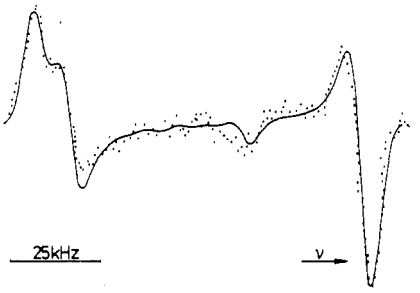

Figure 6. ^{11}B NMR spectrum of BS_2 at 7.02 MHz. The solid line represents the single-site fit listed in Table IV.

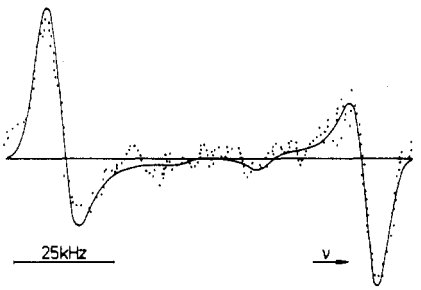

Figure 7. ^{11}B NMR spectrum of BSe_2 at 7.02 MHz. The solid line represents the single-site fit listed in Table IV.

Table IV. Quadrupole Coupling Constants and Asymmetry Parameters in the Subject Compounds Obtained by Computer Simulation

compd	e^2qQ/h, MHz	η	compd	e^2qQ/h, MHz	η
B_2S_3	2.455	0.06	BSe_2	2.070	0.05
BS_2	2.160	0.10			

program of Taylor and Bray.[19] It should be noted here that the fits of Table IV are unique if the discrete site hypothesis[28] is applicable. In the presence of inhomogeneous broadening, however, the spectra observed may also reflect a zero asymmetry parameter and a distribution of e^2qQ.[29] Owing to this uncertainty, the significance of the η values remains, as in many ^{11}B solid-state applications, an open question and shall be omitted in the subsequent discussion. On the other hand, interesting information about bond properties is available from the e^2qQ/h data. Electric quadrupole coupling constants in boron compounds are frequently interpreted in terms of the Townes-Dailey method,[30] which considers the p-electron imbalance at the boron atoms as the main contribution to the electric field gradient. In the case of sp^2 hybridization e^2qQ/h (^{11}B) = 5.39 MHz has been predicted[31] and subsequently almost quantitatively verified in alkylboron compounds.[32] In most triangular substances, bond polarity effects as well as back-donation of nonbonding substituent electrons into the empty boron p_z orbital lead to experimental values about half as large as those theoretically predicted. Since the above effects are difficult to separate, only quadrupole couplings should be compared of compounds that have very similar bond polarities. This condition is certainly fulfilled for the compounds that are the subject of the present investigation. The aforementioned analysis of quadrupole coupling data indicates that the boron-chalcogen bonds in BS_2 and BSe_2 have significantly higher π character than in B_2S_3. This is probably due to the fact that within the five-membered rings the constituents of the S-S and Se-Se bridges supply significantly large amounts of electron density to the boron atom. This kind of behavior has been also revealed by CNDO/2 studies of B_8S_{16}[33] as well as of dihalotrithiadiborolanes[34] and has led to speculations about the possibility of electron delocalization as it is, for instance, observed in borazenes. While, e.g. for 2,4,6-trichloroborazene, the electric quadrupole constant vanishes, thus indicating full π character of the B-N bonds,[35] it is clear from the data in the present study that no appreciable electron delocalization is possible in the BS_2 and BSe_2 trichalcogenadiborolane rings. This result agrees well with conclusions drawn from ^{11}B NMR chemical shift data on the dihalotrithiadiborolanes,[36] which contain the same five-membered rings. Nevertheless, the present study indicates that ^{11}B solid-state NMR can serve as a sensitive measure of bonding characteristics in boron chalcogenide systems. This makes it a valuable tool in order to design appropriate compounds in which the electronic features can be correlated with structural properties.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for substantial support of our work.

Registry No. BS_2, 12045-25-9; BSe_2, 12505-78-1; B, 7440-42-8; S, 7704-34-9; Se, 7782-49-2; Te, 13494-80-9; ^{11}B, 14798-13-1.

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Assignment of the Deuteron NMR Spectra of Chromium(III) Complexes with edta and Related Ligands

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The deuteron NMR spectra of $[Cr(cdta)]^-$, $[Cr(pdta)]^-$, $[Cr(edta)]^-$, and $[Cr(edda)(mal)]^-$ have been assigned by using stereospecific isotopic substitution of cdta and pdta coordinated to substitution-inert Cr(III) and Co(III). Deuteron NMR spectroscopy demonstrates that the Cr(III) complexes of cdta and pdta are structurally similar to $[Cr(edta)]^-$ whose structure was determined to be sexidentate at intermediate pHs in a previous study. The present study also provides the first example of stereospecific isotopic substitution to be carried out on Cr(III).

Introduction

Until recently it was not thought possible to do NMR studies on the paramagnetic complexes of substitution-inert chromium(III). We have demonstrated that deuteron NMR spectroscopy can be used to characterize the solution structures of simple Cr(III) complexes,[2,3] and more recently this method has been extended

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Table I. Materials and Reaction Conditions for Selective Deuteration of H_4cdta

total deuterium[a]	vol ^2HCl, mL	time, h	yield, g (%)	extent of deuteration, % H_A	H_B
41	0.70	3	2.8 (57)	72	8
76	0.70	6	3.2 (65)	98	54
97	1.40	16	1.5 (30)	100	94

[a] This is the total incorporation of deuterium into two of the ligand arms.

to more complex Cr(III) chelates of edta[4] and medtra.[1] To date, only a few Cr(III) complexes have been studied by ^2H NMR spectroscopy, but the technique is already showing great promise for the structural characterization of Cr(III) amine carboxylate complexes in solution. Structural assignments have been made on the basis of the symmetry of the complexes without assignment of the resonances to specific deuterons. The objective of this study was to use the property of sterespecific isotopic substitution of chelated amine carboxylate ligands to assign the resonances in the spectra of these compounds. The knowledge that a resonance of a given chemical shift is a product of a particular structural feature would add a great deal to our ability to characterize Cr(III) complexes in solution. The results of these studies also confirm the structures previously reported for $[Cr(edta)]^{-1}$ and *sym-cis*-$K[Cr(edda)(mal)]\cdot 3H_2O$[2] and are used to assign the structures to the analogues $[Cr(cdta)]^-$ and $[Cr(pdta)]^-$.

Experimental Section

Materials. Reagent grade H_4cdta and H_4pdta were purchased from Sigma Chemical Co. and used without further purification.

Synthesis. Selectively Deuterated H_4cdta-α-d_4.[4] This ligand was prepared with a total deuterium incorporation of 41%, 76%, and 97% by a modification of a previously reported method.[5] A 7-g portion of $K[Co(cdta)]\cdot 3H_2O$[6] was dissolved in 25 mL of ^2H_2O. Concentrated ^2HCl was added, and the solutions were heated on a steam bath (Table I). After the required time the p^{2}H was adjusted to 9.4 with solid K_2CO_3, 6.0 g of KCN was added, and the solution was heated to 60 °C for 10 min. *In a hood*, the p^{2}H was then adjusted to 2 with concentrated HNO_3, the solution was cooled in ice, and the pinkish powder was filtered and washed with ethanol. The powder was suspended in 30 mL of water, 1 M NaOH was added dropwise until the ligand had completely dissolved, and then the pH was adjusted to 3.5 with 1 M HNO_3. The resulting white powder was filtered and washed with ethanol and ether. Proton NMR was used to determine the degree of deuterium enrichment (Table I).

Selectively Deuterated H_4pdta-α-d_3. This ligand was prepared with a total deuterium incorporation of 33% by the method of Terrill and Reilley.[5] The yield was 2.1 g (41%).

$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot {}^3/_2H_2O$. This compound was prepared by methods differing from those previously reported.[7] In a typical preparation, a solution of H_4cdta-α-d_4 (2.0 g) and Na_2CO_3 (1.52 g) dissolved in 10 mL of H_2O was added to a solution of $Cr(OAc)_3\cdot 6H_2O$ (1.85 g) in 10 mL of H_2O. The solution was heated on a steam bath in a covered beaker for 1.5 h, after which the cover was removed and the volume was reduced to 7 mL. The complex crystallized as it cooled and was then filtered and washed with ethanol and ether. The yields ranged from 60 to 75%.

$Na[Ca(pdta)]\cdot {}^1/_2H_2O$. This complex was prepared by methods similar to those used previously.[6,8] A 19-g sample of H_4pdta and 16.5 g of $CrCl_3\cdot 6H_2O$ were suspended in 125 mL of water, and Na_2CO_3 was added until all of the ligand dissolved (pH 1). The solution was heated on a steam bath for 8 h while the volume was maintained at 50 mL. Concentrated HNO_3 (10 mL) was added, and the complex was precipitated by addition of ethanol. The product was recrystallized from a 0.1 M solution of NaOAc adjusted to pH 4.0 with HCl and then from a 75/15/5 methanol/ethanol/water solution. The yield was 12 g (50%).

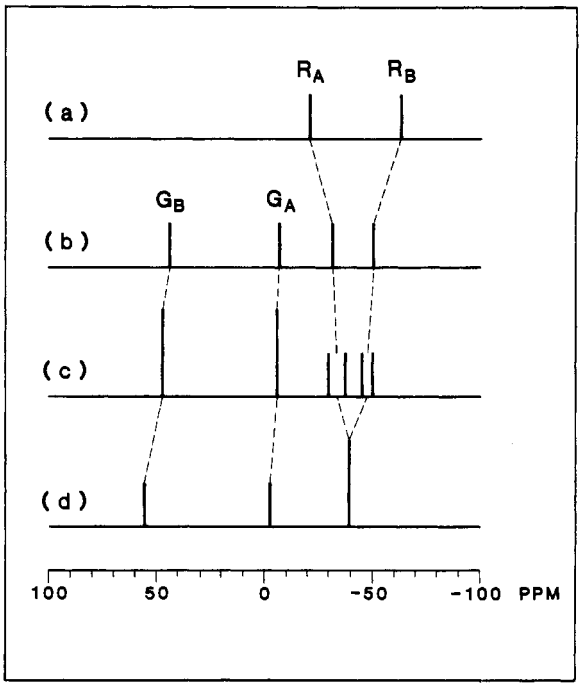

Figure 1. Schematic representation of the deuteron NMR spectra: (a) $[Cr(edda\text{-}\alpha\text{-}d_4)(mal)]^-$; (b) $[Cr(edta\text{-}\alpha\text{-}d_8)]^-$; (c) $[Cr(pdta\text{-}\alpha\text{-}d_8)]^-$; (d) $[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$ (equivalent to the α-d_8 complex).

$Na[Cr(pdta\text{-}\alpha\text{-}d_8)]\cdot H_2O$. A 2-g sample of $Na[Cr(pdta)]\cdot {}^1/_2H_2O$ was dissolved in 40 mL of ^2H_2O and the p^{2}H adjusted to 10.6 with K_2CO_3. The solution was heated on a steam bath for 30 h and cooled and the p^{2}H readjusted to 4.1 with glacial acetic acid. The complex was precipitated with 800 mL of ethanol, filtered, and washed with ethanol and ether. The product was then recrystallized from a solution of 80/20 ethanol/water. The yield was 0.4 g (20%).

$Na[Cr(pdta\text{-}\alpha\text{-}d_3)]\cdot {}^5/_2H_2O$. This complex was prepared by a method similar to that used for the undeuterated complex. H_4pdta-α-d_3 (1.50 g) and $CrCl_3\cdot 6H_2O$ (1.31 g) were suspended in 15 mL of water, and then Na_2CO_3 was added until all of the ligand had dissolved (pH 1). The solution was heated on a steam bath for 8 h, maintaining a volume of 5 mL. Concentrated HNO_3 (0.9 mL) was added, and the complex was precipitated by addition of ethanol. The yield was 0.6 g (32%).

Reprotonation of $Na[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$. $K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot {}^3/_2H_2O$ (0.3 g) was dissolved in 5 mL of water, and the pH was adjusted to 7.5 with 10 mM NaOH. The solution was placed in a 12-mm NMR tube and heated at 75 °C. ^2H NMR spectra were run periodically to determine which resonances were losing intensity.

Physical Measurements. Analysis. Carbon, hydrogen, and nitrogen analyses were obtained from Canadian Microanalytical Service Ltd., Vancouver, B.C., Canada, the CH&N Analytical Facility, University of Idaho, Moscow, ID, and Galbraith Laboratories, Inc., Knoxville, TN. Chromium was determined by spectrophotometric analysis of CrO_4^{2-} at 372 nm after oxidation of the complexes with hot alkaline hydrogen peroxide.[9] Analyses for the compounds are reported in Table II.

UV–Visible Spectra. UV–visible spectra were recorded on a Varian/Cary 219 spectrophotometer and are reported in Table III.

NMR Spectra. The 31-MHz ^2H NMR spectra were recorded at 20 °C on a Nicolet NT-200 spectrometer operating at a field of 4.7 T. A 5-mL portion of 100–200 mM solutions in 12-mm tubes was used in the data collection. The spectral region isolated was ±200 ppm with respect to Me_4Si. An external standard of C^2HCl_3 was assigned a chemical shift of 7.24 ppm. Note that downfield shifts are defined as positive. NMR data are summarized in Tables IV and V in Figures 1–3 and 5.

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(4) Abbreviations: cdta = 1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetate; edta = ethylenediamine-*N,N,N',N'*-tetraacetate; pdta = 1,2-propanediamine-*N,N,N',N'*-tetraacetate; medtra = *N*-methylethylenediamine-*N,N',N'*-triacetate; edda = ethylenediamine-*N,N'*-diacetate; OAc = acetate; mal = malonate. The notation α-d_n refers to the deuteration of *n* positions on the methylene carbons α to the carboxylates. Thus, cdta-α-d_4 signifies that four of the eight α-methylene hydrogens in cdta have been partially or completely replaced by deuterium.
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Table II. Elemental Analysis

complex	% C		% H		% N		% Cr	
	calcd	found	calcd	found	calcd	found	calcd	found
$K[Cr(cdta)]\cdot{}^3/_2H_2O$	36.51	36.85	4.61	4.69	6.09	6.12	11.3	11.6
$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot{}^3/_2H_2O$[a]	36.36	36.04			6.03	5.78	11.2	10.9
$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot{}^3/_2H_2O$[b]	36.36	35.95			6.06	6.04	11.2	11.4
$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot{}^3/_2H_2O$[c]	36.36	36.41			6.06	6.12	11.2	10.9
$Na[Cr(pdta)]\cdot{}^1/_2H_2O$	34.20	34.45	3.92	3.79	7.25	7.17	13.5	13.2
$Na[Cr(pdta\text{-}\alpha\text{-}d_8)]\cdot H_2O$	32.76	32.68			6.95	6.74	12.9	12.7
$Na[Cr(pdta\text{-}\alpha\text{-}d_3)]\cdot{}^5/_2H_2O$	31.06	30.77			6.59	6.62		

[a] 97% ^2H incorporation. [b] 76% ^2H incorporation. [c] 41% ^2H incorporation.

Table III. UV-Visible Spectra in Solution

complex	band posn[a] (ϵ)		pH
	I	II	
$K[Cr(cdta)]\cdot{}^3/_2H_2O$	542 (214)	391 (105)	5.5
$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot{}^3/_2H_2O$[b]	542 (211)	391 (103)	5.5
$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot{}^3/_2H_2O$[c]	542 (211)	391 (103)	5.5
$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot{}^3/_2H_2O$[d]	541 (208)	390 (100)	5.5
$Na[Cr(cdta)]\cdot 4H_2O$[7]	548 (215)	394 (103)	*e*
$Na[Cr(pdta)]\cdot{}^1/_2H_2O$	541 (191)	391 (105)	6.2
$Na[Cr(pdta\text{-}\alpha\text{-}d_8)]\cdot H_2O$	541 (189)	391 (101)	6.2
$Na[Cr(pdta\text{-}\alpha\text{-}d_3)]\cdot{}^5/_2H_2O$	541 (187)	391 (106)	6.2
$Na[Cr(pdta)]\cdot 2H_2O$[8]	540 (181)	389 (95)	6.2

[a] In n; ϵ in M^{-1} cm^{-1}. [b] 97% ^2H incorporation. [c] 76% ^2H incorporation. [d] 41% ^2H incorporation. [e] Reported as pH independent from pH 3.3 to 7.7.

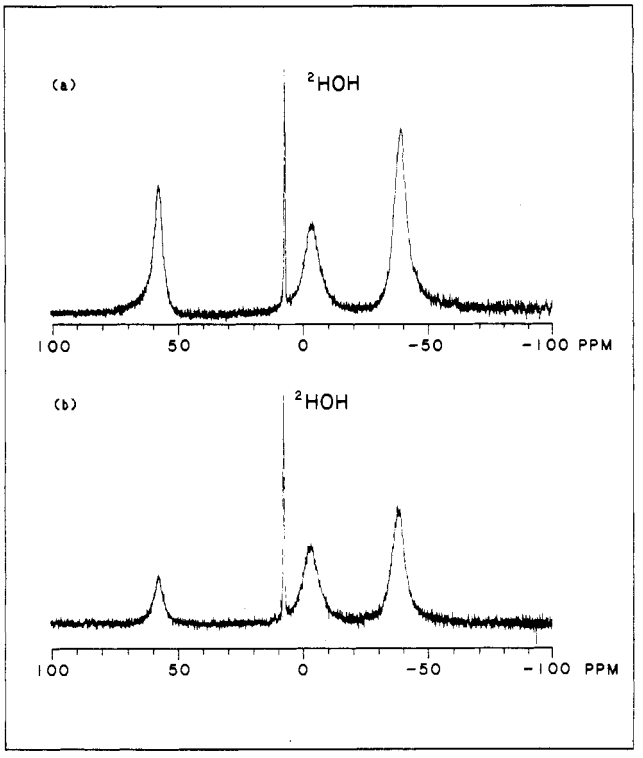

Figure 2. Deuteron NMR spectrum of $[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$ at pH 5.5: (a) 97% incorporation; (b) 41% incorporation.

Results and Discussion

Structural Assignments. A schematic representation of the spectra of $[Cr(edda)(mal)]^-$,[4] $[Cr(edta)]^-$, $[Cr(pdta)]^-$, and $[Cr(cdta)]^-$ is shown in Figure 1 for easy reference.

$[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$.[10] When the sexidenatate ligands cdta or edta are fully coordinated to a substitution-inert metal ion, there are two sets of equivalent acetate rings related by symmetry (C_2 rotation axis), each with two inequivalent protons[11] (Figure 4).

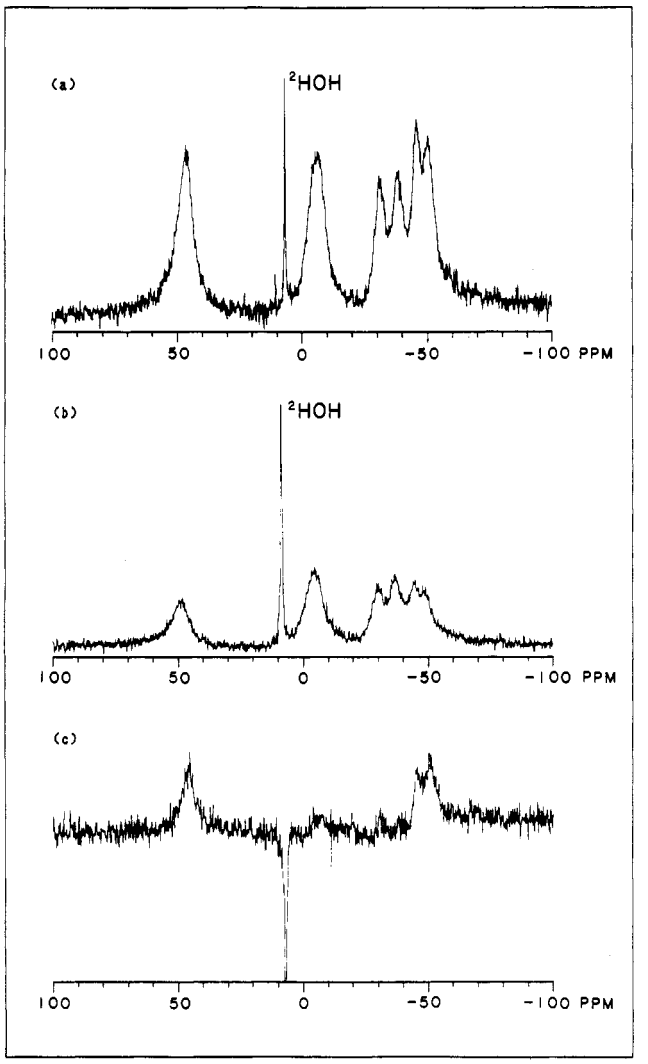

Figure 3. pH 4.0 dueteron NMR spectra: (a) $[Cr(ptdta\text{-}\alpha\text{-}d_8)]^-$; (b) $[Cr(pdta\text{-}\alpha\text{-}d_3)]^-$; (c) difference spectrum of a and b.

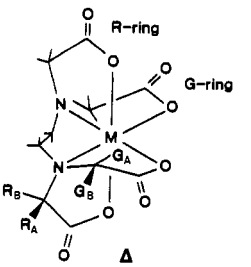

Figure 4. Ring and substituent nomenclature for a sexidentate diamine tetraacetate complex.

Thus, the sexidentate complexes of these ligands are expected to show four resonances of equal intensity as is observed for $[Cr(edta)]^-$[1,12] (Figure 1b). The ^2H NMR spectrum of fully deu-

(10) This complex is equivalent to $[Cr(cdta\text{-}\alpha\text{-}d_8)]^-$, as will be discussed in a subsequent section.
(11) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549.

Table IV. Deuteron NMR Spectra

peak posn[a] (integration)					pH
		$K[Cr(cdta\text{-}\alpha\text{-}d_4)]\cdot 3/2H_2O$[b]			
57 (1)	−3 (1)	−39 (2)			4.0
57 (1)	−3 (1)	−39 (2)			6.3
19 (1)	−4 (2)	−36 (1)			10.6
		$Na[Cr(pdta\text{-}\alpha\text{-}d_8)]\cdot H_2O$			
47 (2)	−6 (2)	−30 (1)	−38 (1)	−45 (1)	−50 (1)	4.0
41 (2)	−7 (2)	−28 (1)	−37 (1)	−40 (1)	−49 (1)	7.0
	−10 (5)	−16 (1)	−34 (1)		−43 (1)	10.0
		$H[Cr(edta\text{-}\alpha\text{-}d_8)]\cdot H_2O$[1]			
44 (1)	−7 (1)	−32 (1)			−50 (1)	6.3
		$K[Cr(edda\text{-}\alpha\text{-}d_4)(mal)]\cdot 3H_2O$[2]			
		−21 (1)			−63 (1)	c

[a] In ppm relative to Me_4Si. [b] Equivalent to the α-d_8 complex. [c] The spectrum of the compound dissolved in H_2O; pH not measured.

Table V. Reprotonation Spectrum of $[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$ [a]

heating time, h	rel peak area, % 57 ppm	−3 ppm	−39 ppm	^{2}HOH
0	23	22	51	3
32	24	27	18	30
56	21	25	9	45

[a] 97% ^{2}H incorporation.

terated $[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$ at several pHs is given in Table IV, and the spectrum at pH 5.5 is shown in Figure 2a. The presence of three lines with relative integrations of 1:1:2 (two of the four expected resonances are accidentally coincident) is consistent with a complex having C_2 symmetry. It is therefore reasonable to conclude that cdta forms a sexidentate complex with Cr(III) below pH 9. The dependence of the spectrum on pH is small below pH 9, but at higher pHs the resonance at 57 ppm shifts upfield. This behavior is consistent with the spectral changes observed for $[Cr(edta)]^-$ at high pH where dissociation of a G ring (Figure 4) occurs to give a quinquedentate complex.[1] The pH range in which the sexidentate complex is stable is somewhat larger for $[Cr(cdta)]^-$ than for $[Cr(edta)]^-$. For instance, at pH 7.5 sexidentate $[Cr(cdta)]^-$ is still the predominant species in solution, whereas a solution of the Cr–edta complex contains about 50% of the quinquedentate species.[1]

$[Cr(pdta\text{-}\alpha\text{-}d_8)]^-$. The spectrum of $[Cr(pdta)]^-$ as a function of pH is also quite similar to that of $[Cr(edta)]^-$[1] (Table IV; Figure 3a), although it is somewhat more complex. When a methyl group is attached to the ethylene backbone of $[Cr(edta)]^-$, it removes the C_2 symmetry of the complex. This small perturbation could split the four resonances observed in the spectrum of $[Cr(edta)]^-$ into as many as eight resonances in the spectrum of the analogue $[Cr(pdta)]^-$. Comparison of the spectrum of $[Cr(pdta)]^-$ at pH 4.0 to the spectrum of $[Cr(edta)]^-$ at pH 6.3 (Table IV; Figure 1) shows that this small perturbation is in fact sufficient to split the two upfield resonances into four and produce a six-line spectrum for the former. The Gaussian line shape of the resonance at −7 ppm (Figure 3a) suggests the presence of two unresolved peaks, but the resonance of 47 ppm is apparently unaffected. Thus, it is reasonable to assign $[Cr(pdta)]^-$ a sexidentate structure at this pH. The observed integration values (Table IV) substantiate this conclusion. At pH 7.0, the spectrum of this complex is essentially unchanged and the sexidentate structure is maintained.

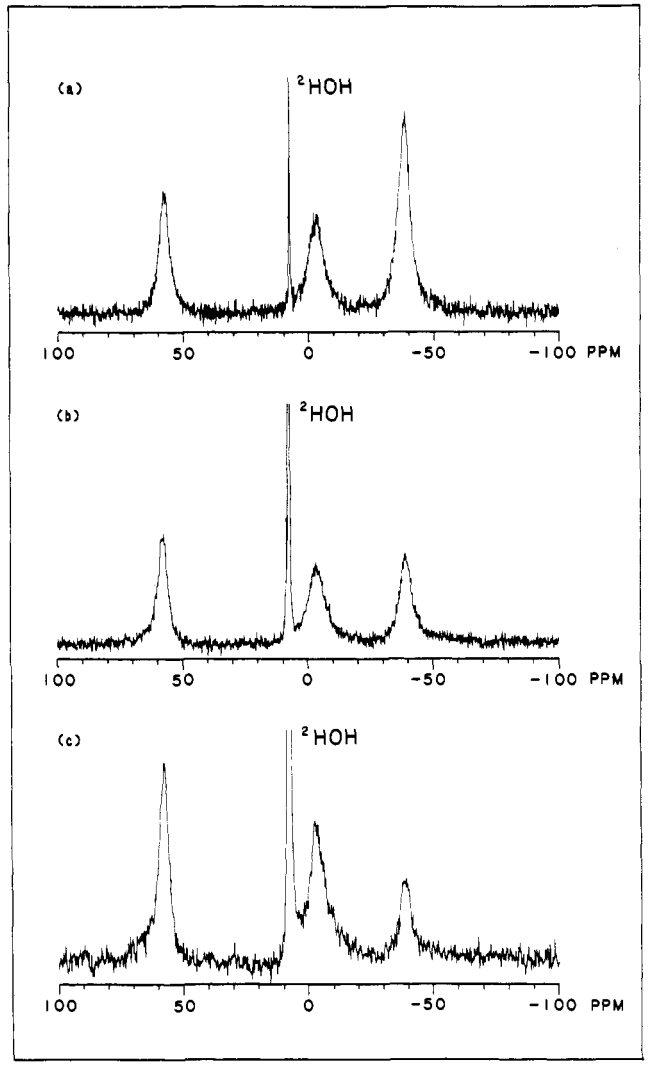

Figure 5. Reprotonation spectrum of $[Cr(cdta\text{-}\alpha\text{-}d_4)]^-$ at pH 7.5: (a) T = 0; (b) T = 32 h; (c) T = 56 h.

As the pH is raised to 10, the spectrum changes significantly, increasing in complexity in much the same way that the spectrum of $[Cr(edta)]^-$ changes at high pH (Table IV) and the complex is probably quinquedentate.

In summary, the ^{2}H NMR data support a sexidentate structure for the Cr(III) complexes of cdta and pdta at intermediate pHs as was found for $[Cr(edta)]^-$ (a structure not commonly accepted for the edta complex in previous studies),[1] but the sexidentate structure of the two former complexes is maintained over a wider pH range. Confirmation of these assignments is obtained from the selective isotopic substitution studies discussed below.

Stereochemistry. To understand how selective deuteration on the chelated acetate rings can be used to specifically assign resonances, it is necessary to review the interrelationship between the ring stereochemistry and the methylene hydrogens (deuterons) on the rings. The nomenclature to be used is that developed by Hoard and co-workers[11] (Figure 4). There are three cases to consider: (a) If the G and R rings belonging to a given nitrogen of $[Cr(edta)]^-$ are interchanged (racemization about the nitrogen) without racemization of the complex, then the R_A position would become G_A and the R_B position would become G_B etc. (b) If the complex undergoes a Δ to Λ conversion[13] (racemization about both the metal ion and the nitrogen), then the R_A position would become G_B and the R_B position would become G_A etc. (c) If the ligand is completely removed from the metal ion and then allowed to

(12) Since the observed line widths are 2–3 orders of magnitude larger than the ^{2}H–^{2}H or ^{2}H–^{1}H coupling constants, nuclear spin–spin coupling is not observed and the spectra behave as though they are zero order. As a consequence, one resonance should be observed for each symmetrically distinct deuteron or set of deuterons. See: Harris, R. K.; Mann, B. E. In "NMR and the Periodic Table"; Academic Press: London, 1978; p 107 and references therein.

(13) For absolute configuration nomenclature, see: *Inorg. Chem.* **1970**, 9, 1. See also: Legg, J. I.; Douglas, B. E. *J. Am. Chem. Soc.* **1966**, *88*, 2697.

recoordinate, all of the positions would be scrambled since both Δ to Λ isomerization and racemization around the nitrogen would occur.

When a substituent group such as a methyl (pdta) or cyclohexyl (cdta) is added to the ethylene backbone, the ligand itself becomes optically active. These substituent groups also impose a steric restriction such that (*R*)-pdta and (*R,R*)-cdta form the Δ isomer almost exclusively when fully coordinated to Co(III) or Cr(III)[5,11,14] (the (*S*)-pdta and (*S,S*)-cdta form the Λ isomer and *meso*-cdta cannot form a sexidentate chelate) (Figure 4). It can be seen that adding these substituent groups allows G,R ring interchane to occur (case a), but a change in absolute configuration about the metal ion (case b), is not possible. This stereochemical restriction when combined with selective deuteration of the ligands makes it possible to distinguish all of the C-^{2}H positions (A,B) on the acetate arms in the ^{2}H NMR spectra as will be shown in the following section. The stereospecific properties just summarized for these ligands have been used with considerable success to make assignments in the ^{1}H NMR spectra for the corresponding Co(III) complexes.[15]

Selective Deuteration of the Ligands. In order for the methylene groups on the chelated acetate rings of a metal complex to exchange deuterons for protons, they must be able to assume a planar conformation to accommodate the sp^2 carbon of the enolate that is thought to be formed during the reaction.[16] The chelate rings in metal complexes, however, tend to be puckered. In edta-like comlexes (Figure 4), the puckering of the R rings is slight and they are able to assume a planar conformation easily, but the G rings, which are severely puckered and strained, cannot.[11] Also, one of the protons on the R ring acetate methylenes is canted into the complex (R_B) and the other proton is canted out (R_A) (Figure 4). Thus, the "outside" (R_A) protons are more exposed to the surrounding medium and will exchange more rapidly. The methyl group on the ethylene backbone of pdta and the methylenes at the 3- and 6-positions of the cyclohexane ring in the cdta backbone tend to block the "inside" (R_B) protons, which further reduces their exposure to the surrounding environment and slows their rate of exchange relative to R_A.[5] In several studies investigating the exchange of deuterium for protium on the acetate arms of multidentate Co(III) complexes, it has been shown that deuterium exchange takes place predominantly on the R rings and that H_A exchanges at a greater rate than H_B.[5,17] This behavior is especially true for [Co(cdta)]$^-$ and [Co(pdta)]$^-$ where H_B is also blocked by substituents attached to the backbone.[5] In addition, in the latter complex, H_B on the R ring adjacent to the methyl substituent was found to exchange more slowly than the H_B proton on the R ring opposite to the methyl substituent due to steric interference from the methylene protons.

Since the exchange at the R_A position is somewhat faster than at the R_B position, careful control of the reaction conditions yields a product for which the major component has deuterium substituted predominantly at R_A with a much smaller incorporation at R_B (Figure 6). Thus, in a molecule that has been selectively deuterated, a new center of chirality is introduced into the ligand at the acetate methylenes. For (*R,R*)-cdta and (*R*)-pdta, which form the Δ isomer on metal ion coordination, the absolute configuration around the selectively deuterated carbons becomes *S* as illustrated in Figure 6. This selectivity is very important because on removal of the ligand from the metal ion the acetate methylenes (which are now chiral) *retain their absolute configuration with respect to the absolute configuration of the ligand backbone.* Replacing the protons at the R_A positions of [Co(pdta)]$^-$ and

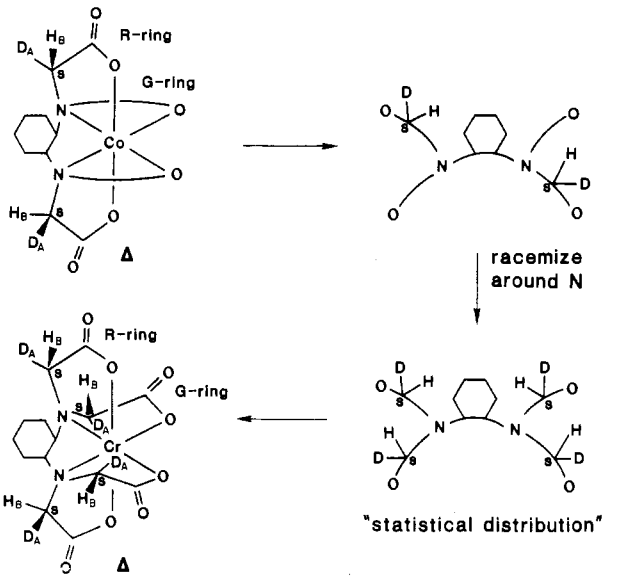

Figure 6. Outline of the selective deuterium (D) labeling of [Cr(cdta-α-d_4)]$^-$.

[Co(cdta)]$^-$ with deuteron followed by removal of the ligand (with concomitant racemization about the nitrogens) and subsequent recoordination gives rise to a complex that has one deuteron stereospecifically substituted on each methylene of the four acetate arms as illustrated for the cdta complex in Figure 6. When the ligand is recoordinated to Cr(III), it assumes the same absolute configuration as when it was originally coordinated to Co(III), and the deuterium that was in the R_A position in the Co(III) complex is again at the R_A position in the Cr(III) complex. The racemization about the nitrogen leads to the presence of deuterium at the G_A positions, but there is *no* conformation that will ever interchange the A and B positions. This behavior makes it possible to assign all the resonances in a ^{2}H NMR spectrum to either a type A or type B position.

Reprotonation of Deuterated Ligands. The reprotonation of a deuterated ligand complex of Cr(III) is identical in concept with the deuteration of the corresponding Co(III) complex. Under controlled conditions it should be possible to selectively reprotonate the ligand predominantly at the R_A position. This allows the G and R positions of type A to be distinguished. If protonation is continued for a long enough period, the R_B position will begin to reprotonate and it is then possible to distinguish R_A and R_B from $G_{A,B}$. This information together with the information obtained from the selective deuteration experiments permits unambiguous assignment of all resonances as outlined below.

Spectral Assignments. [Cr(cdta-α-d_4)]$^-$. The spectrum of this compound with various degrees of deuterium incorporation into the ligand is shown in Figure 2. In both cases, the G_A and R_A positions are nearly saturated with deuterium (Table I), and what is observed in the spectra are the G_B and R_B resonances growing in intensity as the incorporation of deuterium into the ligand increases. On the basis of the intensities of these resonances, the peak at 57 ppm is assigned to either G_B or R_B, the peak at −3 ppm as either G_A or R_A, and the peak at −39 ppm as the sum of either G_A, G_B; G_A, R_A; G_A, R_B; G_B, R_A; G_B, R_B; or R_A, R_B. It is clear from the results of the reprotonation experiment (Figure 5; Table V) that selective reprotonation occurs. The resonances at 57 and −3 ppm retain their intensity as compared to the total deuterium in the spectrum (including the solvent peak) even after 56 h of heating in H_2O at pH 7.5. On the other hand, the resonance at −39 ppm loses about 65% of its intensity after 32 h and over 80% after 56 h. The only reasonable explanation for this phenomenon is that the deuteron in the R_A position reprotonates first followed by the deuteron at R_B as explained earlier. Therefore, the peak at −39 ppm is the sum of R_A and R_B, and the peaks at 57 and −3 ppm must be G_B and G_A, respectively. This behavior is analogous to the behavior of [Co(cdta)]$^-$.[5] It is also consistent with our previous observation that the downfield resonance of

(14) Koine, N.; Tanigaki, T. *Chem. Lett.* **1983**, 785.
(15) Hawkins, C. J. "Absolute Configuration of Metal Complexes"; Wiley: New York, 1971.
(16) Keyes, W. E.; Caputo, R. E.; Willett, R. D.; Legg J. I. *J. Am. Chem Soc.* **1976**, *98*, 6939. Keyes, W. E.; Legg J. I. *J. Am. Chem. Soc.* **1976**, *98*, 4970. Sudmeier, J. L.; Occupati, G. *Inorg. Chem.* **1968**, *7*, 2524. Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133.
(17) Denhart, C. A.; Spoelhof, G. D.; Swartz, T. A.; Williams, D. H. *Inorg. Chem.* **1975**, *14*, 2948.

$[Cr(edta)]^-$ is probably associated with a G ring since it was present only at intermediate pHs where the complex is sexidentate.[1] As the pH is raised, one of the G rings is displaced by a water molecule (or hydroxide ion), and this resonance shifts to high field.

If the acetate arms were scrambling about the nitrogen atoms during the reprotonation process, the R_A position would be interchanged with the G_A position and decreases in intensity of all type A peaks should be observed simultaneously. Scrambling, however does not occur since the peak at −3 ppm (which is also type A) does not lose intensity with time. Another possible explanation for the spectral behavior is that the complex is undergoing Δ to Λ racemization. This would interchange the R_A and G_B positions, which could account for the intensities observed. Racemization should not occur in a sexidentate complex of pdta or cdta, however, since the added prosthetic group on the backbone would be forced to assume a conformation that is very strained,[5,14] and this mechanism of substitution can also be ruled out.

$[Cr(pdta\text{-}\alpha\text{-}d_n)]^-$. The spectrum of this compound with various degrees of deuterium incorporation into the ligand is shown in Figure 3a,b. The situation for the partially deuterated complex of pdta is very similar to that of the complex of cdta but somewhat more complicated. As the extent of deuteration of the ligand increases, so do the intensities of the resonances at 47 (2), −45, and −50 ppm (Figure 3c). As with the spectrum of $[Cr(cdta)]^-$, these resonances are assigned as some combination of G_B, G_B', R_B, and R_B' and the resonances at −6 (2), −30, and −38 ppm are then a combination of G_A, G_A', R_A, and R_A'. The prime recognizes that the deuterons on the acetates that are on the same side of the ligand as the methyl group are inequivalent to the acetates on the other side of the ligand.[18] By analogy to the spectrum of $[Cr(cdta)]^-$, the resonance at 47 ppm is assigned as the sum of G_B and G_B', the resonance at −6 ppm is assigned as the sum of G_A and G_A', and the resonances at −30 and −38 ppm are assigned as R_A and R_A' while the resonances at −45 and −50 ppm are assigned as R_B and R_B'.

$[Cr(edta\text{-}\alpha\text{-}d_8)]^-$. The spectrum of this complex,[1] Table IV and Figure 1, is assigned by comparison with the previous complexes. The resonances at 44 and −7 ppm are assigned as G_B and G_A respectively while the resonances at −32 and −50 ppm are assigned to R_A and R_B respectively.

***sym-cis*-$[Cr(edda\text{-}\alpha\text{-}d_4)(mal)]^-$.** In the spectra of $[Cr(pdta)]^-$ and $[Cr(edta)]^-$ it is seen that the R_B resonance is shifted to higher fields than R_A. On this basis the resonance at higher field in the spectrum of *sym-cis*-$[Cr(edda)(mal)]^-$[2] (Table IV; Figure 1) is assigned as R_B and the resonance at lower field as R_A.

Trends in Chemical Shifts

There appears to be a correlation between the chemical shift of the R ring resonances and the flexibility of the ligand backbone (Table IV; Figure 1).[19] Thus, $[Cr(edda)(mal)]^-$, which has the most flexible backbone, has the largest chemical shift difference between the R_A and R_B resonances while $[Cr(cdta)]^-$, which has the least flexible backbone, shows no detectable difference in chemical shift for these resonances. The complexes of edta and pdta are intermediate with $[Cr(pdta)]^-$, showing a somewhat smaller chemical shift difference (with respect to the center of gravity of R_A, R_A' and R_B, R_B'). It is also observed that the chemical shift of the G_B resonance of $[Cr(cdta)]^-$ is greater than that of $[Cr(pdta)]^-$, which is about equal to the case of $[Cr(edta)]^-$. In all the sexidentate complexes studied so far, the G_B resonance shows a large downfield shift. When the G ring dissociates at high (or low) pH, this downfield resonance disappears. Dissociation of one G ring relaxes the strained ring system present in the sexidentate complex (including the remaining G ring), which could account for the change in chemical shift.

Summary

The ^2H NMR data support a sexidentate structure for the Cr(III) complexes of cdta and pdta at intermediate pHs, as was found for $[Cr(edta)]^-$. The deuteron NMR spectra of $[Cr(cdta)]^-$, $[Cr(pdta)]^-$, $[Cr(edta)]^-$, and $[Cr(edda)(mal)]^-$ have been assigned by stereospecific isotopic substitution.

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Registry No. K[Cr(edda-α-d_4)(mal)], 95464-61-2; K[Cr(cdta-α-d_4)], 95464-62-3; Na[Cr(pdta-α-d_8)], 95464-63-4; H[Cr(edta-α-d_8)], 95464-64-5; deuterium, 7782-39-0.

(18) The complex $[Co(pdta\text{-}\alpha\text{-}d_3)]^-$, from which the ligand was isolated for the preparation of the partially deuterated Cr(III) complex, is deuterated primarily at the two R_A positions and at the R_B position of the ring opposite to the methylene substituent (see the discussion in Selective Deuteration of the Ligands). Thus, in principle it should be possible to differentiate the two R_B positions since two resonances are observed. However, as seen in the difference spectrum (Figure 3c), these resonances are not sufficiently resolved to discriminate between these two positions on the chelate ring.

(19) Molecular models show that in the complexes studied the conformational flexibility of the two-carbon backbone becomes more restricted with the number of coordinated acetate rings and the complexity of substituents attached to it.