The identified products from the experiments with SiH_4 were shown by ir, mass spectral, and vpc analyses to be methylsilane, acetylene, diacetylene, benzene, and disilane. The high volatility of SiH_4 and the observed pressure increase during this experiment raise some questions as to the nature of the reaction. In ordinary studies the pressure in the cell remains sufficiently low so that the mean free path exceeds substantially the distance from the entry port to the wall. Gas-phase reaction or reactions on the hot electrodes are thereby largely eliminated in normal work. The possibility of such effects cannot be eliminated in the silane case. Thus, acetylene, diacetylene, and benzene may arise from the secondary reaction of hydrogen with the hot carbon electrodes. The low thermal stability of silanes strongly suggests, however, that they are not formed in such secondary processes.

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Substitution Reactions of Copper(II) Chelates with Sodium Maleonitriledithiolate

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Maleonitriledithiolate (mnt^{2-}) is the best known of a series of 1,2-dithiolate ligands that form a wide variety of interesting and unusual metal complexes.[1] Little or nothing has been reported concerning the kinetics and mechanisms of substitution reactions involving these ligands. For this reason we investigated the reactions of several copper(II) chelates with mnt^{2-} as the nucleophile.

Experimental Section

The Na_2mnt was prepared as previously described[2] and was checked for purity by spectrophotometric titration with a standard nickel(II) perchlorate solution. G. F. Smith and Co. copper(II) perchlorate was standardized *via* EDTA titration. Fisher Certified reagent grade $Na_2EDTA \cdot 2H_2O$ was used. The disodium salts of nitrilotriacetic acid (NTA) and iminodiacetic acid (IDA) were purchased from Eastman Kodak. The Na_2NTA was crystallized twice from 50:50 ethanol–water. Spectra were recorded on a Cary 14 spectrophotometer. The reactions were followed at 470 nm in aqueous solution at 25 ± 0.1° on a commercially available[3] stopped-flow apparatus. The ionic strength was adjusted to 0.2 M with sodium perchlorate. The total copper concentration was 5×10^{-5} M and the Na_2mnt concentration was $(5\text{–}45) \times 10^{-4}$ M, thus maintaining pseudo-first-order conditions. The EDTA, NTA, and IDA complexes of copper were prepared *in situ* by combining equimolar quantities of copper perchlorate and ligand, except that a 1:2 molar ratio was used for $Cu(IDA)_2^{2-}$. The pH of the copper(II)-EDTA and -NTA solutions was adjusted to 7.5, thus ensuring the absence of protonated and/or hydroxy forms.[4,5] The fully deprotonated form of IDA, *i.e.*, Na_2IDA, was used so that no pH adjustment was necessary. The pH of the Na_2mnt solutions was about 8.

Results and Discussion

The product spectrum for the reaction $CuL^{z-} + 2mnt^{2-} \rightarrow Cu(mnt)_2^{2-} + L^{(z+2)-}$ was identical with the spectrum of a $Cu(mnt)_2^{2-}$ solution prepared from a copper perchlorate solution. For reaction 1 the form of the pseudo first-order rate constant, k_{obsd}, is given

$$Cu(EDTA)^{2-} + 2mnt^{2-} \longrightarrow Cu(mnt)_2^{2-} + EDTA \tag{1}$$

in eq 2. With NTA as the leaving group (eq 3)

$$k_{obsd}(sec^{-1}) = 5.2 + 7.6 \times 10^3[mnt^{2-}] \tag{2}$$

the results are given in eq 4. For reactions 1 and 3

$$Cu(NTA)^{-} + 2mnt^{2-} \longrightarrow Cu(mnt)_2^{2-} + NTA \tag{3}$$

$$k_{obsd}(sec^{-1}) = 0.88 + 1.6 \times 10^3[mnt^{2-}] \tag{4}$$

excellent first-order kinetics were followed. The reactions with IDA as given in reactions 5 and 6 were

$$Cu(IDA) + 2mnt^{2-} \longrightarrow Cu(mnt)_2^{2-} + IDA \tag{5}$$

$$Cu(IDA)_2^{2-} + 2mnt^{2-} \longrightarrow Cu(mnt)_2^{2-} + 2IDA \tag{6}$$

too rapid to observe. This means that k_{obsd} must have been greater than 100 sec^{-1} for reactions 5 and 6. Figure 1 shows the experimental results.

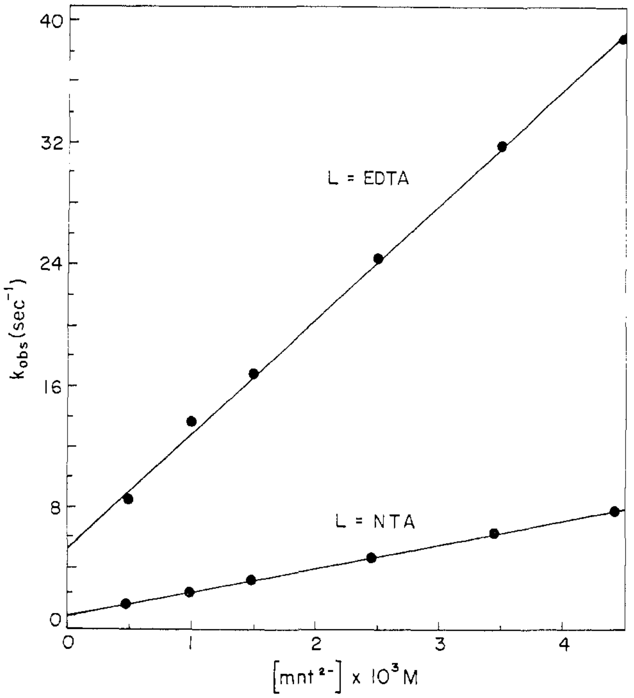

Figure 1.—The dependence of k_{obsd} on mnt^{2-} concentration for the reactions $Cu(L)^{z-} + 2mnt^{2-} \rightarrow Cu(mnt)_2^{2-} + L'$ (z = 1 or 2).

The mechanism proposed to account for the observed kinetics with $Cu(EDTA)^{2-}$ is shown in Figure 2. A similar mechanism is expected for the NTA and IDA complexes. It is expected that the copper–oxygen bonds would be broken in preference to the copper–nitrogen bonds as the first mnt^{2-} group is added.[6] It is generally found, however, that cleavage of the cop-

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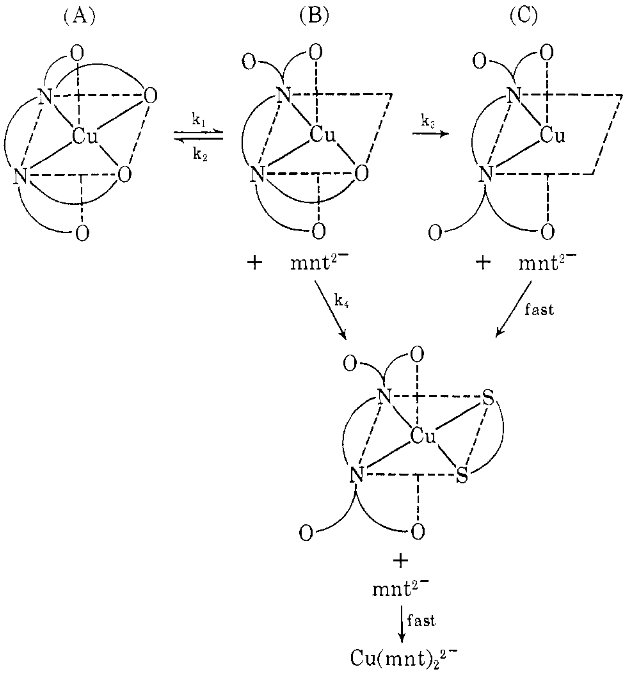

Figure 2.—Mechanism for Cu(EDTA)$^{2-}$ + 2mnt^{2-} → Cu(mnt)$_2$$^{2-}$ + EDTA. Charges have been omitted.

per–nitrogen bonds is rate determining, at least for EDTA.[6] However, mnt^{2-} may well exert a large *trans*-labilizing effect in the Cu(L)(mnt) intermediate causing rapid cleavage of the metal–nitrogen bonds, *i.e.*, addition of the first group is rate determining. It has been reported that mnt^{2-} is high in the *trans*-effect series.[7,8] Supporting the suggestion that the addition of the first group is rate determining, it was found that the entire absorbance change calculated from the reactants and products for reactions 1 and 3 was observed and was a single pseudo-first-order step.

In Figure 2 the EDTA complex is drawn as six-coordinate. It is not clear whether or not the complex is best described as four-coordinate planar or six-coordinate octahedral.[9,10] At any rate there would be a tetragonal distortion[11] and cleavage of the axial bonds would be very rapid. The rate-determining step is cleavage of equatorial bonds. The proposed mechanism gains support from its similarity to the general mechanism proposed for acid hydrolysis of metal chelate compounds.[12]

Assuming the steady-state approximation for B in Figure 2 one calculates, with L = mnt^{2-}

$$k_{\text{obsd}} = \frac{k_1(k_3 + k_4[\text{L}])}{k_2 + k_3 + k_4[\text{L}]} \tag{7}$$

$$\lim_{[\text{L}]\to 0} k_{\text{obsd}} = \frac{k_1k_3}{k_2 + k_3} \tag{8}$$

The intercept is hence predicted to be $k_1k_3/(k_2 + k_3)$. Although the experimentally found form of k_{obsd} (Figure 1) contains a term first order in mnt^{2-}, in principle at much higher ligand concentrations than could be used, k_{obsd} would reach a limiting value equal to k_1.

Cu(EDTA)$^{2-}$ has a stability constant[13] log β = 18.7 at 25°. For Cu(NTA)$^-$ the value[14] is about 13 at 25°. For Cu(IDA)$_n$ log β_1 = 10.5 and log β_2 = 16.1 at 30°.[15] Assuming a planar or distorted octahedral (tetragonal) structure for these complexes, one expects the order of decreasing rate of substitution to be: Cu(IDA), Cu(IDA)$_2$$^{2-}$ > Cu(NTA)$^-$ > Cu(EDTA)$^{2-}$. The different charges on these complexes would most likely enhance this order. It was found that the order is: Cu(IDA), Cu(IDA)$_2$$^{2-}$ > Cu(EDTA)$^{2-}$ > Cu(NTA)$^-$ (see Figure 1). Finding that IDA is more easily displaced than EDTA is no surprise. The results for Cu(NTA)$^-$ were unexpected. Note that both the second-order term (slope) and the intercept in k_{obsd} for Cu(NTA)$^-$ (eq 4) are less than those of Cu(EDTA)$^{2-}$ (eq 2). See Figure 1.

Several structures can be envisioned for the Cu(NTA)$^-$ complex. Models show that a planar structure would demand considerable steric strain. Furthermore, one would not expect a planar complex to react at a slower rate than the EDTA analog. Smith and Sawyer[16] have studied the NTA complex of palladium(II), a metal that almost always forms planar complexes. In order to form a planar complex and yet reduce the steric strain that such a structure implies a dimer is formed, [Pd(NTA)]$_2$$^{2-}$, in which each NTA has three bonds to one metal and one bond to the other. We consider a dimeric structure to be unlikely for copper(II) because the formation constant for Cu(NTA)$^-$ was calculated[17] by standard procedures, the data not requiring the assumption of polynuclear species. If polynuclear species formed, it is unlikely that consistent stability constants would be obtained by assuming their absence.[18] The low copper concentration used in this study (5×10^{-5} *M*) also makes dimeric species less likely. A *cis*-octahedral structure with three donor groups in the equatorial plane is conceivable, but it is difficult to understand why such a complex would react more slowly than Cu(EDTA)$^{2-}$ and Cu(IDA)$_2$$^{2-}$. The last possibility is a tetrahedral structure. Models show that there exists relatively little strain in this configuration. One example of a tetrahedral NTA complex has been reported.[19] Our conclusion is that Cu(NTA)$^-$ is probably tetrahedral

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or at least distorted from planar toward tetrahedral. The addition of the first mnt^{2-} group would then involve a change of stereochemistry from tetrahedral to planar (tetragonal). Swift reported[20] evidence that a stereochemical change from tetrahedral to octahedral can be slow relative to many ligand-substitution reactions for cobalt(II) and zinc(II). It is possible that the displacement of NTA from copper(II) by mnt^{2-} is slow compared to IDA and EDTA because the former displacement involves tetrahedral copper converting to planar whereas the latter involves planar or tetragonal copper without a change in stereochemistry. Even if the stereochemical change is not rate determining, we suggest that the difference in kinetics is due to the NTA complex being tetrahedral and hence possessing energy requirements for substitution qualitatively different from the planar complexes.

The electronic spectra of the copper(II) complexes reported herein have been published.[21] The spectra of the EDTA and NTA complexes are not sufficiently different to allow any conclusions as to structure. None of the possible structures for $Cu(NTA)^-$ possesses a center of inversion so intensity arguments are not really useful. Actually, destruction of a center of symmetry does not always lead to increased intensity.[22]

We have found that the displacement of EDTA and NTA from cadmium(II) with mnt^{2-} under the conditions stated above is too rapid to observe on a stopped-flow device. The displacement of NTA from zinc(II) with mnt^{2-} is about ten times faster than from copper(II), but mnt^{2-} will not displace EDTA from zinc(II).

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Kinetics and Mechanisms of the Substitution Reactions of Five-Coordinate Cobalt Formally in Oxidation State III

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Maleonitriledithiolate (mnt) readily forms the complex $Co(mnt)_2^-$ which has cobalt in a formal oxidation state of III. This complex forms a wide variety of five- and six-coordinate adducts.[1-3] The substitution reactions of these adducts are usually very rapid. It has been shown[1] that $Co(mnt)_2^-$ displays many properties at variance with the usual behavior of cobalt(III) and the metal resembles a d^8 system more closely than a d^6 system. We have initiated an investigation of the kinetics of the unusual cobalt(III) and iron(III) maleonitriledithiolate systems.

Herein we report the kinetics of reaction 1, where L = en, bipy, phen, mnt^{2-}, i-mnt^{2-}, and triphenyl phosphite.

$$Co(mnt)_2P(C_6H_5)_3^- + L \longrightarrow Co(mnt)_2L^{3-} + P(C_6H_5)_3 \quad (1)$$

Experimental Section

Sodium maleonitriledithiolate (Na_2mnt) and its isomer sodium 1,1-dicyanoethylene-2,2-dithiolate ($Na_2(i$-$mnt)$) were prepared and purified by published methods.[4,5] The other nucleophiles were purchased. The reactions were studied in methanol, purified as previously described,[6] at 25° on a commercially available[7] stopped-flow device. The ionic strength was maintained at 0.1 M with sodium perchlorate. The $Co(mnt)_2P(C_6H_5)_3^-$ complex was prepared *in situ* from triphenylphosphine and $[(CH_3)_4N]Co(mnt)_2$ prepared by a published method.[8] *Anal.* Calcd for $C_{12}H_{12}N_5S_4Co$: C, 34.9; H, 2.9; N, 16.9. Found: C, 34.9; H, 2.8; N, 16.9. Spectra of reactants and products agreed with those previously reported.[1-3] For the kinetic runs $Co(mnt)_2^-$ was made 10^{-4} M and then triphenylphosphine was made either 10^{-4} M or 6×10^{-4} M, the latter representing a fivefold excess of triphenylphosphine over $Co(mnt)_2P(C_6H_5)_3^-$.

Results and Discussion

Figure 1 shows the mechanism proposed to account for the observed kinetics with bidentate nucleophiles. We propose a similar mechanism for unidentate nucleophiles except that C represents the product so k_4, k_5, and k_7 do not operate. The results are presented in Figures 2–4. Table I lists the results for cases when linear k_{obsd} *vs.* nucleophile concentration plots were obtained. Assuming the steady-state approximation for B and C one obtains, for excess L-L

TABLE I
THE DEPENDENCE OF k_{obsd} ON NUCLEOPHILE CONCENTRATION IN THE CASES EXHIBITING LINEAR BEHAVIOR

Nucleophile[a]	k_{obsd}, sec^{-1} No excess $P(C_6H_5)_3$	Fivefold excess $P(C_6H_5)_3$ (5×10^{-4} M)
mnt^{2-}	$3.4 + 1900[mnt^{2-}]$	$0.32 + 507[mnt^{2-}]$
i-mnt^{2-}	$3.3 + 1140[i\text{-}mnt^{2-}]$	$0.21 + 262[i\text{-}mnt^{2-}]$
phen	$0.24 + 425[phen]$	$79[phen]$

[a] Nucleophile concentration was in the range $(1–7) \times 10^{-3}$ M.

$$k_{obsd} = \frac{k_1k_3k_5[L\text{-}L] + k_5k_6K[L\text{-}L](k_2[P] + k_3[L\text{-}L])}{(1 + K[L\text{-}L])(k_2[P](k_4 + k_5 + k_7[P]) + k_3[L\text{-}L](k_5 + k_7[P]))} \quad (2)$$

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