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# The Rates and Mechanisms of Substitution Reactions of Square-Planar Nickel(II) Dithiolate Complexes

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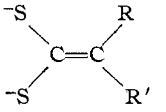
The kinetics of the substitution reactions of bis(dithiolato)nickel(II) complexes with dithiolate nucleophiles have been studied in aqueous solution at 25° using a stopped-flow technique. Nucleophilic reactivity, leaving-group effects, and *trans* effects are discussed. Mechanisms for bidentate and unidentate nucleophiles are proposed. Several five-coordinate intermediates were detected and their stabilities were estimated. The *trans* effect operates *via* the stability of the five-coordinate intermediate which in turn is correlated to the extent of involvement of the nickel 4p$_z$ orbital in $\pi$ bonding. Stability constants for the bis(dithiolato)nickel(II) complexes have been measured in aqueous solution at 25°. Kinetics of formation of several nickel(II) dithiolato complexes is reported. Tris(ethylenediamine)nickel(II) reacts with dithiolate ligands in a dissociative manner. A bis(dithiolato)copper(II) substitution reaction is reported.

## Introduction

Most studies of the substitution reactions of d$^8$ planar complexes have been limited to platinum(II) systems.[1] Relatively little work has been reported for nickel(II) planar systems mainly because the reactions are usually very rapid, requiring flow or relaxation techniques to study the kinetics. The fact that most common ligands form octahedral rather than planar complexes with nickel(II) has also been a deterrent. The sparse work that has been reported on planar nickel(II) systems agrees with the two-term rate law found for platinum(II) substitutions.[1]

Recently a new series of water-soluble planar nickel(II) complexes with ethylene-1,1-dithiolate (I) and ethylene-1,2-dithiolate (II) ligands has been reported.



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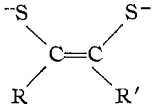

II

The 1,2-dithiolates, of which maleonitriledithiolate (mnt) is perhaps best known, have been extensively studied largely because of the unusual redox properties of their metal complexes.[2] The 1,1-dithiolate complexes possess less well-defined redox properties, presumably due to the lack of $\pi$ delocalization as present in 1,2-dithiolate systems.[3-5] Nevertheless both of these ligand systems are ideally suited for the study of substitution reactions of nickel(II).

This study was undertaken to ascertain the mechanism of ligand substitution for planar nickel(II) systems, to study the reactivities of the dithiolate complexes, to study the nucleophilic reactivities of the dithiolate ligands, and to study the effect of the group *trans* to the ligand being displaced. In view of the existence of many five-coordinate nickel(II) complexes,[6] especially[7] Ni(CN)$_5{}^{3-}$, it was hoped that five-coordinate adducts could be detected and their stabilities estimated. Table I shows the structures of the dithiolate ligands used in this work.

## Experimental Section

**Preparation of Ligands.**—All the ligands described below were checked for purity by spectrophotometric titration with a standard nickel perchlorate solution.

**Potassium N-cyanodithiocarbimate, K$_2$cdc,** was prepared by a published method.[4] **Sodium 1,1-dicyanoethylene-2,2-dithiolate, Na$_2$-*i*-mnt,** was prepared as described in the literature.[8] **Potassium 1-nitroethylene-2,2-dithiolate, K$_2$ned,** was prepared by the synthesis of Freund.[9] **Sodium 1-cyano-1-phenylethylene-2,2-dithiolate, Na$_2$cpd,** was prepared according to the method of Coucouvanis.[10] **Potassium dithiooxalate, K$_2$dto** (Eastman Kodak), was purified as previously described.[11] **Sodium maleonitriledithiolate, Na$_2$mnt,** was prepared according to a published method.[12]

**Preparation of Metal Complexes.** **[(CH$_3$)$_4$N]$_2$Ni(cdc)$_2$.**—This complex was prepared by a published method.[4] *Anal.* Calcd for C$_{12}$H$_{24}$N$_6$S$_4$Ni: C, 32.8; H, 5.5; N, 19.1. Found: C, 32.5; H, 5.6; N, 19.1.

**[(CH$_3$)$_4$N]$_2$Ni(*i*-mnt)$_2$.**—The synthesis of this complex followed a published method.[4] *Anal.* Calcd for C$_{16}$H$_{24}$N$_6$S$_4$Ni: C, 39.4; H, 5.0; N, 17.2. Found: C, 39.0; H, 4.8; N, 17.1.

**[(CH$_3$)$_4$N]$_2$Ni(mnt)$_2$.**—The synthesis of this compound is described in the literature.[13] *Anal.* Calcd for C$_{16}$H$_{24}$N$_6$S$_4$Ni: C, 39.4; H, 5.0; N, 17.2. Found: C, 39.5; H, 4.9; N, 17.2.

**K$_2$Ni(ned)$_2$.**—This compound was prepared by adding, with stirring, 6.2 g (0.025 mol) of NiSO$_4\cdot$6H$_2$O in 40 ml of hot water to 10.6 g (0.05 mol) of K$_2$ned in 40 ml of water. Crystals of K$_2$Ni(ned)$_2$ formed upon cooling in an ice bath. The product was filtered and washed with ethanol and then ethyl ether. The compound was crystallized from 50:50 ethanol–water and washed with ethanol and ether and air dried. Fine purple-red crystals were obtained in a yield of approximately 60%. *Anal.* Calcd for K$_2$C$_4$H$_2$N$_2$O$_4$S$_4$Ni: C, 11.8; H, 0.5; N, 6.9. Found: C, 11.7; H, 0.3; N, 6.5.

**K$_2$Ni(dto)$_2$.**—This compound was prepared according to a

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(3) J. A. McCleverty, *ibid.*, **10**, 213 (1968).

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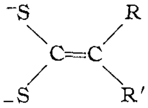
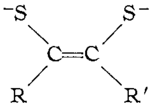
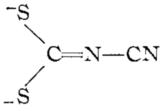
Table I

The Ligands Used in This Study

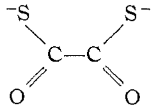




| R | R′ | Name | R | R′ | Name |
|---|---|---|---|---|---|
| CN | CN | *i*-mnt | CN | CN | mnt |
| CN | $C_6H_5$ | cpd | $CF_3$ | $CF_3$ | tfd |
| H | $NO_2$ | ned | | | |



cdc



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published method.[14] *Anal.* Calcd for $K_2C_4O_4S_4Ni$: C, 12.7; H, 0.0; Ni, 22.4. Found: C, 12.4; H, 0.0; Ni, 22.3.

**$K_2Cu(dto)_2$.**—The complex was prepared by adding 4.5 g (0.023 mol) of $K_2dto$ in 20 ml of warm water to 2.5 g (0.01 mol) of $CuSO_4 \cdot 5H_2O$ in 30 ml of hot water. The precipitate was filtered and washed with methyl alcohol. Crystallization from 67% methyl alcohol yielded black crystals. *Anal.* Calcd for $K_2C_4O_4S_4Cu$: C, 12.6; H, 0.0. Found: C, 12.4; H, 0.0.

**Bis(tetraethylammonium)bis(*cis*-1,2-ditrifluoromethylethylene-1,2-dithiolato)nickel(II), $[(C_2H_5)_4N]_2Ni(tfd)_2$.**—This compound was prepared by a published method[15] using bis(trifluoromethyl)-1,2-dithietene prepared by the gas-phase reaction of sulfur and hexafluorobutyne-2 according to Krespan.[16] *Anal.* Calcd for $C_{24}H_{40}F_{12}N_2S_4Ni$: C, 37.4; H, 5.2; N, 3.6. Found: C, 37.3; H, 5.3; N, 3.5.

Several mixed complexes, *e.g.*, $Ni(mnt)(i\text{-}mnt)^{2-}$, were prepared *in situ* by adding slowly and with vigorous stirring, in a 1:1 molar ratio, an aqueous solution of the ligand yielding the stronger complex to a solution of the nickel complex of the weaker ligand. Electronic spectra clearly showed that mixed complexes were present as the major species. The stopped-flow oscilloscope scans of the reactions of the mixed complexes also demonstrated that the major species in solution had to be a mixed complex. Several mixed complexes of nickel with dinegative sulfur ligands have been reported.[17,18]

**Kinetic Runs.**—Kinetic runs were made on a commercially available stopped-flow device previously described.[19] All kinetic runs were made in aqueous solution under pseudo-first-order conditions at 25°. The temperature was maintained constant to within ±0.1°. The ionic strength was maintained constant using sodium perchlorate as the inert electrolyte. In order to obtain a second-order rate constant the usual procedure was to study the reaction at five different concentrations of excess nucleophile. Usually three kinetic runs were analyzed at each concentration. When the kinetics was other than simple second order, a more extensive study was made.

**Spectra.**—Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer. A Beckman DU-2 spectrophotometer was used to determine the stability constants.

**Stability Constants.**—The $\beta_2$ values of the nickel dithiolate systems were determined in water at 25° and an ionic strength of 0.2 *M* (sodium perchlorate). The method was to add the sodium or potassium salt of the dithiolate ligand to a solution containing tris(ethylenediamine)nickel(II) and enough excess ethylenediamine such that the reaction ($(S\text{–}S)^{2-}$ means a dithiolate ligand)

$$Ni(en)_3^{2+} + 2(S\text{–}S)^{2-} = Ni(S\text{–}S)_2^{2-} + 3en$$

proceeds only part way. The absorbance of the solution is measured as a function of the total amount of dithiolate ligand present. Spectra suggest that mixed ethylenediamine–dithiolate complexes are not formed. The solutions were assumed to contain the species $Ni(en)_3^{2+}$, $Ni(en)_2^{2+}$, en, $Ni(S\text{–}S)_2^{2-}$, and $(S\text{–}S)_2^{2-}$. The extinction coefficients of these species are known. The formation constants of $Ni(en)_n^{2+}$ were assumed to be $\log \beta_2 = 13.9$ and $\log \beta_3 = 18.25$.[20] This information together with knowledge of the total concentration of metal, ethylenediamine, and dithiolate allows one to solve for the value of $\beta_2$ for the dithiolate complex. The uncertainty in the log $\beta_2$ values is estimated to be approximately 0.2 log unit.

**Analyses.**—Microanalyses for C, H, and N were performed in our department by Miss H. Beck.

## Results

**Stability Constants and Structures.**—Crystal structure determinations for $[(C_6H_5)_4As]_2Ni(CS_3)_2$,[21] $[(CH_3)_4N]_2Ni(mnt)_2$,[22] $[(C_6H_5)_4As]_2Ni(cdc)_2$,[23] and $K_2Ni(dto)_2$[14] show these complexes to be planar. Spectral investigations and X-ray powder patterns[4,13,24–28] of the solids show that the other nickel(II) dithiolate complexes are planar as well. Thus $NiL_2^{2-}$ complexes, where L = dto,[25] mnt,[13,24] and 1,1-dithiolates,[27] display similar spectra in various solvents, including pyridine, showing the lack of axial perturbation. Molecular orbital calculations have been reported for some of these complexes.[2,25]

Table II

Formation Constants of Nickel(II) Dithiolate Complexes in Aqueous Solution at 25°[a]

| Ligand | Log $\beta_2$ | Ligand | Log $\beta_2$ |
|---|---|---|---|
| $CN^-$ | 30.5[b,c] | $dto^{2-}$ | 16.1 |
| $tfd^{2-}$ | >36[d] | $ned^{2-}$ | 14.4 |
| $mnt^{2-}$ | ≤25[e] | $cdc^{2-}$ | 13.7 |
| $cpd^{2-}$ | 20.3 | $i\text{-}mnt^{2-}$ | 12.2 |

[a] Ionic strength 0.2 *M* (sodium perchlorate). Estimated uncertainty is approximately 0.2 log unit. [b] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968). Ionic strength 0.1 *M* (sodium perchlorate). [c] This value is log $\beta_4$. [d] From results in 50% ethanol solution. Ionic strength 0.2 *M* (NaCN). [e] Ionic strength not adjusted.

Table II lists the formation constants obtained for the nickel(II) complexes using a competition reaction between ethylenediamine and the dithiolate ligand (see the Experimental Section for details).

Deskin[29] reported that $\log \beta_2 = 9.72$ for $Ni(dto)_2^{2-}$ in water at 25° and ionic strength 0.1 *M* (potassium sulfate). This value must be in error because experimentally ethylenediamine must be in a greater than tenfold excess to displace the $dto^{2-}$ from a $10^{-4}$ *M*

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(27) D. Coucouvanis and J. P. Fackler, Jr., *ibid.*, **6**, 2047 (1967).

(28) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **6**, 814 (1964).

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solution of $Ni(dto)_2^{2-}$, yet the value of log $\beta_2$ for $Ni(en)_2^{2+}$ is reliably known to be about 14.[20] The formation constant of $Ni(dto)_2^{2-}$ was determined by three methods: addition of $K_2dto$ to a solution of $Ni(en)_3^{2+}$ and en, addition of en to a solution of $Ni(dto)_2^{2-}$, and addition of $K_2dto$ to a solution of $Ni(dien)_2^{2+}$ which has a log $\beta_2$ of approximately 18.5 at 25°.[30] For all three cases the value of log $\beta_2$ for $Ni(dto)_2^{2-}$ was $16.1 \pm 0.2$.

It has been reported[13] that a substantial excess of $CN^-$ is needed to displace the $mnt^{2-}$ from $Ni(mnt)_2^{2-}$. Although the displacement of $mnt^{2-}$ from $Ni(mnt)_2^{2-}$ by $CN^-$ is very slow at low $CN^-$ concentrations, our results show that a large excess of $CN^-$ is not needed. It is difficult to obtain an accurate value of $\beta_2$ for $Ni(mnt)_2^{2-}$ by using $CN^-$ because mixed complexes are formed and the liberated $mnt^{2-}$ slowly decomposes in solution. Hence it was only possible to put a limit on log $\beta_2$ for $Ni(mnt)_2^{2-}$ at $\leq 25$.

A solution of $[(C_2H_5)_4N]_2Ni(tfd)_2$ ($10^{-4}$ *M*) and NaCN ($10^{-1}$ *M*) in 50:50 ethanol–water under nitrogen shows virtually no spectral change over 25 hr. Taking log $\beta_4 = 30$ for $Ni(CN)_4^{2-}$ in water,[31] one estimates for $Ni(tfd)_2^{2-}$ log $\beta_2 > 36$, also in water solution.

The other $\beta_2$ values reported in Table II were obtained without any difficulty.

**Rates of Formation of $Ni(i\text{-}mnt)_2^{2-}$ and $Ni(cdc)_2^{2-}$.**—The kinetics of formation of $Ni(i\text{-}mnt)_2^{2-}$ and $Ni(cdc)_2^{2-}$ in water at 25° and ionic strength of 0.1 *M* (sodium perchlorate) were studied using the stopped-flow apparatus. The results are in agreement with the work of Pearson and Ellgen,[11] who reported the kinetics of formation of $Ni(mnt)_2^{2-}$ and $Ni(dto)_2^{2-}$. For $i\text{-}mnt^{2-}$, with the ligand in excess, $k_{obsd}(sec^{-1}) = 4.5 \times 10^4[i\text{-}mnt^{2-}]$ and for $cdc^{2-}$ $k_{obsd}(sec^{-1}) = 9.1 \times 10^4[cdc^{2-}]$. The absorbance changes observed in the kinetic runs were the same as that calculated from the reactants and products. This, coupled with the fact that only one reaction was seen, means that the mono complex probably never becomes a major species in solution. Following Pearson and Ellgen,[11] the mechanism is postulated to be the usual ion-pair dissociation process

$$Ni(OH_2)_6^{2+} + L^{2-} \overset{K_0}{\rightleftharpoons} Ni(OH_2)_6^{2+},L^{2-} \qquad (1)$$

$$Ni(OH_2)_6^{2+},L^{2-} \xrightarrow{k_0} Ni(OH_2)_4L + 2H_2O \qquad (2)$$

$$Ni(OH_2)_4L + L^{2-} \xrightarrow{\text{fast}} NiL_2^{2-} + 4H_2O \qquad (3)$$

Reaction 1 is the diffusion-controlled formation of an ion pair and (2) represents the rate-determining loss of solvent water. For excess ligand one calculates

$$k_{obsd} = \frac{K_0k_0[L^{2-}]}{1 + K_0[L^{2-}]} \qquad (4)$$

Taking the approximate value[11] of $K_0$ to be 14 $M^{-1}$, the $k_0$ value is $3.2 \times 10^3$ $sec^{-1}$ for $i\text{-}mnt^{2-}$ and $6.5 \times 10^3$ $sec^{-1}$ for $cdc^{2-}$. These values are, as expected, somewhat lower than the water-exchange rate of $Ni(OH_2)_6^{2+}$.[32]

TABLE III

RATE CONSTANTS FOR PLANAR NICKEL(II) SUBSTITUTION REACTIONS IN AQUEOUS SOLUTION AT 25°[a]

| Reactant | Nucleophile | Product | $10^{-3}k$, $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|
| $Ni(dto)(dto)^{2-}$ | $mnt^{2-}$ | $Ni(dto)(mnt)^{2-}$ | 0.33 |
| $Ni(dto)(mnt)^{2-}$ | $mnt^{2-}$ | $Ni(mnt)(mnt)^{2-}$ | 0.019 |
| $Ni(dto)(cpd)^{2-}$ | $mnt^{2-}$ | $Ni(cpd)(mnt)^{2-}$ | 0.11 |
| $Ni(cdc)(cdc)^{2-}$ | $mnt^{2-}$ | $Ni(cdc)(mnt)^{2-}$ | ~150 |
| $Ni(cdc)(mnt)^{2-}$ | $mnt^{2-}$ | $Ni(mnt)(mnt)^{2-}$ | 0.20 |
| $Ni(cdc)(dto)^{2-}$ | $mnt^{2-}$ | $Ni(dto)(mnt)^{2-}$ | 23 |
| $Ni(cdc)(cpd)^{2-}$ | $mnt^{2-}$ | $Ni(cpd)(mnt)^{2-}$ | 2.8 |
| $Ni(i\text{-}mnt)(i\text{-}mnt)^{2-}$ | $mnt^{2-}$ | $Ni(i\text{-}mnt)(mnt)^{2-}$ | Very fast |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $mnt^{2-}$ | $Ni(mnt)(mnt)^{2-}$ | 0.58 |
| $Ni(i\text{-}mnt)(dto)^{2-}$ | $mnt^{2-}$ | $Ni(dto)(mnt)^{2-}$ | 53 |
| $Ni(i\text{-}mnt)(cpd)^{2-}$ | $mnt^{2-}$ | $Ni(cpd)(mnt)^{2-}$ | 7.35 |
| $Ni(ned)(ned)^{2-}$ | $mnt^{2-}$ | $Ni(ned)(mnt)^{2-}$ | Very fast |
| $Ni(ned)(mnt)^{2-}$ | $mnt^{2-}$ | $Ni(mnt)(mnt)^{2-}$ | 0.29 |
| $Ni(ned)(cpd)^{2-}$ | $mnt^{2-}$ | $Ni(cpd)(mnt)^{2-}$ | 14.5 |
| $Ni(cpd)(cpd)^{2-}$ | $mnt^{2-}$ | $Ni(cpd)(mnt)^{2-}$ | 0.021 |
| $Ni(cpd)(mnt)^{2-}$ | $mnt^{2-}$ | $Ni(mnt)(mnt)^{2-}$ | Slow |
| $Ni(cdc)(cdc)^{2-}$ | $dto^{2-}$ | $Ni(cdc)(dto)^{2-}$ | 6.0 |
| $Ni(cdc)(dto)^{2-}$ | $dto^{2-}$ | $Ni(dto)(dto)^{2-}$ | 0.55 |
| $Ni(cdc)(mnt)^{2-}$ | $dto^{2-}$ | $Ni(mnt)(dto)^{2-}$ | 0.0057 |
| $Ni(cdc)(CN)_2^{2-}$ | $dto^{2-}$ | $Ni(dto)(CN)_2^{2-}$ | 0.25 |
| $Ni(i\text{-}mnt)(i\text{-}mnt)^{2-}$ | $dto^{2-}$ | $Ni(i\text{-}mnt)(dto)^{2-}$ | 28 |
| $Ni(i\text{-}mnt)(dto)^{2-}$ | $dto^{2-}$ | $Ni(dto)(dto)^{2-}$ | 1.6 |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $dto^{2-}$ | $Ni(mnt)(dto)^{2-}$ | 0.025 |
| $Ni(i\text{-}mnt)(CN)_2^{2-}$ | $dto^{2-}$ | $Ni(dto)(CN)_2^{2-}$ | 0.80 |
| $Ni(i\text{-}mnt)(cpd)^{2-}$ | $dto^{2-}$ | $Ni(cpd)(dto)^{2-}$ | 0.52 |
| $Ni(cpd)(cpd)^{2-}$ | $dto^{2-}$ | $Ni(cpd)(dto)^{2-}$ | 0.00087 |
| $Ni(i\text{-}mnt)(i\text{-}mnt)^{2-}$ | $cdc^{2-}$ | $Ni(i\text{-}mnt)(cdc)^{2-}$ | Very fast |
| $Ni(i\text{-}mnt)(cdc)^{2-}$ | $cdc^{2-}$ | $Ni(cdc)(cdc)^{2-}$ | 26 |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $cdc^{2-}$ | $Ni(mnt)(cdc)^{2-}$ | 0.047 |
| $Ni(i\text{-}mnt)(CN)_2^{2-}$ | $cdc^{2-}$ | $Ni(cdc)(CN)_2^{2-}$ | 6.8 |
| $Ni(i\text{-}mnt)(dto)^{2-}$ | $cdc^{2-}$ | $Ni(dto)(cdc)^{2-}$ | ~10 |
| $Ni(i\text{-}mnt)(cpd)^{2-}$ | $cdc^{2-}$ | $Ni(cpd)(cdc)^{2-}$ | 0.68 |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $ned^{2-}$ | $Ni(mnt)(ned)^{2-}$ | 0.52 |
| $Ni(ned)(ned)^{2-}$ | $cpd^{2-}$ | $Ni(ned)(cpd)^{2-}$ | Very fast |
| $Ni(ned)(cpd)^{2-}$ | $cpd^{2-}$ | $Ni(cpd)(cpd)^{2-}$ | 4.9 |
| $Ni(dto)(mnt)^{2-}$ | $cpd^{2-}$ | $Ni(mnt)(cpd)^{2-}$ | 0.0049 |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $cpd^{2-}$ | $Ni(mnt)(cpd)^{2-}$ | *b* |
| $Ni(dto)_2^{2-}$ | en | $Ni(en)_3^{2+}$ | 0.15 |
| $Ni(cdc)_2^{2-}$ | en | $Ni(en)_3^{2+}$ | 47 |
| $Ni(i\text{-}mnt)_2^{2-}$ | en | $Ni(en)_3^{2+}$ | ~130 |
| $Ni(dto)_2^{2-}$ | dien | $Ni(dien)_2^{2+}$ | 0.10 |
| $Ni(cdc)_2^{2-}$ | dien | $Ni(dien)_2^{2+}$ | ~70 |
| $Ni(i\text{-}mnt)_2^{2-}$ | dien | $Ni(dien)_2^{2+}$ | ~300 |

[a] Ionic strength 0.2 *M* (sodium perchlorate). [b] The reaction is not first order in nucleophile: $k_{obsd} = 73[cpd]\{1 + 170 \cdot [cpd]\}^{-1}$.

**Substitution Reactions.**—The second-order rate constants found with bidentate and tridentate nucleophiles are listed in Table III. The nucleophile dependence of the observed first-order rate constants when the entering group is $CN^-$ is shown in Table IV. The

TABLE IV

RATE CONSTANTS FOR PLANAR NICKEL(II) SUBSTITUTION REACTIONS WITH CYANIDE ION AS THE NUCLEOPHILE[a]

| Reactant | Product | $k_{obsd}$, $sec^{-1}$ [b] |
|---|---|---|
| $Ni(dto)(dto)^{2-}$ | $Ni(dto)(CN)_2^{2-}$ | $40 \times 10^6[CN]^2$ |
| $Ni(dto)(CN)_2^{2-}$ | $Ni(CN)_4^{2-}$ | $12 \times 10^6[CN]^2$ |
| $Ni(i\text{-}mnt)_2^{2-}$ | $Ni(CN)_4^{2-}$ | Very fast |
| $Ni(cdc)_2^{2-}$ | $Ni(CN)_4^{2-}$ | Very fast |
| $Ni(mnt)_2^{2-}$ | $Ni(CN)_4^{2-}$ | Slow |
| $Ni(dto)(mnt)^{2-}$ | $Ni(mnt)(CN)_2^{2-}$ | $3.1 \times 10^4[CN]^2$ |
| $Ni(ned)(mnt)^{2-}$ | $Ni(mnt)(CN)_2^{2-}$ | $56 \times 10^4[CN]^2/(1 + 160[CN])$ |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $Ni(i\text{-}mnt)(mnt)(CN)^{3-}$ | $5.5 \times 10^3[CN]$ |
| $Ni(i\text{-}mnt)(mnt)(CN)^{3-}$ | $Ni(mnt)(CN)_2^{2-}$ | $230[CN]$ |
| $Ni(cdc)(mnt)^{2-}$ | $Ni(cdc)(mnt)(CN)^{3-}$ | $2.8 \times 10^3[CN] + 3.1$ |
| $Ni(cdc)(mnt)^{2-}$ | $Ni(mnt)(CN)_2^{2-}$ | $31 \times 10^4[CN]^2/(1 + 820[CN])$ |
| $Ni(CN)_4^{2-}$ | $Ni(CN)_5^{3-}$ | *c* |

[a] Reactions are in aqueous solution at 25° and ionic strength 0.2 *M* (sodium perchlorate). [b] $k_{obsd}$ is the pseudo-first-order rate constant obtained with cyanide in excess. [c] Studied by temperature-jump method. Second-order formation rate constant is greater than $5 \times 10^3$ $M^{-1}$ $sec^{-1}$. See Discussion.

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(30) Reference 20, p 422.

(31) G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968).

(32) R. E. Connick and D. Fait, *J. Chem. Phys.*, **44**, 4103 (1966).

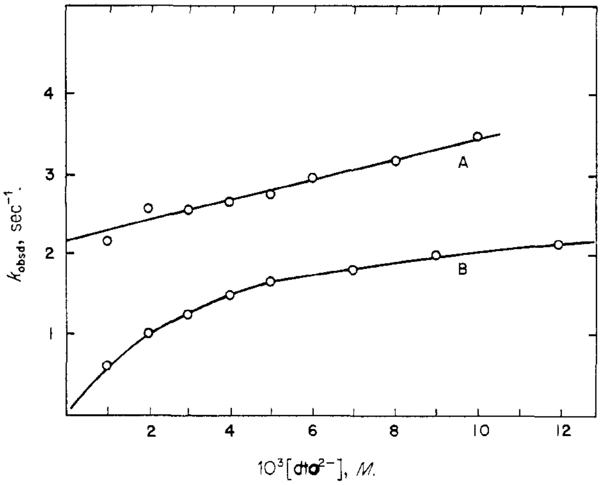

Figure 1.—Plot of $k_{obsd}$ *vs.* $dto^{2-}$ ion concentration for $Ni(en)_3^{2+} + 2dto^{2-} \rightarrow Ni(dto)_2^{2-} + 3en$ at 25° (total complex concentration (5–10) × $10^{-5}$ *M*): curve A, no excess en; curve B, en in $10^{-3}$ molar excess.

mixed-ligand complexes were prepared *in situ*. The other solutions were prepared by adding the appropriate amount of a salt of the complex to water. Some of the compounds were found to decompose slowly in water. Solutions of these compounds were prepared and used within a period of time that ensured negligible decomposition. Wavelengths offering large absorbance changes were selected for the kinetic runs. Some of the products listed in Tables III and IV react further with the nucleophile. In some cases an isosbestic point was used, thus eliminating the problem of observing secondary reactions. In most cases, however, this was not necessary as the rate constants describing the main reaction and the subsequent ones are separated by at least a factor of 10, permitting a straightforward determination of the rate constants.

For a typical kinetic run the total complex concentration was 5 × $10^{-5}$ *M* and the nucleophile concentration was varied from $10^{-3}$ to $10^{-2}$ *M*. To several of the reaction solutions sodium hydroxide was added ($10^{-3}$–$10^{-2}$ *M*) with no observable effect on the kinetics.

Kinetic runs with en and dien as the nucleophiles show only one step and this step has the absorbance change calculated from the reactants and products. Hence it seems probable that the reaction sequence is

$$NiL_2^{2-} + en \xrightarrow{k} Ni(en)L + L^{2-} \qquad (5)$$

$$Ni(en)L + 2en \xrightarrow{fast} Ni(en)_3^{2+} + L^{2-} \qquad (6)$$

**Reactions of $Ni(en)_n^{2+}$.**—For the reaction

$$Ni(en)_2^{2+} + 2dto^{2-} \longrightarrow Ni(dto)_2^{2-} + 2en \qquad (7)$$

the nucleophile dependence of the observed pseudo-first-order rate constant at 25° and ionic strength of 0.2 *M* (sodium perchlorate) is

$$k_{obsd}(sec^{-1}) = \frac{33 \times 10^3[dto^{2-}]}{1 + 350[dto^{2-}]} \qquad (8)$$

The $dto^{2-}$ concentrations used were between 5 × $10^{-4}$ and 120 × $10^{-4}$ *M*. The entire absorbance change between the reactants and products was observed in the kinetic runs suggesting the scheme

$$Ni(en)_2^{2+} + dto^{2-} \xrightarrow{k} Ni(en)(dto) + en \qquad (9)$$

$$Ni(en)(dto) + dto^{2-} \xrightarrow{fast} Ni(dto)_2^{2-} + en \qquad (10)$$

All of the nickel(II) complexes with sulfur donor ligands used in this study are diamagnetic. $Ni(en)_2^{2+}$ is not a low-spin planar system in solution, but it is likely that reaction 9 proceeds by the same mechanism as the dithiolate-substitution reactions. This is discussed below.

The same reaction with $mnt^{2-}$ as the nucleophile is too fast to allow a detailed study.

Figure 1 shows the nucleophile dependence of the pseudo-first-order rate constants observed at 25° and ionic strength of 0.2 *M* (sodium perchlorate) for reaction 11. When no en is present other than that generated during the course of the reaction, the form of $k_{obsd}$ is (curve A)

$$Ni(en)_3^{2+} + 2dto^{2-} \longrightarrow Ni(dto)_2^{2-} + 3en \qquad (11)$$

$$k_{obsd}(sec^{-1}) = 2.2 + 120[dto^{2-}] \qquad (12)$$

When $10^{-3}$ molar excess en is present, all $k_{obsd}$ values are lowered and $k_{obsd}$ curves toward zero as $[dto^{2-}]$ approaches zero (curve B). The mechanism proposed to account for the data is

$$Ni(en)_3^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (en)_2Ni\text{–}N\text{—}N^{2+} \xrightarrow{k_3} Ni(en)_2^{2+} + N\text{—}N$$

$$Ni(en)_2^{2+} + dto^{2-} \xrightarrow{k_5} Ni(en)(dto) + en \xrightarrow[dto^{2-}]{fast} Ni(dto)_2^{2-} + en$$

$$Ni(en)_2^{2-} + en \xrightarrow{k_7} Ni(en)_3^{2+}$$

$$(en)_2Ni\text{–}N\text{—}N^{2+} + en \xrightarrow{k_9} Ni(en)_3^{2+} + N\text{—}N$$

$$(en)_2Ni\text{–}N\text{—}N^{2+} + dto^{2-} \xrightarrow{k_4} \text{mixed complex} \xrightarrow{fast} Ni(dto)_2^{2-}$$

Using the steady-state approximation for $Ni(en)_2^{2+}$ and $(en)_2Ni\text{–}N\text{—}N^{2+}$ and letting [L] mean $[dto^{2-}]$ one calculates

$$k_{obsd} = k_1\left[\frac{k_3k_5}{k_5[L] + k_7[en]} + k_4\right](k_2 + k_3 + k_4[L] + k_9[en])^{-1}[L] \qquad (13)$$

When no excess en is present, one can approximate $k_{obsd}$ as

$$k_{obsd} = \frac{k_1(k_3 + k_4[L])}{k_2 + k_3 + k_4[L]} \qquad (14)$$

and

$$\lim_{[L]\rightarrow 0} k_{obsd} = \frac{k_1k_3}{k_2 + k_3} \qquad (15)$$

The limiting value of eq 15 can be estimated from published reports[33] on the rate of dissociation of $Ni(en)_3^{2+}$. The value of $k_1$ is about 87 $sec^{-1}$ at 25° and $(k_2 + k_3)/k_3$ is approximately 30.[33] Hence the limiting rate constant should be 2.9 $sec^{-1}$. The limiting rate constant found is 2.2 $sec^{-1}$, a value in excellent agreement with the proposed mechanism.

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[33] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960).

When excess en is present, the limiting value of $k_{\text{obsd}}$ as [L] approaches zero should be zero according to eq 13. Figure 1 shows that this is precisely what happens. Although Figure 1 shows that $k_{\text{obsd}}$ is linear in [L] within the range of concentrations used (curve A), at much higher concentrations of nucleophile than could be used in this study $k_{\text{obsd}}$ would become nonlinear in [L] and finally reach a limiting value given by $k_1$.

When $\text{mnt}^{2-}$ is the nucleophile, analogous results are found. With no excess en, at 25° and ionic strength of 0.2 *M* (sodium perchlorate), it is found that

$$k_{\text{obsd}}(\text{sec}^{-1}) = 2.2 + 380[\text{mnt}^{2-}] \qquad (16)$$

Again when excess en is present, $k_{\text{obsd}}$ approaches zero as $[\text{mnt}^{2-}]$ approaches zero.

**Reaction of $\text{Cu(mnt)(dto)}^{2-}$ with $\text{mnt}^{2-}$.**—$\text{Cu(mnt)(dto)}^{2-}$ was prepared *in situ* by adding slowly and with vigorous stirring a dilute solution of $\text{Na}_2\text{mnt}$ to a solution of $\text{Cu(dto)}_2^{2-}$. Although the spectra are not as definitive as for most of the nickel(II) dithiolate analogs, a mixed complex is indicated. It appears[13] that $\text{Cu(mnt)}_2^{2-}$ is square planar. One would expect $\text{Cu(dto)}_2^{2-}$ and $\text{Cu(mnt)(dto)}^{2-}$ also to be planar. For reaction 17 the same stopped-flow oscilloscope traces

$$\text{Cu(dto)}_2^{2-} + 2\ \text{mnt}^{2-} \longrightarrow \text{Cu(mnt)}_2^{2-} + 2\text{dto}^{2-} \qquad (17)$$

were observed whether starting with $\text{Cu(dto)}_2^{2-}$ or a solution corresponding to equimolar $\text{Cu(mnt)(dto)}^{2-}$. This supports the existence of $\text{Cu(mnt)(dto)}^{2-}$ and suggests the scheme

$$\text{Cu(dto)}_2^{2-} + \text{mnt}^{2-} \xrightarrow{\text{fast}} \text{Cu(mnt)(dto)}^{2-} + \text{dto}^{2-} \qquad (18)$$

$$\text{Cu(mnt)(dto)}^{2-} + \text{mnt}^{2-} \xrightarrow{k} \text{Cu(mnt)}_2^{2-} + \text{dto}^{2-} \qquad (19)$$

Because the reaction is very fast, only an approximate second-order rate constant could be obtained: $k \approx 1.4 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ at 25° and ionic strength 0.2 *M*. This would mean that copper(II) reacts about 7000 times faster than nickel(II) for this reaction (Table III). Such a factor seems reasonable.[1]

## Discussion

**Stability Constants.**—Table II shows that the 1,2-dithiolates usually form nickel(II) complexes of greater stability than the 1,1-dithiolates. This is partly due to the fact that the former complexes have five-membered rings while the latter are four-membered. That complexes with five-membered rings are considerably more stable than analogous four-membered ring complexes is well known. Another reason is that the 1,2-dithiolate complexes possess extensive $\pi$ delocalization not possible with the 1,1-dithiolates.[3-5,24,34] This is not to say, however, that $\pi$ interactions are of no importance with the 1,1-dithiolates. From Table II the order of decreasing stability is: $\text{Ni(tfd)}_2^{2-} > \text{Ni(mnt)}_2^{2-}$ and $\text{Ni(cpd)}_2^{2-} > \text{Ni(ned)}_2^{2-} > \text{Ni(}i\text{-mnt)}_2^{2-}$. A consideration of substituent effects[35] shows that stability decreases as inductive and resonance removal of electronic density from the nickel center increases. This is as expected.

TABLE V

EFFECT OF THE LEAVING GROUP FOR PLANAR NICKEL(II) SUBSTITUTION REACTIONS IN AQUEOUS SOLUTION AT 25°[a]

| *trans* group | Nucleophile | Leaving group |
|---|---|---|
| $\text{dto}^{2-}$ | $\text{dto}^{2-}$ | $i\text{-mnt}^{2-} > \text{cdc}^{2-}$ |
| | | 2.9 1 |
| $\text{mnt}^{2-}$ | $\text{dto}^{2-}$ | $i\text{-mnt}^{2-} > \text{cdc}^{2-}$ |
| | | 4.6 1 |
| $\text{mnt}^{2-}$ | $\text{mnt}^{2-}$ | $i\text{-mnt}^{2-} > \text{ned}^{2-} > \text{cdc}^{2-} > \text{dto}^{2-} > \text{cpd}^{2-}$ |
| | | 30.5 15.5 10.5 1 . . . |
| $\text{CN}^-$ | $\text{CN}^-$ | $i\text{-mnt}^{2-}, \text{cdc}^{2-} > \text{dto}^{2-} > \text{mnt}^{2-}$ |
| $\text{cpd}^{2-}$ | $\text{dto}^{2-}$ | $i\text{-mnt}^{2-} > \text{cpd}^{2-}$ |
| | | 1200 1 |
| $\text{cpd}^{2-}$ | $\text{mnt}^{2-}$ | $\text{ned}^{2-} > i\text{-mnt}^{2-} > \text{cdc}^{2-} > \text{dto}^{2-} > \text{cpd}^{2-}$ |
| | | 1350 690 260 11 1 |
| $\text{mnt}^{2-}$ | $\text{CN}^{-\,b}$ | $\text{ned}^{2-} > \text{cdc}^{2-} > \text{dto}^{2-} > \text{mnt}^{2-}$ |
| | | 18 10 1 . . . |

[a] Ionic strength 0.2 *M* (sodium perchlorate). General reaction is $\text{Ni(T)(L)}^{2-} + \text{Nu}^{2-} \rightarrow \text{Ni(T)(Nu)}^{2-}$ where T is the *trans* group, L is leaving group, and $\text{Nu}^{2-}$ is the nucleophile. Numbers under the leaving group-ligands are relative reactivities. [b] Relative reactivities are for the limit $[\text{CN}^-] \rightarrow 0$.

**Leaving-Group Effect.**—Table V summarizes the relative ease of displacement of a group, holding the *trans* group and nucleophile constant, from a nickel(II) dithiolate complex. With the exception of $\text{ned}^{2-}$ the relative leaving-group effects are seen to remain fairly constant as the nucleophile and *trans* group are changed. The ease of displacement decreases: *i*-mnt, ned > cdc > dto > cpd > mnt. The stability of $\text{NiL}_2^{2-}$ decreases (Table II): mnt > cpd > dto > ned > cdc > *i*-mnt. Thus with the sole exception of $\text{ned}^{2-}$ the two series correspond nicely. This shows that bond breaking is important in the overall substitution mechanism.

**Nucleophilic Reactivity.**—Table VI summarizes the nucleophilic reactivities for the substitution reactions holding the leaving group and *trans* group constant. The series remain fairly constant as the substrate is changed. The general ordering for the nucleophiles is: CN > mnt > ned > cpd > cdc > dto and dien, en > cdc. Cyanide ion cannot be rigorously compared to the other nucleophiles because most of its reactions are greater than first order in nucleophile. The fact that dien and en are not charged probably places them higher in the series than would otherwise be the case. The nucleophilic reactivities only very roughly parallel stability. As with the leaving-group effect, $\text{ned}^{2-}$ seems to be somewhat anomalous.

**Mechanism of the Substitution Reactions.**—Square-planar substitution reactions of platinum(II) proceed *via* an associative mechanism.[1] The form of the observed pseudo-first-order rate constant is usually given by

$$k_{\text{obsd}} = k_{\text{S}} + k_{\text{L}}[\text{L}] \qquad (20)$$

In eq 20 $k_{\text{S}}$ refers to the solvent path and $k_{\text{L}}$ the reagent path. Such a two-term rate law was found[36] for

$$\textit{trans}\text{-Ni(P(C}_2\text{H}_5)_3)_2(o\text{-CH}_3\text{C}_6\text{H}_4)\text{Cl} + \text{py} \longrightarrow \textit{trans}\text{-Ni(P(C}_2\text{H}_5)_3)_2(o\text{-CH}_3\text{C}_6\text{H}_4)\text{py}^+ + \text{Cl}^- \qquad (21)$$

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[34] G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

[35] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 4.

[36] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

Table VI

Nucleophilic Reactivity for Planar Nickel(II) Substitution Reactions in Aqueous Solution at 25°[a]

| Substrate | Nucleophile |
|---|---|
| Ni(*i*-mnt)$_2^{2-}$ [b] | CN, mnt$^{2-}$, ned$^{2-}$, dien > en, cdc$^{2-}$ > dto$^{2-}$<br>very fast fast |
| Ni(cdc)$_2^{2-}$ [b] | CN$^-$ > mnt$^{2-}$ > ned$^{2-}$ > dien > en > dto$^{2-}$<br>25 ~17 11.5 8 1 |
| Ni(ned)$_2^{2-}$ [b] | CN$^-$, mnt$^{2-}$, cpd$^{2-}$<br>very fast |
| Ni(dto)$_2^{2-}$ [b] | CN$^-$ [c] > mnt$^{2-}$ > en > dien<br>3.3 1.5 1 |
| Ni(cpd)$_2^{2-}$ [b] | mnt$^{2-}$ > dto$^{2-}$<br>24 1 |
| Ni(cdc)(mnt)$^{2-}$ [d] | CN$^-$ [e] ~ mnt$^{2-}$ > dto$^{2-}$<br>35 1 |
| Ni(cdc)(dto)$^{2-}$ [d] | mnt$^{2-}$ > dto$^{2-}$<br>42 1 |
| Ni(*i*-mnt)(mnt)$^{-}$ [f] | mnt$^{2-}$ > ned$^{2-}$ > cpd$^{2-}$ [g] > cdc$^{2-}$ > dto$^{2-}$<br>23 21 2.9 1.9 1 |
| Ni(*i*-mnt)(dto)$^{2-}$ [f] | mnt$^{2-}$ > cdc$^{2-}$ > dto$^{2-}$<br>33 ~6 1 |
| Ni(*i*-mnt)(cpd)$^{2-}$ [f] | mnt$^{2-}$ > cdc$^{2-}$ > dto$^{2-}$<br>14 1.3 1 |
| Ni(dto)(mnt)$^{2-}$ [h] | CN$^-$ [c] > mnt$^{2-}$ > cpd$^{2-}$<br>4 1 |
| Ni(ned)(mnt)$^{2-}$ [f] | CN$^-$ [e] > mnt$^{2-}$ |
| Ni(ned)(cpd)$^{2-}$ [i] | mnt$^{2-}$ > cpd$^{2-}$<br>3 1 |

[a] Ionic strength 0.2 *M* (sodium perchlorate). The numbers listed under the nucleophiles are relative reactivities. [b] Reactivities refer to displacement of the first ligand. [c] Reaction is second order in CN$^-$. [d] The cdc$^{2-}$ group is displaced. [e] Reaction is between first and second order in CN$^-$. [f] The *i*-mnt$^{2-}$ group is displaced. [g] Value of nucleophilic reactivity is for the limit [cpd$^{2-}$] → 0. [h] The dto$^{2-}$ group is displaced. [i] The ned$^{2-}$ group is displaced.

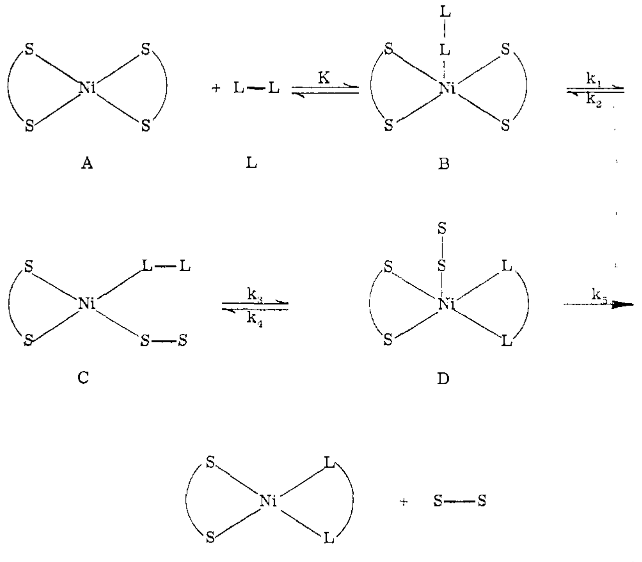

Figure 2.—Mechanism of substitution reactions of nickel(II) dithiolate complexes with bidentate nucleophiles. Charges are omitted. The five-coordinate intermediates are shown as square pyramidal; however, no real evidence is available about their structure.

No solvent path was detected for the dithiolate substitution reactions reported here. This could simply mean that $k_L[L] \gg k_S$.

The mechanism proposed to account for the substitution reactions of nickel(II) dithiolates with bidentate nucleophiles is given in Figure 2. The first step, for which $K$ is the equilibrium constant, is the rapid formation of a five-coordinate adduct. Assuming the steady-state approximation for C and D, one calculates, for excess L

$$k_{\text{obsd}} = \frac{k'K[L]}{1 + K[L]} \tag{22}$$

where $k'$ is a collection of rate constants

$$k' = \frac{k_1k_3k_5}{k_2(k_4 + k_5) + k_3k_5} \tag{23}$$

The transformation C $\rightleftharpoons$ D can be treated as an equilibrium and by assuming the steady-state approximation for the sum (C + D), eq 22 is generated except that a minor change in $k'$ occurs.

The proposed mechanism for unidentate nucleophiles is given in Figure 3. Rapid equilibria are represented by $K_1$ and $K_2$. Assuming the sum (C + D) is in a steady-state and that $k_2 \gg k_5K_2[X]$, one obtains, for excess X

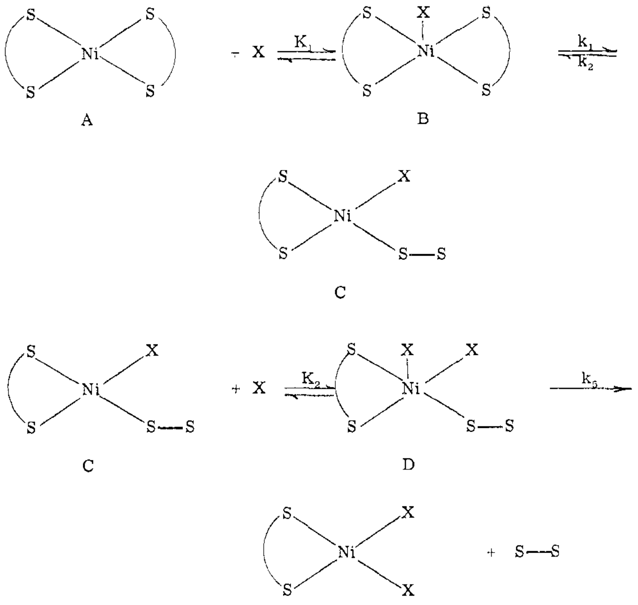

Figure 3.—Mechanism of substitution reactions of nickel(II) dithiolate complexes with unidentate nucleophiles. Charges are omitted. The five-coordinate intermediates are shown as square pyramidal; however, no real evidence is available about their structure.

$$k_{\text{obsd}} = \frac{k''K_1[X]^2}{1 + K_1[X]} \tag{24}$$

where

$$k'' = \frac{k_1k_5K_2}{k_2} \tag{25}$$

Similar results are obtained if $K_2$ is replaced by the rate constants $k_3$ and $k_4$ and both C and D are assumed to be in a steady-state. A reasonable value of $K_2[X]$ for the compounds reported here will be shown later to be less than unity for the concentrations of X used. Because of this and the fact that one expects $k_2 \gg k_5$, the assumption that $k_2 \gg k_5K_2[X]$ seems safe. Were $K_2$ very large and/or [X] large, however, it would be possible for $k_{\mathrm{obsd}}$ to become zero order in X.

The differences in the $k_{\mathrm{obsd}}$ dependence on nucleophile concentration for bidentate and unidentate nucleophiles is fortunate because it provides a tool with which to test the mechanisms as is demonstrated below.

**Evidence for the Substitution Mechanisms.**—There is considerable evidence in favor of the proposed mechanisms. All reactions with bidentate nucleophiles except one are first-order in the entering group. The exception is less than first order (Table III). This agrees with eq 22. Likewise all reactions with $CN^-$ are somewhere from first to second order in nucleophile (Table IV) as demanded by eq 24. Also the mechanisms proposed are associative in nature, agreeing with the associative nature of the mechanisms proposed for platinum(II) substitutions.

Several reactions are strictly second order in $CN^-$ as the entering group (Table IV). This is expected if $K_1[CN] \ll 1$ in eq 24. Strong support for the mechanism in Figure 3 is obtained from the results of the reaction $Ni(L)(mnt)^{2-} + 2CN^- \rightarrow Ni(mnt)(CN)_2^{2-} + L^{2-}$ where L = *i*-mnt, cdc, ned, or dto. With L = dto the reaction is second order in $CN^-$ over the range of $[CN^-]$ used ($10^{-3}$ to $15 \times 10^{-3}$ $M$). With L = *i*-mnt two reactions were seen both of which were first order in $CN^-$. The absorbance change remained constant for both steps as the concentration of the nucleophile was varied. This is predicted from eq 24 when $K_1[X] \gg 1$. The first step is attributed to the adduct formation

$$Ni(i\text{-mnt})(mnt)^{2-} + CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(i\text{-mnt})(mnt)(CN)^{3-} \quad (26)$$

The $k_{\mathrm{obsd}}$ value for (26) is given by eq 27. As shown

$$k_{\mathrm{obsd}} = k_1[CN^-] + k_{-1} \quad (27)$$

in Table IV a plot of $k_{\mathrm{obsd}}$ *vs.* $[CN^-]$ gave $k_{-1} \approx 0$. This simply means that $K_1 = k_1/k_{-1}$ is too large to allow the detection of $k_{-1}$ experimentally. The second step, which is about 24 times faster than the initial step, is attributed to reaction 28. Although a precise value of $K_1$ cannot be obtained from the data, its magnitude must be greater than 1000 $M^{-1}$ for $k_{-1}$ to appear to be zero and for (28) to be first order in $CN^-$.

$$Ni(i\text{-mnt})(mnt)(CN)^{3-} + CN^- \longrightarrow Ni(mnt)(CN)_2^{2-} + i\text{-mnt}^{2-} \quad (28)$$

With L = cdc again two steps are seen. The steps are attributed to reactions analogous to (26) and (28) where cdc is the leaving group instead of *i*-mnt. This time the first step has $k_{\mathrm{obsd}}(\mathrm{sec}^{-1}) = 2.8 \times 10^3[CN^-] + 3.1$. This agrees nicely with eq 27. From this one calculates $K_1 = k_1/k_{-1} = 900$ $M^{-1}$. The second step has a rate form identical with eq 24, as shown in Table IV. The best fit is obtained with $K_1 = 820$ $M^{-1}$, determined by plotting $[CN^-]^2/k_{\mathrm{obsd}}$ *vs.* $[CN^-]$. The proposed mechanism (Figure 3) demands that the $K_1$ in eq 24 be identical with the $K_1$ obtained as $k_1/k_{-1}$ from eq 27. The values of 820 and 900, though not identical, are certainly within experimental error and lend strong support to the proposed mechanism.

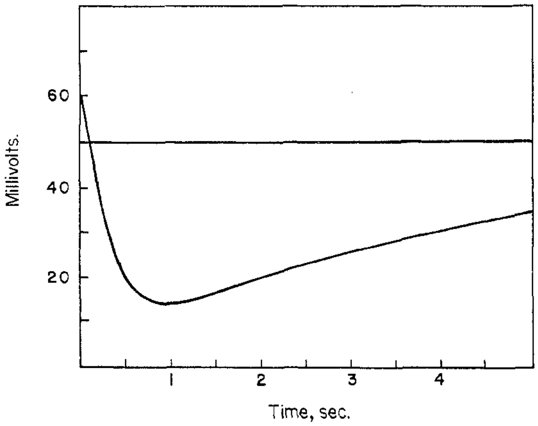

Figure 4.—Representation of a typical oscilloscope trace for the reaction $Ni(i\text{-mnt})(mnt)^{2-} + cpd^{2-} \rightarrow Ni(cpd)(mnt)^{2-} + i\text{-mnt}^{2-}$ at 25°. The wavelength is 420 mμ. The complex concentration is $10^{-4}$ $M$ and the $cpd^{2-}$ concentration is $6 \times 10^{-3}$ $M$. The horizontal line is the infinity reading.

With L = ned again two steps are seen. The absorbance change for the first step is, however, too small at the wavelengths used to allow accurate rate constant determinations. The second step has the rate form given in Table IV. A plot of $[CN^-]^2/k_{\mathrm{obsd}}$ *vs.* $[CN^-]$ gives $K_1 = 160$ $M^{-1}$.

The equilibrium constant, $K = k_1/k_{-1}$, for $Ni(CN)_4^{2-} + CN^- \rightarrow Ni(CN)_5^{3-}$ is reported[37] as 0.21 $M^{-1}$ at 23° and an ionic strength of 2.5 $M$. This means that a very large excess of cyanide ion is needed to drive the equilibrium to the right to an appreciable extent. An attempt was made to measure the kinetics of this reaction using the temperature-jump relaxation technique. At 0°, 35,000 V was discharged through an aqueous solution containing $5 \times 10^{-3}$ $M$ total nickel ion and 0.5 $M$ sodium cyanide. Although an absorbance change occurred, the relaxation time was too short to detect. On the instrument used this meant that the half-life for the relaxation process was $\leq 40 \times 10^{-6}$ sec. One obtains $k_1 \geq 5 \times 10^3$ $M^{-1}$ $\mathrm{sec}^{-1}$ if the reciprocal relaxation time is assumed to be of the form $k_1[CN^-] + k_{-1}$. Table IV shows that the formation rate constants of the cyanide adducts of the dithiolate complexes discussed above are 2.8 × $10^3$ and 5.5 × $10^3$ $M^{-1}$ $\mathrm{sec}^{-1}$.

There is also evidence strongly in favor of the mechanism with bidentate nucleophiles (Figure 2). For reaction 7 the form of $k_{\mathrm{obsd}}$ is given by eq 8. Although $Ni(en)_2^{2+}$ is not a planar dithiolate system, it seems reasonable to expect a similar mechanism for its substitution reactions. A plot of $1/[L]$ *vs.* $1/k_{\mathrm{obsd}}$ or $[L]/k_{\mathrm{obsd}}$ *vs.* $[L]$ gives $K = 350$ $M^{-1}$. This $K$ cannot be an ion-pair formation constant as it is much too large.[11] The form of eq 8 agrees with (22).

The best evidence favoring the mechanism in Figure 2 is given by reaction 29. Figure 4 shows a typical oscilloscope trace observed for this reaction. The ab-

$$Ni(i\text{-mnt})(mnt)^{2-} + cpd^{2-} \longrightarrow Ni(cpd)(mnt)^{2-} + i\text{-mnt}^{2-} \quad (29)$$

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[37] A. L. van Geet and D. N. Hume, *Inorg. Chem.*, **3**, 523 (1964).

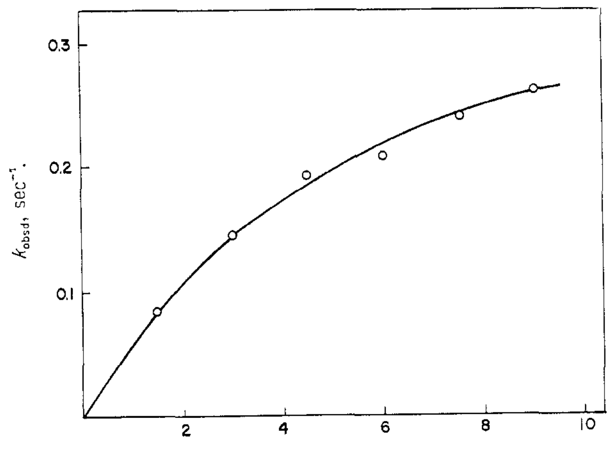

Figure 5.—Plot of $k_{obsd}$ vs. $cpd^{2-}$ concentration for $Ni(i\text{-}mnt)(mnt)^{2-} + cpd^{2-} \rightarrow Ni(cpd)(mnt)^{2-} + i\text{-}mnt^{2-}$.

sorbance change associated with the initial decrease in Figure 4 increases as the $cpd^{2-}$ concentration is increased. This suggests reaction 30, which does not

$$Ni(i\text{-}mnt)(mnt)^{2-} + cpd^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(i\text{-}mnt)(mnt)(cpd)^{4-} \quad (30)$$

go to completion except at high nucleophile concentration. The second step in Figure 4 is attributed to reaction 31. By choosing a wavelength where ab-

$$Ni(i\text{-}mnt)(mnt)(cpd)^{4-} \longrightarrow Ni(cpd)(mnt)^{2-} + i\text{-}mnt^{2-} \quad (31)$$

sorbance changes due to the second step were minimized to almost zero, the $k_{obsd}$ form of (30) was obtained as

$$k_{obsd}(\sec^{-1}) = 0.32 \times 10^3[cpd^{2-}] + 1.2 \quad (32)$$

Equation 32 gives $K = 270\ M^{-1}$. Unfortunately this value is only approximate because reaction 30 does not go far enough to completion at low nucleophile concentrations to allow $k_{obsd}$ determinations under these conditions. The overall reaction (eq 29) goes to completion at all $[cpd^{2-}]$ values, however. Further proof that the initial step is an equilibrium step that does not go to completion at low nucelophile concentrations was obtained by finding a wavelength (430 m$\mu$) where, at higher $[cpd^{2-}]$ values ($\sim 10^{-2}\ M$), only an absorbance change due to the initial step was seen, *i.e.*, at an isosbestic point with respect to $Ni(cpd)(mnt)^{2-}$ and $Ni(i\text{-}mnt)(mnt)(cpd)^{4-}$. By going to low $[cpd^{2-}]$ values at this wavelength an oscilloscope trace was obtained that showed two steps, the slower one yielding the same $k_{obsd}$ as that obtained for reaction 31 at other wavelengths. Regardless of the nucleophile concentration, the total absorbance changes were identical. This is precisely what reactions 30 and 31 predict. Although there is no absorbance change associated with (31), reaction 30 does not go to completion; so as (31) proceeds, reaction 30, which is a rapid equilibrium with respect to reaction 31, is shifted to the right thus producing the absorbance change at a rate determined by reaction 31. A plot of $k_{obsd}$ vs. $[cpd^{2-}]$ of the second step (eq 31) is given in Figure 5. The form of $k_{obsd}$ is given by

$$k_{obsd}(\sec^{-1}) = \frac{73[cpd^{2-}]}{1 + 170[cpd^{2-}]} \quad (33)$$

The $K$ value of 170 $M^{-1}$ thus indicated is probably more accurate than the 270 $M^{-1}$ value obtained from eq 32. All these results for reaction 29 agree well with the mechanism given in Figure 2.

It is felt that the above results with $CN^-$ and $cpd^{2-}$ as nucleophiles lend strong support to the proposed mechanisms for the substitution reactions of nickel(II) dithiolates.

**Adduct Stability.**—In $D_{2h}$ or $D_{4h}$ symmetry the nickel $4p_z$ orbital is purely $\pi$ ($\perp$) bonding. It is well known[13,24,38] that a good way to stabilize a square-planar geometry is to involve the metal $4p_z$ orbital in extensive $\pi$ bonding with the ligands. Adduct formation would remove the $4p_z$ orbital from the $\pi$ network as it involves $\sigma$-bond formation to the entering group. Hence much of the stability due to $\pi$ delocalization is lost. Similar reasoning has been used to explain the lack of axial perturbation of the dithiolate and dithiooxalate complexes when dissolved in coordinating solvents.[13,24,25,27]

Table VII

Approximate Formation Constants of Five-Coordinate Adducts of Nickel(II) Complexes in Aqueous Solution at 25°[a]

| Reactant | Nucleophile | Adduct | $K$, $M^{-1}$ |
|---|---|---|---|
| $Ni(en)_2^{2+}$ | $dto^{2-}$ | $Ni(en)_2(dto)$ | 350 |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $cpd^{2-}$ | $Ni(i\text{-}mnt)(mnt)(cpd)^{4-}$ | 200 |
| $Ni(i\text{-}mnt)(mnt)^{2-}$ | $CN^-$ | $Ni(i\text{-}mnt)(mnt)(CN)^{3-}$ | >1000 |
| $Ni(ned)(mnt)^{2-}$ | $CN^-$ | $Ni(ned)(mnt)(CN)^{3-}$ | 160 |
| $Ni(cdc)(mnt)^{2-}$ | $CN^-$ | $Ni(cdc)(mnt)(CN)^{3-}$ | 850 |
| $Ni(dto)(mnt)^{2-}$ | $CN^-$ | $Ni(dto)(mnt)(CN)^{3-}$ | <50 |
| $Ni(CN)_4^{2-}$ | $CN^-$ | $Ni(CN)_5^{3-}$ | 0.21[b] |

[a] Ionic strength 0.2 $M$ (sodium perchlorate). Formation constants were extracted from kinetic data. [b] From A. L. van Geet and D. N. Hume, *Inorg. Chem.*, **3,** 523 (1964). Ionic strength 2.5 $M$ and temperature 23°.

Table VII lists the adduct formation constants described above. The constants are necessarily rather approximate. From Table VII the stability of the cyanide adducts decreases: *i*-mnt > cdc > ned > dto. This is also the inverse of the stability series for the bis-dithiolato complexes. Considering resonance and inductive effects one expects $Ni(L)(ned)^{2-}$ to contain more $\pi$-electron density in the nickel $4p_z$ orbital than $Ni(L)(i\text{-}mnt)^{2-}$. It seems probable that the order of decreasing $\pi$-electron density in the $4p_z$ orbital is: ned > cdc > *i*-mnt. The adduct constants agree with the idea that the greater the $\pi$ density in the $4p_z$ the lesser the tendency for a nucelophile to form a strong $\sigma$ bond along the $z$ direction.

Only one dithiolate, cpd, displayed kinetic evidence of being able to form a strong $\sigma$ bond to the nickel $4p_z$ orbital in a dithiolate complex. The stability of $Ni(cpd)_2^{2-}$ suggests that cpd should be better than any other dithiolate ligand reported here for forming

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(38) H. B. Gray, *Transition Metal Chem.*, **1,** 240 (1965).

adducts. Although $Ni(mnt)_2^{2-}$ is of greater stability than $Ni(cpd)_2^{2-}$, much of this stability is due to the more extensive $\pi$ bonding possible with mnt. This $\pi$ stabilization results upon ring closure so that bonding through only one sulfur atom may well be stronger with cpd; *i.e.*, cpd is a better $\sigma$ donor to the $4p_z$ orbital than is mnt.

Table VII shows that the formation constant of $Ni(CN)_5^{3-}$ from $Ni(CN)_4^{2-}$ is about 0.2.[37] This value is much smaller than the formation constants of the cyanide adducts of some of the dithiolate complexes listed in Table VII. The instability of $Ni(CN)_5^{3-}$ has been explained[38] as being due to the large amount of $\pi$ bonding in $Ni(CN)_4^{2-}$ which is lost when a fifth group is added. In at least one case Table VII shows that cyanide ion is better than a dithiolate anion in forming five-coordinated adducts.

***trans* Effect.**—Table VIII summarizes the effect of the *trans* group, holding the nucleophile and leaving group constant, on the kinetics of nickel(II) dithiolate substitution reactions. The *trans*-effect series decreases in the order $i$-mnt > cdc > dto > CN > cpd > mnt and ned > cpd. Except for $CN^-$ this is just the stability series. With mnt there is very extensive $\pi$ delocalization involving the nickel $4p_z$ orbital. This means that $K$ for adduct formation is expected to be very small relative to complexes containing *trans*-1,1-dithiolate groups, which participate in $\pi$ bonding to a significant but much smaller extent than the 1,2-dithiolates. A small $K$ value reduces the rate constant accordingly. With $i$-mnt, cdc, dto, and cpd as the *trans* groups, the stability of the five-coordinate adduct also seems to control the rate. For reasons stated above the $\pi$-electron density in the nickel $4p_z$ orbital probably decreases: cpd > ned, dto > cdc > $i$-mnt. The cyanide adduct stability decreases in the order $i$-mnt > cdc > ned > dto. The suggestion is that the rate increases as the adduct stability increases and that the major part of the *trans* effect operates *via* the stability of the five-coordinate adduct which must form before substitution can occur. Of course, one should also consider the effect of the *trans* group on the bond strengths of the leaving group but there is no simple way to do this.

TABLE VIII

EFFECT OF THE *trans* GROUP FOR PLANAR NICKEL(II)-SUBSTITUTION REACTIONS IN AQUEOUS SOLUTION AT 25°[a]

| Leaving group | Nucleophile | *trans* group |
|---|---|---|
| $i$-mnt$^{2-}$ | dto$^{2-}$ | $i$-mnt$^{2-}$ > dto$^{2-}$ > CN$^-$ > cpd$^{2-}$ > mnt$^{2-}$<br>560 64 32 21 1 |
| cdc$^{2-}$ | dto$^{2-}$ | cdc$^{2-}$ > dto$^{2-}$ > CN$^-$ > mnt$^{2-}$<br>530 96 44 1 |
| $i$-mnt$^{2-}$ | mnt$^{2-}$ | $i$-mnt$^{2-}$ > dto$^{2-}$ > cpd$^{2-}$ > mnt$^{2-}$<br>. . . 91 13 1 |
| ned$^{2-}$ | cpd$^{2-}$ | ned$^{2-}$ > cpd$^{2-}$ |
| cdc$^{2-}$ | mnt$^{2-}$ | cdc$^{2-}$ > dto$^{2-}$ > CN$^-$ > cpd$^{2-}$ > mnt$^{2-}$<br>375 115 50 14 1 |
| dto$^{2-}$ | mnt$^{2-}$ | dto$^{2-}$ > cpd$^{2-}$ > mnt$^{2-}$<br>8.6 6 1 |
| dto$^{2-}$ | CN$^-$ | dto$^{2-}$ > CN$^-$ > mnt$^{2-}$<br>655 390 1 |
| $i$-mnt$^{2-}$ | cdc$^{2-}$ | $i$-mnt$^{2-}$ > cdc$^{2-}$ > dto$^{2-}$ > CN$^-$ > cpd$^{2-}$ > mnt$^{2-}$<br>. . . 560 213 144 14.5 1 |
| cpd$^{2-}$ | mnt$^{2-}$ | cpd$^{2-}$ > mnt$^{2-}$ |
| ned$^{2-}$ | mnt$^{2-}$ | ned$^{2-}$ > cpd$^{2-}$ > mnt$^{2-}$<br>. . . 49 1 |

[a] Ionic strength 0.2 $M$ (sodium perchlorate). The general reaction is $Ni(T)(L)^{2-} + Nu^{2-} \rightarrow Ni(T)(Nu)^{2-}$ where T is the *trans* group, L is the leaving group, and $Nu^{2-}$ is the nucleophile. Numbers under *trans*-group ligands are relative reactivities.

## Conclusion

Substitution reactions of the planar nickel(II) complexes reported herein follow an associative path as expected. The solvent path is not important. Although for platinum(II) formation of a five-coordinate intermediate may be rate determining, for nickel(II) this is rapid compared to subsequent steps. The formation constant of the five-coordinate intermediate does, however, markedly affect the rates. The *trans* effect for nickel(II) operates *via* the stability of the five-coordinate intermediate.

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