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# Solution Structure of the Chromium(III) Complex with edta by Deuteron NMR Spectroscopy[1]

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Deuteron NMR spectroscopy has been shown to be a valuable method for the structural characterization of simple Cr(III) complexes in solution. In order to explore the potential of this technique in more complex systems, $[Cr(edta)]^-$ and $[Cr(medtra)(H_2O)]$ have been investigated, where $^2H$ is selectively substituted for $^1H$ on the methylene carbons of the acetate arms. The $^2H$ NMR spectrum of the Cr(III)–edta complex is pH independent between pH 3.5 and pH 6.5. In this pH range edta forms a sexidentate complex with Cr(III), a structure that is not currently widely accepted. At pHs outside this range significant changes occur in the spectra. At high and low pHs the spectrum of the complex is similar to that of the quinquedentate $[Cr(medtra)(H_2O)]$ complex. The $^2H$ NMR spectrum of $[Cr(medtra)(H_2O)]$ shows only minor changes with variations in pH.

## Introduction

The sexidentate ligand edta[2] has most certainly been at the forefront of interest of the chelating agents that have been studied. Although full sexidentate coordination might be expected due to the chelate effect, quite often edta is known to have a quinquedentate or lower coordination number. Crystal structure investigations on numerous metal complexes of this ligand have shown this to be the case. Model studies suggest that a considerable amount of strain is present in these complexes when edta is fully coordinated, an observation supported by crystal structure data and chemical studies.

Establishing the structure of metal complexes of edta in solution is considerably more difficult. Although Cr(III)–edta complexes have been studied extensively since the first preparation of $H[Cr(edta)(H_2O)]$ 40 years ago,[3] the structure of this complex in solution has not yet been established definitively. Most of the studies related to this complex can be grouped into one of two categories, those relating to the structure of the complexes and those of kinetic interest.

Dwyer and Garvin were able to show from IR data that edta forms a quinquedentate complex with the Cr(III) ion in solid $H[Cr(edta)(H_2O)]$.[4] The same year Sawyer and McKinnie assigned $Na[Cr(edta)]\cdot 2H_2O$ a sexidentate structure, also by IR data.[5] The assignment of the quinquedentate complex was later confirmed by a crystal structure, where the water molecule was shown definitively to be bound to the metal.[6]

Hoard and co-workers were able to show that the ammonium and rubidium salts of $[Cr(edta)]^-$ are isomorphous with the sexidentate $[Co(edta)]^-$ complex[7] and that the hydrogen salt is isomorphous with the quinquedentate Fe(III) and Ga(III) complexes of edta.[8] Thorneley and Sykes attempted to repeat this work but were unable to prepare anything but a quinquedentate complex, and furthermore, they were unable to remove the bound water molecule either by dehydration or by heating.[9] Tsuchiya et al., however, demonstrated that the bound water could be removed with the resultant formation of the sexidentate complex.[10] The analogous complex of Cr(III) with pdta is observed to have both quinquedentate and sexidentate coordination in the solid state.[11,12]

Studies of $[Cr(edta)]^-$ in solution have been primarily by UV/visible spectroscopy.[9,13–22] Although the sexidentate complex is observed in the solid state, and it has been suggested that it might also exist in solution at slightly acidic pHs,[7,22] the conclusions of several studies have always described the structure of this complex as quinquedentate coordination of the edta with the sixth position occupied by a water molecule.[13,15,22] The unbound carboxylate is described as being deprotonated above pH 2.3 and the bound water deprotonated above pH 7.4. At very high pHs (above pH 12.2) the description is that of a quadridentate Cr–edta–dihydroxo complex. Subsequent workers have cited the quinquedentate structure as the species participating in the reactions being investigated.[9,16–21]

A considerable amount of effort has gone into investigating the lability of the sixth coordination position, which appears to be associated with the distorted nature of the complex and with the pendant acetate (or other functional groups in related ligands). Kinetic data show that the rate constants for the anation of the complex are generally 1 order of magnitude higher at pHs where the free carboxylate arm is considered to be deprotonated than at pHs where it is protonated.[19,20] The interpretation given to these data is that the free carboxylate arm has a labilizing effect on the coordinated water, with a fast transient coordination of the free carboxylate arm to the metal followed by the attack of the anating species.[19,21] A prior investigation, however, was unsuccessful at detecting this intermediate.[22]

Structural studies of Cr(III) complexes in solution have been

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(1) Wheeler, W. D.; Kaizaki, S.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 3248.

(2) Abbreviations: edta = ethylenediamine-*N,N,N′,N′*-tetraacetate; edtra = ethylenediamine-*N,N,N′*-triacetate; medtra = *N*-methylethylenediamine-*N,N′,N′*-triacetate; pdta = 1,2-propanediamine-*N,N,N′,N′*-tetraacetate.

(3) Brintzinger, H.; Thiele, H. *Z. Anorg. Allg. Chem.* **1943**, *251*, 285.

(4) Dwyer, F. P.; Garvin, F. L. *J. Am. Chem. Soc.* **1960**, *82*, 4823.

(5) Sawyer, D. T.; McKinnie, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 4191.

(6) Gerdom, L. E.; Baenziger, N. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1606.

(7) Hoard, J. L.; Smith, G. S.; Lind, L. "Advances in the Chemistry of the Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961, p 296.

(8) Hoard, J. L.; Kennard, C. H. L.; Smith, G. S. *Inorg. Chem.* **1963**, *2*, 1316.

(9) Thorneley, R. N. F.; Sykes, A. G. *Chem. Commun.* **1968**, 340.

(10) Tsuchiya, R.; Uehara, A.; Kyuno, E. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1886.

(11) Dwyer, F. P.; Garvan, F. L. *J. Am. Chem. Soc.* **1961**, *83*, 2610.

(12) Suarez Cardeso, J. M.; Gonzalez Garcia, S. *An. Quim.* **1972**, *68*, 1227; *Ibid.* **1973**, *69*, 483.

(13) Schwarzenbach, G.; Biedermann, W. *Helv. Chim. Acta* **1948**, *31*, 459. Schwarzenbach, G.; Heller, J. *Helv. Chim. Acta* **1951**, *34*, 576.

(14) Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670.

(15) Furlani, Von C.; Morpurgo, G.; Sartori, G. *Z. Anorg. Allg. Chem.* **1960**, *303*, 1.

(16) Andersen, P.; Berg, T.; Jacobsen, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 219.

(17) Chen, Z.; Chimolino, M.; Adamson, A. W. *Inorg. Chem.* **1983**, *22*, 3035.

(18) Ogino, H.; Watanabe, T.; Tanaka, N. *Inorg. Chem.* **1975**, *14*, 2093.

(19) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1979**, *18*, 2497.

(20) Leupin, P.; Sykes, A. G.; Weighardt, K. *Inorg. Chem.* **1983**, *22*, 1253.

(21) Sulfab, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2388.

(22) Thorneley, R. N. F.; Sykes, A. G.; Gans, P. *J. Chem. Soc. A* **1971**, 1494.

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Table I. Elemental Analyses

| complex | % C calcd | % C found | % H calcd | % H found | % N calcd | % N found | % Cr calcd | % Cr found |
|---|---|---|---|---|---|---|---|---|
| $[Cr(medtra)(H_2O)]\cdot H_2O$ | 32.43 | 32.09 | 5.15 | 5.56 | 8.41 | 8.27 | 15.6 | 15.9 |
| $[Cr(medtra\text{-}d_6)(H_2O)]\cdot H_2O$ | 31.86 | 31.84 | | | 8.26 | 8.24 | 15.3 | 15.4 |
| $H[Cr(edta)(H_2O)]$ | 33.43 | 33.13 | 4.22 | 4.86 | 7.80 | 7.47 | 14.5 | 14.0 |
| $H[Cr(edta\text{-}d_8)(H_2O)]$ | 32.71 | 32.50 | | | 7.63 | 7.52 | 14.2 | 13.6 |

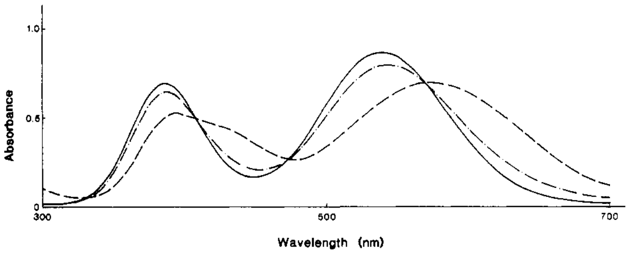

**Figure 1.** UV/visible spectrum of $[Cr(medtra)(H_2O)]$ as a function of pH: (—) pH 4.0; (–·–) pH 6.0; (- -) pH 8.1.

severely hampered by the lack of any viable NMR technique. The extreme broadening of the NMR signals by the paramagnetic metal ion has led the scientific community to believe that NMR is useless as a structural probe of Cr(III) complexes. However, it was recently demonstrated that the substitution of deuterons for protons on the ligand(s) bound to the Cr(III) ion yields complexes whose solution $^2H$ NMR spectra are resolved to the extent that detailed structural information can be obtained.[1]

We report here the first study of two closely related complexes of Cr(III) with edta-like ligands by $^2H$ NMR. Our results show that edta forms a *sexidentate* complex with Cr(III) between pH 3.5 and 6.5, in disagreement with the quinquedentate structure so often cited in the literature. This assignment is supported by comparison with $^2H$ NMR data obtained for the closely related complex of medtra.

## Experimental Section

**Materials.** Reagent grade $H_4edta$ was purchased from the J. T. Baker Chemical Co.

**Syntheses. $H_4edta\text{-}d_8$.** The Co(III) complex of this ligand[23] was deuterated by the method of Terrill and Reilley,[24] and the ligand was removed by the method of Denhart et al.[25] The yield was 2.7 g (50%), and the $^1H$ NMR showed $^2H$ incorporation on the acetate methylenes to be 80%.

**$H[Cr(edta\text{-}d_n)(H_2O)]$ ($n$ = 0, 8).** These complexes were prepared from their respective ligands by a method similar to that of Hamm,[14] except that the crude material was passed over a 3 × 30 cm column of Dowex 50W-X4 ($H^+$ form). Two volumes of absolute ethanol were added to the eluate, and the solution was refrigerated overnight. The resulting crystals were filtered and washed with ethanol and ether.

**$[Cr(medtra)(H_2O)]\cdot H_2O$.** This complex was prepared by the method of Ogino et al.[18]

**$[Cr(medtra\text{-}d_6)(H_2O)]\cdot H_2O$.** This complex was prepared by dissolving 2.7 g of $[Cr(medtra)(H_2O)]\cdot H_2O$ in 50 mL of $^2H_2O$ and adjusting the $p^2H$ to 10.6 with 40% $NaO^2H$. The solution was heated on a steam bath for 24 h. After cooling, the $p^2H$ was readjusted to 6.0 with concentrated $HNO_3$. Chromatography on a 5 × 30 cm column of Dowex 50W-X4 ($H^+$ form), eluted with water, gave two bands. The first band was violet and represented about 10% of the reaction mixture. A red-purple solution, which eluted second, was evaporated to 20 mL on a steam bath and then refrigerated. The purple crystals that formed were filtered, washed with ether, and recrystallized from hot water; yield 1.8 g (67%).

**Physical Measurements. Analyses.** Carbon, hydrogen, and nitrogen analyses were obtained from Canadian Microanalytical Service Ltd., Vancouver, B.C., Canada and CH&N Analytical Facility, University of Idaho, Moscow, ID. Chromium was determined by spectrophotometric analysis of $CrO_4^{2-}$ at 372 nm after oxidation of the complexes with hot alkaline hydrogen peroxide.[26] Analyses of the compounds are reported in Table I.

**UV/Visible Spectra.** UV/visible spectra were recorded on a Varian/Cary 219 spectrophotometer and are reported in Tables II and III and in Figure 1.

**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. Five milliliters of 100–200 mM solutions in 12-mm tubes were used. The spectral region isolated was ±200 ppm with respect to $Me_4Si$. An external standard of $C^2HCl_3$ was assigned a chemical shift

Table II. UV/Visible Spectra in Solution

| complex | $\lambda^a$ ($\epsilon^b$) I | $\lambda^a$ ($\epsilon^b$) II | pH |
|---|---|---|---|
| $[Cr(medtra)(H_2O)]\cdot H_2O$ | 538 (139) | 385 (112) | 4.4 |
| $[Cr(medtra\text{-}d_6)(H_2O)]\cdot H_2O$ | 538 (143) | 385 (114) | 4.4 |
| $[Cr(medtra)(H_2O)]\cdot {}^3/_2H_2O$[18] | 539 (143) | 386 (113) | *c* |
| $H[Cr(edta)(H_2O)]$ | 540 (200) | 392 (112) | 3.6 |
| $H[Cr(edta\text{-}d_8)(H_2O)$ | 540 (200) | 392 (112) | 3.6 |
| $H[Cr(edta)(H_2O)]$[15] | 542 (202) | 391 (117) | 3.5 |

[a] In nm. [b] Molar absorptivity in $M^{-1}$ $cm^{-1}$. [c] The pH was not reported.

Table III. UV/Visible Spectra as a Function of pH

| complex | $\lambda^a$ ($\epsilon^b$) I | $\lambda^a$ ($\epsilon^b$) II | $\lambda^a$ ($\epsilon^b$) III | pH |
|---|---|---|---|---|
| $[Cr(medtra)(H_2O)]\cdot H_2O$ | 539 (139) | 386 (112) | | 4.0 |
| | 543 (127) | 387 (103) | | 6.0 |
| | 573 (109) | 393 (81) | 420 (72) | 8.1 |
| $H[Cr(edta)(H_2O)]$[15] | 542 (202) | 391 (117) | | 3.5 |
| | 555 (150) | 391 (105) | | 7.5 |
| | 581 (124) | 391 (86) | 431[c] | 10 |
| $Na[Cr(pdta)]\cdot 2H_2O$[12] | 543 (190) | 391 (118) | | 2.3 |
| | 540 (181) | 389 (95) | | 6.2 |
| | 583 (115) | 392 (51) | 432 (66) | 9.0 |
| $[Cr(medtra)(OAc)]^{2-}$[18] | 549 (154) | 394 (112) | | *d* |
| $[Cr(edta)(OAc)]^{2-}$[18] | 565 (147) | 394 (112) | | *d* |

[a] In nm. [b] Molar absorptivity in $M^{-1}$ $cm^{-1}$. [c] The $\epsilon$ value was not reported. [d] The pH was not reported.

Table IV. Deuteron NMR Spectra

| $\delta^a$ (integration) | | | | | | pH |
|---|---|---|---|---|---|---|
| | | $[Cr(medtra\text{-}d_6)(H_2O]\cdot H_2O$ | | | | |
| −9 (1) | −20 (1) | | −39 (3) | | −61 (1) | 4.0 |
| −8 (1) | −17 (1) | | −31 (3) | | −52 (1) | 6.3 |
| −6 (1) | −13 (1) | −18 (1) | −24 (1) | −27 (1) | −46 (1) | 10.1 |
| | | $H[Cr(edta\text{-}d_8)(H_2O)]$ | | | | |
| | −11 | | −22 | −39 | −62 | 0.9 |
| 30 | −8 | | | −32 | −53 | 2.3 |
| 44 (1) | −7 (1) | | | −32 (1) | −50 (1) | 6.3 |
| 22 | −7 | | | −28 | −45 | 7.4 |
| | −6 | −15 | −23 | −28 | −47 | 10.6 |
| 45 | −6 | −18 | | −32 | −49 | 4.8[b] |
| 44 (1) | −6 (1) | | | −32 (1) | −50 (1) | 4.8[c] |

[a] In ppm relative to $Me_4Si$. [b] In 1 M potassium acetate. [c] In 1 M sodium perchlorate.

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(23) Moeller, T. *Inorg. Synth.* **1957**, *5*, 186.

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

(25) Denhart, C. A.; Spoelhof, G. D.; Swartz, T. A.; Williams, D. H. *Inorg. Chem.* **1975**, *14*, 2948.

(26) Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *40*, 2331.

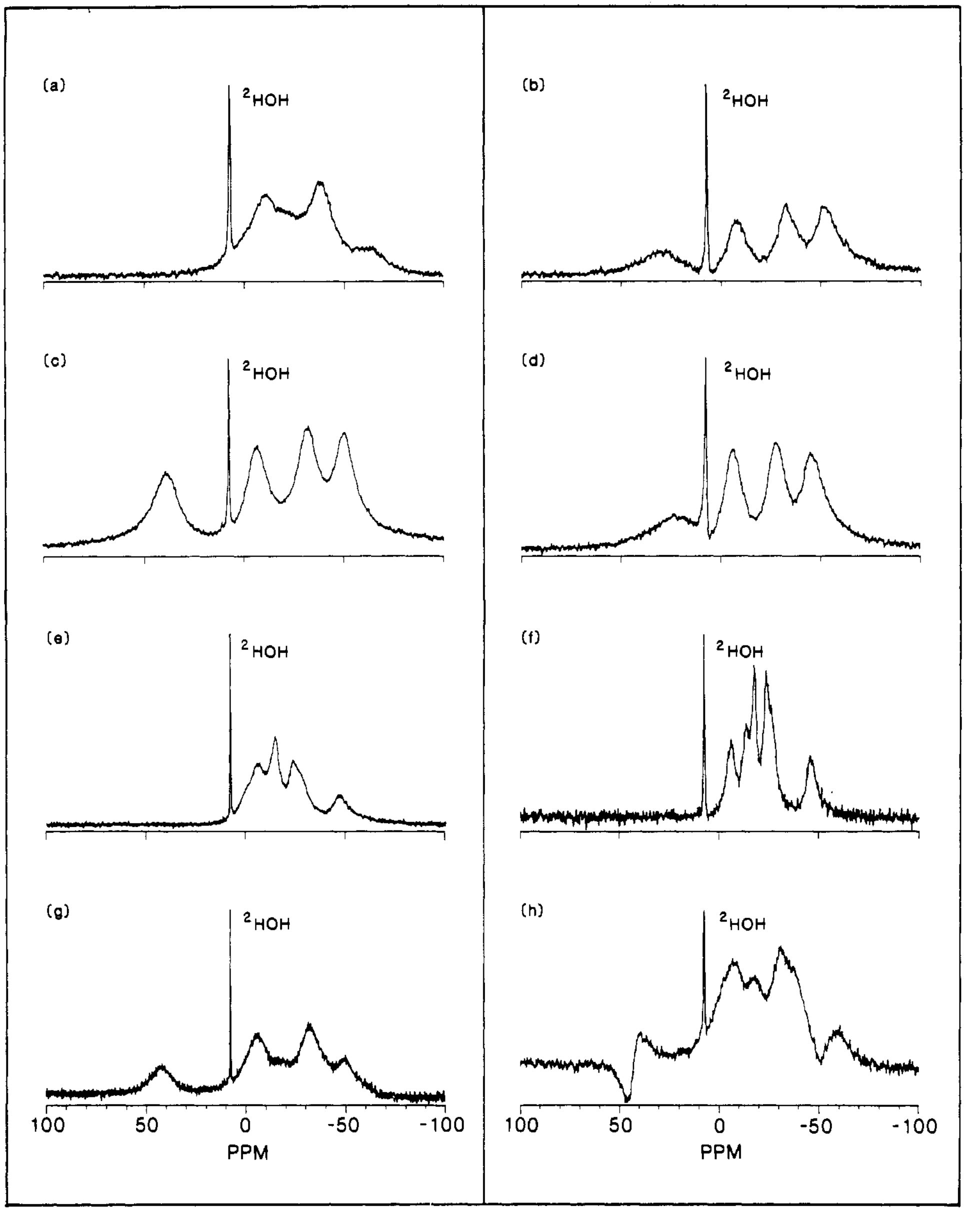

**Figure 2.** Deuteron NMR spectra: [Cr(edta)]$^-$ at (a) pH 0.9, (b) pH 2.3, (c) pH 6.3, (d) pH 7.4, (e) pH 10.6; [Cr(medtra)(OH)]$^-$ at (f) pH 10.1; (g) [Cr(edta)]$^-$ at pH 4.8 in 1 M KOAc; (h) spectrum of [Cr(edta)]$^-$ in 1 M NaClO$_4$ at pH 4.8 subtracted from the spectrum in (g). The "derivative" shape in the spectrum at 40 ppm is due to a slight dependence of chemical shift with ionic strength.

of 7.24 ppm. Note that "downfield" shifts are defined as positive. Deuteron NMR data are summarized in Table IV and in Figure 2.

## Results and Discussion

**NMR Spectra.** 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,[27] nuclear spin–spin couplings are not observed and the spectra behave as though they are zero order. As a consequence, only one resonance should be observed for each symmetrically distinct deuteron or set of deuterons.

**[Cr(medtra-$d_6$)(H$_2$O)].** The ligand occupies at most five of the six possible coordination positions for an octahedral metal complex, with a water molecule filling the remaining position. When medtra forms a quinquedentate complex with a metal, three isomers are possible (Figure 3). The trans-equatorial and cis-polar isomers are strained, and the cis-equatorial isomer is expected to predominate. Both the cis- and trans-equatorial isomers of [Co(edtra)NO$_2$]$^-$ have been isolated, and the cis-equatorial isomer predominates.[28] It appears that in our preparations of the Cr(III) complex of this ligand, a small amount (<10%) of a second isomer was obtained, although it was not isolated.

Since all of the isomers of this complex have $C_1$ symmetry, and all six of the protons on the acetate arms have been replaced with deuterons, it is expected to show six resonances for each isomer in its $^2$H NMR spectrum. The spectrum of this complex shows a slight pH dependence between pH 4.0 and 10.1 (Table IV), with the magnitude of the shifts decreasing with increasing pH. At high pH the spectrum clearly shows the six expected signals (Figure 2f), while at low pH three of these signals coalesce to form one broad peak with the remaining resonances still clearly resolved (Table IV).

**[Cr(edta-$d_8$)]$^-$.** In solution this complex is expected to show a $^2$H NMR spectrum with as many as eight resonances if $C_1$ symmetry is present and as few as four resonances if the ligand is fully coordinated ($C_2$ symmetry). It is evident from the spectra in Figure 2 and Table IV that the behavior of [Cr-

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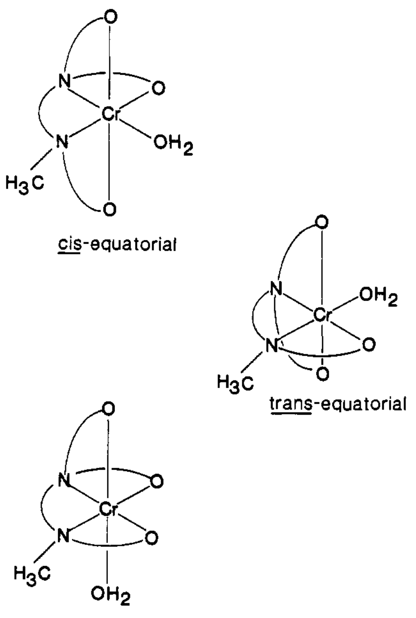
[27] Harris, R. K.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: London, 1978; p 107 and references therein.

[28] Blackmer, G. L.; Hamm, R. E.; Legg, J. I. *J. Am. Chem. Soc.* **1969**, *91*, 6632. Bause, D. E.; Chang, C. A.; Douglas, B. E. *J. Coord. Chem.* **1979**, *6*, 211.



cis-equatorial

trans-equatorial

cis-polar

**Figure 3.** Isomers of [Cr(medtra)($H_2O$)].

(edta)]$^-$ as a function of pH is complicated. The spectrum at pH 6.3 consists of four resonances indicative of a complex with $C_2$ symmetry (Figure 2c). This is also true at pH 4.8 in 1 M $NaClO_4$ (Table IV), but at pHs 0.9 and 10.6 the spectrum becomes more complex (Figure 2a,e). Most noticeably, the signal at 44 ppm is now shifted upfield into the −15 to −25 ppm range. The spectrum of [Cr(medtra)($H_2O$)] (Figure 2f), exhibits no downfield signal at any pH, and as it cannot be sexidentate, the downfield signal present in the Cr–edta spectrum at intermediate pHs is most likely a feature indicative of a sexidentate complex. The presence of this resonance appears to be associated with the G-ring of a fully coordinated sexidentate ammine carboxylate ligand where these rings are under considerable strain. Although most of the resonances observed for these complexes are shifted to high field, shifts to low field have been reported previously.[1] The spectra of [Cr(edta)(OH)]$^{2-}$ at pH 10.6 and [Cr(medtra)(OH)]$^-$ at pH 10.1 are easily compared in Figure 2e,f. Although there are two resonances buried in the spectrum of the latter that do not appear in the former,[29] the striking similarity leaves little doubt that [Cr(edta)(OH)]$^{2-}$ is quinquedentate at this pH. The spectrum of [Cr(edta)($H_2O$)]$^-$, at pH 0.9 (although poorly resolved) (Figure 2a), is quite similar to the spectra of [Cr(edta)(OH)]$^{2-}$ and [Cr(medtra)(OH)]$^-$, and quinquedentate coordination is again implicated.

The $^2H$ NMR spectrum of [Cr(edta)]$^-$ in 1 M potassium acetate at pH 4.8 is shown in Figure 2g. Under these conditions the sexidentate Cr–edta complex is in equilibrium with a Cr–edta–acetate complex where the acetate complex is present as about 10% of the mixture.[18] If the Cr–edta complex is really sexidentate at pH 4.8, then subtraction of the spectrum of [Cr(edta)]$^-$ in 1 M $NaClO_4$ at pH 4.8 from the spectrum of the mixture should leave a spectrum similar to the one at pH 10.6. This is in fact the case (Figure 2h).

**UV/Visible Spectra.** A great deal of effort has gone into the interpretation of the UV/visible spectra of Cr–edta like complexes. In light of the NMR data just presented, another examination of the UV/visible spectra is in order. In addition we also report for the first time the pH dependence of the UV/visible spectrum of [Cr(medtra)($H_2O$)] in Figure 1. The similarity in behavior of the spectra of [Cr(edta)]$^-$, [Cr(pdta)]$^-$, and [Cr(medtra)($H_2O$)] as a function of pH is noteworthy (Table III). The primary difference in the spectra of the edta and pdta complexes from the spectrum of the medtra complex is in the magnitude of the molar absorptivities ($\epsilon$). The $\epsilon$'s for the former complexes are 170–200 $M^{-1}$ $cm^{-1}$ for the first absorption band[30] in the pH region 2–7, whereas the medtra complex has an $\epsilon$ of 130–140 for band I in this pH range. As the pH is rasied to about 9 for [Cr(edta)]$^-$ and [Cr(pdta)]$^-$ and to around 8 for [Cr(medtra)($H_2O$)], the first absorption band is shifted 30–40 nm to lower energy for all three complexes. The $\epsilon$ values decrease by 60–80 for [Cr(edta)]$^-$ and [Cr(pdta)]$^-$ but decrease by only 30 for [Cr(medtra)($H_2O$)]. This behavior would be somewhat anomalous if the parent complexes of the Cr–edta and Cr–pdta complexes had the same quinquedentate structure as [Cr(medtra)($H_2O$)] throughout the pH range investigated. It is also interesting to note that the $pK_a$ for [Cr(medtra)($H_2O$)] is much different from that of [Cr(edta)]$^-$ (6.25 and 7.39, respectively).[18] The shifts in band position are most likely due to the replacement of an acetate arm by hydroxide ion in the former complexes and by the ionization of the coordinated water in the latter complex. The trend in $\epsilon$'s can be explained as arising from the release of one of the acetate arms of the sexidentate complexes of [Cr(edta)]$^-$ or [Cr(pdta)]$^-$, which provides a direct reduction in steric strain and a lower $\epsilon$. Since a change in chelation does not occur for [Cr(medtra)($H_2O$)], a smaller change in the UV/visible spectrum is expected with a change in pH.

Similar behavior is observed when acetate ion is coordinated to these complexes. The first absorption band of [Cr(edta)(OAc)]$^{2-}$ and [Cr(medtra)(OAc)]$^-$ is shifted by 11 and 25 nm, respectively, as compared to the absorption spectra of [Cr(edta)]$^-$ and [Cr(medtra)($H_2O$)] (Table III). The $\epsilon$'s, however, decrease by about 55 for the Cr–edta–OAc complex but increase slightly for the Cr–medtra–OAc complex. These results are easily explained by noting that acetate ion and a chelate acetate arm have very similar ligand field strengths while hydroxide ion is quite different. As a result, the spectral band positions are shifted by a smaller amount on acetate substitution than when hydroxide is substituted. The behavior of the $\epsilon$'s is consistent with this behavior as previously discussed.

**Kinetic Behavior.** Although this study has centered on the structure of Cr(III)–edta like complexes in solution, the results provide some insight into the rates at which one species is converted into another. When the $^2H$ NMR spectrum of [Cr(edta)]$^-$ in 1 M acetate is compared to that of the complex in 1 M perchlorate both at pH 4.8 (Figure 2g; Table IV), it is seen that there is a decrease in intensity of the peaks at 45 and −50 ppm when acetate is present, with a new peak growing in at −18 ppm. These spectral changes are consistent with the behavior expected for two complexes in equilibrium where the rate of exchange is slow compared to the chemical shift difference of the deuterons. This is in agreement with the results of Ogino et al. who have found the forward rate constant of this reaction (eq 1) to be 3.3 $M^{-1}$ $s^{-1}$ with an equilibrium constant of 0.62 at pH 4.8.[18]

$$[\mathrm{Cr(edta)}]^- + \mathrm{OAc}^- \rightleftarrows [\mathrm{Cr(edta)(OAc)}]^{2-} \qquad (1)$$

Comparison of the spectrum of the Cr–edta complex at pH 6.3 to the spectra of this complex at pH 0.9 and 10.6 shows that the downfield signal is absent at pH 0.9 and 10.6, with a new signal appearing between −15 and −25 ppm. As the pH is varied from 6.3 through the $pK_a$'s of the complex (2.3 and 7.4), the downfield signal shifts upfield (to 30 and 22 ppm,

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(29) The relative integrations above and below ca. −40 ppm in the spectra of [Cr(medtra)(OH)]$^-$ and [Cr(edta)(OH)]$^{2-}$ integrate to 5:1 and 7:1, respectively, as expected.

(30) Chromium(III) complexes typically show two absorption bands in the UV/visible region of the spectrum. The first (low-energy) band is due to the $^4A_2 \rightarrow {}^4T_2$ electronic transition while the second band is due to the $^4A_2 \rightarrow {}^4T_1$ transition.

respectively) and is broadened (Figure 2). This behavior is consistent with two species in equilibrium, which are exchanging at a rate that is rapid compared to the chemical shift difference of the deuterium nuclei. At pHs well removed from the p$K_a$'s, where the equilibrium is shifted predominantly to the right side of eq 2 and 3, the spectrum that is predicted is

$$[Cr(edta)]^- + OH^- \rightleftarrows [Cr(edta)(OH)]^{2-} \qquad (2)$$

$$[Cr(edta)]^- + H_3O^+ \rightleftarrows [Cr(Hedta)(H_2O)] \qquad (3)$$

essentially the same regardless of the exchange rate (i.e., there is no exchange). Although it is not possible to extract a rate constant directly, it is possible to estimate a lower limit if it is assumed that the resonance at 45 ppm in the spectrum of $[Cr(edta)]^-$ at pH 6.3 and the resonance at −15 ppm in the spectrum at pH 10.6 are the resonances associated with the exchanging G-ring.[31] The conditions for fast exchange dictate that the rate must be large (2×) compared to the chemical shift difference of the resonances of the two exchanging species.[32] Since the differences in chemical shifts are on the order of 60 ppm (1800 Hz), the exchange rates for the complex at pHs near the p$K_a$'s must be on the order of several thousand per second. In an experiment in which $[Cr(edta)(OH)]^{2-}$ (in 0.1 M hydroxide) is added to a pH 4 buffer, Thorneley and Sykes found an apparent rate constant that is greater than $10^3$ $s^{-1}$.[9]

Is it interesting to speculate why it is that the substitution by hydronium/water/hydroxide is so fast at pH 2.3 and 7.4 and not at other pHs. Considering that the concentration of water remains constant regardless of pH, the concentrations of $H_3O^+$ and $OH^-$ are negligible (ca. $10^{-2}$ and $10^{-7}$ M in $H_3O^+$, respectively), and that small changes in pH are responsible for dramatic changes in both structure and reactivity, it becomes apparent that the phenomenon found here is a very subtle one. One possible explanation is that the sexidentate complex (with respect to edta) is really a seven-coordinate Cr(III) ion where water is bound as the seventh ligand. Although there is no precedent for this behavior in Cr(III) systems (nor is there any direct evidence presented here), Cr(III) compounds are known to undergo substitution via an associative mechanism[33] and seven-coordination has been observed in crystalline $[Fe(edta)(H_2O)]^-$ complexes.[34] The Fe(III) complex is also known to have acid–base properties similar to those of the Cr(III) complex in the neutral pH region.[7] The rapid equilibrium at pH 7.4 could then be viewed as the deprotonation of the bound water to form the dianionic complex, which converts to the six-coordinate quinquedentate $[Cr(edta)(OH)]^{2-}$ by losing one of the bound acetate arms of the edta. The process at pH 2.3 could be viewed as the protonation of the bound carboxylate arm followed by rearrangement to the quinquedentate complex.

## Conclusions

It is found from $^2H$ NMR data that edta forms a sexidentate complex with Cr(III) in the pH range 3.5–6.5. Above and below these pHs there is a rapid equilibrium between the sexidentate and the quinquedentate species that favors the quinquedentate species at the more extreme pHs. At pHs near the p$K_a$'s the equilibrium between these two species is fast on the time scale of the NMR experiment with an exchange rate greater than $10^3$ $s^{-1}$. The Cr–medtra complex is quinquedentate at all pHs studied and provides a reference point for our structural assignments. We have reinterpreted the UV/visible spectra of these complexes as a function of pH and found that they are consistent with our NMR data.

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**Registry No.** $[Cr(edta)]^-$, 16091-77-3; $[Cr(edta)(H_2O)]^-$, 19610-17-4; $[Cr(edta)(OH)]^{2-}$, 21729-57-7; $[Cr(medtra)(H_2O)]$, 55622-36-1; $[Cr(medtra)(OH)]^-$, 92055-18-0.

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(31) It appears that there is a direct correspondence of many of the resonances in the spectra at different pHs even though the complexes are undergoing large structural changes.

(32) Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Chapman and Hall: New York, 1979; Chapter 12.

(33) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

(34) Lind, M. D.; Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 34.

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# Ab Initio Direct Calculation of the Singlet–Triplet Splitting in a μ-Oxalato Copper(II) Binuclear Complex

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The singlet–triplet (S–T) splitting of (μ-oxalato)bis((*N,N,N′,N′*-tetramethyl-1,2-ethanediamine)aquacopper(II)) perchlorate has been calculated in an ab initio scheme. The method, based on a perturbation development of the configuration interaction problem, directly gives the S–T energy separation, after an ab initio SCF–MO calculation on the open-shell system, using pseudopotentials. The $2K_{ab}$ ferromagnetic potential-exchange contribution is important (720 $cm^{-1}$) and not balanced by the second-order kinetic-exchange mechanism (∼−450 $cm^{-1}$). The other second-order contributions are the double-spin polarization (−38 $cm^{-1}$), the ligand–metal charge transfer (−146 $cm^{-1}$), and the kinetic-exchange + polarization (−177 $cm^{-1}$). The fourth-order terms allow one to reach a total value of −295 $cm^{-1}$ not too far from the experimental one of −385 $cm^{-1}$. The magnitude of the different contributions is discussed and compared to that of a μ-dithiooxamido copper(II) binuclear complex.

There are only few works dealing with non-semiempirical calculations of the singlet–triplet splitting in exchange-coupled systems. Two of us performed an ab initio direct calculation of this kind on the cupric acetate hydrate dimer.[2] The same