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Deuteron Nuclear Magnetic Resonance Study of $[Cr(edda)X_2]^n$ Complexes (X_2 = Two Monodentates or a Bidentate) and Complete Assignment of the Deuteron NMR Spectrum of $[Cr(1,2\text{-pdta-}\alpha\text{-}d_8)]^-$

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The stereochemistry of Cr(III) complexes with the linear quadridentate ligand ethylenediamine-*N,N'*-diacetic acid (H_2edda) has been studied by deuteron nuclear magnetic resonance (^{2}H NMR) spectroscopy. The isomers *sym-cis*-$[CrX_2(edda\text{-}\alpha\text{-}d_4)]^n$ (X_2 = $2H_2O$, $2F^-$, acetylacetonate, oxalate) and *unsym-cis*-$[CrX_2(edda\text{-}\alpha\text{-}d_4)]^n$ (X_2 = $2H_2O$, acetylacetonate) were assigned by ^{2}H NMR. The conversion of *unsym-cis*-$[Cr(H_2O)_2(edda\text{-}\alpha\text{-}d_4)]^+$ to the more stable sym-cis configuration was followed by ^{2}H NMR, and an equilibrium distribution constant (sym-cis/unsym-cis) of 4 was obtained. Preferential deuteration of *sym-cis*-[Cr(edda)(malonate)]$^-$ permitted specific assignments to be made for the geminal deuterons on the edda glycinate chelate rings. The complete ^{2}H NMR spectrum for the previously reported, related complex $[Cr(1,2\text{-pdta-}\alpha\text{-}d_8)]^-$ was also assigned by preferential deuteration of the stereoselective ligand 1,2-propylenediamine-*N,N,N',N'*-tetraacetate (1,2-pdta) on Co(III) followed by transferral to Cr(III).

Introduction

We have been investigating deuteron nuclear magnetic resonance (^{2}H NMR) spectroscopy as a probe of the solution chemistry of paramagnetic chromium(III) complexes.[1-5] Previous to these studies an effective NMR technique for Cr(III) investigations had not been developed, although the potential of ^{2}H NMR had been demonstrated.[6] The long electron spin relaxation times associated with Cr(III) cause severe line broadening for most NMR-active nuclei.[7]

Linear quadridentate ligands provide a variety of stereochemical permutations, and linear diamine diacetate ligands are of particular interest for Cr(III) studies since the acetate components can be readily deuterated. In an earlier study, the stereochemistry of Cr(III) complexes of 1,3-propanediamine-*N,N'*-diacetate (1,3-pdda)[8] was elucidated, and the three possible geometric isomers of $[CrF_2(1,3\text{-pdda})]^-$ (Figure 1) were characterized by ^{2}H NMR and an X-ray crystallographic study.[4] For the analogous linear quadridentate ligand edda, with one less carbon in the diamine backbone, ring strain apparently prevents the formation of the trans isomer, and only the sym-cis and unsym-cis (Figure 1) isomers have been reported for Co(III) and Cr(III) complexes of edda.[9] For Cr(III), only one unsym-cis isomer has been reported along with the predominant and more stable sym-cis isomer.[10] The close similarity between the ligand field spectra of the two isomers precludes definitive characterization by electronic absorption spectroscopy. As with the 1,3-pdda complexes of Cr(III),[4] it was anticipated that ^{2}H NMR would provide the necessary information to differentiate the edda isomers. The data obtained in this study confirmed this expectation and, in addition, permitted us to monitor the solution dynamics as these systems approached equilibrium. Our interest in Cr(III)–edda complexes stems not only from their interesting stereochemistry but from the use of substitution-inert complexes of edda as probes of protein structure/function relationships.[11]

Structural assignments do not usually require specific assignment of deuteron resonances, but elucidation of the mechanisms that give rise to the large observed ^{2}H NMR isotropic shifts require this information. To this end we have been making specific assignments whenever possible. In this study preferential deuteration of *sym-cis*-[Cr(edda)(mal)]$^-$ permitted specific assignment of the NMR resonances and, by comparison, assignment of the resonances to the other sym-cis isomers synthesized.

Specific assignment of deuteron resonances can require the use of stereospecific ligands, ligands whose structures predetermine deuteron/proton positions due to structural constraints imposed on the mode of ligand coordination. In order to assign the ^{2}H NMR spectra obtained for the unsym-cis isomers, 1,2-propanediamine-*N,N'*-diacetic acid (1,2-pdda) would have had to have been used. To date attempts to synthesize this ligand with deuterium labels have been unsuccessful.[12] However, in the course of these studies we were able to complete the assignment of the ^{2}H NMR spectrum of the Cr(III) complex of 1,2-pdta, a ligand closely related to 1,2-pdda. The partial assignment of the ^{2}H NMR spectrum of [Cr(1,2-pdta)]$^-$ has been reported.[1]

Experimental Section

Materials. All materials were reagent grade quality and were used without further purification. Deuterium oxide was purchased from Aldrich Chemical Co., Milwaukee, WI, and was at least 99.8 atom % ^{2}H.

Synthesis. Deuterated Ethylenediamine-*N,N'*-diacetic Acid Dihydrochloride (H_2edda-α-d_4·2HCl). Freshly prepared ethylenediamine-*N,N'*-diacetronitrile dihydrochloride[13] (8.6 g, 0.04 mol) was added to a stirred solution of KO^{2}H (10 g in 40 mL of ^2H_2O). An air stream was passed through the solution while being heated at 80 °C for 2 h. During this period the strong odor of ammonia diminished. After the mixture cooled to room temperature, methanol (100 mL) was added and the reaction mixture was stored at 0 °C overnight. A white crystalline salt was removed on a medium-glass-fritted funnel and washed with portions of methanol until the filtrate was clear. The yellow filtrate was acidified with 6 M HCl until it became cloudy, and then it was cooled to 0 °C. A tarry yellow-white precipitate was collected, washed with ethanol and anhydrous ether, and vacuum-dried. An additional crop of material was

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(1) Wheeler, W. D.; Legg, J. I. *Inorg. Chem.* **1985**, *24*, 1292.
(2) Wheeler, W. D.; Legg, J. I. *Inorg. Chem.* **1984**, *23*, 3798.
(3) Green, C. A.; Bianchini, R. J.; Legg, J. I. *Inorg. Chem.* **1984**, *23*, 2713. Broderick, W. E.; Legg, J. I. *Inorg. Chem.* **1985**, *24*, 3724.
(4) Bianchini, R. J.; Geiser, U.; Place, H.; Kaizaki, S.; Morita, Y.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 2129.
(5) Wheeler, W. D.; Kaizaki, S.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 3248.
(6) Everett, G. W., Jr.; Johnson, A. *J. Am. Chem. Soc.* **1972**, *94*, 6397. Johnson, A.; Everett, G. W., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 1419. Reuben, J.; Fiat, D. *J. Am. Chem. Soc.* **1969**, *91*, 1243.
(7) Holm, R. H.; Hawkins, C. J. In *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. DeW, Jr., Holm, R. H., Eds.; Academic: New York, London, 1973; Chapter 7, pp 287–289.
(8) Abbreviations: acac = acetylacetonate or 2,4-pentanedionate; mal = malonate; ox = oxalate; edda = ethylenediamine-*N,N'*-diacetate or 2,5-diazahexanedionate; edda-α-d_4 = 2,5-diazahexanedionate-1,1,6,6-d_4; 1,3-pdda = 1,3-propanediamine-*N,N'*-diacetate or 2,6-diazaheptanedionate; 1,2-pdta = 1,2-propylenediamine-*N,N,N',N'*-tetraacetate. 1,3-pdda = 1,3-propanediamine-*N,N'*-diacetate or 2,6-diazaheptanedionate; 1,2-pdta = 1,2-propylenediamine-*N,N,N',N'*-tetraacetate.
(9) Radanović, D. J. *Coord. Chem. Rev.* **1984**, *54*, 159.
(10) Weyh, J. A.; Pierce, R. L. *Inorg. Chem.* **1971**, *10*, 858.
(11) Pielak, G. J.; Urdea, M. S.; Legg, J. L. *Biochemistry* **1984**, *23*, 596. Pielak, G. J.; Urdea, M. S.; Igi, K.; Legg, J. I. *Biochemistry* **1984**, *23*, 589. Igi, K.; Urdea, M. S.; Legg, J. I. *Inorg. Chem.* **1981**, *20*, 3208. Urdea, M. S.; Legg, J. I. *J. Biol. Chem.* **1979**, *254*, 11868. Urdea, M. S.; Legg, J. I. *Biochemistry* **1979**, *18*, 4984. Urdea, M. S.; Pielak, G. J.; Igi, K.; Legg, J. I. *Abstracts*, Methods for Determining Metal Ion Environments in Proteins; Las Cruces, NM, 1979; No 56.
(12) Bianchini, R. J. Ph.D. Thesis, Washington State University, Pullman, WA, 1985.
(13) Kawato, T.; Kanatami, H.; Morase, I. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1723.

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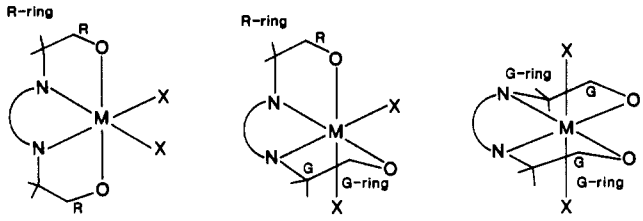


Figure 1. Three geometric isomers for an [M(linear diamine diacetate)X_2]^n complex (sym-cis = symmetrical-cis or α-cis, unsym-cis = unsymmetrical-cis or β-cis; R = out-of-plane or "relaxed" ring, G = in-plane or "girdling" ring).

Table I. Electronic Absorption Spectral Data

complex	band position λ (ε)[a] I	II
sym-cis-[CrF_2(edda)]$^-$	557 (90)	375 (21)
sym-cis-[Cr(edda)(mal)]$^-$[b]	538 (71)	398 (53)
sym-cis-[Cr(edda)(ox)]$^-$[b]	534 (88)	393 (73)
sym-cis-[Cr(H_2O)$_2$(edda)]$^+$[c]	529 (77)	401 (47)
sym-cis-[Cr(acac)(edda)][d]	532 (65)	380 (168)
unsym-cis-[Cr(H_2O)$_2$(edda)]$^+$[c]	527 (119)	392 (72)
unsym-cis-[Cr(acac)(edda)]	530 (84)	414 (sh), 380 (173)

[a] In nm (M^{-1} cm^{-1}). [b] From ref 5 and this study. [c] From ref 10 and this study. [d] From ref 14 and this study.

obtained by reducing the filtrate volume by half, adding ethanol until cloudy, and filtering. the crude product was converted to the dihydrochloride salt by dissolving it in a minimum amount of water, adjusting the pH to 1.0 with 6 M HCl, adding ethanol until cloudy, and refrigerating overnight. Fluffy white crystals were filtered, washed with two 20-mL portions of ethanol and anhydrous ether, and vacuum-dried. Yield: 3.7 g (37%). Proton NMR showed that 65% deuterium had been incorporated.

***sym-cis*- and *unsym-cis*-Diaquo(ethylenediamine-*N*,*N*'-diacetato)chromium(III) Nitrate, *sym-cis*- and *unsym-cis*-[Cr(H_2O)$_2$(edda-α-d_n)]NO_3 (*n* = 0, 4).** These complexes were prepared by a modification of the method of Weyh and Pierce.[10] A suspension of 1.9 g (0.007 mol) of H_2edda-α-d_n (n = 0, 4) in H_2O (25 mL) was adjusted to pH 9.5 with K_2CO_3 (2.3 g in 10 mL of H_2O) and added dropwise to 1.9 g (0.007 mol) of $CrCl_3$·$6H_2O$ dissolved in H_2O (10 mL). The initially green chromium solution turned deep purple as the ligand was added. The mixture was heated on a steam bath until it turned red-violet (~2 h). After cooling to room temperature, the solution was filtered and then introduced onto a column of Dowex 50W-X8 (100–200 mesh, H^+ form) in a cold room at 10 °C. The column was washed with water, and a positively charged species was eluted with 0.5 M HNO_3. After several hours two bands separated. The first band (B-I) was collected and rotary evaporated at 25 °C to a final volume of approximately 200 mL. After the mixture was transferred to a beaker, anhydrous ether (200 mL) was added and a deep red-violet oil was obtained. The ether was decanted and acetone (50 mL) was added followed by ether (100 mL). The ether layer was decanted, and the process was repeated three times. Glittery, crimson-red crystals were obtained by diluting with acetone (250 mL), scraping the beaker with a glass rod, and storing it in a freezer overnight. The product (B-I) was collected, washed with acetone, and ether, and vacuum-dried. Yield: 0.81 g (35%). Anal. Calcd for [Cr(H_2O)$_2$(edda)]NO_3: C, 22.21; H, 4.36; N, 12.95. Found: C, 22.64; H, 4.24; N, 12.55.

The second band (B-II) was eluted with 3 M HNO_3 at <10 °C and was immediately frozen. The band was concentrated by lyophilization in the dark to a final volume of 50 mL. The solid was periodically thawed and adjusted to pH 1–2 by addition of solid K_2CO_3. As found previously, compound B-II could not be isolated in crystalline form.[10] Spectral data were thus taken directly on the concentrated solution. The peak maxima of the electronic absorption spectrum agreed with those reported by Weyh and Pierce (Table I).[10]

***sym-cis*- and *unsym-cis*-(Acetylacetonato)(ethylenediamine-*N*,*N*'-diacetato)chromium(III), *sym-cis*- and *unsym-cis*-[Cr(acac)(edda-α-d_n)] (*n* = 0, 4).** The sym-cis isomer was prepared as previously described.[14] The unsym-cis isomer was prepared as follows. An aqueous solution of the sym-cis isomer (25 mL, 0.1 M) was allowed to stand overnight at room temperature. The solution was poured onto a 5 cm × 50 cm column of QAE-Sephadex (A-25, Cl^- form) at <10 °C in the dark. Two bands (C-I and C-II) separated on elution with H_2O. Compound C-I was present at approximately 10 times the amount of compound C-II. The electronic absorption spectrum for complex C-I corresponded to that reported previously for the sym-cis isomer.[14] Complex C-II was concentrated by lyophilization to 20 mL in the dark. Since it could not be isolated in crystalline form, spectral data were taken directly on the concentrated solution. The molar absorptivities of the complex were calculated on the basis of a quantitative analysis of the Cr(III) content of a concentrated sample using the basic peroxide oxidation method.[15]

Lithium *sym-cis*-Difluoro(ethylenediamine-*N*,*N*'-diacetato)chromate(III), *sym-cis*-Li[CrF_2(edda-α-d_n)] (*n* = 0, 4). A solution of 1.50 g (0.006 mol) of edda-α-d_n·2HCl (n = 0, 4) in 25 mL of H_2O was adjusted to pH 8.0 with potassium carbonate and added dropwise to a stirred solution of 2.84 g (0.006 mol) of *trans*-[CrF_2(py)$_4$]NO_3[16] in 50 mL of H_2O. The reaction mixture was heated on a steam bath at pH 7 for 4 h. After cooling to room temperature, the deep purple solution was poured onto a 5 cm × 45 cm column containing QAE-Sephadex (A-25, Cl^- form). The column was washed with water to remove unreacted starting materials, and the adsorbed purple band was eluted in the dark with aqueous 0.05 M LiCl. A single violet band was eluted halfway down the column, and then the cellulose above the band was removed. The column was washed with H_2O until the eluate was free from Cl^-. The band was eluted with 3 M LiCl into an aluminum foil covered beaker. Acetone (250 mL) was added to the eluate, and an oil formed. The upper layer was decanted. The process was repeated three times, whereupon a violet powder formed. Then, approximately 20 mL of methanol was added followed by acetone until the solution became cloudy. The product was isolated, washed with acetone and ether, and then dried in a vacuum desiccator. Recrystallization was carried out by dissolving the product in H_2O/MeOH (1:3), adding acetone until cloudy, and cooling to 0 °C. Yield: 0.54 g (50%). Anal. Calcd for Li[CrF_2(edda)]·$^1/_4H_2O$: C, 25.95; H, 4.54; N, 10.09. Found: C, 25.81; H, 3.92; N, 9.87.

Potassium *sym-cis*-(Ethylenediamine-*N*,*N*'-diacetato)(oxalate)chromate(III), *sym-cis*-K[Cr(edda-α-d_n)(ox)] (*n* = 0, 4). This complex was prepared by the method of Radanović et al.[17] except H_2edda was titrated to pH 9.0 with 1 M KOH before using.

Preferential Deuteration of *sym-cis*-[Cr(edda)(mal)]$^-$. The complex (250 mg) was dissolved in 4 mL of ^2H_2O in a sealed vial. The pD[18] of the sample was adjusted to 10.2–10.4 with solid K_2CO_3. Six samples were prepared in this manner and heated from 1 to 7 days in a constant-temperature bath at 50 °C. If the samples were heated for more than 1 week, a significant amount of decomposition occurred, as observed in the electronic absorption and ^2H NMR spectra. After being heated, each sample was transferred to a beaker and ethanol/acetone (1:1) was added until the solution became just cloudy. The sample was stored in a refrigerator overnight, and the precipitate that formed was collected, washed with acetone and ether, and vacuum-dried. It was assumed that no appreciable exchange of the acetate deuterons occurred during the ^2H NMR measurements (0.5–2 h at 18 °C), but the resonances of the labile malonate deuterons decreased over this time period.

Preferential Deuteration of K[Cr(1,2-pdta)]. Attempts to perform isotopic substitution directly on [Cr(1,2-pdta)]$^-$ using the mild exchange conditions described for *sym-cis*-[Cr(edda)(mal)] above were unsuccessful. However, preferentially deuterated 1,2-pdta was prepared on Co(III) as previously described.[19] The ligand was removed from Co(III) by adding excess CN^-, as described for the isolation of preferentially deuterated H_4cdta-α-d_4.[1] The Cr(III) complex of deuterated 1,2-pdta was prepared as described by Wheeler and Legg.[1]

Physical Measurements. Analysis. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and the CH & N Analytical Facility, University of Idaho, Moscow, ID.

Electronic Absorption Spectra. Spectra were recorded in H_2O on a Varian/Cary 219 spectrophotometer and are reported in Table I.

Deuteron NMR Spectra. The 31-MHz ^2H NMR spectra were recorded at 18 °C on a Nicolet NT-200WB spectrometer operating at a field of 4.7 T. The instrumental setup parameters have been summarized elsewhere.[4] A 4-mL portion of a 30–200 mM solution in a 12-mm tube was used for the data collection. The free induction decay (FID) signal

(14) Guardalabene, J.; Gulnac, S.; Keder, N.; Shepherd, R. E. *Inorg. Chem.* **1979**, *18*, 22.
(15) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.
(16) Glerup, J.; Josephsen, J.; Michelsen, K.; Pedersen, E.; Schaffer, C. E. *Acta Chem. Scand.* **1970**, *24*, 247.
(17) Radanović, D. J.; Veselinović, D. S.; Grugic, S. A. *Glas. Hem. Drus. Beograd.* **1979**, *44*, 503.
(18) The empirical formula pD = pH + 0.4 was used to correct the measured values. see: Glascok, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188.
(19) Sudmeir, J. L.; Senzel, A. J.; Blackmer, G. L. *Inorg. Chem.* **1971**, *10*, 90.

Table II. Deuteron NMR Spectral Data[a]

complex	δ (ω)[b]	relative integration
sym-cis-$[CrF_2(edda\text{-}\alpha\text{-}d_4)]^-$	−18 (525), −51 (400)	1:1
sym-cis-$[Cr(edda\text{-}\alpha\text{-}d_4)(mal)]^-$[c]	−21 (120), −63 (250)	1:1
sym-cis-$[Cr(edda\text{-}\alpha\text{-}d_4)(ox)]^-$	−29 (280), −68 (400)	1:1
sym-cis-$[Cr(H_2O)_2(edda\text{-}\alpha\text{-}d_4)]^+$	−28 (185), −73 (390)	1:1
sym-cis-$[Cr(acac)(edda\text{-}\alpha\text{-}d_4)]$	−20 (185), −60 (250)	1:1
unsym-cis-$[Cr(H_2O)_2(edda\text{-}\alpha\text{-}d_4)]^+$[d]	−14 (155), −21 (185), −29 (170)	1:1:2
unsym-cis-$[Cr(acac)(edda\text{-}\alpha\text{-}d_4)]$[d]	−14 (215), −24 (155), −76 (400)	2:1:1
$[(Cr(1,2\text{-pdta-}\alpha\text{-}d_8)]^-$[e]	+49 (250), −6 (310), −29 (250), −38 (280), −45 (155), −49 (250)	2:2:1:1:1:1

[a] Data obtained in H_2O at 18 °C unless otherwise indicated. [b] δ = chemical shift with respect to C^2HCl_3; ω = width at half-height in Hz. [c] In 1 mM $HClO_4$. From ref 5. [d] Data obtained at 2 °C. [e] Adjusted to pH 4.7 with 1 mM $HClO_4$. The shifts are slightly different from those in ref 1 due to differences in concentration and ionic strength.

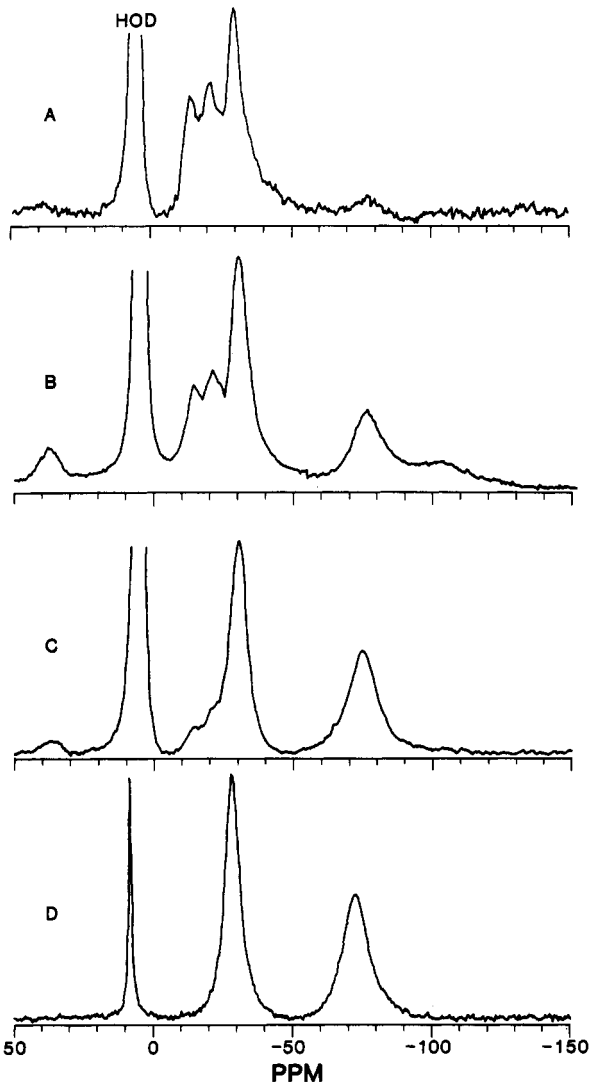


Figure 2. Deuteron NMR spectra of $[Cr(H_2O)_2(edda\text{-}\alpha\text{-}d_4)]^+$: (A) unsym-cis isomer at 2 °C; (B) unsym-cis isomer after 24 h at room temperature; (C) unsym-cis isomer after 7 days at room temperature; (D) sym-cis isomer.

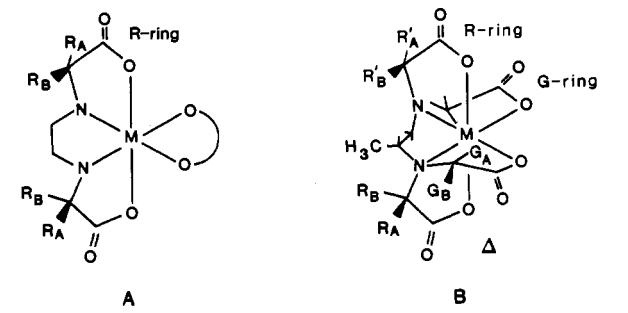


Figure 3. Ring substituent nomenclature for the (A) diaminediacetate complex and the (B) diaminetetraacetate complex.

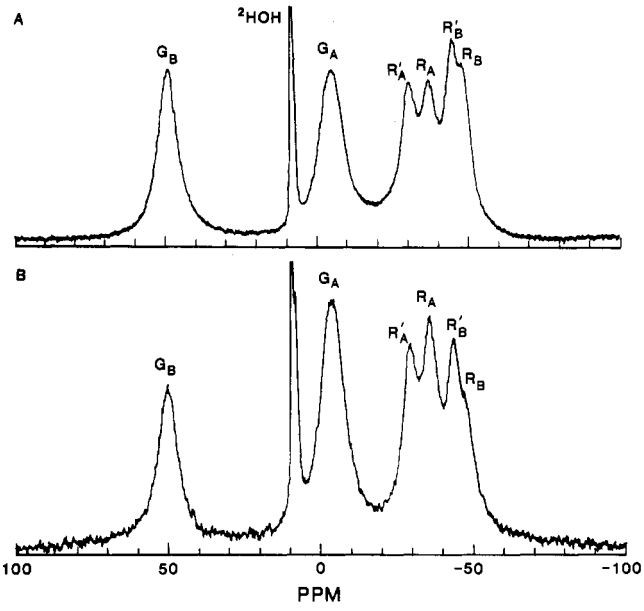


Figure 4. Deuteron NMR spectra of (A) fully deuterated $[Cr(1,2\text{-pdta})]^-$ and (B) preferentially deuterated $[Cr(1,2\text{-pdta})]^-$.

was multiplied by an exponential decay signal before Fourier transformation to improve the signal to noise ratio. This has the effect of broadening the resonances by 5–10 Hz. The spectral region isolated was ±200 ppm with respect to Me_4Si. Integration of overlapping peaks was accomplished by means of a curve-fitting program. An external standard of C^2HCl_3 was assigned a chemical shift of +7.24 ppm. Upfield shifts are defined at (−). NMR data are summarized in Table II and figures 2 and 4.

Results and Discussion

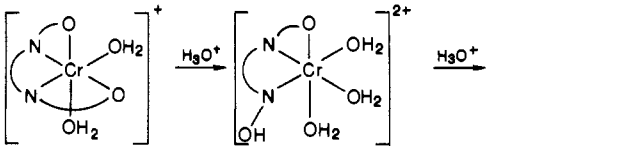
$[Cr(edda)X_2]^n$ Complexes (X = Two Monodentates or One Bidentate). Chelation of edda to Cr(III) is expected to lead to the formation of the sym-cis and unsym-cis isomers but not the trans isomer (Figure 1), as discussed in the Introduction. Electronic absorption spectra were not expected to differentiate conclusively the sym-cis from the unsym-cis isomers for the X_2 = mal, ox, $2H_2O$, and acac complexes since both isomers belong to the general category *cis*-$Cr^{III}N_4O_2$. This expectation is born out for the two cases in which both isomers were isolated (Table I). The absorption maxima for the two isomers of $[Cr(H_2O)_2(edda)]^+$ and $[Cr(acac)(edda)]$ are almost identical. However, the molar absorptivities can be used to make preliminary assignments since the lower symmetry of the unsym-cis isomer would be expected to give rise to a larger ϵ. The data in Table I show that the two isomers of each complex have distinctly different ϵ values. This distinction was the basis for the assignment of the $[Cr(H_2O)_2(edda)]^+$ isomers made by Weyh and Pierce.[10] However, it is clear that the geometry of these isomers and of the remaining complexes where only one isomer was isolated cannot be assigned with certainty by using only the ligand field spectra.

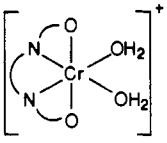
When a polyamino carboxylic acid ligand (e.g., edda, pdda) is deuterated at the acetate proton positions, it becomes possible to distinguish a chemically inequivalent set of geminal deuterons on the chromium complex by ^2H NMR spectroscopy.[1,2,4,20] The sym-cis edda comlexes are expected to give rise to two resonances of equal integration values (C_2 symmetry), and the unsym-cis isomers to four resonances of equal integration values (C_1 symmetry).

Although the trans isomer is not expected to form, it could also give rise to two resonances and make differentiation between a sym-cis and a trans isomer difficult, as was the case for the isomers of $[CrF_2(1,3\text{-pdda})]^-$.[4] The use of a bidentate ligand to complete the coordination sphere of an edda/pdda complex can simplify the problem since formation of the trans isomer is precluded.

In the present study two resonances of equal integration value were observed for the isomer isolated for $[CrF_2(edda)]^-$ and $[Cr(edda)(ox)]^-$ and also for one of the isomers of both $[Cr(H_2O)_2(edda)]^+$ (B-I) and [Cr(acac)(edda)] (C-I). These isomers are assigned the sym-cis configuration (Table II and Figure 2D). Since [Cr(acac)(edda)] cannot form a trans isomer, the isomer that gives two resonances must be the sym-cis isomer. Although the maximum of the first d–d absorption band for $[CrF_2(edda)]^-$ (Table I) is somewhat different from the maxima observed for other *cis(F)*-$Cr(N_2O_2F_2)$ complexes,[4] we assign it the sym-cis configuration by comparison with the NMR data obtained for the other sym-cis isomers in this study (Table II). If this complex had a trans(F) arrangement, a splitting of the first d–d absorption band would also be expected.[4] For the remaining two isomers, $[Cr(H_2O)_2(edda)]^+$ (B-II) and [Cr(acac)(edda)] (C-II), three resonances integrating 1:1:2 and 2:1:1, respectively, were obtained instead of the four resonances expected for an unsymmetrical isomer (Table II). There is thus coincidence in two of the resonances, and these complexes are assigned the unsym-cis configuration.

It is possible to follow the conversion of the less stable unsym-cis isomer to the more stable sym-cis configuration by ^2H NMR. Figure 2 shows a series of ^2H NMR spectra obtained for a solution (30 mM, pH 1.3) of *unsym-cis*-$[Cr(H_2O)_2(edda)]^+$ monitored over a period of 7 days at room temperature. After the solution was allowed to sit 24 h at room temperature, a significant amount of the sym-cis isomer forms, as indicated by the appearance of a resonance at −73 ppm and a broadening of the resonance at −29 ppm (Figure 2B and Table II). The resonances at +39 and −103 ppm are attributed to the presence of an intermediate species formed during the isomerization. A possible explanation is outlined:





The terdentate intermediate is not unreasonable in light of the recent ^2H NMR studies of the solution structure of $[Cr(edta)]^-$ as a function of pH.[2] The $[Cr(edta\text{-}d_8)]^-$ complex was found to undergo major changes in the ^2H NMR spectrum in acidic solution. On the basis of a model study, a quinquedentate structure was proposed where the edta ligand has one "glycinate arm" uncoordinated.[2] No further changes in the ^2H NMR are observed after 7 days (Figure 2C). At equilibrium the sym-cis isomer is clearly the major species present, as indicated by the dominant resonances at −28 and −73 ppm (see reference spectrum in Figure 2D). A small amount of intermediate remains at equilibrium as evidenced by a residual resonance at +39 ppm.[21] The isomer distribution constant (sym-cis/unsym-cis) was calculated to be 4 by curve-fitting analysis of the resonances at −14 and −73 ppm.[22] The equilibrium spectrum could be reproduced by allowing a solution of pure *sym-cis*-$[Cr(H_2O)_2(edda)]^+$ to sit for 1 week at room temperature. The calculated equilibrium value is smaller than that estimated previously.[10]

Table III. Isotopic Exchange Results for *sym-cis*-$[Cr(edda)(mal)]^-$

days heating	pD^{13}	peak ratio[a]	days heating	pD^{13}	peak ratio[a]
1	10.4	1.4	5	10.4	1.7
2	10.4	1.4	6	10.4	2.0
4	10.2	1.3	7	10.4	2.1

[a] Area of resonance at −21 ppm/area of the resonance at −63 ppm (Table II).

Preferential Deuteration of *sym-cis*-$[Cr(edda)(mal)]^-$. The R_A and R_B deuteron (Figure 3A) resonances of this complex have been tentatively assigned by comparison with data obtained for related, preferentially deuterated Cr(III) complexes.[1] The method employed in this study to assign the resonances definitively has been used successfully with analogous Co(III) complexes.[19,23,24] Isotopic exchange of the edda glycinate protons was performed directly on the complex as described in the Experimental Section. Table III gives the ratio of the peak areas for the ^2H NMR spectra of this complex as a function of time. The complex was heated in ^2H_2O at pD 10.2–10.4 over 7 days. It can be seen from the data in Table III that as the heating time increases, the resonance at −21 ppm grows in more rapidly than the resonance at −63 ppm. Thus, the resonance at −21 ppm is R_A, the deuteron more accessible to the solvent (Figure 3A), in agreement with what has been observed for the analogous Co(III) complexes.[19,23,24] These results are also consistent with the assignments made for related Cr(III) complexes.[1]

Complete Assignment of the Deuteron NMR Spectrum of $[Cr(1,2\text{-pdta-}\alpha\text{-}d_8)]^-$. The ^2H NMR spectrum of this complex has been partially assigned.[1] However, specific resonances resulting from the asymmetry of the complex were not assigned. Figure 3B shows the labeling scheme used for this complex. Due to the presence of the methyl group on the amine hydrocarbon "backbone", the complex has C_1 symmetry, and the fully deuterated complex is expected to give rise to as many as eight resonances in the ^2H NMR spectrum. At intermediate pH, a total of six resonances were observed (Figure 4A).[1] Relative integration values demonstrated that accidental degeneracy occurs for two sets of resonances. Through selective isotopic substitution on the analogous complex $[Cr(cdta\text{-}\alpha\text{-}d_8)]^-$, the two degenerate sets of resonances were assigned to the G_A and G_B deuterons (Figures 3 and 4). The R_A and R_B set of deuterons (4 peaks total) were also assigned, but the R_A, R_A' and R_B, R_B' deuterons, resulting from the asymmetry of the corresponding $[Cr(1,2\text{-pdta-}\alpha\text{-}d_8)]^-$ complex (Figure 3B), were not distinguished. By preferentially

(20) Since the line widths observed are at least 2–3 orders of magnitude larger than the ^2H–^2H or ^2H–^1H coupling constants, nuclear spin–spin couplings are not observed. Thus, the spectra behave as though they are zero order, and only one resonance should be observed for each symmetrically distinct deuteron or set of deuterons. See: Harris, R. K.; Mann, B. E. *NMR and The Periodic Table*; Academic: London, 1978; p 107 and references therein.

(21) For the amino carboxylate Cr(III) chelate complexes studied thus far, the only case in which a positive resonance has been observed is when sexadentate ligands (e.g. edta, pdta) are fully coordinated. This resonance has been associated with the in-plane, coordinated glycinate ring (G ring, Figure 1), and it is absent when one of the acetates dissociates.[2] Thus, an alternate but less likely explanation for the observed spectrum of this intermediate is that isomerism of the unsym-cis to the sym-cis isomer produces a small amount of the strained trans isomer, a situation very similar to the in-plane portion of fully coordinated edta. Attempts to chromatographically isolate the intermediate have thus far been unsuccessful.

(22) The Nicolet NT-200 curve-fitting program was used to calculate the peak area of the resonances at −14 ppm (1 deuteron) and −73 ppm (2 deuterons).

(23) Coleman, P. F.; Legg, J. I.; Steel, J. *Inorg. Chem.* **1970**, *9*, 937. Sudmeier, J. L.; Occupati, G. *Inorg. Chem.* **1968**, *7*, 2524.

(24) Terrill, J. B.; Reilley, C. N. *Inorg. Chem.* **1966**, *5*, 1988.

deuterating 1,2-pdta on Co(III), removing the ligand, and then complexing it to Cr(III), we have been able to completely assign the ^2H NMR spectrum of $[Cr(1,2\text{-pdta-}\alpha\text{-}d_8)]^-$.

The different rates of exchange of the four chemically distinct R glycinate protons of $[Co(1,2\text{-pdta})]^-$ have been well documented.[19,24] The order of exchange was found to be $R_A > R_A' > R_B' > R_B$. The G rings do not normally exchange. In this study, $[Co(1,2\text{-pdta})]^-$ was deuterated to the extent that the R_A resonances at 3.4 and 4.1 ppm in the ^1H NMR spectrum began to diminish. We anticipated that the remaining protons at R_A', R_B', and R_B had also partially exchanged at this point since the integration showed that one total deuteron had been incorporated. As noted earlier, the 1,2-pdta ligand is stereospecific.[1] Therefore, preferential ^2H substitution of 1,2-pdta on one metal ion permits specific assignments to be made after the 1,2-pdta is transferred to a new metal ion. The R resonances can be assigned for $[Cr(1,2\text{-pdta})]^-$, as shown in Figure 4, by noting the relative enrichment obtained on Co(III). In addition, transfer of the ligand from one metal ion to another leads to racemization around the nitrogen atoms. This places labels in the G positions as well as the R positions in the same proportion. Thus, the area under the G_A resonance should be equal to the combined areas of the R_A and R_A' resonances, and the area under the G_B resonances should be equal to the combined areas of the R_B and R_B' resonances. This, indeed, was the result obtained from a curve-fitting analysis of the resonances observed.

Summary. Deuteron NMR spectroscopy was used to establish the stereochemistry of a series of Cr(III)-edda complexes. As with most Co(III) complexes, edda was found to favor the sym-cis configuration on Cr(III). In the two instances where an unsym-cis isomer was isolated, the isomer was obtained in small quantities and found to be unstable relative to the sym-cis isomer, as evidenced by ^2H NMR spectroscopy.[9] Preferential deuteration of a sym-cis isomer permitted definitive specific assignments to be made to the geminal deuterons on the glycinate chelate rings. Although specific assignments could not be made for the unsym-cis isomers, efforts to this end led to the complete assignment of all the resonances previously reported for the Cr(III) complex of the related ligand 1,2-pdta.

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Free-Radical Pathways to Alkyl Complexes of a Nickel Tetraaza Macrocycle

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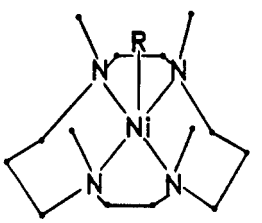
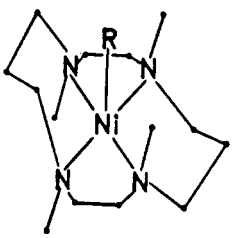
The cationic nickel(I) macrocycle (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), abbreviated *R,S,R,S*-$[Ni(tmc)]^+$, reacts in aqueous, alkaline solutions on the stopped-flow time scale with alkyl halides to form a new series of organonickel complexes. Kinetic data were obtained for a large number of alkyl halides. The trends in the rate constants are benzyl > allyl > secondary > primary > methyl > cyclopropyl, and RI > RBr > RCl. These trends suggest that carbon-centered free radicals R• are produced by a bimolecular reaction between $Ni(tmc)^+$ and RX and are then captured by a second $Ni(tmc)^+$. Further evidence for free-radical involvement comes from cyclization of the radical produced from 6-bromo-1-hexene, from the yields of products in those instances where dimerization of the free radical competes with its capture by $Ni(tmc)^+$, and from the nonreactivity of alkyl tosylates. The organonickel complexes slowly hydrolyze in unimolecular processes to yield hydrocarbon and the nickel(II) complex *R,S,R,S*-$[Ni(tmc)]^{2+}$. The organonickel complexes do not undergo unimolecular homolysis but react with Co(II) macrocycles with a 1:2 stoichiometry to form cobalt-carbon bonds. This reaction most likely occurs not by homolytic displacement but by electron transfer followed by radical capture.

Introduction

Despite an extensive chemistry of organonickel complexes,[1] efforts directed toward alkyls of nickel macrocycles have been relatively limited. Some success was realized[2] in the preparation by Grignard routes of several alkylnickel complexes containing the "tetramethylcyclam" or "tmc" macrocycle. In the series of compounds reported,[2] the chirality at the nitrogen donors defines the stereochemistry[3] as *R,R,S,S*; we abbreviate the formulas of the organometallic compounds as *R,R,S,S*-$[RNi(tmc)]^+$. An alternative route to them, the reaction of alkyl halides with the nickel(I) macrocycle, was shown to proceed by a free-radical mechanism.[4] Previous studies of organonickel macrocycles, both preparative[2] and mechanistic,[4] have concentrated on that isomer. We consider here the nickel(I) complex *R,S,R,S*-$[Ni(tmc)]^+$, the isomer with "four methyls up", which is the other reasonably stable and well-characterized stereoisomer[5,6] in the Ni(tmc) series.



R,S,R,S-[RNi(tmc)]$^+$



R,R,S,S-[RNi(tmc)]$^+$

Interest in this area derives in part from observations that have identified nickel macrocycles as catalysts for the electrochemical

(1) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1974; Vol. I, Chapter IV and references therein.
(2) D'Aniello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1976**, *98*, 1610.
(3) The complex used here is (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetrazacyclotetradecane)nickel(I), which we abbreviate as *R,S,R,S*-$[Ni(tmc)]^+$ or (when it is not confusing) simply as $Ni(tmc)^+$. It has also been referred to in the literature as the trans-I isomer. This complex is an isomer of that we studied previously,[4] *R,R,S,S*-$[Ni(tmc)]^+$, also known as the trans-III form. The nickel(II) complexes do not interconvert in aqueous solution over extended periods of time (weeks or longer), but in the nickel(I) state, a mixture of the two, in an approximate 3:1 ratio in favor of *R,S,R,S*, results when either stands several hours at room temperature.
(4) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713.
(5) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(6) Moore, P.; Sachinidis, J.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1323.

0020-1669/86/1325-3267$01.50/0