

(pya<sub>2</sub>tn)(H<sub>2</sub>O)L]<sup>2+</sup> (L = ethylamine), 39262-41-4; [Ni(py<sub>2</sub>a<sub>2</sub>-tn)(H<sub>2</sub>O)L]<sup>+</sup> (L = alanine (*dl*)), 37339-51-8; [Ni(py<sub>2</sub>a<sub>2</sub>tn)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 39262-42-5.

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## Kinetics and Mechanism of the Reactions of Substituted 8-Mercaptoquinoline Complexes of Nickel(II) with Some Alkyl Halides

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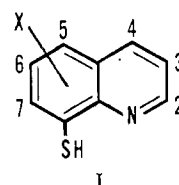
A series of X-8-mercaptoquinoline complexes of nickel(II) (X = 5-chloro, 5-bromo, 6-methoxy, 5-nitro, 7-methyl, 2-methyl) has been synthesized. The rates of reaction of these complexes with benzyl bromide and methyl iodide have been determined as a function of temperature. The enthalpies and entropies of activation for the reactions of these complexes with benzyl bromide are in the ranges 10–16 kcal/mol and –28 to –38 eu, respectively. The rates of reaction of the 5- and 6-substituted complexes with methyl iodide and benzyl bromide were correlated with the substituent by means of the Hammett equation.  $\rho$  was found to be –2.9 for the reactions of these complexes with both of the alkyl halides studied. The results have been interpreted on the basis of a mechanism involving the prior coordination of the alkyl halide to the nickel ion.

In investigations on the nature of homogeneous metal catalysis, one approach to the elucidation of these mechanisms involves the study of kinetic alterations arising from metal coordination to one of the organic moieties. A specific system utilizing this approach is the alkylation of coordinated mercaptans where one of the simplest and most completely studied reactions is the alkylation of the nickel complexes of 2-aminoethanethiol.<sup>1,2</sup> The reaction of bis(2-aminoethanethiol)nickel(II) with either methyl iodide or benzyl halides yields the 2:1 thioether complexes.<sup>1,2</sup> More recently, Burke and Brink extended this area by showing that bis(8-mercaptoquinoline)nickel(II), Ni(8-mq)<sub>2</sub>, reacts with alkyl halides under mild conditions.<sup>3</sup> The reaction of Ni(8-mq)<sub>2</sub> with methyl iodide yields bis(5-methyl-8-mercaptoquinoline)nickel(II) iodide as a reaction product. The magnetic moment of 3.18 BM for this dimethylated product reported by Lindoy, *et al.*, is consistent with the spin-free octahedral configuration anticipated if the iodide ions are coordinated to the metal.<sup>4</sup>

The kinetic parameters for the reactions involving 8-mercaptoquinoline and 2-aminoethanethiol as ligands show close similarities suggesting that the reactions proceed *via* the same mechanism. There is evidence, in the case of bis(*N*-alkyl-2-aminoethanethiol)nickel(II), to suggest that a preequilibrium involving the metal ion and the alkyl halide may be considered to polarize the carbon-halogen bond resulting in an enthalpy of activation for the reaction which is lower than anticipated for an SN<sub>2</sub> attack at a saturated carbon atom.<sup>5</sup>

By using the nickel complexes of appropriately substituted 8-mercaptoquinolines it has been possible to study the effect of substituents on the rate of alkylation of coordinated mer-

captans. The nickel complexes of 5-chloro-8-mercaptoquinoline, 5-Cl-8-mq, 5-bromo-8-mercaptoquinoline, 5-Br-8-mq, 5-nitro-8-mercaptoquinoline, 5-NO<sub>2</sub>-8-mq, 6-methoxy-8-mercaptoquinoline, 6-CH<sub>3</sub>O-8-mq, 7-methyl-8-mercaptoquinoline, 7-CH<sub>3</sub>-8-mq, and 2-methyl-8-mercaptoquinoline, 2-CH<sub>3</sub>-8-mq, have been synthesized. The ligands used to prepare these complexes are shown in I. Reaction rates of these complex-



es with benzyl bromide and methyl iodide in chloroform have been determined spectrophotometrically as a function of temperature. For those complexes containing a substituent in the 5 or 6 position, the reaction rates have been correlated with the substituent by means of the Hammett equation.<sup>6</sup> Substituents in the 2 or 7 position are used to provide information regarding steric effects on both the geometry of the complex and the rates of alkylation.

### Experimental Section

**Preparation of the Ligands.** Whenever feasible, the mercaptans were oxidized by dilute hydrogen peroxide to the disulfides. Such a conversion facilitated storage and purification of the ligand. Reduction of the disulfide to the mercaptan was easily accomplished with hypophosphorous acid. The disulfides were prepared according to modified published procedures and are summarized below.

**5-Bromo-8-mercaptoquinoline and 5-Chloro-8-mercaptoquinoline.** The 5-bromo-8-mercaptoquinoline was prepared from 5-bromoquinoline<sup>7</sup> and the 5-chloro-8-mercaptoquinoline was prepared from 5-chloroquinoline.<sup>8</sup> The 5-haloquinolines were readily obtained from

(1) D. H. Busch, J. A. Burke, D. C. Jicka, M. C. Thompson, and M. L. Morris, *Advan. Chem. Ser.*, No. 37, 143 (1963).

(2) E. L. Blinn and D. H. Busch, *Inorg. Chem.*, 7, 820 (1968).

(3) J. A. Burke and E. C. Brink, *Inorg. Chem.*, 8, 386 (1968).

(4) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, 19, 1391 (1966).

(5) E. L. Blinn and D. H. Busch, *J. Amer. Chem. Soc.*, 90, 4280 (1968).

(6) H. H. Jaffe, *Chem. Rev.*, 53, 191 (1953).

(7) J. Bankovskis, D. Zaruma, and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 100 (1963).

(8) J. Bankovskis, Z. U. Misulovira, J. Circule, and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 134 (1962).

5-aminoquinoline by the Sandmeyer reaction. Both mercaptans were oxidized in a slightly basic solution with dilute hydrogen peroxide. Recrystallization from benzene of the appropriate oxidized product yielded (1) white crystals of bis(5-bromo-8-quinolyl) disulfide, mp 219°, lit. mp 204°, and (2) cream-colored crystals of bis(5-chloro-8-quinolyl) disulfide, mp 208–209°, lit. mp 209°.

**5-Nitro-8-mercaptoquinoline.** The preparation of this ligand was from 8-chloroquinoline according to the procedure of Winter and Reinhart.<sup>9</sup> The 8-chloroquinoline was obtained from 8-aminoquinoline by the Sandmeyer reaction. Attempts to recrystallize the mercaptan from ethanol resulted in oxidation of the mercaptan to the disulfide (mp 246–247°, lit. mp 245°). It was necessary to use the crude mercaptan immediately since the disulfide cannot be efficiently reduced due to the presence of the nitro group.

**6-Methoxy-8-mercaptoquinoline.** This ligand was prepared from 6-methoxy-8-aminoquinoline (Aldrich Chemical Co.) and thiourea by a method similar to that reported by Kealey and Freiser for the synthesis of 8-mercaptoquinoline from 8-aminoquinoline.<sup>10</sup> Dilute hydrogen peroxide was added to ensure the complete oxidation of the mercaptan and the solid material was collected by filtration. Recrystallization from benzene yielded the white bis(6-methoxy-8-quinolyl) disulfide, mp 238–239°.

**7-Methyl-8-mercaptoquinoline.** The synthesis of this ligand begins with 7-methylquinoline (Eastman Organic Chemicals). The methylquinoline was nitrated by the procedure of Tomisek, *et al.*, to yield 7-methyl-8-nitroquinoline in 72% yield.<sup>11</sup> Iron reduction of the nitro group gave 7-methyl-8-aminoquinoline which was diazotized and then treated with thiourea. Decomposition of the isothiuronium salt in a hot basic solution yielded, after treatment with hydrogen peroxide, bis(7-methyl-8-quinolyl) disulfide. Recrystallization from benzene gave white crystals of the disulfide, mp 176–178°.

**2-Methyl-8-mercaptoquinoline.** This ligand was prepared from 8-aminoquinoline (Aldrich Chemical Co.) and thiourea by a previously reported method.<sup>10</sup> Oxidation of the mercaptan with hydrogen peroxide yielded, after recrystallization from benzene, bis(2-methyl-8-quinolyl) disulfide which melted at 260–262°.

**Preparation of the Complexes.** With the exception of Ni(5-NO<sub>2</sub>-8-mq)<sub>2</sub>, the complexes were all prepared in the same manner. The appropriate disulfide was reduced to the mercaptan by refluxing for 1 hr in a 5:1 ethanol-hypophosphorous acid solution. The mercaptan solution was cooled to room temperature and filtered to remove any unreacted disulfide. A stoichiometric amount of nickel chloride hexahydrate in ethanol was slowly added to the mercaptan solution, and in all cases the insoluble complex formed immediately. The solid material was collected on a sintered-glass funnel and washed with water and ethanol. Recrystallization from boiling chlorobenzene, followed by drying *in vacuo*, yielded the Ni(X-8-mq)<sub>2</sub> complexes.

Ni(5-NO<sub>2</sub>-8-mq)<sub>2</sub> was prepared from nickel chloride hexahydrate and 5-NO<sub>2</sub>-8-mq by stirring a 2:1 mole ratio of ligand to metal ion in a 5:1 ethanol-hypophosphorous acid solution. The precipitated complex was collected on a sintered-glass funnel, washed successively with water, ethanol, and chloroform, and then dried *in vacuo*. The highly insoluble nature of this complex prevented effective recrystallization.

The elemental analyses of the Ni(X-8-mq)<sub>2</sub> complexes in Table I are consistent with a 2:1 ligand to metal mole ratio. For the case of X = 5-NO<sub>2</sub>, the analyses are in better agreement with a structure which includes 0.5 mol of nickel sulfide per mole of the 2:1 complex. Attempts to purify the 5-NO<sub>2</sub> complex were not successful.

**Electronic spectra** of the complexes were obtained in chloroform with either a Beckman DB-G or a Beckman DU-2 spectrophotometer. Molar absorptivities of the more soluble complexes were obtained in chloroform solutions (Table II). The reported values are the average of at least two determinations and are precise to ±3%. Difficulties in solubilizing the 5-NO<sub>2</sub> and 5-Cl complexes prevented any accurate determination of molar absorptivities for these two complexes. The peculiar solubility properties of these two complexes is noteworthy. Extraction of the solid complex for up to 24 hr in the case of Ni(5-NO<sub>2</sub>-8-mq)<sub>2</sub> is required to obtain a reasonably concentrated solution. These two complexes are difficult to dissolve but once solution is complete they remain in solution. A similar property has been reported for the parent complex, Ni(8-mq)<sub>2</sub>, but in this case dissolution is not nearly as difficult.<sup>12</sup>

(9) H. C. Winter and F. E. Reinhart, *J. Amer. Chem. Soc.*, **62**, 3508 (1940).

(10) D. Kealey and H. Freiser, *Talanta*, **13**, 1381 (1966).

(11) A. Tomisek, B. Graham, A. Griffith, C. S. Pease, and B. E. Christensen, *J. Amer. Chem. Soc.*, **68**, 1587 (1946).

(12) E. C. Brink, Jr., M.S. Thesis, Trinity University, San Antonio, Tex., 1967.

**Magnetic moments** were obtained on some of the samples by the Gouy method. The system consisted of a water cooled electromagnet and dc power supply. At a current of 30 A the magnetic field at the center of the pole pieces measured 8200 G as recorded by a rotating coil gaussmeter. All magnetic moments reported were measured at this field strength. Weight changes in the samples were obtained with a Mettler Model H6 balance and were reproducible to ±0.2 mg. The sample tubes were constructed from plastic tubing and suspended from the balance by a fine gold chain. Tube calibration constants were determined using Hg(Co(NCS)<sub>4</sub>) as the standard. A determination of the magnetic susceptibility for ferrous ammonium sulfate at 23° served to check the apparatus. A value of 33.0 × 10<sup>-6</sup> cm<sup>3</sup>/g agrees within experimental error with the reported value of 32.3 × 10<sup>-6</sup> cm<sup>3</sup>/g.<sup>13</sup> Molar susceptibilities were corrected for the diamagnetism of the ligands by the use of Pascal's constants.<sup>14</sup>

**Kinetic measurements** were made on the reactions of the Ni(X-8-mq)<sub>2</sub> complexes with benzyl bromide and methyl iodide in chloroform. Benzyl bromide and methyl iodide were supplied by Eastman Organic Chemicals and Aldrich Chemical Co., respectively, and used without further purification. Possible variations in the reaction rates of these complexes, due to the presence of small amounts of ethanol used to stabilize commercially supplied chloroform, were investigated. No significant variation in reaction rates was observed when freshly distilled chloroform was substituted for reagent grade chloroform. Baker Analyzed reagent chloroform was used as the solvent. Standard techniques for measuring rates of reactions spectrophotometrically were used to obtain the kinetic parameters. The absorption band indicated in Table II was used to follow the change in concentration of complexes with time. A reaction for kinetic study was carried out under conditions that would ensure pseudo-first-order conditions by using a 100–1000-fold excess of the organic halide.

## Results

**Structures of the complexes** in the solid state can be inferred from magnetic moment data and electronic spectra. The Ni(7-CH<sub>3</sub>-8-mq)<sub>2</sub> and Ni(6-CH<sub>3</sub>O-8-mq)<sub>2</sub> complexes are essentially diamagnetic (0.39 and 0.51 BM, respectively) in the solid state as anticipated for planar nickel(II) complexes. On this basis a planar configuration is assigned as the solid-state geometry of these complexes. Electronic spectra of these complexes in chloroform, given in Table II, show two principal absorption bands in the visible region. The high molar absorptivities of these bands, coupled with the lack of any absorbance bands in the region 8300–14,000 cm<sup>-1</sup>, where octahedral and tetrahedral complexes of nickel(II) normally absorb, indicate that the 7-methyl- and 6-methoxy-substituted complexes are essentially planar in chloroform solutions.

The room-temperature magnetic moment of 3.39 BM for Ni(5-Br-8-mq)<sub>2</sub> would indicate that the complex cannot have a planar geometry. The magnitude of the moment is within the range (3.3–3.5 BM) found for tetragonal polymeric complexes of nickel(II).<sup>4</sup> The parent complex, Ni(8-mq)<sub>2</sub>, has a room-temperature magnetic moment of 3.32 BM. The magnitude of the magnetic moment, the lack of metal-metal interaction, and the adherence of this complex to the Curie-Weiss law (Θ = 6°) are all consistent with a polymeric structure involving bridging sulfur atoms.<sup>4</sup>

The essential features of the electronic spectra for 5-bromo-, 5-chloro-, and 5-nitro-substituted complexes are markedly similar to each other and to the 7-methyl species. Intense ligand bands for 5-nitro-8-mercaptoquinoline mask any absorption above 28,000 cm<sup>-1</sup>. These results indicate that the absorbing species in all these cases is most likely one approximating a square-planar geometry around the nickel ion in chloroform solution.

In contrast, the electronic spectrum of Ni(2-CH<sub>3</sub>-8-mq)<sub>2</sub> in chloroform differs from those observed for the other complexes. The appearance of two weak bands at 13,200 cm<sup>-1</sup>

(13) J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 405.

(14) Reference 13, p 403.

Table I. Elemental Analyses of the Bis(X-8-mercaptoquinoline)nickel(II) Complexes

Compd	% C		% H		% N	
	Calcd	Found <sup>a</sup>	Calcd	Found <sup>a</sup>	Calcd	Found <sup>a</sup>
Ni(5-Br-8-mq) <sub>2</sub>	40.27	39.10	1.86	1.90	5.21	4.96
Ni(5-Cl-8-mq) <sub>2</sub>	48.28	47.40	2.23	2.25	6.26	5.94
Ni(5-NO <sub>2</sub> -8-mq) <sub>2</sub> ·0.5NiS <sup>b</sup>	41.98	42.01	1.94	2.07	10.90	10.49
		42.40		2.27		10.33
Ni(6-CH <sub>3</sub> O-8-mq) <sub>2</sub>	54.71	54.76	3.64	3.77	6.37	6.21
Ni(7-CH <sub>3</sub> -8-mq) <sub>2</sub>	58.98	58.84	3.93	3.75	6.87	6.78
Ni(2-CH <sub>3</sub> -8-mq) <sub>2</sub>	58.98	59.02	3.93	4.02	6.87	6.84
Ni(7-CH <sub>3</sub> -8-mqSCH <sub>3</sub> ) <sub>2</sub> I <sub>2</sub>	38.23	36.27	3.21	3.11	4.05	3.75
Ni(6-CH <sub>3</sub> O-8-mqSCH <sub>3</sub> ) <sub>2</sub> I <sub>2</sub>	36.54	35.05	3.07	2.95	3.88	3.79
Ni(5-Br-8-mqSCH <sub>3</sub> ) <sub>2</sub> I <sub>2</sub>	29.26	28.13	1.96	1.93	3.41	3.11

<sup>a</sup> Analyses were performed by Galbraith Laboratories, Inc. <sup>b</sup> Per cent S: calcd, 15.55; found, 15.02.

Table II. Electronic Spectra of the Bis(X-8-mercaptoquinoline)nickel(II) Complexes in Chloroform

Compd	$\tilde{\nu}$ , cm <sup>-1</sup> ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
Ni(5-Br-8-mq) <sub>2</sub>	17,850 <sup>a</sup> (6535), 25,180 sh <sup>c</sup> (7900), 29,500 (12,100)
Ni(5-Cl-8-mq) <sub>2</sub>	17,850 <sup>a</sup> (b), 25,250 sh (b), 29,600 (b)
Ni(5-NO <sub>2</sub> -8-mq) <sub>2</sub> ·0.5NiS	17,090 <sup>a</sup> (b), 25,000 (b)
Ni(6-CH <sub>3</sub> O-8-mq) <sub>2</sub>	19,260 <sup>a</sup> (5130), 25,500 sh (6700), 27,300 sh (8000), 30,700 (17,900)
Ni(7-CH <sub>3</sub> -8-mq) <sub>2</sub>	18,600 <sup>a</sup> (6030), 25,500 (7570), 29,300 (13,500)
Ni(2-CH <sub>3</sub> -8-mq) <sub>2</sub>	8300 (33), 13,200 sh (170), 16,700 <sup>a</sup> sh (2000), 21,200 (6085), 26,300 (4860)

<sup>a</sup> Frequency at which kinetic measurements were made. <sup>b</sup> Not measured. <sup>c</sup> sh = shoulder.

and about 8300 cm<sup>-1</sup>, in conjunction with two intense bands in the visible region which differ substantially from the pattern observed in the other complexes, indicates that this complex is not planar in solution. In this case, the appearance of the two weak bands suggests a pseudotetrahedral configuration. The 3.14-BM magnetic moment observed for this complex is within the range found for octahedral nickel(II) and tetrahedral nickel(II) with orbitally degenerate ground states.<sup>15</sup> Pseudotetrahedral configurations have been assigned to NiX<sub>2</sub>mmq (X = Cl, Br; mmq = *S*-methyl-2-methyl-8-mercaptoquinoline) where the magnetic moments are 3.29 and 3.20 BM for the chloro and bromo complexes, respectively.<sup>4</sup> On this basis the data would indicate that Ni(2-CH<sub>3</sub>-8-mq)<sub>2</sub> is tetrahedral in the solid state and this configuration is maintained in chloroform solutions.

When a planar configuration is considered, both *cis* and *trans* isomers are theoretically possible for the complexes in this series. Preliminary steric consideration would favor a *trans* structure since the relative size of the ligand is such that if the two sulfur atoms are located *cis* to each other, distortion of the plane would occur. This steric strain is relieved in the *trans* isomer. An opposing argument would, however, favor a *cis* configuration in that this arrangement would allow more effective overlap of the vacant d orbitals of the sulfur atom with both the filled d<sub>xz</sub> and d<sub>yz</sub> as well as the d<sub>xy</sub> orbitals of the nickel ion. If the orbital overlap in the *trans* configuration with either the d<sub>xz</sub> or d<sub>yz</sub> orbitals cannot provide the necessary stabilization energy to cause spin pairing, then a *cis* structure would be preferred.

van der Waals radii models show that in the *cis* isomer there is distortion from a true square-planar geometry caused by the strong steric interaction between any moiety located in the 2 position on the quinoline ring. The introduction of a methyl group in this position prevents any reasonable *cis* planar structure from being constructed. Conversely, the

molecular scale models fail to reveal any steric effects to prohibit the *trans* isomer from forming in all of these complexes including the 2-methyl complex. The only anomalous electronic spectrum noted in this series is that of the 2-methyl-substituted complex. For this complex the data obtained suggest a tetrahedral configuration. A consistent explanation is that the preferred spatial configuration for these complexes is the *cis* isomer since the *trans* cannot provide the necessary stabilization energy. When strong steric interactions prevent the formation of the *cis* isomer, as in the case of Ni(2-CH<sub>3</sub>-8-mq)<sub>2</sub>, then the next energetic alternative is a tetrahedral configuration.

**Kinetic data** are presented for the 2:1 complexes 5-chloro-, 5-bromo-, 5-nitro-, 6-methoxy-, and 7-methyl-8-mercaptoquinoline reacting with benzyl bromide and methyl iodide in chloroform solution. In most cases the rate equation exhibited first-order dependence in both complex and organic halide. The absorbance determined as a function of time for the thermostated reaction solution followed the characteristic logarithmic decrease. A zero absorbance at the monitoring wavelength suggests, by analogy to the bis(8-mercaptoquinoline)nickel(II) work,<sup>3</sup> that the product of the reaction is the thioether complex. Products of the reaction of representative complexes with methyl iodide were isolated and analyzed (Table I). The analyses for the methyl iodide products are consistent with the formation of the thioether complexes.

An anomalous feature of the kinetics of the two 5-halo-substituted complexes involves an induction time at the beginning of the reaction with methyl iodide. The complex concentration, as monitored spectrophotometrically, remains essentially constant during this portion of the reaction. The induction period lasts for 10-20% of the time required for the reaction to proceed through 3 half-lives; however, after this period, the reaction follows pseudo-first-order dependence. The rate constants listed for these complexes in Table IV were determined from data after this initial period was complete.

Although initial attempts were made to investigate the reactions of Ni(2-CH<sub>3</sub>-8-mq)<sub>2</sub> with organic halides, the reactions involved produced the free thioether ligand. This observation is in accord with results of Chia and Livingstone<sup>16</sup> which produced only (*S*-methyl-2-methyl-8-mercaptoquinoline)nickel(II) iodide from the thioether ligand and nickel iodide. Although the nature of this reaction awaits further investigation, the deviation of the tetrahedral complex from the pattern established by the planar complexes strongly implicates a structural requirement in the reaction mechanism.

The second-order rate constant evaluated from first-order

(15) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 884.

(16) P. S. K. Chia and S. E. Livingstone, *Aust. J. Chem.*, **21**, 339 (1968).

**Table III.** Rates of Reaction of Bis(X-8-mercaptoquinoline)nickel(II) with Benzyl Bromide<sup>a</sup>

X	Temp, °C	[C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br], M	10 <sup>4</sup> k, M <sup>-1</sup> sec <sup>-1</sup>	No. of determinations
5-Cl	38.9	0.099-0.334	16.5	3
	31.6	0.002-0.200	11.8	9
	20.4	0.123-0.261	5.12	3
5-Br	38.8	0.098-0.396	15.0	3
	31.6	0.098-0.400	9.60	8
	20.0	0.140-0.441	5.06	3
6-CH <sub>3</sub> O	38.8	0.096-0.120	40.4	2
	30.2	0.072-0.096	29.0	2
	19.6	0.072-0.096	13.9	2
5-NO <sub>2</sub>	38.8	1.00-1.34	0.473	2
	30.2	1.34-1.68	0.235	2
	18.0	1.34-1.68	0.075	2
7-CH <sub>3</sub>	37.8	0.033-0.067	79.6	2
	30.2	0.098-0.131	50.7	3
	17.5	0.100-0.134	24.9	2

<sup>a</sup>  $\Delta H^\ddagger$  (kcal/mol) and  $\Delta S^\ddagger$  (eu) for various X: 5-Cl, 11, -35; 5-Br, 10, -38; 6-CH<sub>3</sub>O, 10, -37; 5-NO<sub>2</sub>, 16, -28; 7-CH<sub>3</sub>, 10, -36.

**Table IV.** Rates of Reaction of Bis(X-8-mercaptoquinoline)nickel(II) with Methyl Iodide at 30.4°

X	[CH <sub>3</sub> I], M	10 <sup>5</sup> k, M <sup>-1</sup> sec <sup>-1</sup>	No. of determinations
5-Cl	1.92-3.21	5.36	3
5-Br	1.92-2.57	5.43	3
6-CH <sub>3</sub> O	1.28-1.92	22.7	2
5-NO <sub>2</sub>	1.92-2.57	0.148	2
7-CH <sub>3</sub>	0.64-1.28	30.8	2

plots of the absorbance vs. time and the organic halide concentration are listed in Tables III and IV for the reaction with benzyl bromide and methyl iodide, respectively. The rate constants are precise to 5% or less for two or more determinations. The small enthalpies and large negative entropies of activations determined in the benzyl bromide series parallel those previously reported for reactions of coordinated sulfur atoms.<sup>1,2,3,17</sup> Benzyl bromide reacts 10-20 times faster than methyl iodide with this series of complexes which supports the similarity of these reactions with those previously reported.

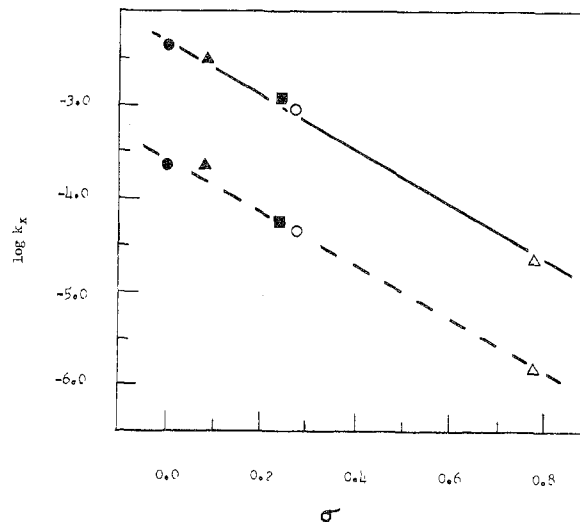
The magnitudes obtained for  $\Delta H^\ddagger$  are somewhat lower than the 20-25 kcal/mol usually found for an SN2 attack on a saturated carbon atom. This observation has also been reported for the complexes of some 2-aminoethanethiols.<sup>1</sup> This decrease in the energy requirements for the reaction suggests that the metal ion is facilitating the reaction. The large negative values obtained for  $\Delta S^\ddagger$  indicate that a large steric requirement is made on the geometry of the transition state. This can be interpreted to mean that the incoming alkyl halide may assume only a limited number of orientations with respect to the complex.

The reaction of Ni(7-CH<sub>3</sub>-8-mq)<sub>2</sub> with benzyl bromide indicates the direction of the attack of the alkyl halide. Molecular models of this complex show that some steric hindrance would be encountered if the alkyl halide is attacking in the molecular plane. In a study of the ultraviolet spectra<sup>18</sup> of a series of methyl-substituted S-methyl-8-mercaptoquinolines, an anomalous behavior was noted in the case of the 7-methyl compound. This behavior has been interpreted in terms of steric interaction of the

**Table V.** Rates of Reaction and Substituent Parameters for the Reactions of Bis(X-8-mercaptoquinoline)nickel(II) with Benzyl Bromide and Methyl Iodide at 30°

Compd	Log k		
	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	$\sigma$
Ni(8-mq) <sub>2</sub> <sup>a</sup>	-3.67	-2.39	0.00
Ni(5-Cl-8-mq) <sub>2</sub>	-4.27	-2.92	0.24
Ni(5-Br-8-mq) <sub>2</sub>	-4.36	-3.02	0.27
Ni(5-NO <sub>2</sub> -8-mq) <sub>2</sub> · 0.5NiS	-5.80	-4.63	0.78
Ni(6-CH <sub>3</sub> O-8-mq) <sub>2</sub>	-3.64	-2.52	0.08

<sup>a</sup> Reference 3.

**Figure 1.** The Hammett plot for the reaction of bis(X-8-mercaptoquinoline)nickel(II) with benzyl bromide (—) and methyl iodide (---): ●, H; ■, 5-Cl; ○, 5-Br; ▲, 6-CH<sub>3</sub>O; △, 5-NO<sub>2</sub>.

methyl group in the 7 position with the methyl group attached to the sulfur atom when the latter moiety is in the plane of the molecule. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are within the range observed in the other complexes indicating that there is negligible steric interaction between the incoming alkyl halide and the methyl group in the 7 position. Such a condition is possible if the attack is perpendicular to the molecular plane. The effects of the substituents on the rate of alkylation of these complexes can be correlated by the Hammett equation, eq 1, where  $k_X$  and  $k_H$  are the rate constants for the substituted and unsubstituted complexes, respectively. The Hammett equation restricts the correlation to those complexes containing substituents in the 5 or 6 position, where these are considered oriented para and meta, respectively, to the coordinated mercaptan.

$$\log k_X = \rho\sigma + \log k_H \quad (1)$$

A summary of the rates of reactions of the appropriate complexes with benzyl bromide and methyl iodide is given in Table V. Included in this table are the rates of reaction of the unsubstituted complex determined previously.<sup>3</sup> Substituent parameters,  $\sigma$ , were taken from the work of Wells.<sup>20</sup> Treatment of the data given in Table V according to eq 1 is shown in Figure 1.  $\rho$ , as determined from the slope of the line, is equal to -2.9 for the reactions with both benzyl bromide and methyl iodide. This indicates that the same mechanism is involved for the reaction of these complexes with the alkyl halides studied. The negative sign of  $\rho$  shows that the reaction is facilitated by an increase in the electron density at the reaction site which can be defined as the sulfur atom. Since the sulfur atom is acting as a nucleophile, an

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(17) E. L. Blinn and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 4280 (1968).

(18) J. Bankovskis, A. Struis, and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, **672** (1967).

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increase in the electron density would be expected to accelerate the rate of reaction.

Treatment of the data given by Hudson and Klopman<sup>21</sup> for the rate of reaction of substituted thiophenols with benzyl bromide gives a  $\rho$  of  $-0.64$ . A comparison of the magnitude of  $\rho$  obtained for the reactions of the free mercaptan and the coordinated mercaptan show that in the latter case a more pronounced substituent effect is observed.  $\rho$  obtained for the coordinated 8-mercaptoquinoline series indicates that a stronger electron demand is being made by the sulfur atom in the transition state. A strong electron demand would be required if the alkyl halide possessed an appreciable positive charge prior to reaching the transition state.

The data in hand are consistent with the mechanism proposed by Busch and coworkers<sup>1</sup> and subsequently supported by steric hindrance studies<sup>2</sup> and solvent-dependence studies.<sup>22</sup> Coordination of the alkyl halide through the halogen bond is indicated since it has been possible to force the reaction to deviate from the normal pseudo-first-order dependence at high concentrations of alkyl halide for *N*-alkyl-2-aminoethanethiol nickel complexes.<sup>2,16</sup> The steric constraints imposed by the *N*-alkyl groups impede the coordination of the halogen of the incoming group. Distances of closest approach in the transition state estimated from the dielectric

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(22) J. A. Burke and S. E. Campbell, *J. Inorg. Nucl. Chem.*, 33, 1163 (1971).

dependence for bis(8-mercaptoquinoline)nickel(II) reactions with methyl iodide are in agreement with this postulate.<sup>22</sup>

Furthermore, a highly polarized carbon-halogen bond, as evidenced by the large negative value of  $\rho$ , in the vicinity of a nucleophile such as the coordinated sulfur atom on the nickel, strongly intimates a four-centered transition state; *i.e.*, the nickel is simultaneously polarizing the alkyl halide and acting as a template to hold the reactive centers in close proximity. Such a transition state would call for large negative entropies of activation and a relatively fast reaction in the case of the 7-methyl derivative, since the incoming group approaches the sulfur away from its shielded side. Both of these demands of the postulate are met.

**Registry No.** Bis(6-methoxy-8-quinolyl) disulfide, 10222-12-5; bis(7-methyl-8-quinolyl) disulfide, 15758-98-2; bis(2-methyl-8-quinolyl) disulfide, 20335-14-2; benzyl bromide, 100-39-0; methyl iodide, 74-88-4; Ni(5-Br-8-mq)<sub>2</sub>, 39526-71-1; Ni(5-Cl-8-mq)<sub>2</sub>, 39556-24-6; Ni(5-NO<sub>2</sub>-8-mq)<sub>2</sub>, 39556-25-7; Ni(6-CH<sub>3</sub>O-8-mq)<sub>2</sub>, 39556-26-8; Ni(7-CH<sub>3</sub>-8-mq)<sub>2</sub>, 39556-27-9; Ni(2-CH<sub>3</sub>-8-mq)<sub>2</sub>, 39556-28-0; Ni(7-CH<sub>3</sub>-8-mqSCH<sub>3</sub>)<sub>2</sub>-I<sub>2</sub>, 39556-29-1; Ni(6-CH<sub>3</sub>O-8-mqSCH<sub>3</sub>)<sub>2</sub>I<sub>2</sub>, 39556-30-4; Ni(5-Br-8-mqSCH<sub>3</sub>)<sub>2</sub>I<sub>2</sub>, 39556-31-5.

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## Metal-Exchange Reaction between Ethylenediaminediacetonickelate(II) and Copper(II)

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The reaction between copper(II) and ethylenediaminediacetonickelate(II) was studied between pH 3.2 and 5.0 over a 70-fold variation in copper concentration at an ionic strength of 1.25 and a temperature of 25°. The reaction order in ethylenediaminediacetonickelate(II) is first while that for copper varied from first to zero and then back to first as the copper concentration increased. At low copper concentration, the first-order rate constant is pH independent and represents the attack of copper on the nickel complex through a pathway in which EDDA is half unwrapped before reaction with copper. Evidence is given for a stepwise unwrapping mechanism followed by copper attack to give a dinuclear intermediate. The zero-order rate is pH dependent. At high copper concentrations, the shift back to another first-order copper dependence is due to the formation of a weak copper-ethylenediaminediacetonickelate complex which then goes through the dinuclear intermediate to give products. A general mechanism is presented which is consistent with all the kinetic data.

### Introduction

Multidentate ligand transfer between two metal ions, as represented by eq 1, has been subject of extensive study for



a variety of metal ion combinations and aminocarboxylate ligands under many different conditions, using many different methods.<sup>1-11</sup> Detailed studies have shown the mechanism

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