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Formation of Adducts with Bis-dimethylglyoximate Copper(II)

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The distribution of $^{64}Cu(II)$ between chloroform with different concentrations of donors (TBP, hexone, CH_3SCN, $CH_2=CHCH_2NCS$, aniline, dibutyl amine and piperidine) and acetate buffered aqueous solutions containing dimethylglyoxime (H_2D) has been studied as a function of initial concentrations of the donors in the organic phase. The distribution was practically unaffected by the addition of TBP, hexone, CH_3SCN and $CH_2=CHCH_2NCS$. For aniline and dibutyl amine log K was calculated (1.92 and 2.10, respectively) for the adduct formation equilibrium in chloroform.

The adduct formation constants of $Cu(HD)_2$ and dibutyl amine, dodecyl amine and pyridine in dry benzene solutions, have been determined spectrophotometrically (log K equal to 2.50, 3.50, and 3.62 respectively) by measuring the increase of the absorbance of $Cu(HD)_2$-saturated solutions of benzene at 400 nm for different concentrations of the amines. The reaction between $Cu(HD)_2$ and triethyl amine is very weak suggesting that the adduct formation is sterically hindered.

The electronic spectra of $Cu(HD)_2$ in 0.1 M water solutions of sodium hydroxide, ammonia and pyridine, in 0.1 M dry chloroform solutions of dibutyl amine, dodecyl amine, pyridine and ammonia (saturated solution), and in 0.1 M dry benzene solutions of dibutyl amine, dodecyl amine, pyridine and ammonia are given.

Considerable attention is being drawn to adduct formation in the organic phase as a supplement to masking with complexing agents in the aqueous phase in order to achieve better separation of ions with metal chelate extraction systems. Adduct formation of TTA chelates has previously been studied by Healy [1] and Irving [2] among others. Recently Sekine and Dyrssen [3] published a study of the adduct formation between Cu(II) and Zn(II) chelates of TTA and IPT (β-isopropyltropolone) with tributyl phosphate (TBP) and methyl-

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** Reprints and spectrophotometric data are available from this Department.

isobutyl ketone (hexone) as PO and CO donors. The adduct formation of Cu(II) acetylacetone with pyridine bases has been investigated by May and Jones.[4]

It was pointed out some years ago by Dyrssen and Hennichs [5] that Cu(II) dimethylglyoximate, $Cu(HD)_2$, could form a 1:1 adduct with quinoline and dodecyl amine in chloroform, and OH^- in water. Here we wish to report additional results with some other donors. At the same time we wish to report spectra for some of the complexes in water, chloroform, and benzene. Our spectrum of $Cu(HD)_2$ in water has recently been resolved by a least-square minimizing technique.[6]

EXPERIMENTAL

Dimethylglyoxime (Kebo p.a.), copper sulfate (Merck p.a.), allyl mustard oil, $CH_2{=}CHCH_2NCS$ (Kebo), aniline (Merck, p.a.), dibutyl amine (Fluka puriss.), dodecyl amine (Fluka, two white crystallized products), methyl thiocyanate, CH_3SCN (Fluka, purum), piperidine (Kebo, puriss.), pyridine (Kebo p.a.), TBP (Kebo), and benzene (Merck, p.a.) were not further purified. Chloroform (Merck p.a.) was washed with distilled water three times to remove alcohol. Benzene and chloroform were dried with anhydrous sodium sulfate. $Cu(HD)_2$ was prepared according to Chugaev using a modification by Dyrssen and Hennichs.[5]

The solubility experiments were carried out at room temperature (about 22°C) by allowing solutions to pass through a 1 cm Brönsted solubility column with a 8 to 10 cm bed of $Cu(HD)_2$ at a flow rate of about 1 ml/min. The concentrations of $Cu(HD)_2$ and $Cu(HD)_2B$ in the effluent were determined spectrophotometrically.

The spectra were measured at room temperature (about 22°C) by means of a "Beckman DB" ratio recording spectrophotometer equipped with 1 cm cells.

The extraction experiments were carried out at 25°C by Mr. Kjell Rydberg at KTH, Stockholm, who used the same technique as Dyrssen and Hennichs.[5]

DATA

Extraction data. The initial aqueous phase consisted of 10 ml of 0.09 M Na^+, 0.08 M ClO_4^-, 0.01 M CH_3COO^- and 0.01 M CH_3COOH, 0.0025 M H_2D, and radioactive ^{64}Cu. The initial organic phase was a chloroform solution with different concentrations of the donor B. Depending on the distribution constant of B and the acidity constant of BH^+ the donor molecule might react with both CH_3COOH and H_2D. With B = TBP, hexone, CH_3SCN, $CH_2{=}CHCH_2NCS$ and aniline ($pK_a = 4.58$) the formation of BH^+ can be neglected. Bu_2NH ($pK_a \simeq 10.6$) will react with most of the CH_3COOH, but not with H_2D. Piperidine, which is a strong base ($pK_a = 11.21$), reacts even with the weak acid H_2D. In the case of Bu_2NH corrections could be made

Table 1. The distribution of ^{64}Cu between solutions of B in chloroform and acetate buffered aqueous solutions containing H_2D. Values of log D (initial molar conc. of B). For $[B]_{org} = 0$ log $D = -0.93 \pm 0.05$.

For B = aniline: −0.686 (0.01), −0.456 (0.025), −0.269 (0.05), 0.003 (0.1), 0.360 (0.25), 0.659 (0.5),

For B = dibutyl amine: −0.810 (0.01), −0.408 (0.025), −0.084 (0.05), 0.182 (0.1), 0.540 (0.25), 0.788 (0.5).

For B = piperidine: −0.714 (0.01), 0.922 (0.025), 1.27 (0.05), 1.44 (0.1), 1.57 (0.25), 1.57 (0.5).

for the amount of BH^+ formed, but the data (log D *vs* log $[B]_{org}$) with piperidine do not fit the normalized curve $Y = \log(1 + v)$; $X = \log v$ (*cf.* Ref. 5, Fig. 3). Table 1 gives the distribution data for B = aniline, dibutyl amine and piperidine. For B = aniline and dibutyl amine we calculated log $K = 1.92$ and 2.10 for the adduct formation equilibria in chloroform

$$Cu(HD)_2 + B = Cu(HD)_2B \quad (1)$$

$$K = \frac{[Cu(HD)_2B]}{[Cu(HD)_2][B]} \quad (1a)$$

For the donors TBP, hexone, CH_3SCN and $CH_2{=}CHCH_2NCS$ the distribution was practically unaffected by the addition of B. Therefore, one can conclude that $K < 1$ for these donors.

Solubility measurements. The increase of the absorbance of $Cu(HD_2)$ saturated solutions of benzene was measured at 400 nm for different concentrations of the amines. The results are given in Table 2. The total absorbance of these solutions then, is

$$A_{tot} = A_{Cu(HD)_2} + A_{Cu(HD)_2B} = \varepsilon_0[Cu(HD)_2] + \varepsilon[Cu(HD)_2B] \quad (2)$$

and

$$[Cu(HD)_2B] = \frac{A_{tot} - A_{Cu(HD)_2}}{\varepsilon} \quad (3)$$

In the presence of solid $Cu(HD)_2$ we may assume $[Cu(HD)_2]$ and $A_{Cu(HD)_2} = 0.073$ to be constant. Using eqns. (1a) and (3) one can obtain

$$K = \frac{A_{tot} - 0.073}{\varepsilon[Cu(HD)_2][B]} \quad (4)$$

Table 2. The absorbances of $Cu(HD)_2$ saturated solutions of benzene at 400 nm with different concentrations of dibutyl amine, dodecyl amine, and pyridine. The reference solutions contained the concentration of the donors, but no copper.

Absorbances of $Cu(HD)_2B$					
B = dibutyl amine		B = dodecyl amine		B = pyridine	
C_B	A_{tot}	C_B	A_{tot}	C_B	A_{tot}
0	0.073	0	0.073	0	0.073
10^{-3}	0.090	2.5×10^{-3}	0.585	10^{-3}	0.239
5×10^{-3}	0.193	5×10^{-3}	1.055	3×10^{-3}	0.560
10^{-2}	0.302	7.5×10^{-3}	1.590	5.5×10^{-3}	0.974
2.5×10^{-2}	0.542	10^{-2}	2.10	10^{-2}	1.722
5×10^{-2}	0.937	1.25×10^{-2}	2.56		
$\varepsilon = 1400$		$\varepsilon = 1435$		$\varepsilon = 1510$	

The concentration of free amine, [B], can be calculated from the total concentration of amine, C_B,

$$C_B = [B] + [Cu(HD)_2B] = [B] + \frac{A_{tot} - 0.073}{\varepsilon} \quad (5)$$

Fleisher and Freiser [7] have determined the solubility of $Cu(HD)_2$ in benzene as 3.9×10^{-5} M (extrapolated value for 22°C). Using this value and eqns. (4) and (5) we calculated K from

$$K = \frac{A_{tot} - 0.073}{3.9 \times 10^{-5}(\varepsilon\, C_B - A_{tot} + 0.073)} \quad (6)$$

The values of ε were determined for weighed amounts of $Cu(HD)_2$ at high [B]. The values of C_B, A_{tot} and ε for B = dibutyl amine, dodecyl amine and pyridine are given in Table 2. The values of log K obtained from these data are 2.52, 3.50, and 3.62, respectively. The reaction of $Cu(HD)_2$ with triethyl amine is very slight and we could not calculate the adduct formation constant.

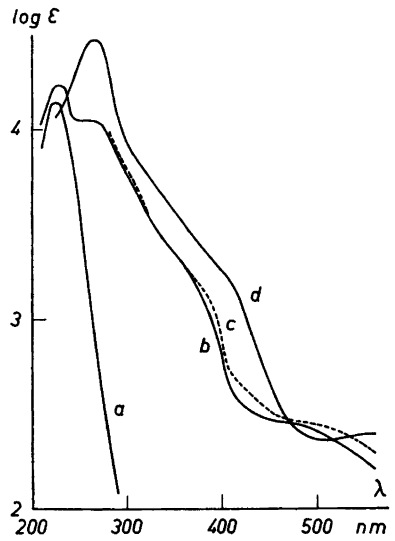

Fig. 1. The molar absorptivity spectra of H_2D (a), $Cu(HD)_2$ (b), and $Cu(HD)_2B$ where B = pyridine (c) and B = OH^- (d).

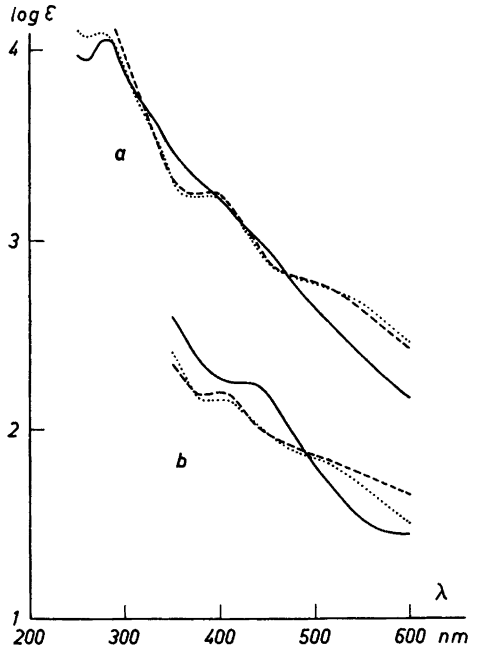

Fig. 2. The molar absorptivity spectra of $Cu(HD)_2$ (solid lines), and $Cu(HD)_2B$, where B = dodecyl amine (dotted lines), and B = pyridine (dashed lines) in dry chloroform (a) and benzene solutions (b). The spectra of the benzene solutions (b) are plotted as log $\varepsilon - 1$ against the wave length in nanometer.

Spectra. The spectra of $Cu(HD)_2$ in 0.1 M water solutions of sodium hydroxide, ammonia and pyridine, in 0.1 M chloroform solutions of dibutyl amine, dodecyl amine, pyridine and ammonia (saturated solution), and in 0.1 M benzene solutions of dibutyl amine, dodecyl amine, pyridine and ammonia were measured. These measurements were carried out from 210 to 600 nm for water solutions, from 250 to 600 nm for chloroform solutions (from 295 nm with pyridine) and from 350 to 600 nm for benzene solutions. Some spectra are shown in Figs. 1 and 2. One can see that with the exception of $Cu(HD)_2$ in 0.1 M NaOH there is a very small difference between the spectra of $Cu(HD)_2$ and $Cu(HD)_2B$ in water solutions. It may mean that adduct formation cannot compete with hydration of $Cu(HD)_2$, *i.e.* the main adduct reaction is the reaction of $Cu(HD)_2$ with solvent. The same explanation can, however, be given for the spectra in chloroform solutions where we know from the distribution and solubility experiments that adducts are formed between the bases and $Cu(HD)_2$. In the case of benzene as a solvent the influence of amines on the spectra of $Cu(HD)_2$ is more pronounced. These observations reflect the solvent interaction with $Cu(HD)_2$, which is discussed further below. For a theoretical treatment of the spectra of $Cu(HD)_2$ and $Cu(HD)_2B$, a plot of log ε against the wave number can be more convenient (Fig. 3).

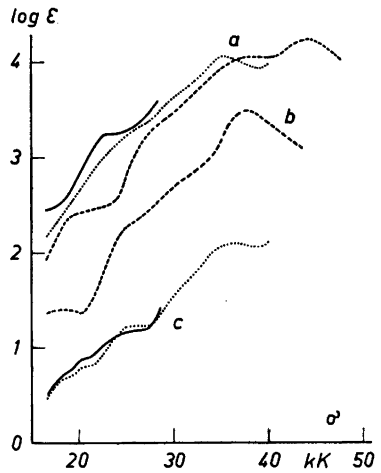

Fig. 3. The molar absorptivity spectra of $Cu(HD)_2$ (a), $Cu(HD)_2$ in 0.1 M NaOH (b), and $Cu(HD)_2B$ (c) where B = dodecyl amine. The solid lines show spectra in benzene solutions, the dotted lines show spectra in chloroform solutions, and the dashed lines show spectra in water solutions. The spectra of $Cu(HD)_2$ in 0.1 M NaOH are plotted as log $\varepsilon - 1$ and the spectra of $Cu(HD)_2B$ are plotted as log $\varepsilon - 2$ against the wave number in kilokayser (1000 cm^{-1}).

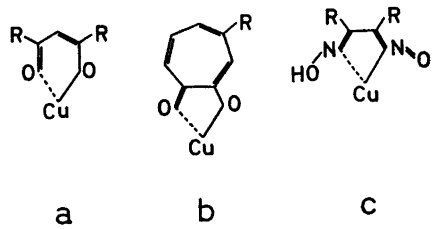

Fig. 4. The planar structure of some copper chelates: (a) $Cu(AcAc)_2$ and $Cu(TTA)_2$, (b) $Cu(IPT)_2$, and (c) $Cu(HD)_2$.

A preliminary investigation of the spectrum of 2.5×10^{-5} M $Cu(HD)_2$ at different $[OH^-]$ has revealed changes which are not consistent with the assumption that only $Cu(HD)_2OH^-$ is formed in addition to $Cu(HD)_2(H_2O)_x$. An extended investigation may reveal to what extent other complexes such as CuD_2^{2-} are formed.

The data of molar absorptivities of $Cu(HD)_2$ in water solutions of ammonia and pyridine (210—600 nm), and in chloroform and benzene solutions of dibutyl amine, dodecyl amine, ammonia and pyridine (250—600 and 350—600 nm) are available at request (*cf.* the footnote on page 653).

Table 3. The reaction of copper chelates of acetylacetonate ($AcAc^-$), thenoyltrifluoroacetonate (TTA^-), β-isopropyltropolonate (IPT^-), and dimethylglyoximate (HD^-) ions with different donors and in different solvents. The equilibrium constants refer to the adduct formation equilibria $CuL_2 + B \rightleftharpoons CuL_2B$ in the organic solvent.

Acceptor	donor	solvent **	log K	reference
$Cu(AcAc)_2$	pyridine	C_6H_6 (dry)	0.94	4
»	4-picoline	»	1.04	4
»	4-benzoylpyridine	»	1.26	4
$Cu(TTA)_2$	hexone *	$CHCl_3$ (wet)	<0	3
»	»	CCl_4 (wet)	0.47	3
»	TBP	$CHCl_3$ (wet)	0.65	3
»	»	CCl_4 (wet)	2.27	3
$Cu(IPT)_2$	hexone *	»	<0	3
»	TBP *	»	<0	3
$Cu(HD)_2$	triethyl amine *	C_6H_6 (dry)	<0	this work
»	dibutyl amine	$CHCl_3$ (wet)	2.10	»
»	» »	C_6H_6 (dry)	2.52	»
»	dodecyl amine	$CHCl_3$ (wet)	3.36	5
»	» »	C_6H_6 (dry)	3.62	this work
»	pyridine	»	3.50	»
»	quinoline	$CHCl_3$ wet)	2.04	5
»	aniline	»	1.92	this work
»	TBP *	»	<0	»
»	hexone *	»	<0	»
»	CH_3SCN *	»	<0	»
»	$CH_2=CHCH_2NCS$ *	»	<0	»
»	OH^-	H_2O	3.21	5

* No adduct formation was detected for this system.

** Wet solvent indicates that the solvent extraction method was used for determination of log K.

DISCUSSION

In Table 3 we have collected data for the adduct formation of different copper chelates. In our opinion the adduct formation constant K reflects the residual coordination power of the copper chelates for a certain type of donor electrons provided the donor ligand attachment to the copper atom is not hindered sterically or by solvent interaction. The copper chelates of the three different types of ligand (Fig. 4) are planar molecules [8-10] and thus only

triethyl amine would be expected to be sterically hindered. This was confirmed for $Cu(HD)_2$. Furthermore, on comparing pyridine and quinoline we found for $Cu(HD)_2$ a considerably lower value of K for quinoline. As these donors have very close acidity constants for BH^+ we conclude that quinoline is sterically hindered to some extent. For the secondary and primary amines as donors for $Cu(HD)_2$ the difference may also very well be explained by steric hindrance.

The values of K are also largely influenced by the solvent. Chloroform presumably interacts with the oxygen and nitrogen atoms of the chelate ligands by hydrogen bond formation. Furthermore, chloroform can form a hydrogen bond complex with donors such as TBP, pyridine and aliphatic amines, thus lowering the free concentration of B. From Table 3 we find that the K values in benzene and carbon tetrachloride are larger than those in chloroform. We may therefore conclude that chloroform reacts more readily with B or CuL_2 than with the adduct CuL_2B.

In spite of steric and solvent influence on K we find great differences in the adduct forming ability of the different types of chelates. In the tropolonate complex of copper, $Cu(IPT)_2$, as in $Cu(HD)_2$, there are no unsaturated electron levels that can accept the electrons from the phosphoryl donor. This is not the case, however, with the β-diketonate chelate, $Cu(TTA)_2$. On comparing $Cu(AcAc)_2$ and $Cu(HD)_2$ as acceptors for pyridine we find a much larger K value for $Cu(HD)_2$. This may reflect the ability of these copper chelates to accept the p electrons supplied by the nitrogen donor. May and Jones [4] have shown that the electron withdrawing power of substituents in the ligand may have some influence on the values of K (as well as the acid dissociation constants of BH^+), but our results with dodecyl amine and pyridine indicate that the base strength of B (amines have more than 10^5 times lower dissociation constants of BH^+ than pyridines) has very little influence on K.

The adduct formation with $Cu(HD)_2$ has rather little effect on the spectrum of $Cu(HD)_2$. However, differences are quite discernible and the hidden peaks in the spectra can be resolved by a least-square technique developed by Roos.[6] Theoretical calculations on such spectra are in progress at the Department of Theoretical Physics at the University of Stockholm. That work might offer further explanation about the electron energy levels involved in the adduct formation of copper chelates.

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