

SOME THEORETICAL AND PRACTICAL PROBLEMS IN THE USE OF ORGANIC REAGENTS IN CHEMICAL ANALYSIS, VIII*

INFLUENCE OF THE CHELATE EFFECT AND RING SIZE
ON THE STABILITY OF THE DIOXIME COMPLEXES OF TRANSITION METALS

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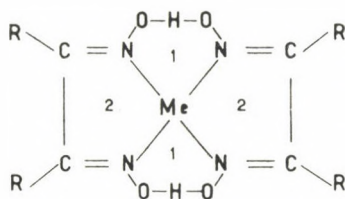
I. Introduction

In our earlier communications [1, 2] we showed the importance of two effects among the other factors stabilizing the dioxime complexes of transition metals; these are 1. the stabilizing action of hydrogen bridges formed in the complexes, and 2. the effect of metal \rightarrow ligand donor π bonds. The former factor is significant mainly in the complexes of metals of small ionic radius. Owing to this effect, in solutions of such complexes the constant of formation of a complex having the composition $\text{Me}(\text{dmg})^+$ (where $\text{dmg} = \text{dimethylglyoxime}$) deviates from the statistical case, and it is even lower than that of the complex of composition $\text{Me}(\text{dmg})_2$ [1]. The effect of the donor π bond is shown in the infrared spectra of the complexes by a decrease of the $\text{C}=\text{N}$ vibration frequency of the ligand in the order $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$, $\text{Fe}(\text{II})$ [2] indicating that on passing from $\text{Cu}(\text{II})$ to $\text{Fe}(\text{II})$, the conjugation increases in the chelate ring which contains the $\text{C}=\text{N}$ double bond. The participation of the d-electrons of the central metal ion in the π electron system of the conjugated ring is the greater, the lower the bond energy of the d-electrons of the metal ion which do not participate in a σ bond. This can be measured, in first approximation, by the ionization work $\text{Me}(\text{II})-\text{Me}(\text{III})$. That explains the reason why maximum stabilizing effect of the donor π bond is found in case of the $\text{Fe}(\text{II})$ complex of the mentioned series where the work of ionization is the smallest.

On basis of the frequencies of the $\text{O}-\text{H}$ valence vibrations we succeeded in proving the presence of more or less strong hydrogen bridges in the dioxime complexes of all divalent transition metals [2]. Thus, it is likely that these dioxime complexes have an approximately square-planar arrangement. Their formula may be written as follows on page 144.

It can be seen in this structural formula that the molecule actually consists of four condensed rings. The stabilizing effect of the hydrogen bridges is due to the formation of the two rings denoted by 1, while in the two five-

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membered rings, denoted by 2, conjugation is extended through the metal ion (quasi-aromatization). Consequently, the stabilizing effect of the donor π bond manifests itself primarily through these rings.

In dioxime complexes both stabilizing effects appear parallel to each other, contributing to the stabilization of the ligand field. Thus, it appeared promising to carry out investigations by which these two effects may separately be studied. Such an investigation can be conducted in two different ways:

1. Investigating the complexes of a ligand where the formation of hydrogen bridges is somehow inhibited. A comparison of the stability of these complexes with those of the corresponding dioxime chelates affords information as regards the extent of stabilization by the hydrogen bridge. In order to prevent the formation of the hydrogen bridge, *e.g.*, one oxime group may be converted into an $=N-O-CH_3$ group. Investigations of this type have been carried out by CHARLES and FREISER [3] with dimethylglyoxime monomethyl ether. However, this substitution may lead, in addition to inhibiting the formation of the hydrogen bridge, to changes in the electron distribution of the molecule, and may even cause steric hindrance. Consequently, this method gives only an approximative information about the stabilizing effect of the hydrogen bridge.

2. The second possibility involves the use of a ligand where the formation of the "aromatic" ring (denoted by 2) is inhibited or at least hindered. In this way information may be obtained concerning the extent of the stabilizing effect of the donor π bond. The formation of the "aromatic" ring can be inhibited by applying in place of dimethylglyoxime (dmg) ligand, *e.g.*, the unidentate ligand acetaldoxime (aao). Using the latter, the decrease of stability compared with the corresponding dimethylglyoxime complex is due to two factors: (a) to chelate effect and (b) to the absence of the stabilizing action of an aromatic ring.

In order to study these two effects separately, a ligand is to be selected in which only one of the effects is possible. In the case of acetylacetonedioxime (aado) as the ligand, the ring is six-membered, in contrast to dimethylglyoxime complexes. A continuous conjugation in this ring is impossible, and stabilization due to aromatization cannot take place. However, the chelate effect is not suspended, because acetylacetonedioxime is a bidentate ligand.*

* It must be noted that any changes in the number of carbon atoms of the ring also affect the strength of chelate effect. Still, according to literature [12], this factor is negligible compared with the effect examined in our present study.

On the basis of the above considerations, the scope of our present investigations was the determination of the stabilities of the acetaldoxime and acetylacetonedioxime complexes of transition metals. Thus far, of these complexes only the acetylacetonedioxime complexes of copper(II) [4, 5] and nickel(II) [6] have been investigated by preparative studies and by measurements by ultraviolet and infrared spectrophotometry. BEN BASSAT and BINENBOYM [5, 6] reported that these complexes have the composition $\text{Me}(\text{aado})_2$, and that binuclear hydroxo mixed complexes are precipitated from an aqueous copper(II) solution in which the ratio metal: aado is 1 : 1. In respect to the cobalt(II) complex of acetylacetonedioxime, the mentioned authors referred merely to their observation that it may be utilized as a sensitive reagent for the detection of cobalt(II) ions in the presence of nickel(II). On the basis of the Job curve of the nickel(II) complex of acetylacetonedioxime, the apparent stability constant of the complex was established, but the acidic dissociation constant of the ligand was not taken into account in the calculations.

The acetaldoxime complexes have been studied so far only in non-aqueous media, mainly from preparative aspects [7].

2. Experimental

2.1. Reagents and instruments

The potentiometric measurements were carried out with an instrument "Radiometer Type pH meter 28", the ultraviolet spectrophotometric investigations with a Unicam SP 700 spectrophotometer, while the infrared spectra were established in potassium bromide discs with a Zeiss UR 10 spectrometer. The magnetic measurements were made with the magnetic proton resonance measuring instrument of the Department for Nuclear Physics of the L. Eötvös University, Budapest.

Acetaldoxime was prepared according to the prescriptions of PETRACZEK [8] (b. p. 114–115°).

The acetylacetonedioxime (Eastman Organic Chemicals) was of analytical grade.

The metal salts and perchloric acid were Merck reagents of analytical grade.

Sodium perchlorate used for adjusting a constant ionic strength was prepared from concentrated perchloric acid with sodium carbonate of analytical grade.

2.2. Determination of the acidic dissociation constant of the ligands

The acidic dissociation constant of acetaldoxime was measured owing to its low value, by spectrophotometry in carbonate-free solutions of sodium hydroxide of various concentrations prepared by accurate weighing, at an aao concentration of $5 \cdot 10^{-4}$ mole ($I = 0.3$). The extinction was determined at the point of maximum absorption of the dissociated ligand, *i.e.*, at $37\,000\text{ cm}^{-1}$.

The acidic dissociation constant of acetylacetonedioxime was determined at $2 \cdot 10^{-4}\text{ M}$ concentration in aqueous solution and in a 50% aqueous dioxane solution, at an ionic strength of 0.3 *M*, by spectrophotometry at $34\,000\text{ cm}^{-1}$.

2.3. Determination of the stability constants of the complexes

The stability constants of the acetylacetonedioxime complexes were determined by the potentiometric method of BJERRUM [10] modified by CALVIN and MELCHIOR [9]. In the aqueous and 50% aqueous dioxane solutions, the following concentrations were used: in case of the nickel(II) and cobalt(II) complexes $C_{\text{Me(II)}} = 10^{-3}\text{ M}$ and $C_{\text{aado}} = 5 \cdot 10^{-3}\text{ M}$; 100.0 ml

of this solution was titrated with 0.2 *N* sodium hydroxide; in case of copper(II): $C_{\text{Cu(II)}} = 10^{-4} M$ and $C_{\text{aado}} = 10^{-2} M$; 100.0 ml of this solution was titrated with 0.01 *N* sodium hydroxide.

The stability constant of the copper(II) complex of acetaldoxime was determined by potentiometry, by titration with 0.01 *N* sodium hydroxide at a copper(II) concentration of $10^{-4} M$ and an acetaldoxime concentration of $10^{-2} M$. Stability measurements by spectrophotometry were carried out at a copper(II) concentration of $10^{-4} M$ and a ligand concentration of $10^{-2} M$, in the p_{H} range between 3 and 10; measurements were also made at ligand concentrations varying between 10^{-4} and $10^{-1} M$.

The magnetic proton resonance spectra were determined in complex solutions of $10^{-2} M$.

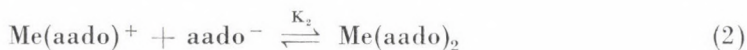
All measurements were made at an ionic strength of $I = 0.3 M$. The potentiometric titrations were carried out at $25 \pm 0.01^\circ$.

3. Evaluation methods

The following equilibria of acetylacetonedioxime complexes must be taken into account in the solutions:



and



Thus, the formation function of Bjerrum reads

$$\bar{n} = \frac{[\text{Me(aado)}^{+}] + 2[\text{Me(aado)}_2]}{[\text{Me}^{2+}] + [\text{Me(aado)}^{+}] + [\text{Me(aado)}_2]} \quad (3)$$

or, applying the conventional expressions for K_1 and K_2 :

$$\bar{n} = \frac{K_1 [\text{aado}^{-}] + 2 K_1 K_2 [\text{aado}^{-}]^2}{1 + K_1 [\text{aado}^{-}] + K_1 K_2 [\text{aado}^{-}]^2} \quad (4)$$

If

$$v = K_1 [\text{aado}^{-}] \quad (5)$$

and

$$p = \frac{K_2}{K_1} \quad (6)$$

then it follows from Equation (4):

$$\bar{n} = \frac{v + 2pv^2}{1 + v + pv^2} \quad (7)$$

On comparing, according to the usual Sillén method of normalization (11), the functions $\bar{n} = f(\lg v; p)$ and $\bar{n} = f(-\lg [aado^-])$ (the latter being obtainable experimentally), the values of K_1 and K_2 can be determined (Fig. 1).

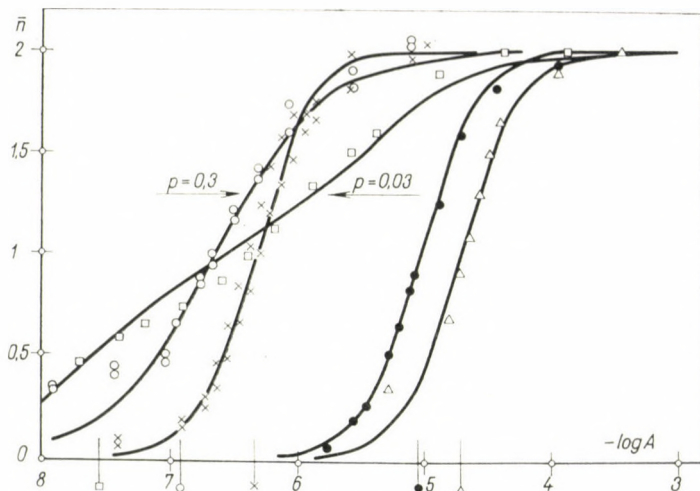
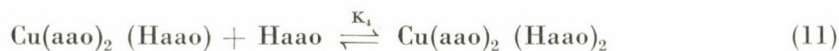
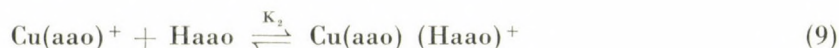
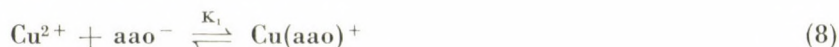


Fig. 1. Curves of formation of the transition metal complexes of acetylacetonedioxime. $\triangle \triangle \triangle$ Co(aado)_2 in water; $\bullet \bullet \bullet$ Ni(aado)_2 in water; $\square \square \square$ Cu(aado)_2 in water; $\times \times \times$ Ni(aado)_2 in 50% dioxan; $\circ \circ \circ$ Co(aado)_2 in 50% dioxan. Curves drawn in full lines are the best fitting normalized curves (the corresponding site $\lg v = 0$ is denoted in the curve by a vertical line)

In the case of the acetaldoxime complex, the equilibria prevailing in the solution can be expressed by the following equations (on the basis of evidence to be discussed later):



From the above equilibria, for the function of formation we have:

$$\bar{n} = \frac{\beta_1 [\text{aao}^-] + 2\beta_2 [\text{aao}^-][\text{Haao}] + 3\beta_3 [\text{aao}^-]^2 [\text{Haao}] + 4\beta_4 [\text{aao}^-]^2 [\text{Haao}]^2}{1 + \beta_1 [\text{aao}^-] + \beta_2 [\text{aao}^-][\text{Haao}] + \beta_3 [\text{aao}^-]^2 [\text{Haao}] + \beta_4 [\text{aao}^-]^2 [\text{Haao}]^2} \quad (12)$$

where

$$\beta_n = K_1 K_2 \dots K_n \quad (13)$$

When the analytical concentration of acetaldoxime in the solution (c_{HaaO}) is sufficiently high, its portion consumed by dissociation and complex formation can be neglected, therefore:

$$[\text{HaaO}] \approx c_{\text{HaaO}} \quad (14)$$

On introducing the symbols

$$\beta'_2 = \beta_2 [\text{HaaO}] \quad (15)$$

$$\beta'_3 = \beta_3 [\text{HaaO}] \quad (16)$$

$$\beta'_4 = \beta_4 [\text{HaaO}]^2 \quad (17)$$

Equation (12) can be simplified as follows:

$$\bar{n} = \frac{(\beta_1 + 2\beta'_2)[\text{aao}^-] + (3\beta'_3 + 4\beta'_4)[\text{aao}^-]^2}{1 + (\beta_1 + \beta'_2)[\text{aao}^-] + (\beta'_3 + \beta'_4)[\text{aao}^-]^2} \quad (18)$$

Now let us introduce the term

$$v = \sqrt{(3\beta'_3 + 4\beta'_4)[\text{aao}^-]} \quad (19)$$

as a new variable. Then, we have

$$\bar{n} = \frac{p_1 v + v^2}{1 + p_2 v + p_3 v^2} \quad (20)$$

where

$$p_1 = \frac{\beta_1 + 2\beta'_2}{\sqrt{3\beta'_3 + 4\beta'_4}} \quad (21)$$

$$p_2 = \frac{\beta_1 + \beta'_2}{\sqrt{3\beta'_3 + 4\beta'_4}} \quad (22)$$

and

$$p_3 = \frac{\beta'_3 + \beta'_4}{3\beta'_3 + 4\beta'_4} \quad (23)$$

The experimental points were found to fit the curve $\bar{n} = f(\lg v)$ corresponding to the equation

$$\bar{n} = \frac{v^2}{1 + \frac{1}{4}v^2} \quad (24)$$

with the parameters $p_1 = p_2 = 0$ and $p_3 = \frac{1}{4}$ (Fig. 4). According to Equations (21)–(23), this means that $\beta'_4 \gg \beta'_3$.

In the spectrophotometric measurements, the degree of formation

$$\alpha = \frac{[\text{Cu}(\text{aao})_2(\text{HaaO})_2]}{c_{\text{Cu}}} \quad (25)$$

referred to the complex $\text{Cu}(\text{aao})_2(\text{HaaO})_2$ was determined as the function of the p_{H} of the solution. Allowing for the presence of complexes of various composition, and considering the corresponding stability constants, α can be written in the form:

$$\alpha = \frac{\beta_4 [\text{aao}^-]^2 [\text{HaaO}]^2}{1 + \beta_1 [\text{aao}^-] + \beta_2 [\text{aao}^-] [\text{HaaO}] + \beta_3 [\text{aao}^-]^2 [\text{HaaO}] + \beta_4 [\text{aao}^-]^2 [\text{HaaO}]^2} \quad (26)$$

When the conditions (14) to (17) hold, this simplifies to

$$\alpha = \frac{\beta'_4 [\text{aao}^-]^2}{1 + (\beta_1 + \beta'_2) [\text{aao}^-] + (\beta'_3 + \beta'_4) [\text{aao}^-]^2} \quad (27)$$

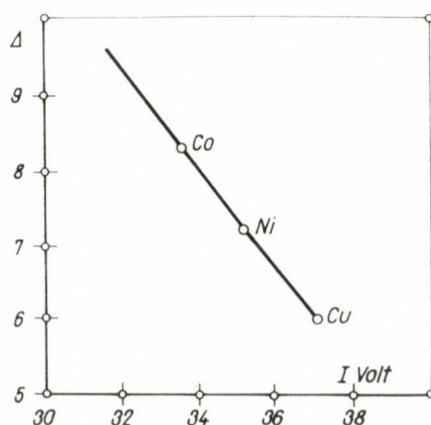


Fig. 2. π bond stabilization of the transition metal complexes of dioxime plotted against the third ionization potential of the metal ion

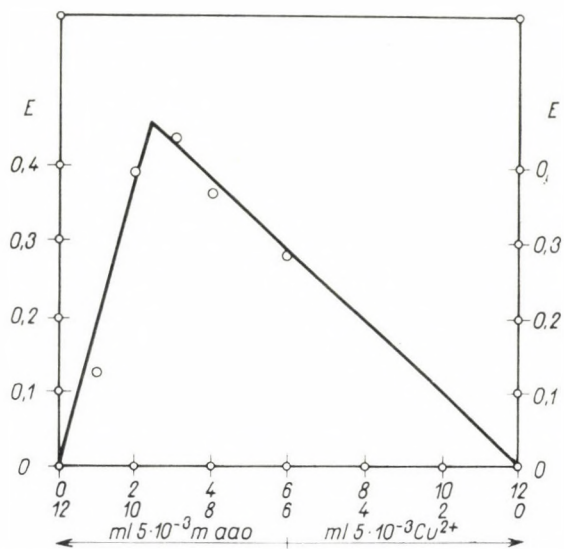


Fig. 3. Job curve of the copper(II) complex of acetaldoxime, measured at 3300 cm^{-1} .

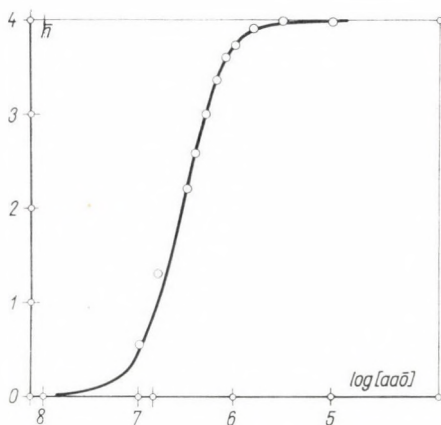


Fig. 4. Potentiometric curve of formation of the complex $\text{Cu}(\text{aao})_2(\text{Haao})_2$
(The curve represents the best fitting normalized curve)

Introducing the new variable

$$v = \sqrt{\beta'_4} [\text{aao}^-] \quad (28)$$

formula (27) will read:

$$\alpha = \frac{v^2}{1 + p_1 v + p_2 v^2} \quad (29)$$

where

$$p_1 = \frac{\beta_1 + \beta'_2}{\sqrt{\beta'_4}} \quad (30)$$

and

$$p_2 = \frac{\beta'_3 + \beta'_4}{\sqrt{\beta'_4}} \quad (31)$$

When the usual normalizations are carried out, the stability constants are obtained. (The experimental points fit the curve $p_1 = 0, p_2 = 1$; see Fig. 5.)

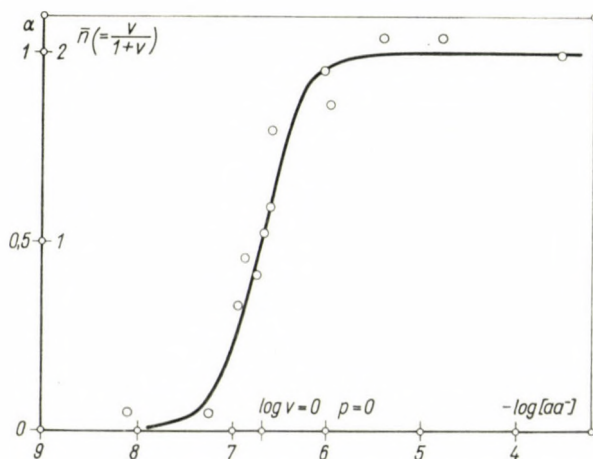


Fig. 5. Spectrophotometrically determined formation function of the complex $\text{Cu}(\text{aao})_2(\text{Haao})_2$ (The curve represents the best fitting normalized curve)

4. Results and discussion

4.1. Acidic dissociation constants

The acidic dissociation constants of the investigated ligands determined at an ionic strength of 0.3 M are summarized in Table I. For the sake of comparison also the corresponding data of dimethylglyoxime are given.

Table I

Acidic dissociation constants of the investigated ligands in 0.3 M sodium perchlorate

Ligand	Solvent	pK_a
Acetaldoxime	water	11.5 ± 0.2
Acetylacetonedioxime ..	water	9.9 ± 0.2
	50% dioxan	11.6 ± 0.2
Dimethylglyoxime	water	10.6
	50% dioxan	11.8

4.2. Effect of ring size

As it has been mentioned in the introduction, the stabilizing effect of ring size and through this that of the π conjugation were studied on the copper(II), nickel(II) and cobalt(II) complexes of acetylaceton dioxime. The determined stability constants are presented in Table II, while the function of formation is shown in Fig. 1.

Table II
Stability constants of acetylaceton dioxime complexes at 25°
($I = 0.3$)

Complex	Solvent	$\lg \beta_1$	$\lg \beta_2$	Δ	Reference
Cu(aado) ₂	water	7.6	13.2	6.0	13
Ni(aado) ₂	water	—	10.1	7.2	14
Co(aado) ₂	water	—	9.4	8.3	15
Ni(aado) ₂	50% dioxan	—	12.7	9.8	1
Co(aado) ₂	50% dioxan	6.9	13.3	7.7	1

The determination of the data shown in Table II was not difficult in case of the nickel(II) and cobalt(II) complexes because these metals, at the concentrations used in the measurements, begin to hydrolyze only at rather high p_H values (7.5 to 8.5). Thus, the p_H range of complex formation (from 6 to 7) is satisfactorily distinct. Accordingly, one need not consider the possibility that hydroxo mixed complexes are formed along with the "regular" complexes which were desired to be studied.

The situation is not so favourable with the complexes of copper(II) and iron(II). Namely, in the first case, as already experienced by BEN BASSAT and BINENBOYM, binuclear or polynuclear copper-hydroxo compounds precipitate from the solution because complex formation occurs (at the same concentrations as used in case of the nickel(II) and cobalt(II) complexes) nearly in the same p_H range where hydrolysis does. Though iron(II) ions begin to hydrolyze only at p_H 7–8, the stability of the corresponding complex is so low that hydroxo mixed complexes are formed in this case as well.

In these instances we attempted to separate the p_H range of hydrolysis from that of complex formation by using a relatively great (hundredfold) excess of the ligand, and the metal ion concentration was decreased by one order of magnitude. Under such circumstances it was possible to determine the stability of the copper(II) complex, but that of the iron(II) complex proved to be so small that its determination by this method was impossible.

Table II also shows the decrease of stability (Δ) in respect to the corresponding dimethylglyoxime complexes:

$$\Delta = \lg \beta_{2,\text{dmg}} - \lg \beta_{2,\text{aado}}$$

This difference in stability, according to what has been said in the introduction, is due mainly to the fact that ring conjugation is no longer possible thus in the aado complex there is no possibility for metal-to-ligand electron transfer (formation of a donor π -bond). This appears in a convincing way in Fig. 2 where the values of Δ have been plotted against the ionization potentials, $\text{Me}^{2+} \rightarrow \text{Me}^{3+}$, of the metal ions. If the work of ionization is higher, this stabilizing effect is decreased, in accordance with the consideration that the probability of the presence on the ligand of electrons belonging to metal orbitals and not involved in σ bonds is greater, if they are bound with less energy to the metal.

In the case of bidentate ligands where there are no incomplete orbitals, and thus the formation of donor π bonds is excluded, the complexes of various central metal ions show, in general, a nearly identical decrease of stability when the number of atoms of the ring is altered. By way of example, the stability of ethylene- and 1,3-propylenediamine complexes can be mentioned [12].

The problem may arise that "ligand exchange" may lead to essential alterations also in the electronic structure of the metal ions. In contrast to the dimethylglyoxime complexes of low spin, the complexes of acetylacetonedioxime may have high spin. Magnetic proton resonance investigations with the $\text{Ni}(\text{aado})_2$ complex proved the presence of diamagnetic complex particles. This result confirms that acetylacetonedioxime is a strong-field ligand in this complex, similarly to dimethylglyoxime. However, this method falls short of permitting an exact determination of the magnetic moments, and other methods could not be applied, owing to the poor solubility of the complex.

4.3. Chelate effect

The extent of chelate effect observed in dioxime complexes can be studied, *e.g.*, by comparing the stabilities of the dimethylglyoxime and acetaldoxime complexes. For this purpose, complex formation has been investigated by potentiometric titrations in aqueous solutions containing iron(II), cobalt(II), nickel(II) or copper(II) ions and acetaldoxime. Of the examined metals, only copper(II) formed a "regular" complex with acetaldoxime, while with the other metals precipitates having colours similar to that of the corresponding metal hydroxides precipitated in the course of titration. The examination of these products by infrared spectrometry showed, indeed, that they consisted of the metal hydroxides containing some, possibly only adsorptively bound, acetaldoxime. In solutions of concentrations higher than $5 \cdot 10^{-4} M$, also copper(II) ions gave the blue hydroxo mixed complexes. However, these mixed complexes have not been studied in greater detail in the present work.

The composition of the "regular" copper(II) complex of acetaldoxime has been established by the Job method (Fig. 3). According to our measurements, this complex has the composition $\text{Cu}(\text{aao})_4$.*

Potentiometric titrations carried out as described in the experimental part indicated, however, a complex formation process involving the liberation of two protons only, proving that the complex has really the composition $\text{Cu}(\text{aao})_2 (\text{HaaO})_2$. By the same potentiometric measurements, the overall stability constant was found to be $\lg \beta_4 = 17.0$ (Fig. 4).

The stability constants were determined by spectrophotometric measurements as well (Fig. 5). These measurements were carried out at the wave number where, according to the Job curve, light is absorbed only by the complex having the composition 1 : 4. This arrangement similarly indicated that in the presence of a hundred-fold excess of acetaldoxime binding of all the four ligands takes place in one step, and the stability constant is $\lg \beta_4 = 17.4$. The stability constant of the copper(II) complex of dimethylglyoxime is $\lg \beta_2 = 19.24$.

The above results show that the decrease of stability of the complex $\text{Cu}(\text{aao})_2 (\text{HaaO})_2$ in comparison with $\text{Cu}(\text{dmg})_2$ is less significant than that of the complex $\text{Cu}(\text{aado})_2$. This can be explained by premising that the absence of the stabilizing effect of a donor π bond and of a chelate effect has been partially compensated by the increase of stabilization due to the hydrogen bridge. Namely, on ring cleavage, the oxygen atoms bound rigidly in the dimethylglyoxime complex may freely move up to an optimum distance required for hydrogen bonding, and thus the stabilizing effect by hydrogen bridge formation may markedly increase.

The authors express their thanks to Mr. E. ANTAL for his assistance in the experiments.

SUMMARY

The stability conditions of the acetylacetonedioxime complexes of cobalt(II), nickel(II) and copper(II), and of the acetaldoxime complex of copper(II) have been investigated. In the case of acetylacetonedioxime, the decrease of stability compared with the corresponding dimethylglyoxime complexes is ascribed to the fact that any conjugation of the ring, and consequently a stabilizing effect by donor π bonds are impossible. The stability decrease of the acetaldoxime complex is attributed to two reasons, (a) chelate effect, and (b) lack of a conjugated ring. This stability decrease is compensated in part by the formation of stronger hydrogen bridges.

Magnetic measurements indicate an electronic arrangement of low spin in acetylacetonedioxime complexes.

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* Obviously, the Job curve is not sufficiently accurate to decide whether the complex has 1 : 4, 1 : 5 or 1 : 6 composition. However, in the present case a coordination number higher than 4 can be excluded on the basis of ligand-field theoretical considerations, and other measurements alike.

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Über einige theoretische und praktische Probleme der analytischen Anwendung organischer Reagenzien, VIII.

Wirkung des Chelateffektes und der Ringgröße auf die Stabilität der Dioximkomplexe von Übergangsmetallen

I. RUFF und K. BURGER

Zusammenfassung. Die Stabilitätsverhältnisse der Acetylaceton-dioximkomplexe des Kobalt(II) Nickel(II) und Kupfer(II), ferner des Acetaldoximkomplexes von Kupfer(II) wurden untersucht. Die im Verhältnis zur Stabilität der entsprechenden Dimethylglyoximkomplexe beobachtete Stabilitätsverminderung wird im Falle des Acetylaceton-dioxims dem Aufhören der Konjugation des Ringes, und dadurch der Einstellung der Stabilisierungswirkung der Donor- π -Bindung zugeschrieben. Die Stabilitätsverminderung des Acetaldoximkomplexes wird durch den Chelateffekt und durch das Verschwinden des konjugierten Ringes erklärt. Diese Stabilitätsverminderung wird teils durch Entwicklung stärkerer Wasserstoffbrücken kompensiert.

Die magnetischen Messungen wiesen auf eine Elektronenverteilung mit kleiner Spinzahl bei den Acetylaceton-dioximkomplexen hin.

О некоторых теоретических и практических вопросах аналитического применения органических реагентов, VIII

Влияние хелатного эффекта и размеров кольца на стабильность комплексов диоксимов с переходными металлами

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Резюме. Были изучены стабильности комплексов ацетилацетон-диоксима с двухвалентными кобальтом, никелем и медью, а также ацетальдоксима с медью(II). Уменьшение стабильности ацетилацетон-диоксимных комплексов по отношению к соответствующим диметил-глиоксимным комплексам приписывается прекращению конюгации в кольце и, в результате этого, ослаблению стабилизирующего влияния донорной π -связи. Уменьшение стабильности ацетальдоксимных комплексов может быть объяснено, с одной стороны, хелатным эффектом, а с другой стороны, исчезновением конюгации кольца. Это уменьшение стабильности частично компенсируется образованием более сильных водородных связей.

Согласно измерениям магнитной восприимчивости было обнаружено, что ацетилацетон-диоксимные комплексы представляют собой электронные упорядочения с низким значением результирующего спина.

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