

tion of the interaction dimer is in accord with our spectrophotometric data and the findings of previous workers.^{1,2}

TABLE X
DEPENDENCE OF EXCHANGE RATE ON TEMPERATURE

Temp., °C.	k (l./mole hr.)
25.0	4.58
37.8	19.3
49.7	88.5 (net)

The effect of temperature on the rate of exchange in 1.00 M Cl⁻ also was studied at three different temperatures (Table X). Once again, non-linear

McKay plots were observed at 49.7°. The original curve is non-linear for the first 140 minutes. Beyond that time a straight line is obtained. Graphical subtraction of the extrapolated straight line results in another straight line, which suggests once again that the higher temperature has accelerated the hydrolysis of the Sn(IV) and the hydrolyzed species is (are) either extremely slow to exchange or possibly does (do) not exchange. The log of the rate, calculated from the slope of the net straight line, when combined with the data from the other temperatures was plotted against the reciprocal of the absolute temperature and the resulting Arrhenius plot is linear with $E_a = 22.6$ kcal./mole.

[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, MALLINCKRODT CHEMICAL WORKS, ST. LOUIS, MISSOURI]

Nickel(II) Complexes of N,N'-Disubstituted Dithiooxamides¹

BY RICHARD N. HURD, GEORGE DELAMATER, GEORGE C. MCELHENY AND LEROY V. PEIFFER

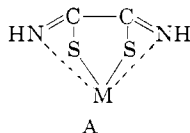
RECEIVED DECEMBER 28, 1959

N,N'-Dimethyl- (I), N,N'-dibenzyl- (II), N,N'-dioctadecyl- (III), N,N'-bis-(2-hydroxyethyl)- (IV), N,N'-bis-(2-acetoxyethyl)- (V) and N,N'-bis-(3-dimethylaminopropyl)-dithiooxamide (VI) formed intensely colored nickel complexes (VII-XII), respectively. N,N'-Dimethyldithiooxamidonickel(II) (VII) is a low polymer whose size and terminal structure are dependent on both the manner of preparation and purification. VII is crystalline and paramagnetic. N,N'-Bis-(2-hydroxyethyl)-dithiooxamidonickel(II) (X) was acetylated, but the product (XIV) contains only half the number of acetyl groups of N,N'-bis-(2-acetoxyethyl)-dithiooxamidonickel(II) (XI) prepared directly from V. The reaction of I with trisethylenediaminenickel(II) ion gave a complex product (XIII) differing from VII. Certain primary alkylamines were found to react with I, and in the case of trisethylenediaminenickel(II) ion, such reaction may have occurred during the formation of XIII.

Introduction

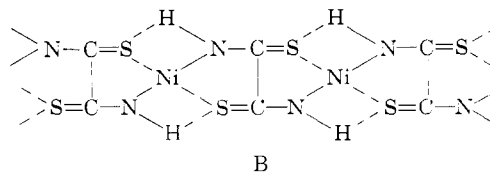
Dithiooxamide (rubeanic acid) has a long record of use as a reagent for the detection² and determination³ of many metals, including nickel. Very little information has been published, however, concerning the structures and properties of dithiooxamidonickel(II) complexes, and until this year nothing had been reported on the structures and properties of N,N'-disubstituted dithiooxamidonickel(II) complexes.

Rây and Rây first proposed a structure (A) for dithiooxamidometal complexes in which "M" represents copper, cobalt or nickel.⁴ This structure is of historical interest primarily, as today it must be regarded as improbable for steric reasons.



The nickel complex was found to be nearly diamagnetic.⁵ Jensen then suggested that dithio-

oxamidonickel(II) was a polymer by analogy to the diamagnetic, tetracoördinate, nickel mercaptides, which were known to be polymers.⁶ Recently, a study of the infrared absorption bands of dithiooxamidonickel(II) led Barceló to conclude that this complex had the polymeric structure B.⁷



Results and Discussion

Formation and Structure of N,N'-Disubstituted Dithiooxamidonickel(II) Complexes.—With all of the dithiooxamide derivatives examined, reaction with a nickel salt occurred instantaneously on admixture of the two starting materials in aqueous alcoholic solution at room temperature.

All of the complexes observed in this work were from dithiooxamides that were monosubstituted at both amido nitrogens. A completely substituted dithiooxamide, tetraethyldithiooxamide, that contains no amido hydrogens, did not react with nickel(II) ion in aqueous alcoholic solution.

N,N'-Dibenzyl dithiooxamide (II), N,N'-dioctadecyldithiooxamide (III), N,N'-bis-(2-hydroxyethyl)-dithiooxamide (IV), N,N'-bis-(2-acetoxyethyl)-dithiooxamide (V) and N,N'-bis-(3-dimethylaminopropyl)-dithiooxamide (VI) formed nickel

(1) Presented in part at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 18, 1959.

(2) F. Feigl, "Spot Tests," Vol. I, 4th Ed., translated by R. E. Osper, Elsevier Publishing Co., New York, N. Y., 1954, pp. 83, 139, 145.

(3) (a) J. M. Pheline and R. Castro, *Congr. groupe avance method. anal. spectrograph produits met. Paris*, **8**, 47, 177 (1947); (b) I. V. Tananaev and S. Y. Levitman, *Zhur. Anal. Khim.*, **4**, 212 (1949); (c) S. V. Vaecck, *Anal. Chim. Acta*, **10**, 48 (1954); (d) F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., New York, N. Y., 1948, p. 148.

(4) P. Rây and R. M. Rây, *J. Indian Chem. Soc.*, **3**, 118 (1926).

(5) P. Rây and H. Bhar, *ibid.*, **5**, 497 (1928).

(6) R. A. Jensen, *Z. anorg. Chem.*, **252**, 227 (1944).

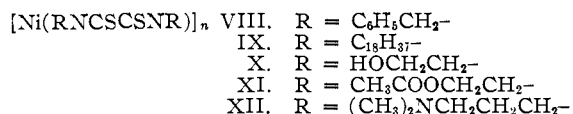
(7) J. Barceló, *Spectrochim. Acta*, **10**, 245 (1958).

TABLE I
 PREPARATION OF N,N'-DIMETHYLDITHIOOXAMIDONICKEL(II) ^a

Experiments	1	2	3	4	5	6	7	8
CH ₃ NHCSCSNHCH ₃ , moles	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Ni(NO ₃) ₂ ·6H ₂ O, moles	0.10	.10	.10	.10	.10	.10	.10	.10
CH ₃ COONa, moles	0	.10	.17	.19	.20	.30	.56	0
(C ₂ H ₅) ₂ N, moles	0	0	0	0	0	0	0	0.20
Relative pH ^{b,c}	1.95	2.25	3.67	4.55	4.60	5.22	5.6	7.0
Yield, g.	2.54	13.1	16.7	17.8	18.0	17.0	17.6	18.7
Analyses ^d : C	24.27							26.13
H	3.45							4.18
N	13.23	12.88	13.08	12.58	12.64	12.86	12.59	12.77
Ni	24.98	26.17	26.82	27.02	27.48	27.80	27.78	26.08
S	32.36	32.29	31.89	31.13	31.27	31.17	31.18	28.62
H ₂ O	1.0	0.5	0.1	0.3	0.4	0.3	0.3	0.7

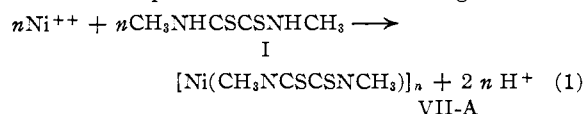
^a Reactions carried out in hot (75°), 50% ethanol (1000 cc.). ^b Measurement by Beckman pH meter of the 50% alcoholic filtrates after removal of the complex. ^c In each experiment the ionic strength was maintained at the same level (0.56) by the addition of a calculated amount of sodium nitrate. ^d Calculated values are given in the Experimental section.

complexes whose analyses were in excellent agreement with formulas VIII–XII. Formulas VIII–XII are represented as polymeric although the analytical data fit equally well for the monomeric case of $n=1$. The polyfunctional nature of the parent dithiooxamides, II–VI, from which these nickel complexes were derived, together with the evidence that dithiooxamidonickel(II) and VII are polymers, strongly suggest that n has a value greater than one in formulas VIII–XII. This conclusion is further supported by the observation that all these complexes, VII–XII, are insoluble in water and nearly all organic solvents. As-



signment of this formula to XII, N,N'-bis-(3-dimethylaminopropyl) - dithiooxamidonickel(II), confirmed the observation of Yoe and Jacobs that in the formation of this complex the reagents combined in equimolar amounts.⁸

The formation of VII, N,N'-dimethyldithiooxamidonickel(II), from N,N'-dimethyldithiooxamide (I) is represented by equation 1, within the limitations presented in the following discussion.



In addition to the failure of tetraethyldithiooxamide to react with nickel(II) ion, other evidence supported the conclusion that two equivalents of acid were formed from replacement of amido hydrogens by nickel. In the experiments summarized in Table I the acidities were determined for a series of aqueous alcoholic reaction mixtures, consisting of 0.1 mole each of I and nickel nitrate and a variable quantity of a weak base incapable of causing precipitation of hydrous nickel oxides. The curve obtained by plotting the measured acidities of the mother liquors *vs.* moles of base used (Table I) resembled a titration curve whose equivalence point corresponded to the neutralization of

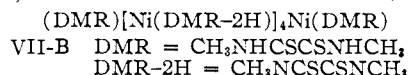
(8) W. D. Jacobs and J. H. Yoe, *Anal. Chim. Acta*, **20**, 435 (1959). This result was based on a study of the ultraviolet spectra.

1.8 equivalents of acid, a value closely approximating the value of 2 called for by equation 1.

The dependence in yield of VII on the quantity of base added to the system suggests that the reaction of equation 1 is reversible and obeys the law of mass action. However an attempt to assign a single equilibrium constant to all of the experiments was not successful. This is not surprising since the experiments were designed and carried out primarily to yield information concerning the composition of the precipitated complex rather than to obtain data from which an equilibrium constant could be calculated.

In another experiment it was demonstrated that the yield of VII is quantitative when an equivalent quantity of base is employed. In the experiments of Table I mechanical losses of VII occurred during isolation, and the recorded yields are therefore low.

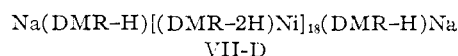
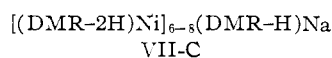
The results of complete analyses of VII suggest that this complex is a low polymer whose size and terminal structure depend on both the manner of preparation and purification. When it was prepared in the absence of base in aqueous, alcoholic solution and purified by Soxhlet extraction with alcohol followed by water (Table I), complete analysis did not give values quite consistent with formula VII-A. The analysis agreed well, however, with formula VII-B in which there is no



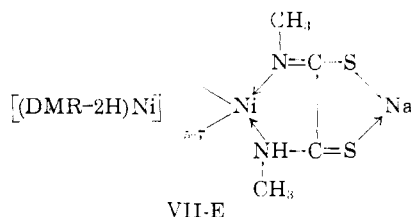
terminally-coordinated nickel. This hypothesis suggests that VII, prepared in the absence of base, is a short polymer containing about six dithiooxamide nuclei. Tetra-coördinate nickel would not be expected to complex at the terminal positions of VII-B where its coördinating power could not be wholly satisfied by strong bonds with thione sulfur and amido nitrogen atoms.

When VII was prepared by reaction of equivalent amounts of nickel ion and N,N'-dimethyldithiooxamide in the presence of two equivalents of sodium hydroxide in aqueous, alcoholic solution, and the product purified by Soxhlet extraction with alcohol only, complete analysis showed that a small amount of sodium was present and that the nickel content was too low for good agreement with

formula VII-A. However, the analysis was in complete agreement with formulas VII-C and VII-D in which some of the nickel atoms of VII-A were replaced by an equal number of sodium atoms. It is probable that such replacement occurred at the terminal positions, as shown in VII-C and VII-D. Replacement of nickel by sodium in a



non-terminal position would require that sodium develop an abnormal coordination number of four. One of the resonance-stabilized structures that can be written for terminally-coordinated sodium is



The conclusion that VII is a polymer is also supported by the observation that the nickel content of the complex increases with the initial presence of increasing amounts of base, as shown by comparison of the nickel analyses of the first five experiments of Table I. Such increase of nickel content would follow for polymers such as VII-C or VII-D in which there are one or two more N,N'-dimethyldithiooxamide nuclei than there are nickel atoms. As the length of such polymeric molecules increases the ratio of nickel to the organic portion approaches unity.

The sodium present in VII, prepared in the presence of either sodium hydroxide or sodium acetate, was displaced readily by hydrogen on Soxhlet extraction with water. Analysis of the displacement product gave no indication of any other change in the polymer.

Properties of N,N'-Disubstituted Dithiooxamidonickel(II) Complexes.—All of the complexes (VII-XII) are intensely colored solids of various shades of blue, violet and brown. In the homologous series of N,N'-dialkyldithiooxamidonickel(II) complexes there is a gradual change in color with increase in molecular weight: for example, VII is blue-violet and IX is red-violet.

As the size of the organic "tail" of the complex becomes larger, it begins to have a moderating effect on certain physical properties of the complex. VII, for example, does not melt below 400° and is nearly insoluble in all organic solvents, whereas IX softens above 200° and dissolves in either hot mineral oil or nitrobenzene, from which it precipitates on cooling.

Complexes VII-XII are much more heat stable than the parent dithiooxamides, I-VI, respectively. Complex VII has been examined in some detail in this respect (see Experimental), and the only volatile decomposition product was found to be hydrogen sulfide.

VII is crystalline with a very small crystallite size. It is paramagnetic with a magnetic susceptibility of about 2.4 Bohr magnetons.⁹ This value is more than 0.4 unit smaller than that often associated with paramagnetic tetracoördinate nickel(II) complexes.¹⁰ This may be explained on the basis that both planar and tetrahedral configurations about nickel occur in VII, with the latter predominantly favored.

The presence of additional functional groups in some of the complexes permits them to be transformed into different complexes. Thus, acetylation of brown X gave a dark blue complex (XIV), similar in appearance to XI. Analysis showed that only half of the hydroxyl groups were acetylated. It is not known whether this represents monoacetylation of each N,N'-bis(2-hydroxyethyl)dithiooxamido group in X or random acetylation.

A Complex from Triethylenediaminenickel(II).—Reaction of I with triethylenediaminenickel(II) ion in aqueous alcoholic solution instantly gave rise to a brown solid complex (XIII). It is an amorphous material with a magnetic moment of 2.4 Bohr magnetons, which suggests that the configuration about nickel is octahedral.⁹

The relative atomic proportions of Ni:N:S in XIII were found by analysis to be 1:3.1:2. On the basis of this analysis it appears that equimolar amounts of I and nickel were consumed and that ethylenediamine participated in complex formation. Complete analysis of XIII does not correspond to any calculable ratio of nickel to I to ethylenediamine. However, these results can be reproduced by independent preparations of XIII.

Although the reaction of I with ethylenediamine¹¹ must be kept in mind in interpreting the analysis of XIII, it appears likely that the greatly different rates of formation of XIII and of reaction of I with ethylenediamine preclude direct reaction of the diamine with I.

Experimental¹²

N,N'-Dimethyldithiooxamidonickel(II) (VII).—The data of Table I were obtained from a series of similar experiments in each of which a solution of nickel nitrate hexahydrate (29.08 g., 0.10 mole) in 50% ethanol (200 cc.) was added dropwise to a hot (75°) vigorously stirred solution of I¹³ (4.82 g., 0.10 mole) in 50% ethanol (800 cc.). The solutions of I contained sodium acetate or triethylamine to the extent shown in Table I. In addition, they contained sodium nitrate in sufficient amount to bring the ionic strength of the initial systems to a common value (0.56). After cooling and standing for 18 hr., each reaction mixture was filtered on a fine grade, sintered glass funnel. The crude

(9) Measurements were made under the direction of J. C. Bailar, Jr., by R. D. Archer, at the Department of Chemistry & Chemical Engineering, University of Illinois, Urbana, Illinois.

(10) J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publishing Co., New York, N. Y., 1956, pp. 360, 602.

(11) Some primary amines were found to react with I in refluxing alcoholic solution. For example, N,N'-dibutyldithiooxamide was isolated in small yield from a refluxing aqueous alcoholic solution of I and excess n-butylamine. Cyclohexylamine, however, did not react with I under similar conditions. Ethylenediamine and I, on long reflux in alcoholic solution, gave rise to four products, all sulfur-free. This reaction was very slow. Dithiooxamide and ethylenediamine have been reported to react to give 2,2'-bisimidazoline (H. Lehr and H. Erlenmeyer, *Helv. Chim. Acta*, **27**, 489 (1944)).

(12) Carbon, hydrogen and Dumas nitrogen analyses were performed by the Clark Microanalytical Laboratory, Urbana, Ill.

(13) O. Wallach, *Ann.*, **262**, 360 (1891).

products were than Soxhlet extracted for 24 hr. with ethanol and then for 24 hr. with water. At the completion of extraction in each case, freshly cycled extract gave a negative nickel(II) ion test with 10% alcoholic dimethylglyoxime reagent or a saturated alcoholic solution of I. The extracted products were dried *in vacuo* (< 0.1 mm.) over either concd. sulfuric acid or phosphorus pentoxide at 118° until the average daily weight losses were less than 0.1%. This generally required about 4 days of drying. Yields and analyses are cited in Table I.

VII-B corresponds to the product prepared in the absence of base (Table I).

Anal. Calcd. for $C_{24}H_{40}N_{12}Ni_6S_{12}$ (VII-B): C, 24.74; H, 3.45; N, 14.43; Ni, 25.19; S, 32.19. Found¹⁴: C, 24.52; H, 3.48; N, 13.36; Na, < 0.1; Ni, 25.23; S, 32.69.

For comparison to the above values the calculated analysis for formula VII-A, $C_4H_6N_2NiS_2$, is as follows: C, 23.45; H, 2.95; N, 13.67; Ni, 28.64; S, 32.89.

The product corresponding to either formula VII-C or VII-D was prepared similarly. An aqueous nickel nitrate hexahydrate (11.63 g., 0.04 mole) solution (50 cc.) was added dropwise to a well-stirred alcoholic solution (250 cc.) of I (5.93 g., 0.04 mole). A 1.0 M solution (122 cc.) of sodium nitrate was added, and the reaction mixture was then neutralized with a 1.0 M solution of sodium hydroxide (78.0 cc., 0.078 mole). The filtered precipitate was Soxhlet extracted for 6 hr. with ethanol and then dried *in vacuo* as before.

Anal. Calcd. for $C_{76}H_{110}N_{36}Na_2Ni_{16}S_{36}$ (VII-D): C, 23.89; H, 3.06; N, 13.93; Na, 1.27; Ni, 25.95; S, 31.89. Found¹⁴: C, 23.35; H, 3.43; N, 13.36; Na, 1.5; Ni, 26.94; S, 31.57.

VII was also prepared from other sources of nickel including other nickel salts, nickel stearate and a nickel anode. No evidence was observed to indicate that the anion portion of other nickel salts participated directly in the reaction. When nickel stearate was used, VII was separated from stearic acid with difficulty. Passage of an electric current through a cell comprising a nickel anode, a platinum cathode and a 66% alcoholic solution of I and sodium acetate yielded a sludge of VII at the anode.

The following solvents did not dissolve VII at the boiling point or 75°, whichever was lower: 2,2'-thiobis(ethanol), glycerol, ethyl acetosuccinate, N-(2-hydroxyethyl)-ethylenediamine, N-(2-aminoethyl)-piperazine, thiophene, dibutyl phosphate, salicylaldehyde, glacial acetic acid, carbon disulfide and 2,4-pentanedione. Very slight solubility was observed in N,N'-dimethylformamide, nitrobenzene and 1-acetylpiperidine on extended refluxing in these solvents. VII was immediately soluble at room temperature in concd. sulfuric acid, giving rise to purple solutions. It dissolves exothermically in nitric acid with gas evolution.

VII was examined for volatile decomposition products by passing pure nitrogen through a slurry of the complex in mineral oil. The effluent gas stream was passed through a series of scrubbers containing reagents for qualitative identification. When the slurry was heated above 150°, hydrogen sulfide was evolved as shown by precipitation of cadmium sulfide from a saturated aqueous solution of tetramminecadmium(II) chloride. No evidence for the presence of a mercaptan by the Wertheim¹⁵ procedure, ammonia by Korenman's method¹⁶ or a primary amine by reaction with phenyl isothiocyanate was observed, even when the slurry was heated to 270°.

VII is very stable to heat, undergoing a weight loss of less than 0.1% when heated to 193° for two days *in vacuo* over various drying agents.

The magnetic susceptibility of VII was measured at 25° by the Curie-Chéneveau balance¹⁷ using Mohr's salt as a comparative standard.⁹ No diamagnetic correction was applied.

Anhydrous VII slowly combined with water on standing until a maximum of one mole of water for each three units of $(CH_3NCSCSNCH_3)_2Ni$ was taken up. This water was removed with difficulty.

(14) Corrected for analyzed amount of water present.

(15) E. Wertheim, *THIS JOURNAL*, **61**, 3661 (1929).

(16) I. M. Korenman, *Z. anal. Chim.*, **90**, 114 (1932).

(17) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 15.

N,N'-Dibenzylidithiooxamidonicel(II) (VIII).—A solution of nickel nitrate hexahydrate (58.1 g., 0.2 mole) in 80% ethanol (200 cc.) was added dropwise to a warm (70°), well-stirred solution of II¹⁸ (60.4 g., 0.2 mole) and sodium acetate (32.8 g., 0.4 mole) in 90% ethanol (2400 cc.). Reaction was immediate. The reaction mixture was worked up, and the product purified, as described in detail for VII. The yield of purple VIII was 89%.

Anal. Calcd. for $C_{16}H_{14}N_2NiS_2$: N, 7.84; Ni, 16.43; S, 17.95. Found¹⁴: N, 7.58; Ni, 16.01; S, 18.48.

N,N'-Dioctadecyldithiooxamidonicel(II) (IX).—A hot (75°) alcoholic solution (750 cc.) of III¹⁸ (31.2 g., 0.05 mole) was added dropwise to a well-stirred, 50% alcoholic solution (800 cc.) of nickel nitrate hexahydrate (14.5 g., 0.05 mole) and sodium acetate (32.8 g., 0.4 mole) at the same temperature. After the mixture had cooled and stood for a day, the product was filtered and Soxhlet extracted with ethanol for 18 hr. to give a 35% yield of purple IX.

Anal. Calcd. for $C_{36}H_{74}N_2NiS_2$: C, 66.93; H, 10.96; N, 4.11; Ni, 8.61; S, 9.41. Found¹⁴: C, 67.96; H, 11.11; N, 4.36; Ni, 7.97; S, 8.78.

N,N'-Bis-(2-hydroxyethyl)-dithiooxamidonicel(II) (X).—A 50% alcoholic solution (200 cc.) of nickel nitrate hexahydrate (29.08 g., 0.10 mole) was added dropwise to a warm (50°), 50% alcoholic solution (800 cc.) of IV¹⁸ (20.83 g., 0.10 mole) and sodium acetate (16.41 g., 0.20 mole). The reaction mixture was worked up and the product purified in the manner described for VII to give a 50% yield of brown X.

Anal. Calcd. for $C_6H_{10}N_2NiO_2S_2$: N, 10.57; Ni, 21.15; S, 24.20. Found¹⁴: N, 10.28; Ni, 21.30; S, 24.20.

The same product was obtained when 0.30 mole of nickel nitrate hexahydrate was used, other conditions remaining the same.

Acetylation of X (XIV).—A mixture of brown X (5.00 g., 0.018 mole) and one drop of concd. sulfuric acid in acetic anhydride (100 cc.) was warmed on the steam-bath for 3 hr., during which time the color of the solid material gradually turned from brown to blue. After filtration, the product (XIV) was Soxhlet extracted for a day with ethanol, then water. The product was dried *in vacuo* (0.04 mm.) over phosphorus pentoxide at 65° for five days to give an 81% yield of blue XIV.

Anal. Calcd. for $C_8H_{12}N_2NiO_2S_2$: N, 9.14; Ni, 19.12; S, 20.88. Found¹⁴: N, 9.20; Ni, 19.12; S, 21.56.

N,N'-Bis-(2-acetoxyethyl)-dithiooxamidonicel(II) (XI).—A 50% alcoholic solution (200 cc.) of nickel nitrate hexahydrate (14.83 g., 0.051 mole) was added dropwise to a warm, 50% alcoholic solution (800 cc.) of V¹⁸ (15.00 g., 0.051 mole) and sodium acetate (13.90 g., 0.102 mole) with good stirring. The reaction mixture was worked up and the product purified in the manner described for VII, to give a 94% yield of dark blue XI.

Anal. Calcd. for $C_{10}H_{14}N_2NiO_4S_2$: N, 8.03; Ni, 16.81; S, 18.37. Found¹⁴: N, 7.96; Ni, 16.70; S, 19.03.

N,N'-Bis-(3-dimethylaminopropyl)-dithiooxamidonicel(II) (XII).—A 50% alcoholic solution (200 cc.) of nickel nitrate hexahydrate (17.45 g., 0.06 mole) was added dropwise to a well stirred, 50% alcoholic solution (800 cc.) of VI¹⁸ (17.43 g., 0.06 mole) and triethylamine (48.58 g., 0.48 mole). The reaction mixture was worked up and the product purified in the manner described for VII to give a 96% yield of red-brown XII.

Anal. Calcd. for $C_{12}H_{24}N_4S_2Ni$: N, 16.14; Ni, 16.91; S, 18.47. Found¹⁴: N, 15.65; Ni, 16.97; S, 18.17.

When sodium acetate was substituted for triethylamine, other conditions remaining the same, a product similar in appearance to XII, but having a different analysis, was obtained.

Anal. Found¹⁴: N, 12.37; Ni, 25.41; S, 26.07.

When the conditions for the preparation of XII were modified so that the molar ratio of VI to triethylamine to nickel salt was 1:2:3, no solid product was obtained. Instead, a dark purple water-soluble oil was formed.

Anal. Found: N, 5.24; Ni, 11.50; S, 5.82; H₂O, 8.80.

(18) The preparation of these compounds will be reported in a subsequent paper dealing with the reactions of dithiooxamide and primary amines.

A portion of this oil yielded a blood-red solid on treatment with ammonia. This solid, unlike XII, was alcohol-soluble and water-insoluble. It was basic, dissolving in dilute hydrochloric acid. This material was purified by Soxhlet extraction with water, then dried *in vacuo*.

Anal. Found¹⁴: N, 15.17; Ni, 16.46; S, 19.12.

A final portion of the oil was diluted with ethanol and treated with VI and triethylamine, whereupon a purple solid precipitated. This product was alcohol-insoluble, and so was Soxhlet extracted for a day with ethanol, then dried *in vacuo*. This product is believed to be XII.

Anal. Found¹⁴: N, 15.62; Ni, 15.09; S, 19.19.

N,N'-Dimethyldithiooxamidoethylenediaminenickel(II) (XIII).—A solution of trisethylenediaminenickel(II) ion was prepared from the reaction of nickel nitrate hexahydrate (392.3 g., 1.35 moles) and ethylenediamine (405.7 g., 6.75 moles) in 80% ethanol (5 l.). To this well-stirred solution was added slowly a hot (65°) alcoholic solution (2720 cc.) of I¹⁸ (200.0 g., 1.35 moles). The brown mixture was diluted with an equal volume of water, whereupon the bulk of the product precipitated. After standing overnight, the product was filtered and Soxhlet extracted with water for a day. The bulk of the water was removed from the wet, extracted XIII as a benzene azeotrope. The brown product was obtained in 58% yield.

Anal. Found¹⁴: C, 28.22; H, 4.72; N, (Dumas) 17.44; (Kjeldahl) 9.83; Ni, 23.58; S, 25.83.

XIII does not melt or decompose below 300°. It was shown to be non-crystalline by X-ray analysis. The mag-

netic susceptibility of XIII was measured in the same manner as that of VII.^{9,17}

The Kjeldahl or Dumas nitrogen determinations gave comparable results for complexes VII–XII. Complex XIII, however, consistently gave low values by the Kjeldahl method.

N,N'-Di-*n*-butyldithiooxamide from N,N'-Dimethyldithiooxamide.—A solution of I¹⁸ (7.41 g., 0.05 mole) and *n*-butylamine (21.94 g., 0.30 mole) in 80% ethanol (600 cc.) was refluxed overnight. The mixture was then poured over cracked ice, and the solid which formed was collected and recrystallized from ethanol to give yellow-orange needles of N,N'-di-*n*-butyldithiooxamide¹⁷, m.p. 36.0–36.3°.

Anal. Calcd. for C₁₀H₂₀N₂S₂: N, 12.05; S, 27.55. Found: N, 11.64; S, 27.73.

When cyclohexylamine was substituted for *n*-butylamine in the above experiment, only I was recovered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

The Reactions of Nickel(II) with 1,2-Ethanedithiol¹

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Ethanedithiol reacts with nickel(II) under alkaline conditions to give the extremely stable complexes Ni₂es₃⁷⁻ and Nies₂⁷⁻. The formation constants for these complexes are about $2 \times 10^{+47}$ and $4 \times 10^{+25}$, respectively, at 30° and at an ionic strength of 0.1. A comparison of the spectra of these complexes with those of the analogous 2,3-dimercapto-1-propanol (DMP) complexes of nickel(II) shows that in these latter complexes coordination takes place only through the sulfur atoms. Relative activities of DMP and ethanedithiol at a given concentration in solution have been determined, and these are shown to have quite a large effect on the relative values of the molar formation constants of Ni(DMP)₂⁷⁻ and Nies₂⁷⁻. The combination of ligand activity effects and complex ion solvation energies obscures conclusions drawn from the relative values of molar formation constants regarding the nature of either bonding or steric factors in a series of complexes.

A recent publication from these Laboratories² describes the reactions of nickel(II) with 2,3-dimercapto-1-propanol (DMP). Exceptionally stable complexes having the composition Ni₂(DMP)₃OH⁷⁻ and Ni(DMP)₂⁷⁻ are reported to form through the displacement of the sulfhydryl protons. The present study was undertaken with 1,2-ethanedithiol to ascertain what changes in the nature of the complexes are brought about by using this simpler ligand. In this way it was hoped to determine the role in the DMP complexes played by the DMP alcohol group. Of particular interest also is the nature of the OH⁻ term which appears in the Ni(II)-DMP dimer.

In addition, the DMP and ethanedithiol system are well suited for determining the effect of ligand activities on the relative values of the molar formation constants which have been obtained in systems of a given metal ion with different ligands. It is quite common to compare formation constants in such systems and attribute the differences to factors such as steric effects, differences in inductive

effects in ligand substituents or to different degrees of σ and π bonding between the metal ion and the various ligands. However, the formation constants usually are calculated using concentration units and the different ligands at any given reference concentration need not have the same activity in solution. Therefore, in any comparison the values of the various formation constants also reflect the differences in the activities of the ligands in addition to reflecting those other factors which contribute to complex stability. Because of their relatively low solubilities and high vapor pressures it is a simple matter to obtain the activities of ethanedithiol and DMP in solution. This effect on the relative molar formation constants of Nies₂⁷⁻ and Ni(DMP)₂⁷⁻ is described below.

Experimental

The symbols esH₂, esH⁻ and es⁷⁻ shall refer to ethanedithiol in its various stages of ionization. Where it is not necessary to distinguish between these in the text just the designation ethanedithiol will be used regardless of its actual state of ionization under the described conditions.

1,2-Ethanedithiol obtained from the Aldrich Chemical Co. was redistilled. The fraction boiling between 65–66° at 43 mm. was used. Air-free stock solutions were prepared by weight and were stored in bottles sealed with

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(2) D. L. Leussing, *THIS JOURNAL*, **81**, 4208 (1959).