It can be asserted, however, that they need not be synchronous, and if the change takes place in steps then the energy profile (Figure 7) must be altered to account for the additional conformational isomers of the deprotonated intermediates.

Acknowledgments. We wish to thank Dr. J. Fildes for the microanalyses, Dr. S. F. Mason for the CD spectrum, and Mr. R. Watts for a computer program. The technical assistance of Mr. S. Brown and Mr. H. Satrapa is also acknowledged.

Ligand-Exchange Reactions of Bis(*cis*-1,2-disubstituted ethylene-1,2-dithiolato)nickel Complexes

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Abstract: Ligand exchange reactions between complexes of the type $[MS_4C_4R_4]^z$ and $[MS_4C_4R_4']^z$, $R \neq R' = C_6H_5$, CF_3, CN, for the nickel group metals are described. In acetonitrile, dichloromethane, and acetone it was found that the mixed species $[M(S_2C_2R_2)(S_2C_2R'_2)]^z$, detected by polarography, was preferentially formed. Because the reorganization reactions were slow at room temperature, it was possible to isolate the mixed species from the equilibrium mixtures and also to devise a direct preparation of a mixed species.

There has been considerable interest in the chemistry of (*cis*-1,2-disubstituted ethylene-1,2-dithiolato)-metal complexes. Much of the current work, however, has been concerned with their characterization,[1] their magnetic properties, and the attempts[2] to elucidate their detailed electronic configurations.

These complexes have been shown[3] to undergo discrete one-electron-transfer reactions and, as a result, most of the subsequent synthetic work has been concerned with the isolation of the various members of the electron-transfer series. It has been tacitly assumed that these complexes are not labile and do not undergo ligand-exchange reactions. In this paper we show that ligand exchange does occur for the planar complexes of the nickel group, and we describe the isolation of mixed ligand species of the type $[Ni(S_2C_2R_2)(S_2C_2R'_2)]^z$, $z = -1, -2$; $R \neq R' = CF_3$, C_6H_5, and CN.

Experimental Section

Preparation of Compounds. The starting materials were prepared by the previously published procedures.[3] All melting points are uncorrected.

$[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CF_3)_2\}]$. A mixture of 0.40 g (0.62 mmole) of $[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$ and 0.42 g (0.62 mmole) of $[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$ was refluxed in 50 ml of acetone for 12 hr. The mixed ligand species was separated from this equilibrium mixture by the following procedure. A 15-ml portion of 2-butanol was added to this solution, and then most of the acetone (*ca.* 45 ml) was removed under reduced pressure without external heating. This caused the small amount of $[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$ to separate. The mixture was filtered and the residual acetone was removed from the filtrate. The product crystallized during 15 min. It was collected and washed with two 5-ml portions of cold 2-butanol, followed by two 5-ml portions of *n*-pentane. It was twice recrystallized from acetone–2-butanol by this procedure to give 0.1 g of pure $[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CF_3)_2\}]$ as brown needles (mp 159–161°).

Anal. Calcd for $C_{26}H_{30}F_6NNiS_4$: C, 47.50; H, 4.60; N, 2.13; S, 19.51; F, 17.34. Found: C, 47.50; H, 4.70; N, 2.20; S, 19.28; F, 17.19.

$[(C_4H_9)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$. A mixture of 0.50 g (0.61 mmole) of $[(C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$ and 0.33 g (0.61 mmole) of $[NiS_4C_4(C_6H_5)_4]$ was refluxed for 6 hr in 150 ml of acetone. The solvent was removed *in vacuo*, and the resultant solid was washed with two 30-ml portions of methanol. The residue was dissolved in 150 ml of acetone–2-butanol (2:1 v/v). The acetone was stripped off and the mixture was filtered. The dropwise addition of *n*-pentane (*ca.* 5 ml) to the filtrate induced crystallization. The product was recrystallized twice from acetone–2-butanol to give 0.2 g of shiny black needles of pure $[(C_4H_9)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$, mp 158–159°.

Anal. Calcd for $C_{34}H_{46}N_3NiS_4$: C, 59.73; H, 6.78; N, 6.15; S, 18.76. Found: C, 59.50; H, 6.83; N, 6.19; S, 18.96.

$[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$. This compound was made from an equimolar mixture of either $[NiS_4C_4(C_6H_5)_4]$ and $[(C_2H_5)_4N]_2[NiS_4C_4(CN)_4]$ or $[(C_2H_5)_4N][NiS_4C_4(CN)_4]$ and $[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$, by a procedure similar to that described above, as shiny black needles, mp 160–161°.

Anal. Calcd for $C_{26}H_{30}N_3NiS_4$: C, 54.66; H, 5.29; N, 7.35; S, 22.45. Found: C, 54.30; H, 5.30; N, 7.55; S, 22.32.

$[(C_4H_9)_4N]_2[Ni\{S_2C_2(CF_3)_2\}\{S_2C_2(CN)_2\}]$. A solution of 1.5 g (6.6 mmoles) of $(CF_3)_2C_2S_2$ in 10 ml of benzene was added to a suspension of 1.5 g (2.1 mmoles) of $[(C_6H_5)_3P]_2NiS_2C_2(CN)_2$ in 40 ml of the same solvent. The mixture was refluxed for 5 min and then the solvent was removed under reduced pressure. The residual oil was treated with 30-ml portions of *n*-pentane to extract the small amounts of $[NiS_4C_4(CF_3)_4]$. The residue was treated with 50 ml of ethanol, and the mixture was filtered after 30 min to remove $(C_6H_5)_3PS$.

The dark brown filtrate was treated with 5 ml of hydrazine. To the resulting red solution was added 1.35 g (4.2 mmoles) of $[(C_4H_9)_4N]Br$ dissolved in 10 ml of ethanol. Sufficient water was added to induce crystallization. The crude product separates slowly on standing. It was dissolved in 10 ml of acetone, treated with 25 ml of 2-butanol, and then most of the acetone was removed under reduced pressure. After 5 min the mixture was filtered to remove small amounts of $[(C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$. The filtrate was concentrated to 15 ml under reduced pressure, causing the product to separate as small red platelets. This ma-

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terial was recrystallized four times from ethanol-water, to which a drop of hydrazine had been added. The final product was collected, washed with ether, and dried *in vacuo* at 80° to give 0.40 g of cardinal red needles, mp 137–138°.

Anal. Calcd for $C_{40}H_{72}F_6N_4NiS_4$: C, 52.80; H, 7.98; N, 6.16; S, 14.09; F, 12.52. Found: C, 52.80; H, 8.08; N, 6.29; S, 12.70; F, 13.97.

A polarogram of this material showed that there was still a small amount of $[(C_4H_9)_4N]_2[NiS_4C_4(CF_3)_4]$ present in the sample. Attempts to prepare analytically pure samples using other cations were also unsatisfactory.

Physical Measurements. The polarographic data were obtained using a Heath-Built EUA-19-2 polarograph equipped with three electrodes. Both dichloromethane[4] and Spectrograde acetonitrile were employed as solvents with $[(C_4H_9)_4N][PF_6]$ and $[(C_3H_7)_4N][ClO_4]$, respectively, as the supporting electrolytes. Additional details are given in Table I.

Table I. Polarographic Half-wave Potentials[a]

For the Couple $NiLL'^- + e^- \rightleftharpoons NiLL'^{2-}$			
L[b]	L′	CH_3CN[c]	CH_2Cl_2[d]
dtb	dtb	−0.82	−0.83
dtb	dtfa	−0.55	−0.55
dtb	mnt	−0.35	−0.38
dtfa	dtfa	−0.12	−0.22
dtfa	mnt	+0.06[e]	−0.01
mnt	mnt	+0.23	+0.12
For the Couple $NiLL' + e^- \rightleftharpoons NiLL'^-$			
dtb	dtb	+0.12	−0.01
dtb	dtfa	+0.43	+0.35
dtb	mnt	+0.57	+0.43
dtfa	dtfa	+0.92	+0.80

[a] Measured in volts *vs.* sce. [b] dtb = $(C_6H_5)_2C_2S_2$; dtfa = $(CF_3)_2C_2S_2$; mnt = $(CN)_2C_2S_2$. [c] Measured with a rotating platinum electrode using 0.042 *M* $[(C_3H_7)_4N][ClO_4]$ as the supporting electrolyte, except as otherwise noted. [d] Measured with a dropping mercury electrode (dme) using 0.10 *M* $[(C_4H_9)_4][PF_6]$ as the supporting electrolyte. [e] Measured with a dme, using $[(C_3H_7)_4N][ClO_4]$ as the supporting electrolyte.

Conductivities were measured in Spectrograde acetonitrile on a Serfass bridge using a cell calibrated with a 1 *M* aqueous potassium chloride solution. The following molar conductivities (ohm^{-1} cm^2 mole^{-1}) were observed for 10^{-3} *M* solutions: $[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CF_3)_2\}]$, $\Lambda_m = 134$; $[(C_4H_9)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$, $\Lambda_m = 114$; $[(C_4H_9)_4N]_2[Ni\{S_2C_2(CF_3)_2\}\{S_2C_2(CN)_2\}]$, $\Lambda_m = 290$. In addition, $[(C_4H_9)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$ was established as a 1:1 electrolyte from the slope of a plot of the equivalent conductivity as a function of $\sqrt{\bar{c}}$ using a method previously described.[1] For this compound, the observed slope was 340 and the extrapolated value for the equivalent conductivity at infinite dilution was 126 ohm^{-1} cm^2 equiv^{-1}. For comparison, the theoretical slope of a 1:1 electrolyte in acetonitrile is 320.

Results and Discussion

The redox behavior and the solubilities of the various species $[MS_4C_4R_4]^{0,-,2-}$ (with a given cation) are markedly dependent on the nature of *R*. Previous synthetic studies[5] utilized these facts, as, for example, in the one-electron oxidation reactions employing $[NiS_4C_4(CF_3)_4]$.

$$[NiS_4C_4(CF_3)_4] + [(C_4H_9)_4N]_2[NiS_4C_4(CN)_4] \longrightarrow [(C_4H_9)_4N][NiS_4C_4(CF_3)_4] + [(C_4H_9)_4N][NiS_4C_4(CN)_4]$$

It was assumed that ligand reorganization would not occur or, at worst, would be very slow in comparison to the primary redox reaction. The reasonableness of this assumption was evident in the oxidation of $[(C_4H_9)_4N]_2[MS_4C_4(CN)_4]$ to $[(C_4H_9)_4N][MS_4C_4(CN)_4]$, M = Ni, Pd, or Pt, where the latter salts were sparingly soluble in the reaction solvent and crystallized rapidly from it. However, the intriguing possibility that ligand "scrambling" reactions could occur, under suitable conditions, prompted our detailed examination of these systems.

Polarography proved to be a particularly convenient technique to detect both the occurrence and the extent of the reorganization reactions. Equimolar amounts (*ca.* 10^{-3} *M*) of two nickel complexes having different ligand substituents, together with the supporting electrolyte necessary for the polarographic measurements, were allowed to react in either CH_2Cl_2 or CH_3CN, and polarograms were recorded periodically. Initially these polarograms consisted only of those waves characteristic of the starting materials. Gradually, however, a new wave appeared at a potential between those of the initially observed waves, and there was a concomitant decrease in the diffusion currents of the reacting species. The relevant data for this type of reaction are summarized in Tables I and II.

Table II. Ligand-Exchange Reactions in Solution

Species[a]	Solvent	Equilibrium time[b]	% mixed species[c]
$[Ni(dtb)(dtfa)]^-$	CH_3CN	13 days at 25°	92
	CH_2Cl_2	6 days at 40°	77
$[Ni(dtb)(mnt)]^-$	CH_3CN	4 hours at 82°	88
	CH_2Cl_2	6 days at 40°	81
$[Ni(dtfa)(mnt)]^-$	CH_2Cl_2	37 days at 40°	74

[a] See Table I for abbreviations. [b] Time required until polarograms of a solution initially containing equimolar amounts (*ca.* 10^{-3} *M*) of the parent compounds showed no further change. [c] Equilibrium values determined from polarograms recorded at 25°. Estimated error, ±3%.

The significant features of our studies are that the mixed species are formed to a much greater extent than expected for random reorganization. The position of equilibrium is solvent dependent, the mixed species occurring to approximately 75–80% in CH_2Cl_2 and to approximately 90% in CH_3CN. While all of the reactions are slow, there is a considerable difference between the rates at room temperature and those at reflux in CH_3CN.

We have shown that these "scrambling" reactions also occur in the other metal systems in the nickel group. The reaction of equimolar amounts of $[NiS_4C_4(C_6H_5)_4]^-$ and $[PtS_4C_4(CF_3)_4]^-$ is expected to give six different species at equilibrium, but the polarogram of the mixture is simplified since the half-wave potentials for the symmetrical nickel and platinum complexes with a given ligand are practically identical. As before, we observed the appearance of an intermediate wave, in this case at −0.49 v, which we assume to be the composite wave for the mixed species $[M\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CF_3)_2\}]^-$, M = Ni and Pt. The rate of ligand exchange is much slower that that for nickel complexes alone.

With the information obtained from the polarographic experiments, we have devised excellent synthetic routes to the mixed ligand complexes. In refluxing acetone or acetonitrile, the "scrambling" re-

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actions were complete in 4–6 hr for R = C_6H_5 and R′ = CN or CF_3. The solubilities of the three species present at equilibrium were sufficiently different (with a suitable counterion) to allow a straightforward separation at room temperature of the desired products. However, the ligand-exchange reaction between $[NiS_4C_4(C_6H_5)_4]^-$ and $[NiS_4C_4(CN)_4]^-$ is complicated by the redox reaction

$$[NiS_4C_4(C_6H_5)_4]^- + [NiS_4C_4(CN)_4]^- \rightleftharpoons [NiS_4C_4(C_6H_5)_4] + [NiS_4C_4(CN)_4]^{2-}$$

which occurred very rapidly, as evidenced by the immediate precipitation of $[NiS_4C_4(C_6H_5)_4]$ on mixing. Polarographic studies of dilute (*ca.* 10^{-3} *M*) solutions in CH_2Cl_2 indicated that, while the redox equilibrium lay to the right, ligand exchange occurred gradually to give $[Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]^-$. Because the redistribution reaction occurred extremely slowly (Table II) for R = CN and R′ = CF_3, a direct synthesis of the mixed species was attempted by the reaction of $[(C_6H_5)_3P]_2NiS_2C_2(CN)_2$ with excess bis(trifluoromethyl)-dithietene. However, it was not possible to obtain the mixed species completely free of $[NiS_4C_4(CF_3)_4]^{2-}$ even by repeated recrystallization. The complexes $[Ni(S_2C_2R_2)(S_2C_2R_2')]^z$, as expected, have properties intermediate to those of the corresponding symmetrical species. The polarograms of freshly prepared solutions of these new compounds exhibit only those waves which were attributed (Table I) to the mixed species in the exchange studies. However, if these solutions are allowed to stand, "scrambling" of the ligands occurs to give an equilibrium mixture of all three species. Thus the isolation and purification of the mixed species must be effected as rapidly as possible, preferably without heating the solutions.

Although there is no evidence that the nickel monoanions are associated in solution, single crystal X-ray diffraction studies[6] of $[(C_6H_5)_3(CH_3)P][NiS_4C_4(CN)_4]$ clearly demonstrate a pairwise interaction in the solid state. It is tempting to suggest that the transient intermediate in the ligand exchange reactions may be dimeric. It is evident that other dithiolato complexes should undergo these "scrambling" reactions, and further investigations are in progress.

Acknowledgment. Financial support by the National Science Foundation (Grant G.P. 3468) is gratefully acknowledged. E. T. S. was a Woodrow Wilson Fellow, 1964–1965, and a National Science Foundation Graduate Fellow, 1965–1967.

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New Multidentate Ligands. V. Transition Metal Chelates of Triethylenetetraminehexaacetic Acid[1]

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Received March 30, 1966

Abstract: Further studies of the interactions of transition metal ions with triethylenetetraminehexaacetic acid (TTHA) have elucidated the equilibria between the mononuclear chelates and several protonated species. Equilibrium constants are reported for mono-, di-, tri-, and tetraprotonated mononuclear Cu(II), Ni(II), and Co(II) chelates, as well as the simple 1:1 chelates. The decadentate ligand TTHA is found to be unique in its ability to combine simultaneously with a metal ion and from one to four protons. Probable arrangements of coordinate bonding in the aqueous chelates are inferred.

In a recent publication, the formation of mono-, di-, and ternuclear alkaline earth chelates of triethylenetetraminehexaacetic acid was described, and the corresponding equilibrium constants were reported,[3] together with the acid dissociation constants of the ligand and dissociation constants of protonated alkaline earth chelates. Reasonable arrangements of donor–ligand bonds were suggested as an aid in the interpretation of the equilibrium data reported. Because of the unusual properties of this new ligand, further studies of metal complex formation equilibria seemed warranted. This paper describes a further extension of the earlier work to successive protonation equilibria of mononuclear transition metal chelates.

There are very little equilibrium data on this new ligand in the literature. The work of Pribil and coworkers[4–12] is restricted to analytical applications. The first equilibrium constants reported for TTHA were the acid dissociation constants of the free ligand,

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(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1020.

(2) (a) Abstracted from a thesis submitted by T. A. Bohigian to the Faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of doctor of philosophy, June 1966. (b) To whom inquiries should be addressed: Department of Chemistry, Texas A & M University, College Station, Texas.

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