give a high noise level in data at higher *k*. Over this more limited range, three-wave fits of the first shell became impossible and correlation effects between Fe and other atoms in the second shell increased significantly, increasing the calculated number of Fe atoms.

Conclusions

This investigation has shown that EXAFS spectra of oxo- and hydroxo-bridged iron complexes **1**–**4** are highly sensitive to the presence or absence of a short μ-oxo Fe–O distance and that this geometric feature can be unambiguously determined. This result provides further evidence in confirmation of the conclusions reached about the presence of such a short iron–oxo bridging distance in azidomethemerythrin.[24,26] The ability of EXAFS spectroscopy to differentiate Fe–oxygen bridge bond lengths in the 1.78 vs. 1.95 Å distance ranges should prove to be valuable in assessing the stereochemistry of semimet forms of hemerythrin, of deoxyhemerythrin (cf. ref 25), and of the binuclear iron centers in ribonucleotide reductase and purple acid phosphatase. It has also been demonstrated that great care must be exercised in determining the second-shell contributions to the EXAFS, since the Fe···Fe scattering can be severely influenced by the presence of C or other low *Z* atoms at the same distance range from Fe as Fe itself. This perturbation can affect especially the determination of the number of neighboring Fe atoms, a problem that is further exacerbated if the *k* range of data is more limited, as is often the case with EXAFS data for dilute metalloproteins. On the positive side, however, the dramatic improvement of the fit for the phosphate ester bridged complex **3** upon addition of the P(S) atom to the second shell augurs well for the potential utility of EXAFS spectroscopy to delineate structural details of iron phosphate centers in biology.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 85-12129, to K.O.H.) and the National Institute of General Medical Sciences (GM-32134, to S.J.L.). EXAFS experiments were performed at SSRL, which is supported by the Department of Energy, Office of Basic Energy Sciences, and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. B.H. was the recipient of Swedish Natural Science Research Council Fellowship (K-PD 3890-101), and W.H.A. acknowledges support under NCI Training Grant CA-09112. We thank Dr. A. Spool for preparing the sample of **2**$(I)_2\cdot0.5CH_3CN$ and Dr. J. E. Penner-Hahn for useful discussions.

Registry No. **1**, 86177-70-0; **2**, 103835-68-3; **3**, 96502-34-0; **4**, 90886-30-9; ribonucleotide reductase, 9040-57-7; purple acid phosphatase, 9013-05-2.

Supplementary Material Available: Listings of raw data for compounds **1**–**4** (20 pages). Ordering information is given on any current masthead page.

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Raman Spectral Study on the Solution Structure of the Chromium(III)-edta Complex

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The complex of chromium(III) with ethylenediaminetetraacetate (edta) was first prepared by Britzinger et al.[1] and was formulated as $H[Cr(edta)]$. However, Schwarzenbach et al.[2] later proposed the formula $[Cr(Hedta)(H_2O)]$, in which the edta coordinates as a quinquedentate ligand with a protonated carboxylate group. This structure was later supported by an IR study[3] and recently was confirmed by a single-crystal X-ray analysis.[4] The sodium salt of the chromium(III)–edta complex, however, was shown by IR analysis to contain sexidentate coordinated edta.[5] The sexidentate structure was later confirmed by X-ray crystallographic analysis of the ammonium and rubidium salts of $[Cr(edta)]^-$[6] and, also, of the lithium and potassium salts.[7]

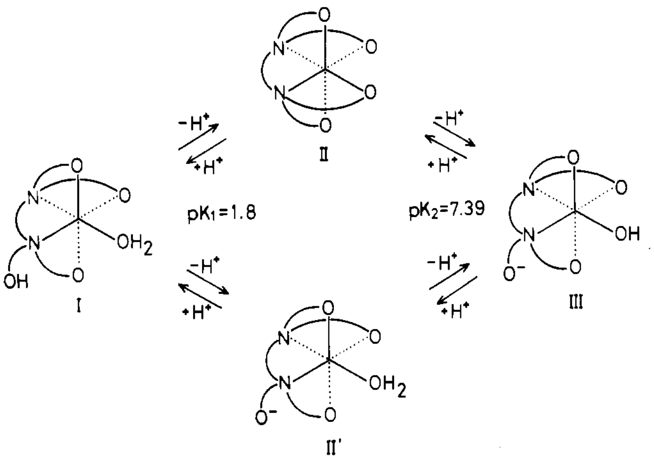

Figure 1. Possible equilibria of Cr(III)–edta (pK_a values from ref 8).

In addition to structural interests, chromium(III)–edta has attracted considerable attention because of its anomalously rapid substitution reactions in solution.[8-11] It is well-known that the edta complex of chromium(III) has two acid dissociation steps, which have been interpreted as the loss of a proton from the uncoordinated carboxylic acid group followed by the loss of a proton from the coordinated water molecule (shown by I ↔ II′ ↔ III in Figure 1).[2,8,10] Thus, it was believed that the edta remained coordinated to Cr(III) as a quinquedentate ligand over a wide pH range, although a sexidentate complex had been proposed at slightly acidic pH. Very recently, however, Wheeler and Legg[12] were able to show by deuterium NMR spectroscopy that edta forms a sexidentate complex with Cr(III) between pH 3.5 and 6.5 (shown as I ↔ II ↔ III in Figure 1).

Raman spectroscopy also has a high potential for characterizing the structure of coordination compounds in aqueous solution.[13-16] Krishnan and Plane[16] reported that the Raman spectra exhibit very intense bands in the 400–500-cm^{-1} region due to skeletal vibrations in complexes where some covalency is expected between metal and ligand. They also noted that the spectra of Cu(II)–edta and Hg(II)–edta complexes changed at both low and high pH, consistent with a single protonation of the ligand in acid solution

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and coordination of hydroxide in basic solution. In this paper, we report a Raman spectral study on the solution structure of the Cr(III)–edta complex as a function of pH.

Experimental Section

$Li[Cr^{III}(edta)]\cdot 2H_2O$. This complex was prepared by the method of Kushi et al.[7]

$[Cr^{III}(Hedta)(H_2O)]$. This complex was obtained by the method of Hamm[10] and purified by the method of Ogino and Tanaka.[17] The purity of the complexes was checked by elemental analyses and electronic absorption spectra.

Raman Spectra. The Raman spectra were recorded on a JASCO R-800 laser Raman spectrometer by use of an Ar^+ ion laser (457.9 nm, 120 mW) as an excitation source. The data were collected from 2000 to 80 cm^{-1} with a spectral slit width of 5 cm^{-1}, a time constant of 0.5 s, and a scan speed of 0.4 cm^{-1}/s. The spectra reported were produced by averaging 32 scans. Distinct Raman bands were only observed between 600 and 350 cm^{-1}. The 457.9-nm line, which falls between the first and second d–d absorption bands of the chromium(III)–edta complex, was found to be the most appropriate for the Raman measurements. To avoid possible thermal decomposition induced by laser illumination, sample-flow and rotating-sample techniques were employed for aqueous solutions and solid samples, respectively. The concentration of the solution used for Raman studies was ca. 3×10^{-2} mol/dm^3. Solutions of higher concentration produced very poor spectra due to the strong absorption of incident and scattered light. Lower concentrations did not give spectra with adequate signal to noise ratio.

Results and Discussion

We were able to observe the Raman bands between 600 and 350 cm^{-1} with the 457.9-nm excitation. No Raman band was observed in the region above 600 cm^{-1} where intraligand vibrations such as CO and CC stretches are expected to appear. Krishnan and Plane[16] observed very intense Raman bands around 500 cm^{-1} for the complexes of divalent metals such as Cu(II) and Hg(II) with edta and assigned these bands to skeletal vibrations. Therefore, we can reasonably assign all of the Raman bands observed in the present study to skeletal vibrations.

There is no controversy over the structure of chromium(III)–edta at low and high pH. Thus, it is generally accepted that the aqua complex, $[Cr(Hedta)(H_2O)]$, is predominant below pH 1.8, while the hydroxo complex, $[Cr(edta)(OH)]^{2-}$, is present above pH 7.4. If the chromium(III)–edta complex equilibrates as shown by I $\leftrightarrow$ II′ $\leftrightarrow$ III in Figure 1, a definite change in the Raman spectra would not be expected for the conversion from I to II′ since the skeletal arrangement of the ligand around the chromium ion would not be affected greatly by deprotonation of the free carboylic acid group. A minor change would be expected in the Raman spectra for the conversion from II′ to III since deprotonation of the aqua ligand would perturb the ligand field slightly. However, the arrangement of the quinquedentate edta ligand around the chromium ion would remain unchanged.

Conversely, if the chromium(III)–edta complex equilibrates by I $\leftrightarrow$ II $\leftrightarrow$ III, the Raman spectral features should change in the course of the conversion from I to II since the edta changes from quinquedentate to sexidentate coordination. This change in coordination would be accompanied by a change in the symmetry of the complex from C_1 to C_2. A reversal of this spectral change would be expected with the subsequent conversion from II to III.

Figure 2 shows the Raman spectral changes as a function of pH. These changes were found to be reversible. The most noticeable variation can be found in the 450–500-cm^{-1} region. Two bands were observed in this region at pH 0.9, whereas only one band was observed when the pH was raised to 3.4. When the pH was raised further, to ca. 10, two bands were again observed. These spectral changes are easily accounted for by the equilibria of I $\leftrightarrow$ II $\leftrightarrow$ III discussed above. The pH values at which the Raman spectral features change agree with the reported pK_a values.[8,10] These observations strongly suggest that edta coordinates as a sexidentate ligand in the range pH 3.4–6.3, and this is consistent with the conclusion deduced from the ^2H NMR spectra by Wheeler and Legg.[12]

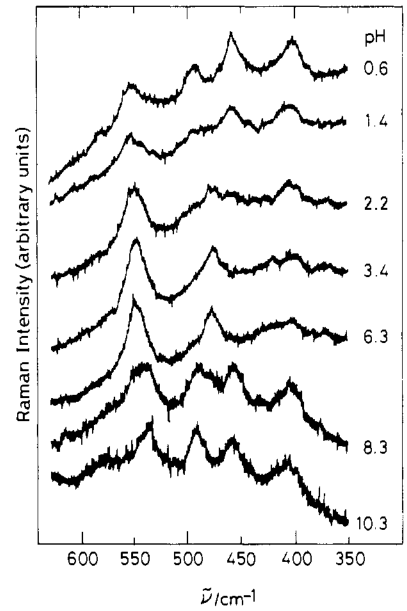

Figure 2. Raman spectra of Li[Cr(edta)] in aqueous solution as a function of pH.

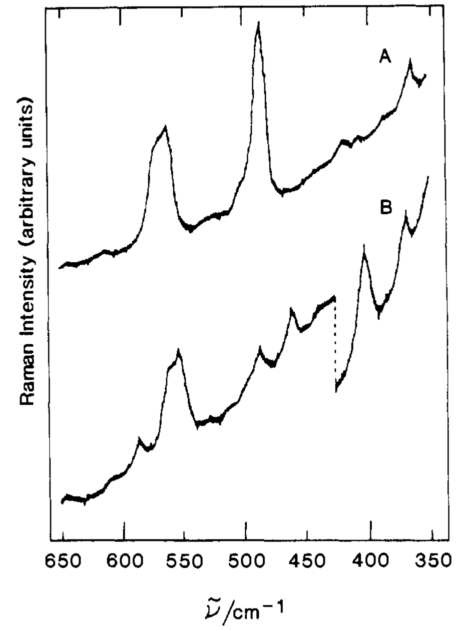

Figure 3. Raman spectra: (A) $Li[Cr(edta)]\cdot 2H_2O$ in the solid state; (B) $[Cr(Hedta)(H_2O)]$ in the solid state.

When coordinated H_2O (or OH) is substituted by D_2O (or OD), an isotope shift, of 0.95 (due to $\nu(Cr-OD_2)/\nu(Cr-OH_2)$), or 0.97 (due to $\nu(Cr(OD))/\nu(Cr(OH))$), is expected. No Raman band in the region of 600–350 cm^{-1} showed an isotope shift of this order, suggesting that the Raman band due to $\nu(Cr-OH_2)$ (or ν(Cr–OH)) was not observed in the spectra at pH 0.6 or at pH 10.3. Therefore, it is probable that the band due to $\nu(Cr-OH_2)$ (or ν(Cr–OH)) is buried in the intense bands due to the other skeletal vibrations. However, much smaller isotope shifts (4–5 cm^{-1}) were observed for the bands in the region of 450–500 cm^{-1} at pH 0.6 and pH 10.3. These shifts possibly arise from mechanical coupling between Cr–OH_2 (or Cr–OH) and Cr–N,O(edta) stretching vibrations. Thus, the behavior of the isotope shifts indirectly supports the existence of Cr–OH_2 and Cr–OH bonds at low and high pHs, respectively. In addition, no isotope shift was detected in the range pH 3.4–6.3. This fact leaves little doubt that the complex having sexidentate coordinated edta is predominant in solution over the range pH 3.4–6.3.

Figure 3 shows the Raman spectra of $Li[Cr(edta)]\cdot 2H_2O$ and $[Cr(Hedta)(H_2O)]$ in the solid state. It should be noted that the

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spectrum of Li[Cr(edta)], which has edta coordinated as a sexidentate ligand, exhibits only one Raman band between 450 and 500 cm^{-1}. In contrast, [Cr(Hedta)(H_2O)], in which the edta is coordinated in a quinquedentate fashion, shows two bands in this region. These observations further support the solution structure of the chromium(III)–edta complex discussed above. The splitting of the Raman band in the quinquedentate complex may be due to the lack of symmetry.

Wheeler and Legg[12] observed continuous shifts, in the positions of the deuteron resonances for deuterated Cr(III)–edta, when the pH of the solution was increased from 0.9 to 10.6. These continuous shifts in the ^{2}H NMR were explained as arising from the rapid equilibria of I ↔ II and II ↔ III as compared to the NMR time scale. On the other hand, the Raman spectra at pH values near the two pK_a's for the chromium(III)–edta system are easily explained by the superposition of the spectra of the coexisting species. This fact is undoubtedly due to the short time scale of the Raman scattering phenomenon.

Registry No. Li[Cr^{III}(edta)], 76547-63-2; [Cr^{III}(Hedta)(H_2O)], 15955-81-4.

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A New Class of Substituted Amine–Boranes: The Amine–(α-Cyanoorgano)boranes

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The general synthesis and chemistry of amine–cyanoboranes, $R_{3-x}NH_x \cdot BH_2CN$ (x = 0–3), have been reported by Spielvogel.[1,2] The trimethylamine derivative shows potent antiarthritic, antihypolipidemic, and antitumor activity on rodents[3] and is the precursor to $(CH_3)_3N \cdot BH_2CO_2H$, the (protonated) boron analogue of the dipolar amino acid betaine, $(CH_3)_3N \cdot CH_2COO^-$.[2] A zinc complex of the amine–cyanoborane has also been reported.[4] We wish to disclose the synthesis, characterization, and preliminary investigations of the chemistry of a new class of compounds whose members are closely related to $(CH_3)_3N \cdot BH_2CN$. This new class of compounds may be represented as $(CH_3)_3N \cdot BH_2CRR'CN$ and referred to as amine–(α-cyanoorgano)boranes.

Experimental Section

Preparation of $(CH_3)_3N \cdot BH_2CHC_6H_5CN$ and $(CH_3)_3N \cdot BH_2C(CH_3)_2CN$. The procedure used is essentially the same for both compounds. The preparation of $(CH_3)_3N \cdot BH_2CHC_6H_5CN$ will be described with differences in the two preparations pointed out. All procedures were carried out under N_2 and all solvents transferred by using inert-atmosphere techniques. All glassware was dried overnight in an oven. The initial procedure is identical with that used by Peters for the preparation of lithium (α-cyanoorgano)trihydroborates.[5] Tetrahydrofuran was dried by distillation from $LiAlH_4$ and sodium and stored over 4A molecular sieves. A 60-mL sample of THF was syringed into flask A (held at −78 °C) followed by 10 mL of 10.1 M *n*-BuLi. The nitrile, $C_6H_5CH_2CN$ (0.025 L, 0.32 mol), was added and the solution stirred for 1 h. THF (50 mL) was then syringed into flask B (−78 °C), followed by $BH_3 \cdot THF$ (0.05 L, 1.0 M). The contents of flask A were transferred to flask B via a double-ended needle by using positive N_2 pressure. The light yellow solution that resulted was stirred for 0.5 h. At this point this procedure differed from that utilized by Peters[5] since $LiBH_3CH(C_6H_5)CN$ was not isolated. Instead, a solution of $(CH_3)_3N \cdot HCl$ (14.3 g, 0.15 mol) in THF (175 mL) was gradually syringed into flask B. The resulting mixture was removed from the −78 °C slush bath and allowed to warm to ambient temperature, with N_2 flowing over the solution. The solution was stirred at ambient temperature for 22 h (16 h for the dimethyl derivative) and filtered to remove LiCl; the filtrate was then concentrated by rotary evaporation to give an oily white material. (When pure $LiBH_3CPhHCN$ is allowed to react with $(CH_3)_3N \cdot HCl$, a solid is obtained directly upon removal of solvent.[5]) With the phenyl derivative, this oily material was washed with diethyl ether (3 × 50 mL), and the resulting white powder was sublimed at 70 °C to give pure product (8.0 g, 85%). With the dimethyl derivative, water (100 mL) was added to the oil, followed by diethyl ether (150 mL). The organic layer was then separated from the aqueous layer and dried over $MgSO_4$, diethyl ether removed by rotary evaporation, and the resulting light yellow oil washed with hexane (3 × 50 mL) to give an oil product (6.2 g, 87%). An oil is also obtained if the intermediate lithium salt is isolated and then allowed to react with $(CH_3)_3N \cdot HCl$. However, crystals were obtained by washing the oil with hexane and allowing the oil–hexane mixture to stand overnight at 18 °C. These crystals may be washed with cold hexane.

Data for $(CH_3)_3NBH_2CH(C_6H_5)CN$: mp 133–134 °C dec; IR (KBr disk) 3037, 3018, 2994, 2938 (CH), 2348 (BH), 2208 (C≡N), 1595, 1485 (Ph, C=C), 1412, 1402 (C—C≡N), 1245 (C—N), 1156 cm^{-1} (BN); ^{1}H NMR ($CDCl_3$) δ 2.63 (s, 9 H, $(CH_3)_3N$), 3.12 (br, s, 1 H, CH), 7.26 (m, 5 H, C_6H_5); ^{11}B NMR ($CDCl_3$) δ −2.23 (t, BH_2, J_{B-H} = 105 Hz). Anal. Calcd for $C_{11}H_{17}BN_2$: C, 70.25; H, 9.11; N, 14.90. Found: C, 70.04; H, 9.25; N, 15.03. The solid is soluble in dichloromethane and tetrahydrofuran and insoluble in hexane, diethyl ether, and water. Data for $(CH_3)_3NBH_2C(CH_3)_2CN$: mp (crystals) 34–35 °C; IR (neat) 3020, 3010, 2960 (CH), 2385 (BH), 2210 (C≡N), 1408 (C—C≡N), 1245 (C—N), 1160 cm^{-1} (BN); ^{1}H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 1.21 (s, 6 H, $C(CH_3)_2$), 2.72 (s, 9 H, $(CH_3)_3N$); ^{11}B NMR ($CDCl_3$) δ −0.17 (t, BH_2, J_{B-H} = 105 Hz). Anal. Calcd for $C_7H_{17}BN_2$: C, 60.05; H, 12.24; N, 20.01. Found (oil product): C, 59.87; H, 12.15; N, 20.20. Found (crystalline product): C, 60.43; H, 11.84; N, 19.97; B, 7.88. The product is soluble in dichloromethane, tetrahydrofuran, and diethyl ether and insoluble in hexane and water.

Results and Discussion

The synthesis of the first two members of this new class of compounds, $(CH_3)_3N \cdot BH_2CH(C_6H_5)CN$ and $(CH_3)_3N \cdot BH_2C(CH_3)_2CN$, has been accomplished by utilizing the method given in eq 1. The reaction of $Li^+BH_3CRR'CN^-$ (generated in situ)

$$Li^+BH_3CRR'CN^- + (CH_3)_3N \cdot HCl \xrightarrow[25\ °C]{THF} (CH_3)_3N \cdot BH_2CRR'CN + H_2 + LiCl \quad (1)$$

and trimethylamine hydrochloride in tetrahydrofuran at room temperature yields the amine–(α-cyanoorgano)boranes (85% yield). (The precursor $Li^+BH_3CRR'CN^-$ salts have been isolated and characterized in our laboratory.[5]) The new compounds were characterized by infrared, proton NMR, and boron-11 NMR spectroscopies and elemental analysis.

The reaction (eq 1) used to synthesize the amine–(α-cyanoorgano)boranes in an 85% yield requires a maximum reaction period of 12 h. In contrast, the reaction used to synthesize $(CH_3)_3N \cdot BH_2CN$ from $NaBH_3CN$ and $(CH_3)_3N \cdot HCl$ requires refluxing in THF for 58 h to achieve a comparable yield.[1] This result indicates that the (α-cyanoorgano)trihydroborates, $BH_3CH(C_6H_5)CN^-$ and $BH_3C(CH_3)_2CN^-$, are much more reactive species with trimethylamine hydrochloride than is cyanotrihydroborate, BH_3CN^-. This increased reactivity is due to the presence of the CRR′ group between the BH_3 and CN groups, which has the effect of reducing the capacity of the nitrile group to withdraw electron density from the BH_3 moiety. Consequently, the B–H hydrogens in the (α-cyanoorgano)trihydroborates are more reactive than those in cyanotrihydroborate. These effects on hydride activity are consistent with the fact that trialkylhydroborates (R_3BH^-)[6] are exceptionally strong reducing agents

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