there can be little doubt that the order of relative chelate stabilities is EDTA < CDTA << DTPA. To the best knowledge of the authors, the DTPA chelate is the most stable aqueous coördination compound of Th(IV) thus far investigated.

The greater hydrolytic tendency of Th(IV)–EDTA over that of Th(IV)–CDTA is in accord with the lower stability of the former chelate compound. The greater interaction of the Th(IV) ion with CDTA thus results in less interaction of the metal with the remaining coördinated water molecules.

It s interesting to note that the equilibrium constants for the formation of the binuclear species from the monohydroxothorium chelates are identical within experimental error for EDTA and CDTA, even though the interaction of Th(IV) with the hydroxyl ion is greater in the EDTA chelate. The equivalence of the two dimerization constants is perhaps the result of the cancelling of two opposing tendencies: 1, the greater tendency for dimerization of the Th(IV)–CDTA chelate as the result of more effective bridging by the OH group, and 2, the somewhat greater steric effects for the CDTA chelate, which would tend to work against formation of the dimer.

It is remarkable that the dimerization constants of these chelate compounds are within the range of dimerization constants noted by Pokras[7] for a series of hydroxo metal ions, as well as the dimerization constant for the Th(IV) ion calculated from the results of Kraus and Holmberg,[3] all of which contain no ligands other than water and hydroxide. This agreement is probably to a large extent fortuitous, since the lower ionic charge in the metal chelates would tend to increase the dimerization tendency over that observed for the more highly charged ions reviewed by Pokras. This effect would be largely balanced by greater steric effects in the chelates, and a reduction in the number of aquo sites through which olate bridging can take place.

[7] L. Pokras, *J. Chem. Educ.*, **33**, 223 (1956).

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

The Interaction of 2-Methyl-2-amino-3-butanone Oxime with Nickel(II) and Copper(II) Ions[1]

BY R. KENT MURMANN

RECEIVED FEBRUARY 28, 1958

The interactions of 2-methyl-2-amino-3-butanone oxime (AO) and some of its derivatives with Cu(II) and Ni(II) ions have been investigated quantitatively. The thermodynamic stability of $[Ni(AO)(H_2O)_4]^{+2}$ is small compared to that of $[Ni(AO)_2(H_2O)_2]^{+2}$ while the Cu(II) complexes follow the normal order. Alkyl substitution on the amine-nitrogen reduces the stability of the nickel complexes but does not prevent hydrogen-bond formation while Cu(II) forms a bi-nuclear structure involving hydroxo bridges. Differences in the thermodynamic stability of the hydrogen bond in the complexes of these ions are great with Ni(II) being the most stable. Addition of acid to complexes of the type $[M(AO)_2{-}H]^+$ results in the instantaneous formation of $[M(AO)_2(H_2O)_2]^{+2}$ which decomposes at a measurable rate. This rate of dissociation follows the law $d[Ni(AO)_2]^{+2}/dt = k[Ni(AO)_2]^{+2}[H^+]$. Substitution of an N-alkyl group has an accelerating effect while increasing the number of chelate rings decreases the rate. These results are discussed with reference to the solubility differences of Cu(II) and Ni(II) dimethylglyoximates.

Introduction

The interaction of transition metal ions with aliphatic *syn*-α-dioximes has long been of importance in analytical chemistry. Recently there has been an increased interest in this type of coordination compound directed primarily toward explaining the solubility differences between Cu(II) and Ni(II) compounds.[2-4] Although these efforts met with considerable success there are some species which do not appear to behave according to the existing theories (*i.e.*, the dioxime of glyoxal). It was felt that stability constant studies would be of value in showing the inherent differences in the chelating ability of closely related metal ions.

The low solubility which characterizes many of the α-dioxime chelates prevents accurate determination in aqueous solution of the thermodynamic quantities involved in their formation. However, (AO)[5a] has been shown to form similar compounds containing only one hydrogen bond, which possess more satisfactory characteristics.[1]

This paper presents the results of studies directed toward elucidation of the properties of intramolecular hydrogen bonds in coördination compounds and toward evaluation of their influence on the configuration of the metal complex and on the stability of intermediate species. The behavior of this ligand provides a further insight into the remarkable difference in solubility of the Cu(II) and Ni(II) dimethylglyoximates.

Previously it was established[1] that with Ni(II) the main species formed in neutral solution with excess (AO) has the structure B. Under basic conditions a second proton can be removed leading to a species of probable structure C. Compound B can be converted under acidic conditions to A which is thermodynamically unstable but somewhat less so kinetically. Copper ions form essentially identical species, the major differences being in the

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[1] For previous paper in this series, see R. Kent Murmann, THIS JOURNAL, **79**, 521 (1957).

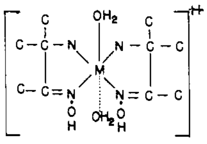
[2] L. E. Godychi and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[3] R. G. Charles and H. Freiser, *Anal. Chim. Acta*, **11**, 101 (1954).

[4] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

[5] (a) The ligands discussed here are designated as follows: (AO) = 2-amino-2-methyl-3-butanone oxime; (*n*-PrAO) = 2-*n*-propylamino-2-methyl-3-butanone oxime; (*n*-AmAO) = 2-*n*-pentylamino-2-methyl-3-butanone oxime; (PhAO) = 2-phenylamino-2-methyl-3-butanone oxime; (EnAO) = 2,2′-ethylenediamino-bis-(2-methyl-3-butanone) dioxime; (En) = ethylenediamine, DMG = dimethylglyoxime, (Gly) = glyoxaldioxime; (b) the designation –H is meant to express the essentially complete ionization of an oxime hydrogen.

relative equilibrium constants and in the increased rates of reaction. The interrelationships between these species are described in terms of equilibrium constants in those cases where measurement is possible.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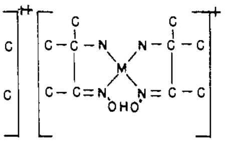
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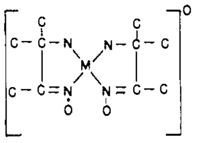

C

Experimental

The organic ligands were prepared as previously described[1] with the exception of EnAO for which an improved method was obtained.

To a cooled (0°) solution of 0.1 mole of anhydrous ethylenediamine dissolved in 220 ml. of anhydrous methanol, 0.24 mole of 2-chloro-2-methyl-3-butanone oxime was added. It was allowed to come to r.t. over a period of 2 hours and then refluxed for 8 hours. The solvent was removed under vacuum and the solid remaining dissolved in cold water (100 ml.). After filtration, neutralization with a slight excess of $NaHCO_3$, and cooling, EnAO was collected on a filter. Recrystallization from 95% ethanol gave colorless needles, m.p. 181–182°, 50–60% of the theoretical.

Anal. Calcd. for $C_{12}H_{26}N_4O_2$: C, 55.77; H, 10.15; N, 21.68. Found: C, 55.71; H, 10.16; N, 21.56.

The dihydrochloride was prepared by passing anhydrous HCl into a mixture of the amine in absolute alcohol and then crystallizing from absolute methanol.

Anal. Calcd. for $C_{12}H_{28}N_4O_2Cl_2$: Cl, 21.41; C, 43.50; H, 8.52; N, 16.92. Found: Cl, 21.50; C, 43.71; H, 8.79; N, 16.46.

The coördination compounds were prepared as previously described,[1] or in the following fashion.

$[Cu(EnAO)\text{-}H]ClO_4$.—A solution containing 0.0057 mole of $CuSO_4 \cdot 5H_2O$, 0.0060 mole EnAO and 30 ml. of H_2O was neutralized to a *p*H of exactly 7.0 with 1 *M* NaOH. After filtration to remove suspended impurities, 2 *M* $NaClO_4$ solution was added slowly with cooling. The product was collected and recrystallized from water as dark blue crystals; yield 80% of theoretical.

Anal. Calcd. for $CuC_{12}H_{25}N_4O_6Cl$: C, 34.11; H, 6.45; N, 13.27. Found: C, 34.41; H, 6.24; N, 13.48.

$[Cu(EnAO)](ClO_4)_2$.—The preparation was identical with that for $[Cu(EnAO)\text{-}H]ClO_4$ except that the *p*H was 2.6 and a higher concentration of ClO_4^- was necessary; bluish-purple crystals; yield 60%.

Anal. Calcd. for $CuC_{12}H_{26}N_4O_{10}Cl$: C, 27.67; H, 5.04; N, 10.75; Cu, 12.20. Found: C, 27.58; H, 5.19; N, 10.56; Cu, 12.11.

$[Cu_2(n\text{-}PrAO)_2(OH)_2\text{-}H]ClO_4$.[5b]—This compound was originally thought to have an analogous structure to that prepared with the unsubstituted ligand.[1] Further study has shown that one cannot obtain $[Cu(n\text{-}PrAO)_2\text{-}H]ClO_4$ from aqueous solution.

To a solution containing 0.01 mole of $CuSO_4 \cdot 5H_2O$, 0.015 mole of *n*-PrAOHCl and 100 ml. of H_2O was added 1 *M* NaOH solution until the *p*H remained at 6.1. The deep green complex was precipitated slowly from solution by the addition of $NaClO_4$(s). Recrystallization was accomplished from water solution and the compound was dried under vacuum; yield 95% of theory.

Anal. Calcd. for $Cu_2C_{16}H_{37}O_8N_4Cl$: Cu, 22.07; ClO_4^-, 17.27; C, 33.36; H, 6.48; N, 9.73. Found: Cu, 22.2; ClO_4, 17.2; C, 33.40; H, 6.40; N, 9.88.

$[Cu_2(n\text{-}AmAO)_2(OH)_2\text{-}H]ClO_4$ and $[Cu_2(PhAO)_2(OH)_2\text{-}H]ClO_4$ were obtained in a like manner.

Anal. Calcd. for $Cu_2C_{20}H_{45}N_4O_8Cl$: Cu, 20.11; N, 8.87. Found: Cu, 20.04; N, 8.79.

Visible spectra were obtained on a Beckman model DU spectrophotometer equipped with "cell-spacers" through which water (at a constant temperature) was pumped. The temperature of the cell compartment was found to differ from the bath by less than 0.1° and was constant to 0.05°.

Infrared spectra were obtained on compressed KBr-complex disks in a Model 21 Perkin–Elmer infrared spectrophotometer equipped with a NaCl prism.[6]

The determinations of magnetic susceptibilities were carried out on a Gouy balance at room temperature and all samples were found to be free of ferromagnetic impurities.

Common reagents were of A.R. grade while C, H and N analyses were conducted by Galbraith Laboratories and metals, halogens, etc., by standard procedures.

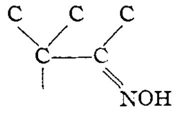
The acid dissociation constants of the amines were determined by *p*H titration at essentially constant ionic strength (μ = 0.27) using a Beckman Model 1190-90 glass electrode in conjunction with a saturated calomel electrode Model E. The solutions contained Ba^{+2} at a concentration equal to that of Cu^{+2} and Ni^{+2} solutions used in the formation constant studies. A Model G Beckman *p*H meter was used and the temperature of the solutions maintained at 24.2 ± 0.1° with a constant temperature bath. Calculation of the constants followed the method described earlier.[7]

Equilibrium constants for the formation of the coördination compounds were obtained by a determination of the *p*H and molar absorbancy of solutions containing HNO_3, $M(NO_3)_2$, ligand and KNO_3. The ionic strength was maintained essentially constant in these determinations (μ = 0.27). Calculation of the constants was carried out by the method previously described[8] suitably modified for this system.

It has been assumed that the two stereoforms of the ligands are in a rapid equilibrium since stoichiometric reactions leading to the production of only one complex are observed. Catalysis of this conversion in solution by many substances (*i.e.*, HCl, LiCl, Br^-) has been shown.[9] In this connection it is interesting to note that the infrared spectra of EnAO, DMG and the dioxime of glyoxal show hydrogen bonding, which favors the *syn*-form. Less than 1% hydrolysis of the ligands occurs in the *p*H range 3.5–9.0 over a period of 5 days at room temperature.

Results

The acid dissociation constants of the amines are listed in Table I. Introduction of the group lowers the basicity of the parent amines while N-alkyl substitution shows very little effect. EnAO is a weaker base than N,N′-dialkylethylenediamines[8] but the separation between successive constants is about the same.



Nickel(II).—It has been established[1] previously that the reaction of this ion with (AO) gives rise to a complex ion containing a maximum of two ligands per metal ion. In the *p*H range 4.5–9.0, no other species containing a different number of AO's can be shown by the method of continuous variations. A study of *n*-PrAO and *n*-AmAO by Job's method shows analogous behavior at a *p*H of 8. However, at *p*H 5, deviations occur which may be explained on the basis of either a mono-complex of limited stability or on the basis of a complex of type A. The reaction of Ni(II) with EnAO (Fig. 1) indicates a 1-1 molar composition. Variation of the *p*H (3.5–11.5) shows no significant deviations from this conclusion. The low stability of the mono-complex of AO has been shown spectro-

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(6) This instrument was obtained by a grant from the National Science Foundation.

(7) F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 2373 (1952)

(8) F. Basolo, Yun Ti Chen and R. K. Murmann, *ibid.*, **76**, 957 (1954).

(9) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 344.

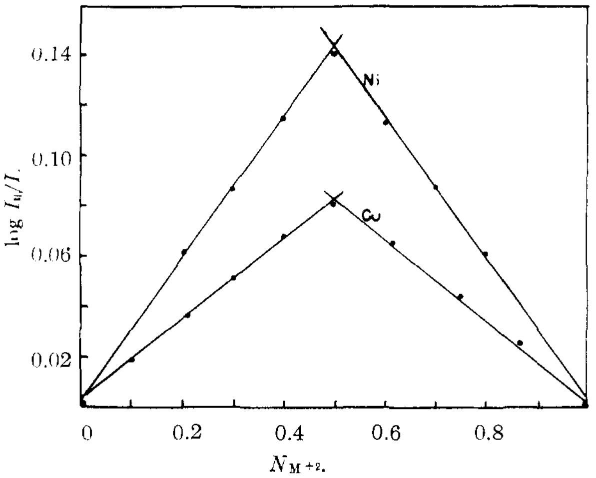

Fig. 1.—Formation of $[M(EnAO)\text{-}H]^+$ *vs.* mole fraction of solutes: $[M^{+2}] = [EnAO] = 8 \times 10^{-4}$; Ni, 390 mμ, *p*H 7.30; Cu, 550 mμ, *p*H 3.90.

photometrically.[1] No change in the absorption spectrum except a lowering of the major peak was observed. If the mono-species were present to any appreciable extent, it would be expected to have a weak absorption in the region 440–580 mμ. Analogous studies with EnAO gave no indication of ions partially coördinated to the ligand while acid–base equilibria involving the hydrogen bond interfered with the interpretation of the *n*-PrAO and *n*-AmAO systems.

TABLE I

ACID DISSOCIATION CONSTANTS[a]

	pK_1	pK_2
EnAO	5.58	8.34
AO	9.12	..
n-PrAO	9.14	..
n-AmAO	9.12	..

[a] Temp. 24.2°, in the presence of $Ba(NO_3)_2$ (9.8×10^{-3} *M*) and KNO_3; $\mu = 0.27$.

Substitution of an alkyl group on the amine nitrogen has a remarkable effect on the α-amine oximes affinity for Ni(II). Figure 2 contains titration curves for the addition of OH^- to solutions containing acid and the theoretical ratio of Ni(II) and ligand. On the basis of base strength, one would expect all of the bidentate donors to have similar coördinating ability. However, a large decrease in stability is noted due to steric hindrance between the alkyl groups. Since the hydrogen bond is present, as shown by infrared studies in the solid state, the *cis* form must be stabilized in spite of this hindrance.

The end-point at 3 equivalents of OH^-, Fig. 2, corresponds to the formation of species of the type $[M(AO)_2\text{-}H]^+$. It is noteworthy that this is absent with *n*-PrAO and *n*-AmAO indicating the weak acidity of $[Ni(n\text{-}PrAO)_2]^{+2}$ compared to $[Ni(AO)_2]^{+2}$. Furthermore, the end-point at 4 equivalents of OH^-, absent in AO and EnAO, shows that $[Ni(n\text{-}PrAO)_2\text{-}H]^+$ is more acidic than the corresponding AO or EnAO complexes. The formation of these compounds is slow with the rate decreasing in the order AO > *n*-PrAO > EnAO.

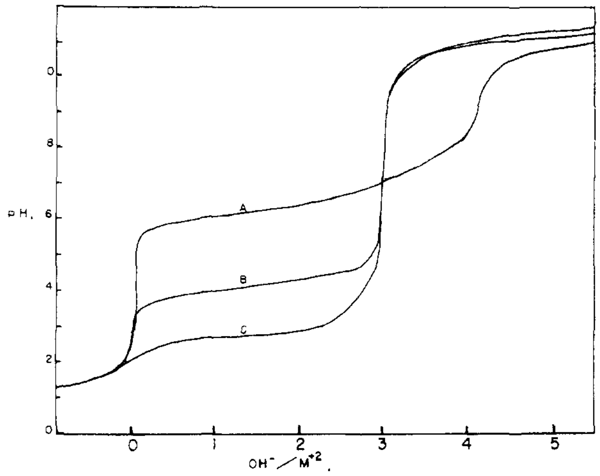

Fig. 2.—Titration curves of Ni^{+2}: A, *n*-PrAO; B, AO; C, EnAO. Ligand/metal ratio: A = 2; B = 2; C = 1.

$[(Ni(AO)_2\text{-}H]^+$.—The reaction $[Ni(AO)_2\text{-}H]^+ + H^+ \rightleftarrows [Ni(AO)_2]^{+2}$ can be observed by the addition of excess acid to a cold solution of $[Ni(AO)_2\text{-}H]^+$. The color changes from yellow, (ϵ_{max} at 419 mμ = 132) to blue (ϵ_{max} at 975 mμ = 8) followed by a gradual decomposition of the complex. That only one H^+ is added can be shown by the method employed on the $[Ni(EnAO)\text{-}H]^+$ system (Fig. 4). K_2 for the reaction $[Ni(AO)_2]^{+2} \rightleftarrows [Ni(AO)_2\text{-}H]^+ + H^+$ was determined by measuring the concentration of $[Ni(AO)_2\text{-}H]^+$ initially present in solutions made by the addition of known amounts of $[Ni(AO)_2\text{-}H]^+$ to buffer solutions. This value was checked by rapid *p*H measurement of solutions of $[Ni(AO)_2\text{-}H]^+$ to which known amounts of H^+ were added. By comparison with identical solutions without complex, the equilibrium constant was calculated and agreed with that determined spectrophotometrically.

Evaluation of the equilibrium constant for the reaction $Ni^{+2} + 2AO \rightleftarrows [Ni(AO)_2\text{-}H]^+ + H^+$ from *p*H titration data was made assuming the contribution from $[Ni(AO)_2]^{+2}$ dictated by K_2. The concentrations of the various species neglecting $[Ni(AO)(H_2O)_4]^{+2}$, were calculated following the method previously described[8] applied to this system. That $[Ni(AO)(H_2O)_4]^{+2}$ does not form in appreciable amounts over 85% of the formation is borne out by Fig. 3. A slope of 1.0 should be obtained if the equation $K_1K_2 = [Ni(AO)_2\text{-}H]^+[H^+]/[Ni]^{+2}[AO]^2$ is obeyed. The slight deviation from this slope probably is due to changes in the ionic strength during titration. As a check on this method and on establishment of equilibrium, individual solutions containing known amounts of $[AO], [Ni^{+2}]$ and $[H^+]$ at $\mu = 0.27$ were equilibrated at constant temperature. $[Ni(AO)_2\text{-}H]^+$ (determined spectrophotometrically) and *p*H were used to evaluate the equilibria. The constants calculated in this manner agreed with those previously obtained and no change was observed after four hours of equilibration.

In alkaline solution (above *p*H 9) the spectrum begins to shift to longer wave lengths and ε increases. The extinction coefficients of both species can be obtained, and the equilibrium constant,

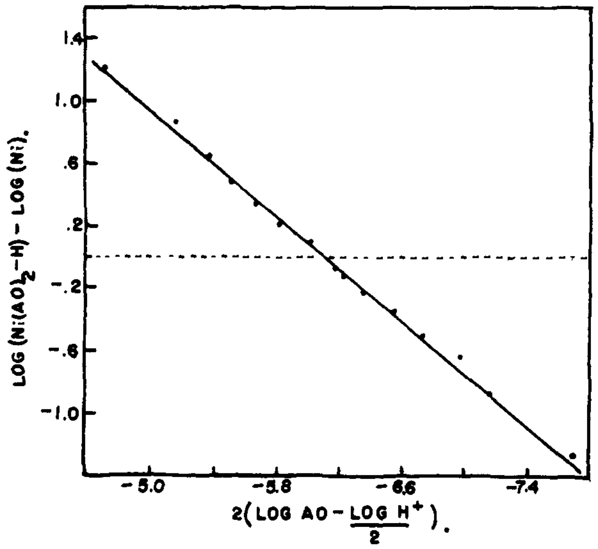

Fig. 3.—Formation of $[Ni(AO)_2\text{-}H]^+$; 24.2°, μ = 0.27.

K_3, for the reaction $[Ni(AO)_2\text{-}H]^+ \rightleftarrows [Ni(AO)_2\text{-}2H]^\circ + H^+$ was estimated from pH and spectrophotometric measurements.

$[Ni(n\text{-}PrAO)_2\text{-}H]^+$ and $[Ni(n\text{-}AmAO)_2\text{-}H]^+$.—Titrations involving the formation of these species come to equilibrium very slowly. Thus the equilibrium constants were determined by measurement of the absorbance and pH of solutions containing known amounts of Ni(II), ligand, HNO_3 and KNO_3 after a two day equilibration period. The values of K_1K_2 found in this manner varied with pH presumably due to the weakly acidic character of $[M(AO)_2]^{+2}$ type species. In the more alkaline solutions, K_1K_2 reached a limiting value which is reported. Because of the approximations involved in their calculation, the values of K_1K_2 for the N-alkyl ligands have only qualitative significance.

Studies of the equilibrium corresponding to K_2 with the N-alkyl ligands were not possible because of the rapid rate of decomposition to Ni(II) in acid solution. K_3 was estimated in the same manner as with the unsubstituted ligands.

$[Ni(EnAO)\text{-}H]^+$.—The combined effect of lowered basicity of the amine and greater stability of the complex lead to the formation taking place in higher acidities than in the AO system. Thus, in spite of the fact that K_2 is only slightly smaller with Ni(II) complexes of EnAO compared to AO, $[Ni(EnAO)]^{+2}$ forms in appreciable amounts in the more acidic solutions. The fact that the extinction coefficient of the protonated species is quite small (ϵ_{max} at 925 mμ = 16) makes it impossible to accurately estimate from spectrophotometric data the concentrations of Ni(II), $[Ni(EnAO)]^{+2}$ and $[Ni(EnAO)\text{-}H]^+$. $[Ni(EnAO)\text{-}H]^+$ can be made to take part in a pseudo equilibrium with $[Ni(EnAO)]^{+2}$ by adding acid to the former complex. Figure 4 shows the changes (extrapolated to 0 time) in absorption observed at the absorption maximum of $[Ni(EnAO)\text{-}H]^+$ (A) and $[Ni(EnAO)]^{+2}$ (B) upon the addition of acid. Only one proton is consumed by the complex in this acid range. It has been assumed that this reaction involves the cleavage of the hydrogen bond. K_2 was evaluated in the same manner as for the corresponding AO complex. Since the rate of formation is slow, separate solutions were equilibrated (containing $[Ni(EnAO)\text{-}H]^+$, EnAO, HNO_3 and KMO_3, μ = 0.27) for two days and the pH and absorbance at 378 mμ measured. A knowledge of K_2 allowed a calculation of K_1K_2 which remained essentially constant throughout 80% of the formation. Table II gives a portion of these calculations. K_3 was determined by calculating the $[Ni(EnAO)\text{-}H]^+/[Ni(EnAO)]^{+2}$ ratio from the spectra of buffered alkaline solutions.

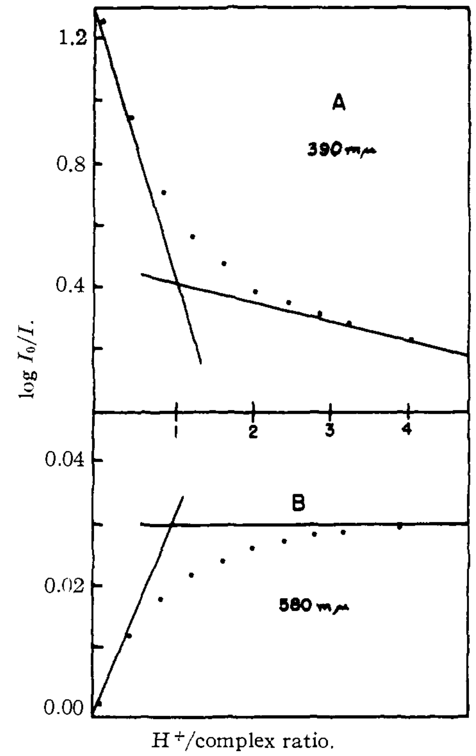

Fig. 4.—$H^+ + [Ni(EnAO)\text{-}H]^+ \rightleftarrows [Ni(EnAO)]^{+2}$; 0°, log I_0/I extrapolated to time of mixing.

TABLE II

FORMATION OF $[Ni(EnAO)\text{-}H]^+$

$Ni_T = 2.00 \times 10^{-3}$, EnAO = 4.00×10^{-3}, ϵ = 320 at 378 mμ (Amine $k_1 = 2.69 \times 10^{-6}$, $k_2 = 4.56 \times 10^{-9}$, K_2 complex = 6.31×10^{-3} 24.2°.)

$[H^+]$ $\times 10^3$	[EnAO] $\times 10^{+10}$	log I_0/I	$[Ni(EnAO)\text{-}H]^+$ $\times 10^{+4}$	$[Ni(EnAO)]^{+2}$ $\times 10^{+4}$	log K_1K_2
1.319	0.228	0.163	5.10	1.35	7.33
0.976	.380	.265	8.29	1.52	7.32
.676	.670	.416	13.00	1.56	7.38
.446	1.372	.515	16.11	1.25	7.30
.364	1.950	.559	17.49	1.06	7.35

Copper(II).—Association between Cu(II) and all of the amine–oximes is much stonger than with Ni(II) corresponding to the normal Irving–Williams order. Also the copper complexes form almost instantaneously in contrast to those of Ni(II). Figure 5 contains titration curves of solutions containing the theoretical Cu/ligand ratio. As is the case with Ni(II), a sharp break occurs at 3 equivalents of OH^- for EnAO and AO, corresponding to

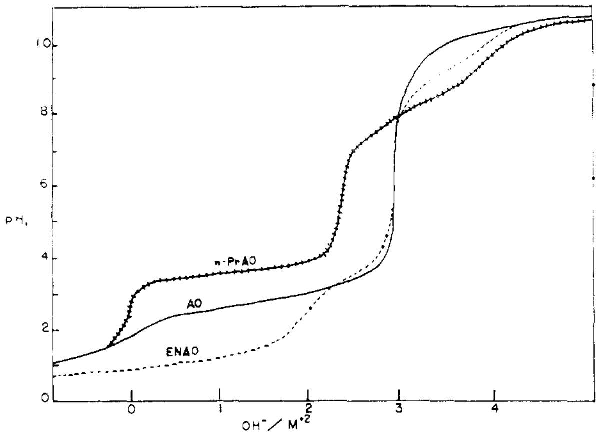

Fig. 5.—Titration curves of $[Cu]^{+2}$, ligand/metal ratio: *n*-PrAO = 2; AO = 2; EnAO = 1.

the formation of $[Cu(EnAO)\text{-}H]^+$ and $[Cu(AO)_2\text{-}H]^+$. In addition there is a weak end-point at 2 equivalents of OH^- for EnAO which is due to the complete formation of $[Cu(EnAO)]^{+2}$. This end-point does not appear with AO. In contrast *n*-PrAO (and *n*-AmAO since they behave almost identically) exhibits a marked increase in slope at about 2.5 equivalents of OH^- and a weak change at 4 equivalents. The color of the EnAO and AO complexes are blue up to 3 equivalents of OH^- and thereafter red-purple. The N-alkyl-substituted AO's form species which are deep green but after the 2.5 equivalent end-point become brown. Alkyl substitution causes a different species to be formed. Analysis of solid compounds and continuous variation studies show a Cu/ligand ratio of 1. In agreement with this, the titration curves for *n*-PrAO show the same shape and spectra (corrected for excess amine present) when the ligand/Cu ratio is 1 or 4. No effort has been made to evaluate the equilibrium constants for the N-alkyl systems because of the uncertainty of their structure.

$[Cu(EnAO)\text{-}H]^+$.—The equilibrium constants K_1, K_2 and K_3 were evaluated from the spectra and *p*H of solutions containing Cu(II), EnAO, HNO_3 and KNO_3. The spectral variation of solutions containing a 2/1 molar ratio of EnAO to Cu(II) with *p*H at constant Cu_T show that three species are formed having ϵ_{max} at 587 mμ = 183, ϵ_{max} at 518 mμ = 306, ϵ_{max} at 622 mμ = 314 which have been ascribed to $[Cu(EnAO)]^{+2}$, $[Cu(EnAO)\text{-}H]^+$ and $[Cu(EnAO)\text{-}2H]^0$, respectively. The variation of absorption with the *p*H of standard solutions allows the calculation of approximate equilibrium constants which were corrected by the method of Spike and Parry.[10]

$[Cu(AO)_2\text{-}H]^+$.—The absorption spectra of solutions of varying *p*H having Cu_T and AO_T constants show that four species are formed. These are believed to be $[Cu(AO)(H_2O)_2]^{+2}$, $[Cu(AO)_2]^{+2}$, $[Cu(AO)_2\text{-}H]^+$ and $[Cu(AO)_2\text{-}2H]^0$, respectively. Approximate constants were obtained by the method described for the EnAO system and were corrected for overlap.

Since the Cu(II) complexes of AO and EnAO form at low *p*H's where $[H^+]$ is rather insensitive to *p*H changes, the final equilibrium constants though satisfying the *p*H and spectrophotometric data are not too accurate. Duplicate determinations at slightly different concentrations reproduced the reported values to ± 0.2 *pK* or log *K* units.

Table III shows the equilibrium constants evaluated in this work. Compounds formed with both Ni(II) and Cu(II) have larger formation constants (K_1) with EnAO than AO which is in agreement with the "Chelate stabilization effect."[10] The acid dissociation of $[M(AO)_2]^{+2}$ type species affects the ratio of AO/EnAO complex stabilities only slightly indicating a minor effect on the stability of the hydrogen-bond by the additional chelate ring. Comparison with the corresponding C-substituted ethylenediamine stabilities shows a marked decrease in stability in the AO series due to the decreased basicity of a —C=N—OH group compared to the -C-NH_2 group. The steric effect of N-alkyl substitution is larger than that observed in the N-alkylethylenediamine series which is to be expected in the light of the hydrogen-bond forced *cis*-configuration. This effect also is observed in the strength of the hydrogen-bond, for pK_3 with the N-alkyl ligands is low.

TABLE III

EQUILIBRIUM CONSTANTS AT 24.2°, μ = 0.27

K_1 $M^{+2} + 2AO \rightleftarrows [M(AO)_2]^{+2a}$

K_2 $[M(AO)_2]^{+2} \rightleftarrows [M(AO)_2\text{-}H]^{+1} + [H^+]$

K_3 $[M(AO)_2\text{-}H]^{+1} \rightleftarrows [M(AO)_2\text{-}2H]^0 + [H^+]$

Nickel	AO	EnAO	*n*-PrAO	*n*-AmAO
log K_1	8.6	10.1	..	..
pK_2	2.5	2.8	..	..
pK_3	11.8	11.8	8.5	8.5
log K_1K_2	6.1	7.3	1.1	1.0
Copper				
log K_1	11.9	13.0		
pK_2	4.1	4.3		
pK_3	9.9	9.8		
log K_1K_2	7.8	8.7		

[a] With (EnAO) complexes, 2 (AO) groups represent 1 (EnAO).

A comparison of the acid dissociation constants of $[M(AO)_2]^{+2}$ type show a larger pK_2 value for Cu(II) compared with Ni(II) while the reverse is true for pK_3. This suggests that the hydrogen bonds of the Ni(II) complexes are more stable thermodynamically than those of Cu(II).

The radical difference in water solubility of Ni(II) and Cu(II) chelates of DMG has been the subject of many investigations. The most reasonable explanation involves the metal to metal interaction which exists only with Ni(II). Sharpe and Wakefield[4] have studied the analogous methylethylglyoximes and attributed the greater solubility of the Ni(II) complex (compared to DMG) to a crowding by the bulky ethyl groups resulting in a longer Ni–Ni distance. If these two effects are the only ones operative, then glyoxal dioxime should be capable of allowing as close metal–metal approach as DMG allowing strong metal bonds and a low solubility. This does not appear to be the case for $[Ni(Gly)_2\text{-}2H]^0$ closely resembles the methyl-

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[10] C. G. Spike and R. W. Parry, THIS JOURNAL, **75**, 2726, 3770 (1953).

ethyl and methyl-*n*-amyl derivatives in color and solubility. Preliminary results indicate that its crystal structure is somewhat different from that of $[Ni(DMG)_2\text{-}2H]^0$.[11] Although a weighting effect is no doubt operative in the DMG case, its magnitude is expected to be smaller than that observed.

This indicates that C-methyl or perhaps C-alkyl groups give rise to strong metal–metal bonds which provide insolubility to the compound. Alkyl substitution has been shown to stabilize the planar configuration of Ni(II) chelates of ethylenediamine[8] and the formation constants are increased in chelates of ethylenediamine and trimethylenediamine.[12]

Even in the EnAO system, methyl substitution is effective in the stabilization of the planar state. Preliminary results indicate that 2,2′-(2-methylethylenediamine)-bis-(2-methyl-3-butanone) dioxime (Me-EnAO) forms $[Ni(MeEnAO)\text{-}H]^+$ which when treated with acid gives diamagnetic $[Ni(MeEnAO)]^{+2}$ in contrast to paramagnetic $[Ni(EnAO)]^{+2}$. These effects cannot be explained on ligand base strength alone.

The stability of the hydrogen bond of Ni(II)–AO complexes when coupled with the stabilization of *bis*-complex over the mono by the change of orbital hybridization leads to essentially one nickel complex in solution in the *p*H range 4.5–8.0. This is in contrast to Cu(II) coördination in which stepwise formation is observed and the hydrogen bond formation occurs superimposed on the last portion of complex formation. Thus Ni(II) and $[Ni(AO)_2\text{-}H]^+$ are the only species present in large concentrations during the majority of the formation while appreciable concentrations of several complex species are always present with Cu(II). With Ni(II) and DMG this situation would be more pronounced and would have the effect of producing the highest concentration of a species which because of its non-ionic character and metal–metal bonds has limited water solubility.

It appears that several factors lead toward the selectivity of DMG as an analytical reagent. (A) The stability of the hydrogen bond leads to a preponderance of the non-ionic species. (B) The methyl groups as well as the hydrogen bond stabilize the planar state of Ni(II) compounds. (C) Metal–metal bonds provide sufficient crystal lattice energy to decrease the solubility of $[Ni(DMG)_2\text{-}2H)^0$. (D) The steric effect of large alkyl groups increases the metal–metal distance and solubility.

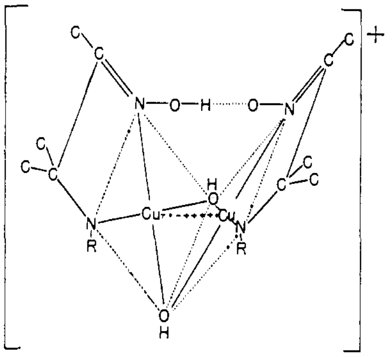
Evidently C is the most important characteristic but the strength of the metal–metal interaction is dependent on the strength of the hydrogen bond and on the presence of methyl groups.

In excess acid $[Ni(AO)_2]^{+2}$ type ions decompose at a measurable rate and at constant H^+ are first order in this species. The $[H^+]$ dependence (0.3–1.0 *M* H^+) shows a first-order dependence and leads to the rates being represented by the expression $d[Ni(AO)_2]^{+2}/dt = k[Ni(AO)_2]^{+2}[H^+]$. The values below show that an increase in the number of chelate rings decreases, while N-alkyl substitution increases, the rate of decomposition.

0°, μ = 1.0 (NaCl)	*k*, l. mole^{-1}, min.$^{-1}$
$[Ni(AO)_2]^{+2}$	0.106
$[Ni(EnAO)]^{+2}$	.0064
$[Ni(N\text{-}AmAO)_2]^{+2}$	.253

The interpretation of the H^+ dependence awaits the completion of studies now in progress on the kinetics of decomposition in neutral and slightly acidic media.

The species formed between Cu(II) and *n*-PrAO, *i*-PrAO, Di-MeAO, *n*-AmAO and PhAO possess radically different chemical and physical characteristics from those formed with the parent ligand. Analyses of the crystalline solids show a Cu/ligand/OH ratio of 1-1-1. The fact that 2.5 equivalents of OH^- are consumed per mole of Cu(II) when prepared from AOH^+ indicates the formation of a dimeric species containing one hydrogen bond. The equivalent conductivity (1.18 × 10^{-3} *M*, 25°) of water solution is 60.6 and 121 when based on a monomer and dimer, respectively. The normal range of 1-1 electrolytes is 100–120. The magnetic moment of the Cu(II) in the solid state is 518 × 10^{-6} (1.12 B.M.). This is considerably lower than the normal value for Cu(II)[13] and may be due to Cu–Cu interaction. That Cu(I) is not present is demonstrated by the lack of reducing properties of the acid-decomposed complex. The infrared spectrum shows the characteristic OH stretching frequency of a weak OHO group. Tentatively, the structures of these substances are



Previous investigators have noted the tendency to dimerize when the formation of the bis-complex is sterically hindered.[14,15] The fact that dimerization occurs with smaller R groups than in the ethylenediamine series is due probably to the great tendency to form the hydrogen bond forcing a *cis*-configuration on the bis-complex with the maximum steric interaction of the R groups. This is substantiated by the fact that with excess ligand in alkaline solutions (*p*H 12) the stable blue complex has a Cu/*n*-PrAO ratio of 1/2 . In this region the hydrogen bond is unstable and loses a second H^+.

AO may be used for the analytical determination of either Cu(II) or Ni(II) if not present together. Spectrophotometric methods give accurate results if the *p*H is carefully controlled. It is also possible to determine these ions by *p*H titration of solutions

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[11] R. Kent Murmann and L. Katz, unpublished results.

[12] J. C. Bailar, Jr., and J. B. Work, THIS JOURNAL, **68**, 232 (1946).

[13] P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1943, p. 181.

[14] F. Basolo and R. K. Murmann, THIS JOURNAL, **76**, 211 (1954).

[15] H. Irving, E. J. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).

made by adding an unknown excess of AO·HCl to a M^{+2} solution at pH 5 and titrating with OH^-. The end-point is sharp with Cu^{+2} but because the Ni^{+2} complexes form slowly it is better to add an excess of OH^- and back titrate with H^+. Zn(II), Pd(II) and Pt(II) interfere with the latter determination.

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

The Stabilities and Absorption Spectra of Complexes of Some Divalent Metal Ions of the First Transition Series with the Thioglycolate Ion[1]

BY D. L. LEUSSING

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The metal ions Mn(II), Co(II), Ni(II) and Zn(II) have been found to react with the thioglycolate ion to form complexes of the type $M(SCH_2CO_2)$ and $M(SCH_2CO_2)_2^=$. The formation constants for these complexes were evaluated and their absorption spectra determined. The changes in the stabilities of the thioglycolato complexes in the series Mn(II) through Zn(II) were found to bear a close relationship to those observed for the oxygen and nitrogen ligands. The formation constants and absorption spectra show that the mercaptide group in the thioglycolate ion is able to exert a strong influence on the metal ion in a complex.

The thioglycolate ion has been found to react in solution with iron(II) to form the light red complex, $Fe(SCH_2CO_2)_2^=$.[2] In alkaline solutions containing the thioglycolate ion in low concentration, the yellow complex $Fe(OH)(SCH_2CO_2)^-$ also forms. The stability constants for these complexes were determined at an ionic strength of zero at 25° as, also, was the solubility product of the slightly soluble compound, $FeSCH_2CO_2$. Evidence was obtained that this latter compound is slow to precipitate and exists in super-saturated solution when the reactants are first mixed. Li and Manning[3] have reported the formation and stabilities of the zinc(II) thioglycolates, $ZnSCH_2CO_2$, and $Zn(SCH_2CO_2)_2^=$ at an ionic strength of 0.15 at 25°.

In order to obtain more information about the complexing of the mercaptide ion as reflected by that of the thioglycolate ion, the stabilities of the complexes with Mn(II), Co(II), Ni(II) and Zn(II) were evaluated and their absorption spectra determined in the present study. Copper(II) reacts rapidly with the thioglycolate ion to form copper(I) and the disulfide so the stabilities of the copper(II) complexes could not be obtained.

Experimental

Stock solutions, approximately 0.10 *M*, were prepared from reagent grade chemicals of $Ni(NO_3)_2$, $NiCl_2$, $MnCl_2$, $CoCl_2$ and $ZnCl_2$. The nickel nitrate solution was standardized with potassium cyanide according to the method of Kolthoff and Stenger.[4] The zinc chloride solution was prepared by dissolving a weighed amount of zinc in a known volume of standard hydrochloric acid. The final composition of this solution was 0.1000 *M* zinc chloride, 0.0407 *M* hydrochloric acid. The manganous chloride and cobaltous chloride solutions were standardized using disodium dihydrogen ethylenediaminetetraacetate.[5] The EDTA solution was standardized against the zinc chloride solution.

Eastman thioglycolic acid was purified as described previously.[6] Dilute stock solutions were freshly prepared from the purified reagent.

A 1.000 *M* potassium hydroxide solution was prepared from a British Drug Houses Concentrated Volumetric Solution. This solution was found to contain less than 0.2% carbonate by potentiometric titration.

The stability constants were determined using the pH-titration method.[7] In most of the experiments, solutions were prepared which contained 0.0100 *M* thioglycolic acid, 0.090 *M* KCl (or KNO_3) and 0.00200 *M* metal ion. These were titrated under an atmosphere of nitrogen with 1.000 *M* KOH using a micro-buret. Additional titrations were run with nickel(II) in 0.00100 and 0.00200 *M* thioglycolic acid and with zinc(II) in 0.00100 *M* thioglycolic acid. The potassium chloride concentration was increased accordingly. A Beckman Model G pH meter was used to determine the pH of the solutions during the titrations. The glass electrodes were calibrated against National Bureau of Standards buffers at an ionic strength of 0.10 at values of pH 1.52, 3.95, 6.85 and 9.20. A linear correction to the pH meter readings was assumed for intermediate values of pH.

To calculate the results obtained in the moderately alkaline range, it was necessary to make a correction for unreacted hydroxide. The relation between the concentration of free hydroxide and the measured pH of the solutions was obtained by titrating the 1.000 *M* potassium hydroxide into 0.100 *M* potassium chloride. The product $a_H M_{OH}$ was found to have the value $12.3 \pm 0.2 \times 10^{-15}$ in the range pH 9.90 to 11.90. Assuming that γ_{OH} is equal to γ_H and using the value 0.63 for $\gamma_H\gamma_{OH}/a_{H_2O}$[8] the activity product of water is calculated to be 9.7×10^{-15}, which is in good agreement within an error of 0.02 pH unit with the accepted value of 10.08×10^{-15}. The value of γ_{OH} equal to 0.76 given by Kielland[9] gives a value of 9.3×10^{-15}.

The ionization constants of thioglycolic acid were determined by titrating 5.02×10^{-3} *M* thioglycolic acid in 0.100 *M* potassium chloride with the standard potassium hydroxide. The constants so obtained were converted to molarity constants using a value of the activity coefficient of hydrogen ion equal to 0.83.[9] The molarity constants were calculated to be 3.83×10^{-4} and 6.35×10^{-11} for K_1 and K_2. The titration curve calculated using the above values agreed excellently within the error of the measurements with that observed when the appropriate corrections were made for the concentration of free hydrogen or hydroxide ions in the solution.

The titration curves in the presence of the divalent metal ions showed the formation of mono- and bis-thioglycolato complexes, designated hereafter as MRS and $M(RS)_2^=$ where $RS^=$ refers to the divalent thioglycolate ion. The complexes presumably are chelates and the water molecules occupying the remaining coördination positions of the metal ion are assumed without writing them in the formula. The

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[1] Financial assistance for this work was made available by a grant from the National Science Foundation.

[2] D. L. Leussing and I. M. Kolthoff, THIS JOURNAL, **75**, 3904 (1953).

[3] N. C. Li and R. A. Manning, *ibid.*, **77**, 5225 (1955).

[4] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd Rev. Ed., Interscience Publishers, Inc., New York, N. Y., 1947.

[5] G. Schwarzenbach, "Die Komplexometrische Titrationen," Ferdinand Enke, Stuttgart, 1955.

[6] D. L. Leussing and I. M. Kolthoff, *J. Electrochem. Soc.*, **100**, 334 (1953).

[7] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

[9] J. Kielland, THIS JOURNAL, **59**, 1675 (1937).