show that the reduction of this salt to potassium tetracyanocobaltate(0) involves the formation of a complex of Co^{+1} as an intermediate. Hence, the first reaction that occurs is most probably the two-electron change

$$K_3Co(CN)_6 + 2K^+ + 2e^- \longrightarrow 2KCN + K_3Co(CN)_4$$

which is followed by the reduction of potassium tetracyanocobaltate(I) to the product reported by Hieber and Bartenstein,[4] *i.e.*, potassium tetracyanocobaltate(0). Attention should be called to the fact that Grube and Schächterle[9] have reported evidence for the existence of cobalt(I) from their studies on the reduction of potassium hexacyanocobaltate(III) in alkaline aqueous media at a cobalt cathode by means of potassium amalgam. Similarly, Hume and Kolthoff[10] have shown that the aquopentacyanocobaltate(III) ion is reduced to a cobalt(I) complex at the dropping mercury electrode.

(9) G. Grube and P. Schächterle, *Z. Elektrochem.*, **32**, 565 (1926).

(10) D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **71**, 867 (1949).

AUSTIN, TEXAS

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Studies on Coördination Compounds. IX. The Solution Stabilities of the Chelate Compounds of a Number of Organic Ligands

BY LEGRAND G. VAN UITERT[1] AND W. CONARD FERNELIUS

RECEIVED JUNE 18, 1953

The chelate compound species formed in solution by a number of chelating agents which coördinate through oxygen, nitrogen and combinations of the two are discussed and their stability constants in 75 vol. % dioxane–25 vol. % water solution are given. Compounds formed by chelating agents bonding through nitrogen show a greater dependency upon metal ion electronegativity than those bonding through oxygen. The following types of chelate species of divalent metal ions are found to exist in solution—for Ch, MCh^{++} and MCh_2^{++}: for HCh, MCh^+, MCh_2 and MCh_3^-; for H_2Ch, MCh and $MCh_2^=$; for H_3CH. MHCh and MCh^-.

Introduction

The potentiometric study of chelate compound formation not only enables one to calculate the solution stability constants for many chelate compounds, but also yields considerable interesting information concerning the chelate compound species that exist in solution. The stability constants for a number of chelate compounds of structurally different ligands have been determined in the course of investigating these relationships. Soluble coördination complexes having charges ranging from +2 to −2 are described and their solution stability constants tabulated. The constants are only applicable in the 75 vol. % dioxane–25 vol. % water solution in which they were determined.

Experimental

The apparatus and procedures that have been employed, except as noted, are as described in a previous paper.[2] The following typical solution was titrated with 0.100 *N* $(CH_3)_4NOH$: 1×10^{-4} mole of metal salt and 4×10^{-4} mole of chelating agent in 75 ml. of dioxane and 25 ml. of water.

The chelating agents were titrated alone in determining their dissociation constants (pK_D values). In the cases of 8-hydroxyquinoline and glycine, 5.8×10^{-4} mole of $HClO_4$ was also present. The solutions were titrated with 0.37 *N* $(CH_3)_4NOH$ in the latter cases. A 0.100 *M* solution of NH_4NO_3 was employed in place of the chelating agent, above, in determining the coördination constant for ammonia. In the case of ethylenediamine, 5.00×10^{-4} mole of $HClO_4$ was added to the solutions. The acid or the acid plus the metal salt was then titrated with 0.100 *N* ethylenediamine solution.

C.P. or reagent grade copper(II), nickel(II), manganese(II), zinc(II) and magnesium(II) perchlorates and ammonium and calcium nitrates were employed. Catechol, 2-acetyl-1-naphthol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 8-hydroxyquinoline, glycine, ethylenediamine, ethyl benzoylacetate, *d*-tartaric acid, ethyl *d*-tartrate, salicylic acid and salicylaldehyde were obtained from the Eastman Kodak Co. Benzoylpyruvic acid and ethyl benzoylpyruvate were student preparations.

The calculation procedures for the compounds involving chelating agents which lose one proton have previously been reported.[3] Briefly

$$pK_D = B + \log U_H + \log 1/\gamma^2$$

where pK_D is the negative logarithm of the dissociation constant of the chelating agent, B the pH meter scale reading, $\log U_H = B - \log C_{H^+}$ = a constant for a fixed solvent and mean electrolyte molality and γ is the mean stoichiometric activity coefficient for HCl of the same mean molality.[4]

For example, in a two millimolal solution containing 75 vol. % dioxane–25 vol. % water, $\log U_H = 0.75$ and $\log 1/\gamma^2 = 0.6$. Also

$$\log K_{f_1} \approx pK_D - B_{n=1/2} - \log U_H - \log C_{HCh\,n=1/2}$$

where n is the average number of chelating agent ions associated with the metal ions per metal ion.

Hence for the above typical conditions in the case of 2-acetyl-1-naphthol with magnesium (see Fig. 1 and Table I).

$$\log K_{f_1} = 13.4 - 8.0 - 0.75 + 2.5 = 7.1 \text{ approximately.}$$

For the chelating agents which lose two protons at a time the relationship $pK_{D_{1,2}} - \log K_{f_{\alpha,\beta}} = -\log [H^+]^2/[H_2Ch]$ when $[MCh] = [M^{++}]$ is employed ($pK_{D_{1,2}} = pK_{D_1} + pK_{D_2}$; $K_{f_{\alpha,\beta}} = [MCh]/[M^{++}][Ch^=]$).

In the case of *d*-tartaric acid where a total of three protons is given up by the chelating agent, the first two at the same time and the third at a higher *B*-value (pH meter reading[3]), the above relationship is employed to find $\log K_{f_{\alpha,\beta}}$ and the relationship $pK_{D_3} - \log K_{f\gamma} = \log 1/[H^+]$ where $[MCh^-] = [MHCh]$ is employed to find $\log K_{f\gamma}$. Then (for MCh^-) $\log K_{f_{\alpha,\beta,\gamma}} = \log K_{f_{\alpha,\beta}} + \log K_{f\gamma}$. The pK_D values and the formation constants obtained are assembled in Table I.

Discussion

It has been shown in a previous paper[5] that the logarithms of the first formation constants for the

---

(1) Union Carbide and Carbon Corporation Fellow 1951–1952.

(2) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

(3) L. G. Van Uitert and C. G. Haas, *ibid.*, **75**, 451 (1953).

(4) H. S. Harned and J. O. Morrison, *ibid.*, **58**, 1908 (1936).

(5) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 2736 (1953).

TABLE I

APPROXIMATE THERMODYNAMIC CONSTANTS IN THE SOLVENT 75 VOL. % DIOXANE–25 VOL. % WATER

				Cu^{++}		Ni^{++}			Zn^{++}			Mn^{++}		Mg^{++}		Ca^{++}		Δ(log K_{M_1} − log K_{M_1})		
	pK_{D_1}	pK_{D_2}	pK_{D_3}	log K_{f_1}	log K_{f_2}	K_{f_1}	K_{f_2}	K_{f_3}	log K_{f_1}	log K_{f_2}	log K_{f_3}	log K_{f_1}	log K_{f_2}	log K_{f_1}	log K_{f_2}	log K_{f_1}	log K_{f_2}	Cu–Mg	Ni–Mg	Coördinating atoms
Et benzoylacetate	14.70			13.30	10.70	10.55	8.85							8.65	7.00			4.65	1.90	O–O⁻
Et benzoylpyruvate	10.20					9.80	8.10							7.85	6.05				1.95	O–O⁻
2-Acetyl-1-naphthol	13.40			12.15	9.80	8.90	7.45							7.15	5.55			5.00	1.75	O–O⁻
1-Nitroso-2-naphthol	11.60					11.50	10.10	6.60	9.50	7.80				6.20	4.40				5.30	NO–O⁻
2-Nitroso-1-naphthol	11.20					10.70	9.20	5.90	8.70	7.00		7.10	5.50	5.80	3.80				4.90	NO–O⁻
Salicylaldehyde	12.20			10.35	8.35	8.25	6.25							6.25	4.30			4.10	2.00	O–O⁻
Dimethyl glyoxime	~15.5			~15.1	~14.1	~14.6	~13.8													
8-Hydroxyquinoline	3.6[a]	14.1[b]				(15.2)[n]	...	7.2				10.8	9.6	8.8	7.4	7.3	5.9		6.4	N–O⁻
Glycine	4.2[c]	10.7[d]				(9.0)[n]	...	4.8	8.3	6.8	3.8	6.3	4.7	4.8	3.2				4.2	N–O⁻
Ethylenediamine	6.2[e]	9.2[f]		11.0		8.2			6.8					(1.8)[n]				9.2	6.4	N–N
Ammonia	8.8			4.7		3.5								(1.2)[n]				3.5	2.3	N
d-Tartaric acid	14.3[g]		*ca.* 16.5[b]			9.9[h]	6.9[i]							7.9[h]	5.3[i]				2.0	⁻O–O⁻
Benzoylpyruvic acid	6.40[c]	12.10[b]			(8.1)[k]	14.4[j]	6.2[k]							12.0[j]	5.0[k]				2.1	⁻O–O⁻
Salicylic acid	7.00[c]	*ca.* 15.5[b]				5.2[l]								4.7[l]					0.5	O–O⁻
Catechol	13.7	14.2		19.5[m]	11.2[k]															

[a] ⩾NH. [b] –OH. [c] COOH. [d] $-NH_3^+$. [e] enH_2^{++}. [f] enH^+. [g] pK_D for loss of both COOH protons, each COOH$\simeq{}^1/_2\ pK_{D_{1,2}}$. [h] For loss of both COOH protons. [i] For the change of attachment of one $-COO^-$ for $-O^-$ in the same molecule. [j] For loss of –COOH and OH protons. [k] For attachment of second Ch$^=$ group. [l] For loss of –COOH protons alone. [m] Loss of both –OH protons at a time. [n] Extrapolated on the basis of a plot of the known log K_{f_1} for NH_3 in H_2O.[4]

metal complexes of β-diketones can be described as an approximately linear function of the metal ion electronegativity for a given chelating agent. Magnesium(II), nickel(II) and copper(II) are typical members of the above metal ion series. In general, these are the ions used herein to indicate the dependency of log K_{f_1} upon metal ion electronegativity for the chelating agents under investigation. Zinc(II), manganese(II) and calcium(II) are employed in those cases where the stability constants for copper and nickel cannot be calculated.

In general, it is found that the relationship described for the β-diketones is also valid for the other chelating agents. However, it will be noted that the slopes of such plots vary from one chelating agent to another being least for O–O coördinating agents and greatest for N–N coördinating agents (see Table I). The further correlation of these data among themselves and with other data is complex in nature and hence has been reserved for a subsequent paper.

2-Acetyl-1-naphthol and 2-Nitroso-1-naphthol.—Figures 1a and 1b show the titration curves for 2-acetyl-1-naphthol and 2-nitroso-1-naphthol. The indicated spacing of the titration curves for 2-acetyl-1-naphthol with magnesium, nickel and copper is typical for the chelating agents coördinating through one enolate and one oxo group. Substituting a nitroso group for the acetyl group more than doubles the B-value difference from magnesium to nickel with an accompanying greater stability for the nickel complex and a lesser stability for the magnesium complex. The copper complex is too stable to be measured in this case. Three 2-nitroso-1-naphtholate ions coördinate with nickel to form $NiCh_3^-$ in solution.

Benzoylpyruvic Acid.—Figure 2 depicts the titration curves of benzoylpyruvic acid alone, and in the presence of Mg, Ni and Cu. The stoichiometry of the titration of benzoylpyruvic acid in the presence of metal ions indicates that two protons are lost from each chelating agent molecule associated with the metal ions present below $B = 5$ yielding

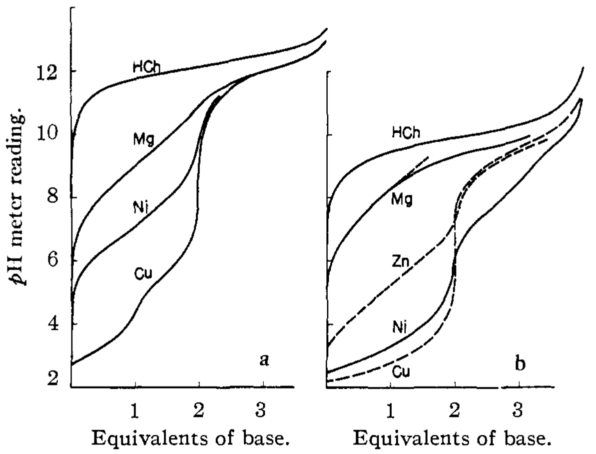


Fig. 1.—Titration of 2-acetyl-1-naphthol (a) and of 2-nitroso-1-naphthol (b) alone and in the presence of metals. The curve for Cu^{++} with the latter reagent is at the limit of accurate measurement of acidity.

the neutral species MCh in solution. A second chelating ion is added at a higher *B*-value giving a final species of $MCh_2^=$ in solution. In the formation of the neutral species, MCh, the carboxyl group lost a proton well below its normal titration level. Hence, the coördination of a metal ion by the *β*-diketone nucleus in pyruvic acid must have an appreciable negative inductive effect upon the carboxyl group or else the coördination is being effected by the carboxyl group and an *α*-enolate group.

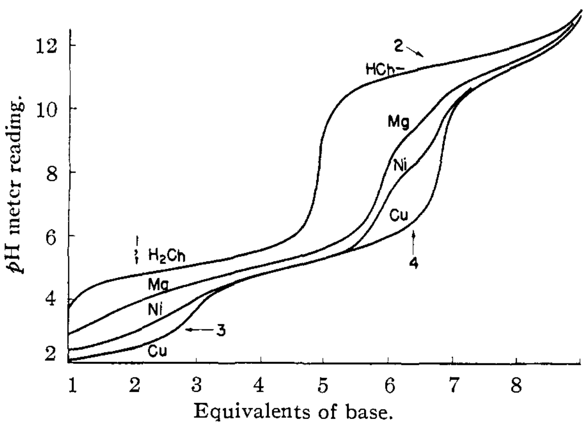


Fig. 2.—Titration of benzoylpyruvic acid alone and in the presence of metals. Along the numbered plateaus, the following reactions occur: (1) $RCOOH \rightarrow H^+ + RCOO^-$; (2) $HCh^- \rightarrow H^+ + Ch^=$; (3) $M^{++} + H_2Ch \rightarrow MCh + 2H^+$; (4) $MCh + RCOO^- \rightarrow MCh_2^= + H^+$.

***d*-Tartaric Acid.**—Figure 3 depicts the titration curves for *d*-tartaric acid alone and in the presence of Mg, Ni and Cu. Only the carboxyl groups could be titrated without exceeding the *B*-values on the *p*H meter scale. The stoichiometry indicates that the *d*-tartaric acid coördinates the metal ions by the loss of the two carboxyl protons at a *B*-value below 5 to give a neutral species which separates from solution during the addition of the second equivalent of base. Upon completion of the titration of the carboxyl groups from the excess tartaric acid in solution, the tartaric acid ions associated with the metal ions lose an additional proton causing the precipitate which separated earlier to go back into solution. This may well represent a change of attachment from one of the two coördinated carboxyl groups to an alkoxide group giving a final product of MCh^-.

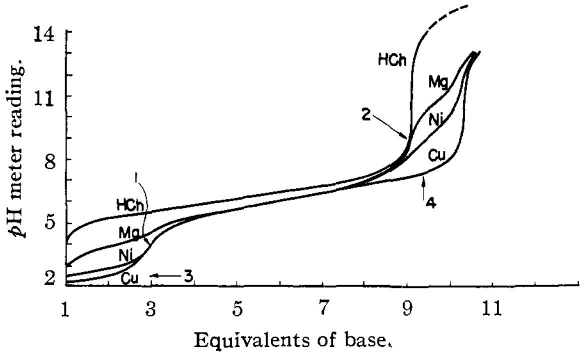
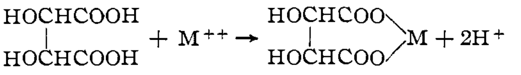
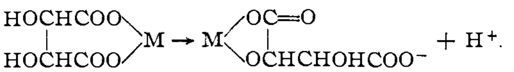


Fig. 3.—Titration of *d*-tartaric acid alone and in the presence of metals. During the metal-ion titrations a precipitate forms at (1) and the solution clears at (2). In region (3) the reaction



$$\begin{array}{l}\text{HOCHCOOH}\\ \;|\\ \text{HOCHCOOH}\end{array} + M^{++} \rightarrow \begin{array}{l}\text{HOCHCOO}\diagdown\\ \;|\qquad\qquad\quad >M\\ \text{HOCHCOO}\diagup\end{array} + 2H^+$$

is taking place and in region (4)



$$\begin{array}{l}\text{HOCHCOO}\diagdown\\ \;|\qquad\qquad\quad >M\\ \text{HOCHCOO}\diagup\end{array} \rightarrow M\begin{array}{l}\diagup\text{OC=O}\\ \quad|\\ \diagdown\text{OCHCHOHCOO}^-\end{array} + H^+.$$

Catechol.—Figure 4 depicts the titration curve for catechol alone and in the presence of copper. Catechol forms a deep blue complex with copper. Two protons are lost at a time in the chelation process. This is shown by the fact that an increase to five times the concentration of catechol lowers the *B*-values of the titration curve by log $\sqrt{5}$ units instead of log 5. Two catechol ions add

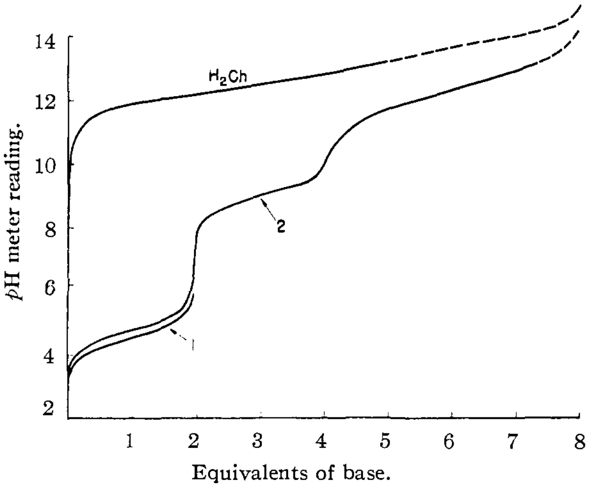


Fig. 4.—Titration of catechol alone and in the presence of copper ion. The concentration of copper for the lowest curve is five times that in the other. Along the numbered plateaus, the following reactions occur: (1) $Cu^{++} + H_2Ch \rightarrow CuCh + 2H^+$; (2) $CuCh + H_2Ch \rightarrow CuCh_2^= + 2H^+$.

to copper about four log units apart on the *B*-scale forming the complexes CuCh and $CuCh_2^=$ in turn. Data for nickel and magnesium were not obtained since this could not be done without using high concentrations of the chelating agent.

8-Hydroxyquinoline and Glycine.—The titration curves for 8-hydroxyquinoline and glycine with excess acid present are given in Fig. 5a. The curves for 8-hydroxyquinoline in the presence of Ca, Mg, Mn, Zn and Ni are given in Fig. 5b and those for glycine with Mg, Mn, Zn and Ni in Fig. 5c. Acid was not added in the chelation titrations since the ring-nitrogen and carboxyl-group buffer areas are too low to allow meaningful calculations to be made in these cases. Also, for the present the best estimates of log K_{f_1} for the Zn, Ni, etc., derivatives of these compounds are obtained by extrapolation of the measurable data.

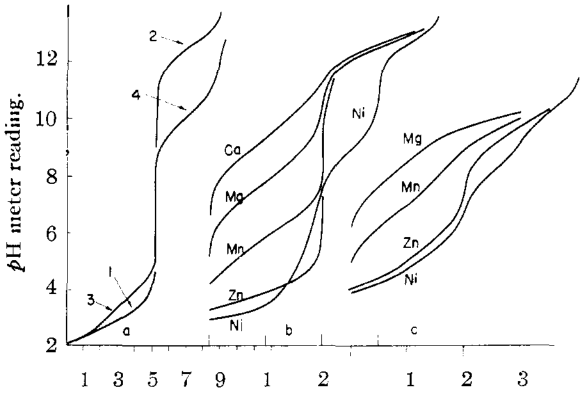


Fig. 5.—Titrations of 8-hydroxyquinoline and glycine alone and in the presence of metals. In (a) the following groups are reacting in the regions designated: (1) $\geqslant NH^+$ and (2) –OH of 8-hydroxyquinoline; (3) –COOH and (4) $-NH_3^+$ of glycine. The titration curves for 8-hydroxyquinoline are given in (b) and those for glycine in (c). 8-Hydroxyquinoline with Ni and glycine with Ni and Zn form species of the type MCh_3^-.

8-Hydroxyquinoline exhibits an unusual titration curve with nickel. The color developed upon mixing the two is quite evident even in the presence of 5 *N* $HClO_4$ indicating that the first product of chelation is very stable. The titration curve has a prolonged rise over the second equivalent of added base that is not compatible with the predictions of any simple mononucleate equilibrium reaction. A third 8-hydroxyquinolate group associates with nickel at a higher *B*-value. This part of the titration curve has the requisite shape for the simple equilibrium

$$MCh_2 + Ch^- \rightleftarrows MCh_3^-$$

in contrast to the shape of the titration curve over the second equivalent. Three glycine ions associate with zinc as well as nickel to form $ZnCh_3^-$ and $NiCh_3^-$ in solution.

The constants for the association of 8-hydroxyquinoline and glycine with the metal ions prior to losing their protons have not been determined here. Hence the constants listed for these substances are not the usual formation constants involving the loss of protons from both coördinating atoms that are listed elsewhere, but should be considered to represent the change of the monodentate group associated with the metal ion through ring nitrogen or the carboxyl ion to the fully chelated bidentate group.

Ammonia and Ethylenediamine.—The results of the titrations with ammonium nitrate and ethylenediamine were comparable to those obtained in water.[6] This is quite in contrast to the approximately 4.5 log unit increase in the constants for the association of the negatively charged chelating-agent ions with the proton and the metal ions in going from water to 75 vol. % dioxane–25 vol. % water solution.

Dimethylglyoxime.—The ligands that have been considered above have been relatively free from influences external to the coördinating nucleus. They and many others which have been studied, such as tropolone and its substitution derivatives[7] and the *o*-hydroxyazo dyes,[8] consistently demonstrate the dependence of log K_{f_1} upon the electronegativity of the metal ion involved. Systems that vary from this relationship, in general, do so as a consequence of structural influences external to the chelating nucleus. Dimethylglyoxime is an example of such a type. Increasing the concentration of dimethylglyoxime in solution by five times the original amount in the magnesium and zinc chelation titrations does not cause a lowering of the titration *B*-values, which would be the case for an equilibrium involving the release of a proton. Instead the *B*-values are raised for the titrations. Copper and nickel, on the other hand, are definitely chelated by dimethylglyoxime with a loss of protons. The difference between the chelating abilities of dimethylglyoxime with copper and nickel equals about 0.5 log unit which is much smaller than would be expected for coördination through alkoxide oxygen.

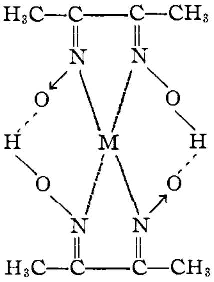
The above relationships are compatible with the following picture. Upon mixing the chelating agent with magnesium or zinc ion in solution, there is a weak association between the metal ions and the nitrogen atoms of the chelating agent that does not lead to the loss of a proton by the =NOH groups. When base is added to the solution it competes with the dimethylglyoxime nitrogen atoms for the metal ions. The higher concentration of chelating agent lowers the "effective" concentration of metal ion and hence the solubility product of the hydroxide is exceeded only at higher *B*-values. If these ions (Mg and Zn) are coördinated tetrahedrally by the nitrogen atoms of the chelating agent, hydrogen bonding between the dimethylglyoxime molecules cannot be effected. In the cases of Ni and Cu the planar hydrogen bonding structures are quite probably in solution

---

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941.

(7) B. E. Bryant, Dissertation, The Pennsylvania State College, 1952.

(8) F. Snavely, Dissertation, The Pennsylvania State College, 1952.



It is the hydrogen bonding of the oxygens in this structure which is responsible for the increased stability of these complexes.[9]

Copper dimethylglyoxime remains in solution as the deep red complex. The nickel compound precipitates after the first few additions of base. The measurements for nickel were made in the supersaturation region for the complex since the complex precipitates without the addition of base if a sufficient period of time is allowed.

The titration curves for 1-nitroso-2-naphthol follow the pattern of Fig. 1b and those for ethyl benzoylacetate, ethyl benzoylpyruvate and salicylaldehyde follow the pattern for Fig. 1a. The formation constants reported for salicylic acid are for the complex formed when only the carboxyl group proton has been lost.

STATE COLLEGE, PENNA.

(9) H. Freiser, University of Pittsburgh, Report of Jan. 31, 1951, on Contract AT(30-1)-860.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Studies on Coordination Compounds. X. Correlation of the Solution Stabilities of the Chelate Compounds of Ligands Coördinating through Nitrogen and Oxygen[1]

BY LEGRAND G. VAN UITERT[2] AND W. CONARD FERNELIUS

RECEIVED JUNE 18, 1953

The correlation of the stability constants of ligands coördinating through oxygen and nitrogen in aqueous solution serve to demonstrate the general factors involved in coördination chemistry. This correlation can be effected through consideration of the electronegativities and the hybrid bond states of the partners, the inductive influences involved, and the number of coördinating positions on the ligand.

The factors governing the solution stabilities of chelate compounds are quite complex. Although it is not possible at present to calculate the stability constant of a given compound from strictly theoretical considerations, it can be shown that the relationships involved are consistent and to a degree predictable.

The approach to the problem that has been employed is based upon the consideration of factors influencing bond stability as presented by Walsh.[3]

Experimental

The compounds referred to by number in Figs. 1, 3 and 4 are the following: 1, ammonia; 2, ethylenediamine; 3, glycine; 4, 2-nitroso-1-naphthol; 5, 1-nitroso-2-naphthol; 6, 8-hydroxyquinoline[4]; 7, 1-(2-hydroxy-5-methylbenzeneazo)-2-benzoic acid; 8, 1-(2-hydroxynaphthylazo)-2-naphthol-4-sulfonic acid; 9, 1-(2-hydroxy-5-nitrobenzeneazo)-2-naphthol; 10, 1-(2-hydroxy-5-chlorobenzeneazo)-2-naphthol; 11, 1-(2-hydroxybenzeneazo)-2-naphthol; 12, 1-phenyl-3-methyl-4-(2-hydroxy-4-sulfonic acid-naphthylazo)-5-pyrazolone; 13, 1-phenyl-3-methyl-4-(2-hydroxybenzene)-5-pyrazolone; 14, 1-phenyl-3-methyl-4-(4-nitrobenzeneazo)-5-pyrazolone; 15, 1-phenyl-3-methyl-4-(4-chlorobenzeneazo)-5-pyrazolone; 16, 1-phenyl-3-methyl-4-(benzeneazo)-5-pyrazolone; 17, 1-phenyl-3-methyl-4-(4-methylbenzeneazo)-5-pyrazolone[5]; 18, salicylaldehyde; 19, 2-acetyl-1-naphthol; 20, ethyl benzoylpyruvate[4]; 21, tropolone[6]; 22, *d*-tartaric acid (2 protons lost); 23, ethyl benzoylacetate[4]; 24, 2,4-pentanedione; 25, 2,2-dimethyl-3,5-hexanedione[7]; 26, *d*-tartaric acid (3 protons); 27, benzoylpyruvic acid; 28, salicylic acid.[4] All values for the above are for 75 volume % dioxane solution, and are expressed as activity constants.

Discussion

Factors Influencing Bond Strength.—It would appear that in the gaseous state the main factors involved in determining bond strength are: (1) the electronegativities of the partners involved, (2) the dipole character of the bond, and (3) the effects of nuclear repulsion in the cases of the highly electronegative atoms. From spectroscopic measurements it has been determined that: (a) the energy of the bond between two partners can be represented as a function of the product of their respective electronegativities, (b) bond strength is weakened by the development of dipole character in a bond, and (c) influences that affect the electronegativity of highly electronegative atoms may result in effects opposite to what would be expected in accordance with a.

Nitrogen and oxygen hold onto their electrons so tightly that appreciable nuclear repulsion is often developed between bonding partners in which one of them is involved. In these cases, a small reduction in the electronegativity of nitrogen or oxygen is more than compensated for by the resulting increase in wave function overlap.

Walsh further indicates that bond stability can be viewed as a function of the total charge interchange between partners. Pauling[8] has calculated the relative hybrid bond stability ratios for the

---

(1) For IX in this series see L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **76**, 375 (1954).

(2) Union Carbide and Carbon Corporation Fellow, 1951–1952.

(3) A. D. Walsh, *J. Chem. Soc.*, 398 (1948).

(4) L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **76**, 375 (1954).

(5) F. A. Snavely, Dissertation, The Pennsylvania State College, 1952.

(6) B. E. Bryant, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 3784 (1953).

(7) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457 (1953).

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 81, 82, 92, 96.