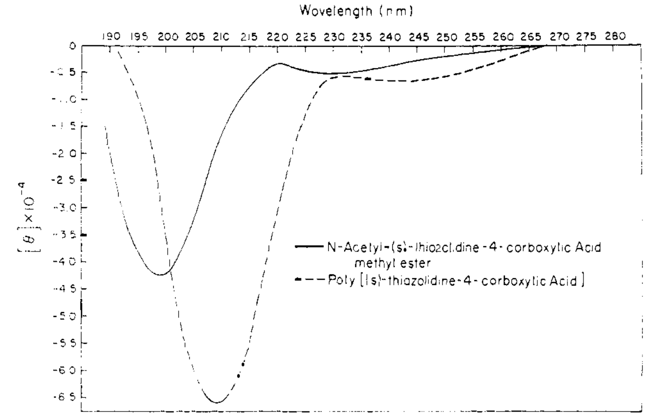

Figure 3. CD spectra of *N*-acetyl-(*S*)-thiazolidine-4-carboxylic acid methyl ester (——) and poly[(*S*)-thiazolidine-4-carboxylic acid] (- - - -) in hexafluoroisopropyl alcohol.

chromophore. These dichroic data are similar to those obtained for poly-L-proline form II.[8] We observed no mutarotations under all experimental conditions employed.

The lack of mutarotation in these systems is fully in agreement with predictions made, based on our conformational energy calculations.

We synthesized (*S*)-thiazolidine-4-carboxylic acid from cysteine hydrochloride and formaldehyde.[9] The total synthetic scheme will be reported in a subsequent paper.

We are currently in the process of preparing an oxygen analog of L-proline and (*S*)-thiazolidine-4-carboxylic acid, namely: (*S*)-oxazolidine-4-carboxylic acid. Our calculations[1] suggest that the polymer made from this compound will have properties intermediate between poly-L-proline and poly[(*S*)-thiazolidine-4-carboxylic acid]. We expect it to exhibit mutarotation.

**Acknowledgment.** We wish to thank the National Science Foundation (Grant No. GB 7558) and the National Institutes of Health (Grant No. GMO8974) for their generous support of this research. This research was also supported in part by the National Science Foundation (Grant No. GB 12278) and a grant from the Research Corporation and the Sloan Foundation to a Consortium at the Rockefeller University for the 220-MHz nuclear magnetic resonance facility.

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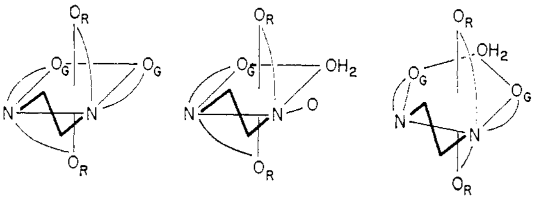
## Carbon-13 and Oxygen-17 Nuclear Magnetic Resonance Studies of the Structure of the Nickel(II)–Ethylenediaminetetraacetate Complexes in Aqueous Solution[1]

*Sir:*

Despite the impressive array of physical techniques that has been applied to the study of the EDTA complexes of divalent metal ions, the structure that these complexes adopt in solution is still a matter of dispute. The crystallographic studies of metal ion–EDTA complexes by Hoard and coworkers[2-4] suggest that the complexes in solution could adopt one of the structures shown in Figure 1.



Ia Ib Ic

Figure 1. Probable structures for metal ion (M)–EDTA complexes in solution. N⌒O represents the $NCH_2CO_2^-$ and N/\/N the $NCH_2CH_2N$ linkages of EDTA.

It has been suggested[5] that, since the M(II)–EDTA complexes exhibit a common p*K* value of ~3 toward protonation, the complexes have structure **1b**. Structure **1b** has also been advanced on the basis of the electronic spectra of aqueous solutions of divalent transition metal ion–EDTA complexes,[6] but Bhat and Krishnamurthy[7] consider that the pH dependence of the electronic spectra of the EDTA complexes of Cu(II), Co(II), and Ni(II) can be explained by an equilibrium between **1a** and **1b** if the free $CO_2$ group of **1b** is protonated. An equilibrium between **1a** and **1b** with a protonated carboxyl group has also been proposed to account for the negative enthalpies and positive entropies of protonation of the M(II)–EDTA complexes.[8] Milner and Pratt[9] interpreted the pmr spectra of the aqueous Ni(II)–EDTA complexes at pH $\cong 11$ and $\cong 2$ in terms of an equilibrium among species having free and coordinated $CO_2$ groups but did not propose structures for the complex species. Wilkins and Yelin[10] argued that since Co(II)–EDTA solutions can be rapidly oxidized predominantly ($\geq 80\%$) to the well-characterized octahedral, substitution-inert Co–EDTA⁻ ion (structure **1a**), the Co–EDTA²⁻ ion must exist in solution as **1a**. However, Margerum and Rosen[11] claim that the kinetic behavior of the aqueous Ni(II)–EDTA system in temperature-jump relaxation studies indicates that the complex has structure **1b**.

We present here $^{13}C$ and $^{17}O$ nmr data which show that the Ni–EDTA complex is predominantly structure **1a** in the pH range 10–4 and that, below pH 4, there is an equilibrium between **1a** and **1b** with protonation of the "free" $CO_2$ group of **1b**. In this study we have taken advantage of the large chemical shifts and relatively small line broadening exhibited by the $^{13}C$ reso-

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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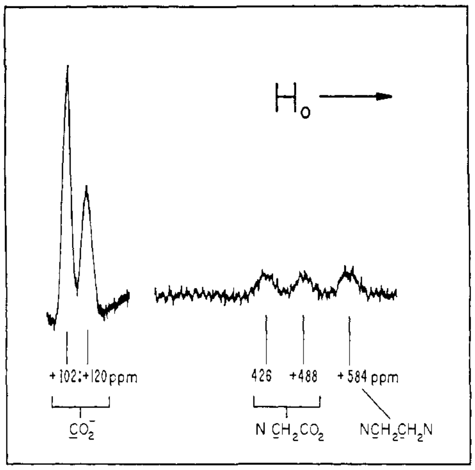

Figure 2. The $^{13}C$ 15.15-MHz nmr spectrum of an aqueous 0.5 *M* Ni–EDTA solution recorded in the derivative of dispersion mode at 32°. The EDTA was selectively enriched to 80% $^{13}C$ in the carboxyl carbon and the $^{13}C$ resonance of the $CO_2$ group was recorded at a lower modulation amplitude and rf field than $^{13}C$ resonances of the $CH_2$ groups. Chemical shifts are with respect to the $^{13}C$ resonance of the appropriate C atom of the free ligand in a 0.5 *M* EDTA solution at pH 7.

nance in paramagnetic complexes.[12] The results also illustrate the value of the multinuclear nmr approach to the study of the structure of metal ion complexes in solution.

The $^{13}C$ nmr spectrum of aqueous Ni–EDTA at pH 7 (Figure 2) exhibits the two $^{13}CO_2$ and two N–$CCO_2$ resonances expected for the stereochemically distinct N–$O_G$ and N–$O_R$ rings of structure **1a**. The large shifts observed are undoubtedly contact shifts due to the interaction between the ligand nuclei and the unpaired electrons of Ni(II). It has been shown[12] that the $^{13}C$ contact shifts of C atoms adjacent to the ligand donor sites in Ni(II) complexes of amino acids and ethylenediamines are shifted *upfield*, but that C atoms more remote from the donor sites experience large *downfield* contact shifts.[13] In this context, the fact that all $^{13}C$ resonances of the Ni–EDTA complex are shifted *upfield* is also consistent with **1a**, in which each C atom is adjacent to a donor atom—for **1b**, we would expect the resonance of the "free" $^{13}CO_2$ group to be shifted *downfield*.

The pH dependence of the $^{13}CO_2$ resonances is summarized in Figure 3. Throughout the pH range depicted, the relative areas of the signals are in a 1:1 ratio consistent with two $CO_2$ groups contributing to each $^{13}CO_2$ site. A plot of the $^{13}CO_2$ shifts *vs.* pH is also provided in Figure 3. The $N^{13}CCO_2$ shifts are also pH dependent, but the low intensity of the natural-abundance $^{13}C$ signals precludes a quantitative analysis of the chemical shifts. The pH–$^{13}C$ chemical shift plot is consistent with a protonation of a $CO_2$ group (p$K$ = 3.10)[14] accompanied by its displacement from the first coordination sphere of Ni(II) by $H_2O$ (eq 1), giving structure **1b** with a protonated free $CO_2$ group.

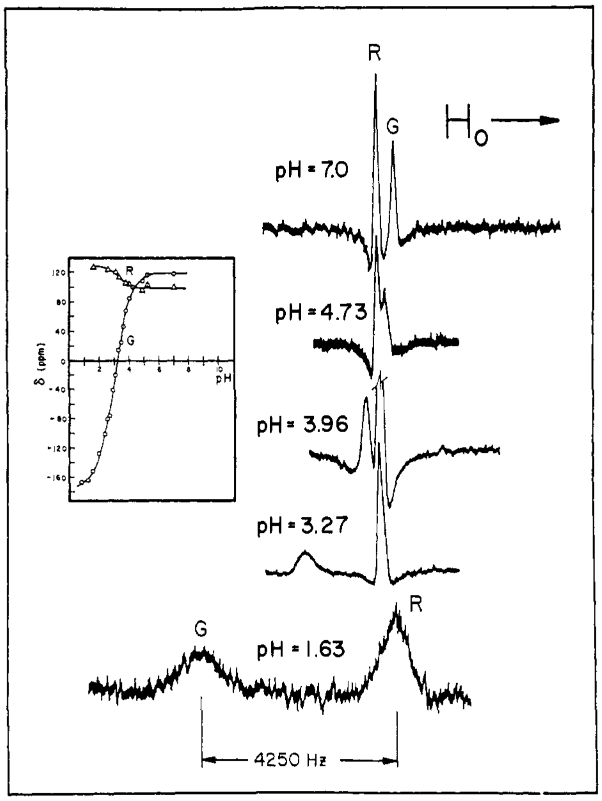

Figure 3. The pH dependence of the $^{13}C$ resonance in the $CO_2$ region of the 15.15-MHz nmr spectra of an aqueous 0.5 *M* Ni–EDTA solution at 32°. Spectra were *not* recorded at the same rf field intensities and modulation amplitudes. Insert: plot of the $^{13}C$ shifts (with respect to the free $CO_2$ group) *vs.* pH; ⊙, $CO_2$ group G; ▽, $CO_2$ group R (Figure 1).

$$[\text{Ni–EDTA}]^{2-} + H^+ + H_2O = [\text{Ni–HEDTA–}H_2O]^- \quad (1)$$

In assigning the $^{13}CO_2$ resonances summarized in Figure 3, we assumed that the $CO_G$ group of the strained N–$O_G$ ring is more easily protonated than the $CO_R$ group. This assumption is based upon the work of Smith and Hoard,[2b] who have shown that *solid* [Ni-$(OH_2)H_2$EDTA] adopts structure **1b**, in which even the coordinated $CO_G$ group may be protonated. The relative areas of the $^{13}CO_2$ signals require that the protonated $CO_G$ group of **1b** rapidly equilibrate, on the nmr time scale, with the coordinated $CO_G$ group but *not* the $CO_R$ groups. This observation, although unexpected, is also consistent with the X-ray studies of crystalline Ni(II)–, Co(III)–, and Fe(III)–EDTA complexes by Hoard and coworkers,[2,4] who showed that the M–$O_G$ bonds are longer (≥0.03 Å) and presumably weaker and more labile than the M–$O_R$ bonds.

The $^{17}O$ relaxation rates ($1/T_2$) of water in these solutions exhibit a pH profile similar to that of the $^{13}CO_G$ shifts in Figure 3. The full width of the water $^{17}O$ resonance at half the maximum intensity of the absorption signal of an aqueous 0.2 *M* Ni–EDTA solution is 118 Hz at pH 6, compared to a water $^{17}O$ line width of 114 Hz for a 0.2 *M* solution of the diamagnetic Mg–EDTA complex at the same pH. In

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[12] C. E. Strouse and N. A. Matwiyoff, *Chem. Commun.*, 439 (1970).

[13] The upfield shifts probably are the result of a spin polarization interaction between the adjacent $^{13}C$ nuclei and the large amount of electron spin delocalized to the N or O donor atoms, whereas the downfield shifts result from the *direct* delocalization of unpaired electron spin to the remote atoms.[12]

[14] This p$K$ value is only approximate and was calculated from the pH dependence of the $^{13}CO_G$ chemical shifts in the pH range 3–5. Analysis of the chemical shifts for pH <3 suggests that protonation of [Ni–HEDTA–$H_2O$] should be taken into account. In addition, we have observed that the $^{13}CO_2$ chemical shifts in the pH range 6–10 depend upon the solution composition, especially at the high ionic strengths employed in these studies.

the pH range 6 ≤ pH ≤ 9, the difference in the water $^{17}$O line widths of the two solutions is ~4 Hz, indicating that there is, at most, only a weak second coordination sphere interaction between $H_2O$ and Ni–EDTA. Below pH 6 there is little change (<10%) in the width of the $^{17}$O resonance of the Mg–EDTA solution but the $^{17}$O line width of the Ni–EDTA solution increases to 350 Hz at pH 2. If the pH dependence of the $^{17}$O relaxation is treated in terms of the formation of **1b**, then a p$K$ value of 3.05 is obtained for reaction 1.[15] Although the $^{13}$C shift data are not inconsistent with structure **1c**, the $^{17}$O relaxation rates in the pH range 6–9 rule out a strong first coordination sphere interaction between Ni(II) and $H_2O$.

The protonation of **1a** is also accompanied by changes in the electronic absorption spectrum. Bhat and Krishnamurthy[7] used dilute solutions ($[Ni^{2+}] = 10^{-3}$–$10^{-2}$ $M$ and ionic strength $\mu = 1$) and obtained p$K$ values of 2.73 and 3.12 for the protonation of Ni–EDTA from changes in the electronic spectrum at 980 and 380 nm, respectively. In our analysis of the pH dependence of the electronic spectra of 0.2 $M$ ($\mu \cong 1$) and 0.5 $M$ ($\mu \cong 2.5$) Ni–EDTA solutions, we obtain p$K$ = 3.1 ± 0.05 for both solutions at 985 and 785 nm.

In contrast to the solution behavior of the Ni–EDTA complex, $^{13}$C and $^{17}$O nmr studies in progress indicate that the Fe$^{III}$–EDTA complex is seven-coordinate in solution (has structure **1c**) and that, if the Co$^{II}$–EDTA complex has structure **1a**, it is stereochemically nonrigid.

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[15] No $^{17}$O contact shifts were observed for these solutions at 32° in the pH range 2–6, indicating that the rate of $^{17}OH_2$ exchange from the Ni(II) coordination sphere of **1b** is much smaller than the $^{17}$O shift. At temperatures above 90°, a large $^{17}$O shift is observable, consistent with the entry of the $^{17}$O relaxation rate into the region of rapid $H_2O$ exchange. Similar observations have been made for the relaxation and chemical shift of $^{17}OH_2$ by the $Ni(OH_2)_6{}^{2+}$ ion.[16]

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[17] (a) Address correspondence to this author; (b) consultant from the University of Texas.

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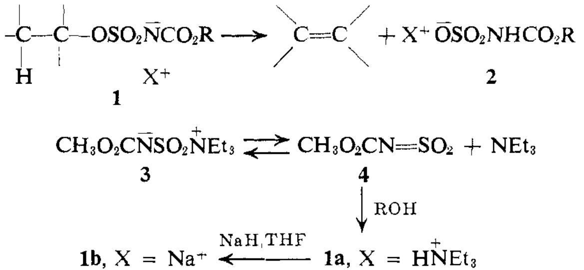
## Synthetic Applications of *N*-Carboalkoxysulfamate Esters

*Sir:*

We have found a synthetically useful and facile method for the mild dehydration of secondary and tertiary alcohols to the corresponding olefins which employs an alcohol-derived new leaving group, trialkylammonium or sodium *N*-carboalkoxysulfamates (**1a,b**). Despite the charge initially associated with this leaving group, such derivatives appear to ionize at low temperatures in nonpolar solvents to provide tight ion pairs which undergo fast stereospecific proton transfer to give high yields of olefins and the corresponding salt of *N*-carboalkoxysulfamic acid (**2**). Similar studies with primary alcohols indicate that thermolysis of such derivatives provides urethanes in high yield by an SN2 (or SNi) pathway.[1]



The triethylammonium *N*-carbomethoxysulfamates employed in this investigation were prepared by the interaction of the alcohol and the readily available methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (**3**) neat or in hydrocarbon solution at 30° or below. The electrophilic species responsible for the observed exothermic reaction even in the case of hindered tertiary alcohols may be methyl *N*-sulfonylcarbamate (**4**).[2]

The *tert*-alkyl sulfamate esters and their salts are sufficiently liable at room temperature as to preclude isolation and characterization. In many cases it was found to be operationally convenient to exchange the triethylammonium for a sodium cation in the more stable primary or secondary sulfamate ester salts and this could be readily accomplished by treatment of **1a** with sodium hydride in THF at 30°. Table I summarizes the results of our product investigation on the thermal decomposition of these *sec*- and *tert*-*N*-carbomethoxysulfamate salts.

A kinetic study of the solvolytic elimination reaction of 1,2-diphenylethyl-*N*-carbomethoxysulfamate triethylammonium salt in ethanol to give only *trans*-stilbene provided a first-order rate constant at 35° of 2.66 ± 0.03 × $10^{-6}$ sec$^{-1}$ with $\Delta H = 21.7$ kcal/mol and $\Delta S = -3.3$ eu.[3] As a probe into the stereochemical requirements we examined the behavior of the corresponding *erythro*- and *threo*-2-deuterio-1,2-diphenylethyl-*N*-carbomethoxysulfamate salts[4] (**5a,b**) in benzene at 50°. The former provided only *trans*-stilbene containing 97% deuterium while the latter gave only protio-*trans*-stilbene as determined by mass spectral analysis and this result remains invariant in substituting dimethylformamide as the solvent.

A small $\beta$-hydrogen isotope effect was kinetically observed with $k_H/k_D = 1.05 \pm 0.02$ and $1.08 \pm 0.03$ for the erythro and threo isomers, respectively, in ethanol at 35°. These kinetic and stereochemical results are consistent with an initial rate-limiting formation of an ion pair followed by a fast cis $\beta$ proton transfer[5] to the departing anion at a rate greater than

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[1] An elegant method for the conversion of alcohols that yields moderately stable carbonium ions to amines *via* the SNi rearrangement of *N,N*-dialkylsulfamate esters has been published: E. H. White and C. A. Elliger, *J. Amer. Chem. Soc.*, **87**, 5261 (1965).

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[3] Product development was followed spectrophotometrically at 295 nm and good first-order kinetics were displayed to 60% reaction.

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