$, $\Delta z = 0.1462$ (placing the Ta atom on a twofold axis) and the coordinates of pairs of symmetry-related atoms were averaged, three full-matrix least-squares refinement cycles led to an R of 0.0303 and a goodness-of-fit of 2.61 for the 2514 F_o and $\sigma(F)$ values recovered from the supplementary material; in the third cycle no shift was greater than 0.19σ (a hydrogen atom). The *C2/c* coordinates for the Ta, Cl, P, and C atoms are given in Table I; their U_{ij} values and the coordinates and isotropic B's of the hydrogen atoms are included as supplementary material.

It is somewhat surprising that the R index and (particularly) the goodness-of-fit are slightly higher than the values 0.0285 and 2.56 reported for the *Cc* model.[2] Accordingly, we attempted to repeat the *Cc* refinement, beginning with the parameters of ref 1. (Such a refinement cannot begin with the *C2/c* parameters, because of exact singularities.) After small adjustments of the scale factor (to 0.993) and the U_{ij} values—perhaps due to slightly different form factors—we obtained essentially the same indexes: $R = 0.0288$, GOF = 2.60. However, continued refinement through four full-matrix least-squares cycles gave no hint of convergence; while the agreement indexes stayed effectively constant, many parameter shifts were appreciably larger than their esd's—up to 3.4σ for two hydrogen atoms and 1.8σ (0.05 Å) for a carbon atom.[3]

Table I. Coordinates (×10^4) for $TaCl_2H_2(PMe_3)_4$, Space Group *C2/c*

atom	*x*	*y*	*z*	B_{eq}[a]
Ta	0	−2710.1 (2)	2500	1.10 (1)
Cl(2,3)	−1079.6 (7)	−1103.9 (9)	2152.8 (9)	1.94 (2)
P(4,7)	224.7 (7)	−2307.6 (9)	446.1 (9)	1.60 (2)
P(5,6)	−1494.5 (7)	−3719.4 (9)	2467.6 (9)	1.56 (2)
C(8,19)	730 (3)	−3357 (4)	−401 (4)	2.21 (8)
C(9,18)	886 (3)	−1077 (4)	182 (4)	2.18 (8)
C(10,17)	−779 (3)	−2035 (4)	−395 (4)	2.41 (8)
C(11,14)	−2452 (3)	−3121 (4)	3120 (4)	2.38 (8)
C(12,16)	−1477 (3)	−5129 (4)	3006 (4)	2.10 (8)
C(13,15)	−2014 (3)	−3959 (5)	1123 (4)	2.52 (8)

[a] $(8\pi^2/3)\sum_{i,j}U_{ij}a_i^*a_j^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

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(2) The "goodness of fit" reported in ref 1 is 1.083. However, using the values of F_o and $\sigma(F)$ in the supplementary material and 2514 and 325 for the numbers of observations and parameters, we obtain 2.56 for the quantity $[\sum(F_o - F_c)/\sigma(F)]^2/2189]^{1/2}$.

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