Monatshefte für Chemie 124, 135–147 (1993)

Monatshefte für Chemie
Chemical Monthly

Metal Chelates of Triazine-Schiff-Bases: Complex Formation of 3-(α-Phenyl)ethylidenehydrazino-5,6-diphenyl-1,2,4-triazine with Copper(II)

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Summary. Complex formation of copper(II)-ions with 3-(α-Phenyl)ethylidenehydrazino-5,6-diphenyl-1,2,4-triazine (*BHT*) has been investigated using UV-VIS-, IR-, and electrochemical methods. Optimal pH for the 1:1 complex formation (and therefore for analytical applications) was found at 5.4. This complex could be isolated. The acid dissociation constant of the free ligand is $pK_a = 13.60$; formation constants for 1:1 and 1:2 complexes were found to be $\log K_1 = 12.0$ and $\log K_2 = 10.4$, respectively. Polarographic reduction of both the free ligand and the Cu(II)-complexes is irreversible, diffusion controlled and like the stability of the complex *pH*-dependent.

Keywords. Copper(II)-complexes; Triazine-Schiff-bases; Polarography; Protonation-deprotonation-reactions.

Metall-Chelate von Schiffschen-Triazin-Basen: Komplexbildung von 3-(α-Phenyl)ethyliden-hydrazino-5,6-diphenyl-1,2,4-triazin mit Kupfer(II)

Zusammenfassung. Die Komplexbildung von Kupfer(II)-ionen mit 3-(α-Phenyl)-ethyliden-hydrazino-5,6-diphenyl-1,2,4-triazin (*BHT*) wurde mittels UV-VIS-, IR-, sowie mit elektrochemischen Methoden untersucht. Der optimale *pH*-Wert der 1:1-Komplexbildung (und damit für analytische Anwendungen) ist 5.4. Dieser Komplex konnte isoliert werden. Die Säure-Konstante des freien Liganden ergab sich als $pK_a = 13.60$, für die Bildungskonstanten der 1:1- und 1:2-Komplexe wurde $\log K_1 = 12.0$ und $\log K_2 = 10.4$ ermittelt. Die polarographische Reduktion des freien Liganden und der beiden Cu(II)-Komplexe war irreversibel, diffusionskontrolliert und ebenso wie die Stabilität der Komplexe *pH*-abhängig.

Introduction

Transition metal complexes of 3-hydrazino-1,2,4-triazines and its derivatives show a series of interesting biological and antiviral properties [1–3]. The ligand is known

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as an analytical reagent for metal ions like Fe(II) [4, 5]. This stimulated our interest in the synthesis and study of 3-(α-phenyl)ethylidenehydrazino-5,6-diphenyl-1,2,4-triazine (*BHT*) which forms stable and coloured complexes preferrably with copper(II) and rare earth elements. To extend the analytical applications of these ligands to such metal ions we investigated the complex formation with Cu(II) in some detail using spectroscopic and electrochemical methods.

Experimental Part

3-Hydrazino-5,6-diphenyl-1,2,4-triazine was prepared according to [6], and condensed with benzaldehyde to obtain yellow crystals of the corresponding Schiff base 3-(α-phenyl)-ethylidene-hydrazino-5,6-diphenyl-1,2,4-triazine (*BHT*; $C_{22}H_{17}N_5$:$M = 351.41$). The crude product was recrystallised from N,N-dimethylformamide (*DMF*). Elemental analysis yielded C 75.20, H 4.84, N 19.94 (calculated values C 76, H 4.84, N 19.71%). The melting point of the substance was 250 °C. IR bands at 3220 cm^{-1} (N–H stretching) and 1610 cm^{-1} (C=N Stretching) and ^{1}H-NMR spectra 7.35–7.83 ppm (q, 15 H, three phenyl groups), 8.32 ppm (s, 1H, –CH=) and 10.50 ppm (br, 1 H, NH) confirmed the structure [7].

The solid Cu(II)-complex was prepared from an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (20 mmol) mixed with *BHT* (40 mmol) dissolved in ethanol. The mixture was refluxed for 30 min, then allowed to cool yielding a brown precipitate of the complex. The complex was filtered, washed several times with ethanol and dried under reduced pressure over P_2O_5. Microanalysis of the solid complex gave C 52.0, H 4.10, N = 16.78 (calculated values for the 1:1 complex $Cu(C_{22}H_{16}N_5)NO_3 \cdot 2H_2O$: C 51.61, H 3.91, N 16.42%). The compound decomposes at 188 °C.

Stock solutions of copper(II) for the measurements were prepared by dissolving copper(II) nitrate (Merck) in double distilled water (standardized by EDTA titration [8]). Dioxane was freshly distilled over sodium metal and $LiAlH_4$. Universal buffer, acetate buffer, and potassium hydroxide were prepared and standardized according to [8].

Electronic absorption spectra of the free ligand and chelate compound were recorded by using Perkin–Elmer 550S spectrophotometer in 75% (*v*/*v*) dioxane-water. The composition of the Cu(II)-ligand system in solution was determined by the molar ratio method [9]. Solutions containing a constant concentration of $Cu(NO_3)_2$ ($2 \cdot 10^{-5}$ *M*) and variable concentrations of *BHT* within the range of $5 \cdot 10^{-6}$ to $7 \cdot 10^{-5}$ *M* were used. IR spectra were recorded using a Perkin–Elmer spectrophotometer (4000–200 cm^{-1}) using KBr pellets. IR spectra in the Far IR range (650–50 cm^{-1}) were recorded on a NICOLET 20F Far IR-FT-spectrometer using polyethylene pellets. ^{1}H-NMR spectra were run on a Brucker 250 MHz NMR spectrophotometer using $CDCl_3$ as solvent. Conductivity measurements were made in dioxane solution (10^{-3} *M*) using a Wayne Kerr B642 Autobalance Universal Bridge.

The *pH*-metric titrations were carried out with a digital WTW *pH*-meter 520 with a conventional *pH*-electrode. Titrations were performed in 75% (*v*/*v*) dioxane-water under nitrogen atmosphere. The values of the hydrogen ion concentrations were corrected by adding 0.28 *pH* units [10].

Polarograms were taken using a capillary with a mercury flow rate of 5.10 mg/s, and a drop time of 7.30 s. The potential was recorded against SCE at 25 °C. Solutions containing $1 \cdot 10^{-4}$ *M BHT* ligand, in 50% (*v*/*v*) dioxane-water were used. The *pH* was adjusted by the addition of 5 ml universal buffer (Britton Robinson) within the range of 2 to 12 and also in acetate buffer in the range 3–6 on solution containing ($4 \cdot 10^{-5}$ *M*) *BHT* ligand. Polarographic studies on the chelate compound were performed in solutions containing $2.5 \cdot 10^{-5}$ *M* Cu(II) and variable concentrations of *BHT* in the range $5.3 \cdot 10^{-6}$–$7.27 \cdot 10^{-5}$ *M* in 50% (*v*/*v*) dioxane-water.

Results

Spectroscopy

The electronic absorption spectra of the free Schiff-base in 75% dioxane-water in acidic and neutral solutions show two bands in the region 200–450 nm (see Fig. 1).

Table 1. pK_a values of *BHT* in 60% (*v*/*v*) dioxane-water, calculated by the modified limiting absorbance method, $\lambda = 375$ nm, $A_{max} = 0.76$, $A_{min} = 0.11$

pH	*A*	$A_{max} - A$	$A - A_{min}$	$\log \frac{A_{max} - A}{A - A_{min}}$	pK_a
12.30	0.16	0.60	0.05	1.08	13.38
12.50	0.18	0.58	0.07	0.92	13.42
12.80	0.22	0.54	0.11	0.69	13.49
13.00	0.275	0.485	0.165	0.47	13.47
13.10	0.32	0.44	0.21	0.31	13.42
13.20	0.38	0.38	0.27	0.15	13.35

Mean value: $pK_a = 13.42 \pm 0.06$
Linear regression analysis: $pK_a = 13.30 \pm 0.1$

The band at 310 nm (λ_1, $\log \varepsilon = 4.43$) can be assigned to an enhanced n-π^* transition (R-band). The band λ_2 located at 212.5 mm ($\log \varepsilon = 4.35$) is assigned to an enhanced π-π^* transition (K-band) over the whole conjugated system [11]. Increasing the *pH* yields decreasing absorptions at λ_1 and increasing absorption at 375 nm of an absorption band which is in acidic and neutral solutions only visible as a shoulder. This is interpreted as a deprotonation of the hydrazo moiety. The acid dissociation constant of the free ligand was calculated from the influence of the *pH* on the spectrum of the ligand in 60% (*v*/*v*) dioxane-water using the limiting absorbance method [12]. A value of $pK_a = 13.42$ was obtained as shown in Table 1.

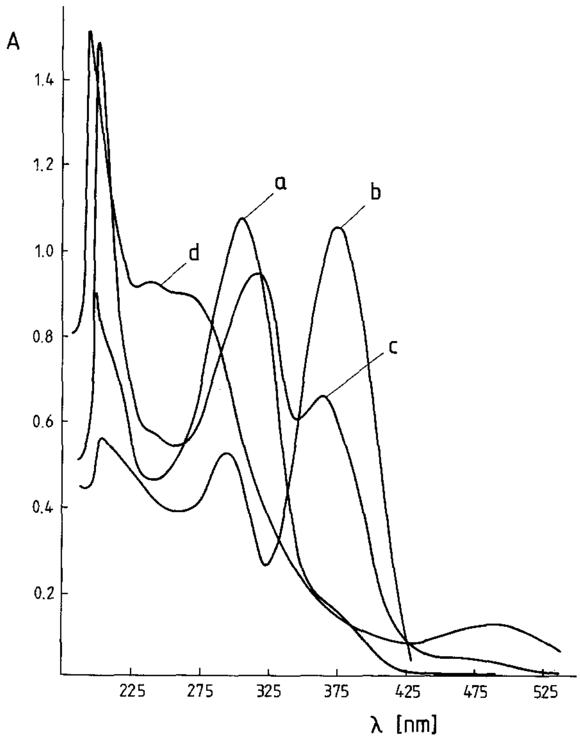


Fig. 1. Absorption spectra of a $4 \cdot 10^{-5}$ *M* *BHT* solution in 75% (*v*/*v*) dioxane-water at 25 °C at $pH = 5$ (a); at *pH* 13.0 (b) and a solution of $4 \cdot 10^{-5}$ *M* Cu(II), $1 \cdot 10^{-4}$ *M* *BHT* in this solvent at *pH* of 5

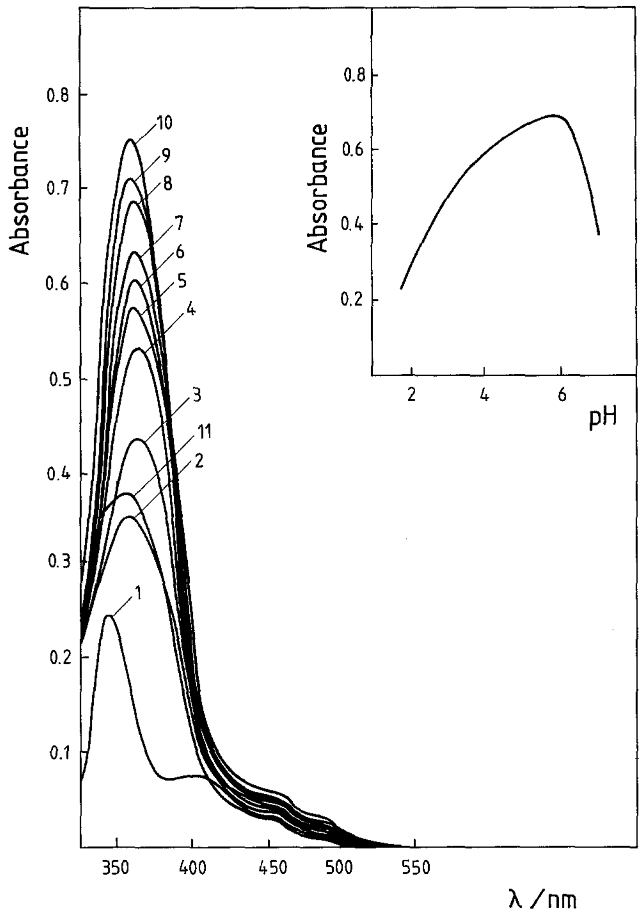


Fig. 2. Absorption spectra of solutions of $2 \cdot 10^{-5} M$ Cu(II), $1 \cdot 10^{-4}$ *M* ligand in 75% (*v*/*v*) dioxane-water at different *pH* values: (1) 2.0, (2) 2.5, (3) 3.0, (4) 3.5, (5) 4.0, (6) 4.5, (7) 5.0, (8) 5.50, (9) 6.0, (10) 6.70, and (11) 7.12. *pH*-absorbance curve at $\lambda = 360$ nm

On the addition of Cu(II) ions ($4 \cdot 10^{-5} M$) to the ligand solution ($4 \cdot 10^{-5} M$) in 75% (*v*/*v*) dioxane-water, a greenish yellow colour developed. The absorption spectra of the complex formed showed absorption bands at 360 nm ($\log \varepsilon = 4.22$), 315 nm ($\log \varepsilon = 4.37$) and 217.5 nm ($\log \varepsilon = 4.57$) (see Fig. 1). The band at 360 nm can be assigned to a π-d transition [13], the other bands are associated with the above mentioned absorption lines. Variation of *pH* using universal buffer revealed that the coloured chelate is formed in the *pH*-range 2.0–7.0 (see Fig. 2). The optimum *pH* range for complex formation was found between 4 and 6.

At $pH = 5.40$ the formation of a 1:1 complex was established by means of the molar ratio method [9] performed at various wave lengths. This was further confirmed by the slope ratio method [14] and Job's "continuous variation" method [15]. The lack of isosbestic behaviour at larger ligand concentrations suggested the formation of higher coordinated species. The results from *pH*-metric studies confirmed this, showing the formation of both a 1:1 and a 1:2 complex (see below).

The complexes of Cu(II) with *BHT* obeyed Beer's law in the concentration range from $2.5 \cdot 10^{-6}$ to $1.75 \cdot 10^{-5} M$ yielding a molar absorption (ε) at 360 nm of $3.69 \cdot 10^4 M^{-1} \mathrm{cm}^{-1}$. Using this value a sensitive method for the determination of copper(II) ions in aqueous (dioxane containing) solution at a *pH* of 5.40 is possible. We used this to determine the stability constant for the formation of the 1:1

complex [9].

$$\mathrm{Cu}^{2+} + \mathrm{H}L \rightleftarrows \mathrm{Cu}L^{+} + \mathrm{H}^{+} \tag{1}$$

$$\mathrm{H}L \rightleftarrows \mathrm{H}^{+} + L^{-}. \tag{2}$$

According to this equilibria the measured total absorbance (A_{tot}) after addition of ligand (HL) can be represented by

$$A_{tot} = A_{\mathrm{Cu}L} - \left(\frac{\varepsilon_{\mathrm{Cu}L}}{\varepsilon_{\mathrm{Cu}L} - \varepsilon_{\mathrm{Cu}}} \cdot \frac{1}{\beta}\right)\left(\frac{A_{tot} - A_{\mathrm{Cu}}}{[\mathrm{H}L]}\right) \tag{3}$$

A_{Cu} is the absorbance of the free metal ion, $A_{\mathrm{Cu}L}$ is the absorbance of the metal complex under excess of ligand, A_{tot} the total absorbance after the addition of a ligand concentration [HL], $\varepsilon_{\mathrm{Cu}L}$ and $\varepsilon_{\mathrm{Cu}}$ represent the molar absorptivity of the complex and the metal ion, respectively. A plot of A_{tot} vs. A_{tot}-A_{Cu}/[HL] gives a straight line with the slope

$$\mathrm{slope} = \frac{\varepsilon_{\mathrm{Cu}L}}{\varepsilon_{\mathrm{Cu}L} - \varepsilon_{\mathrm{Cu}}} \cdot \frac{1}{\beta} \tag{1}$$

from which the complex formation constant is found as $K_1 = (1/\beta)(K^{\mathrm{H}}/[\mathrm{H}^+])$ where K^{H} represents the acid dissociation constant of the ligand and $[\mathrm{H}^+]$ the concentration of hydrogen ions of the medium. This yields a value of $\log K_1 = 11.97$ in good agreement with the value obtained from *pH*-metric studies (see below).

The solid 1:1 complex has been isolated according to the method given in the experimental section. UV-visible spectra of this substance dissolved in pure dioxane show absorption bands at 484, 267, 240 and 200 nm, but no band was found near 360 nm. It appears to be unlikely that in the solid state and in nonaqueous solutions the protonated species is present. Furthermore, the value of the molar conductance in pure dioxane solution at room temperature was found to be $0.26\,\Omega^{-1}\,\mathrm{cm}^2\,M^{-1}$ associated with a weak-electrolyte behaviour. This value shows that the Cu-*BHT* complex behaves in dioxane as a non-electrolyte [18] indicating the coordination of the nitrate ion. Therefore the absence of the band at 360 nm may be interpreted to be due to a change of the coordinating sites and it appears to be possible that the ligand behaves as a tridentate ligand [16].

The band at 484 nm ($\log \varepsilon = 3.52$) appears in all investigated solvents and can be assigned to a d-π transition [13]. The position of this band varies with the solvent and is found in tetrahydrofurane (*THF*) at 507 nm, in 1,2-dichloroethane (*DCE*) at 510 nm, in nitroethane (*NE*) at 512 nm, in ethanol (*Et*OH) at 507 nm, in methanol (*Me*OH) at 504 nm, in acetonitrile (*An*) at 486 nm, in *DMSO* at 500 nm and in *DMF* at 497 nm; the band is therefore shifted to lower wavelengths with increasing donor-number of the solvent.

Characteristic IR-absorption frequencies and absorption maxima observed in the far-IR region are given in Table 2. The band assignments are based on normal coordinate analysis of copper-Schiff-base-complexes [19], copper-pyridine complexes [20], and on the spectra of the free ligand and of $\mathrm{NaNO_3}$. The bands at 645, 424, 405 cm^{-1} are assigned to Cu-triazine ring deformation. Absorptions found at 466, 203, 149, 138 cm^{-1} refer to combined Cu–N stretching vibrations.

The IR spectrum of the Cu(II)-*BHT* complex shows a broad band in the range

Table 2. IR spectra for the free ligand and its copper(II) complex

Free ligand	$[Cu(\mathit{BHT})(NO_3)]\cdot 2H_2O$	Assignment
–	3640–2600	ν(HOH)
3220 m	–	ν(N–H)
3195 m	–	ν(N–H)
3045 w	3045 m	ν(=C–H)
3020 w	3010 m	ν(C–H) aromatic
2920 w	2920 w	ν(C–H)
–	1810 w	$\nu(NO_3^-)$
–	1760 w	$\nu(NO_3^-)$
1610 s	1590 s	ν(C=N)
1585 s	1575 w	ν(C=C) aromatic
1515 m	1525 w	ν(C=C) aromatic
–	1460 s	$\nu(NO_3^-)$
1445 m	1440 s	ν(ring)
1380 s	1380 s	ν(N=N)
1345 s	1320 s	ν(C–N) struct. II
1295 w	–	
	1280 s	$\nu(NO_3^-)$
1270 m	1260 m	ν(C–C)
1230 w	1200 m	ν(C–N) struct. I
1125 m	1175 m	
1080 s	1095 s	δ(C–H)
1055 s	1070 w	
1025 m	1020 w	
955 m	955 w	ν(N–N)
920 w	920 m	
870 w	870 w	
755 s	770 m[a]	
965 s	700 s[a]	
Far IR		
635 w	645 s	ν(triazine ring)
–	625 s	$\nu(Cu–NO_3)$
617 s	613 s	
602 s	594 w	
573 m	576 m	
527 s	539 s	
506 s	516 m	
491 w	477 m	
–	466 m	ν(Cu–N)
–	450 w	$\nu(Cu–NO_3)$
414 m	424 s	ν(triazine ring)
410 m	405 s	ν(triazine ring)
357 m	350 s	
–	295 w	
235 m	239 s	
–	203 m	ν(Cu–N)
–	149 m	δ(Cu–N)
–	138 m	ν(Cu–N)
–	123 w	
–	113 m	
103 w	103 s	

[a] Monosubstituted aromatic ring

3640–2600 cm^{-1} attributed to OH-stretching vibrations in accordance with the bound water molecules found by elementary analysis. The C=N stretching vibrations are shifted from 1610 cm^{-1} observed in the free ligand to 1590 cm^{-1} due to the reduction of the electron density and therefore of the bond strength in the azomethine linkage. The bands at 1810, 1760, 1460, and 1280 cm^{-1} can be assigned to $\nu(NO_3^-)$. The N–N stretching vibrations are shifted from 955 cm^{-1} in the free ligand to 995 cm^{-1} in the complex, due to weaker lone pair-lone pair repulsive forces of the adjacent nitrogen atoms [21]. The shifts of frequencies of the (C=N) and the (N–N)-bands compared to those of free Schiff base (*BHT*) and the absence of a N–H stretching vibration band indicate that the azomethine nitrogen and the NH-site are involved in complexation.

The characteristic IR-absorption frequency of the nitrate ion (a weak combination band at 1750 cm^{-1}) is split into two bands at 1810 and at 1760 cm^{-1} showing that the nitrate ion acts as a bidentate ligand [22, 23]. The two bands at 625 and 450 cm^{-1} may be assigned as Cu–NO_3 stretching vibrations [24].

Potentiometry

Potentiometric titration curves of the free ligand and the solutions containing ligand and molar ratios at 1:1, 1:2 and 1:5 Cu(II) to ligand are given in Fig. 3. They show that the free ligand is monoprotic (H*L*) which is due to deprotonation of the hydrazo moiety. A pK_a-value of 13.63 is obtained from analysing the titration curve. This value is in good agreement with the value obtained by spectrocipic titration taking into consideration the lower dioxane content of the solvent [10]. Titration curves of the Cu-complex are well separated from the titration curves of the ligand showing the liberation of protons in course of the complex formation. A weak inflection point at a molar ratio of base and metal ions of 1:1 is followed by a sharp inflection point

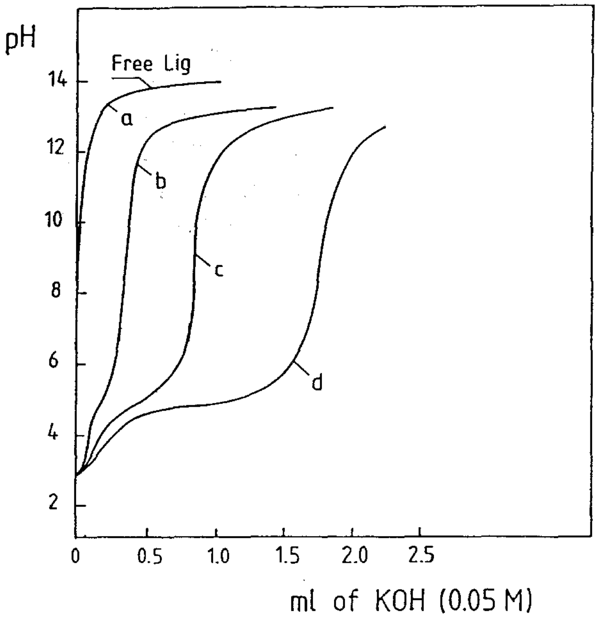


Fig. 3. Potentiometric titration curves of 25 ml of a solution containing $2\cdot 10^{-3}$ *M BHT* in 75% (*v*/*v*) dioxane-water at 25 °C under the addition of 0.05 *M* KOH: (a) free ligand; (b) 1:1, (c) 1:2 and (d) 1:5 molar ratio of Cu(II): *BHT* $V_0 = 25$ ml, $T = 25$ °C

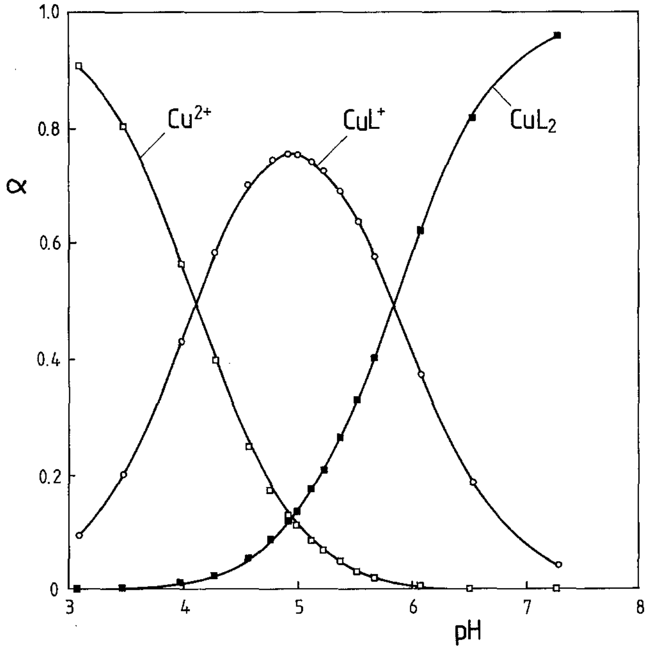


Fig. 4. Distribution diagram of complex species as a function of *pH* in the Cu(II)-*BHT* system

at a molar ratio of 2:1, indicating the stepwise formation of ML and ML_2 species in these solutions (see Fig. 3).

Adopting the method of Irving and Rossotti [25] $\log K_1$ and $\log K_2$ values of 11.97 and 10.40 are obatined, respectively.

The concentration of the complex species as a function of *pH* has been calculated [26]. Fig. 4 shows that $\mathrm{Cu}L^+$ increases rapidly attaining a limiting value at *pH* 5 whereas free Cu(II) and $\mathrm{Cu}L_2$ change monotonically with *pH*.

Polarography

The polarograms obtained for free *BHT* show two polarographic waves within the *pH* range from 2 to 7. In alkaline solutions they fall together yielding only one wave. This behaviour is similar to that observed with *o*-hydroxybenzaldehyde isonicotinyl-hydrazone [27]. $E_{1/2}$ values at different *pH* are given in Table 3. The half-wave potentials are linearly related to the *pH*-values, with a shift of 56 and 45 mV/*pH* towards more negative potential. This *pH* dependence suggests that the first electron transfer occurs prior to a proton transfer. The number of protons involved in the rate determining step can be calculated from the slopes of $E_{1/2}$ vs. *pH* or from $\log i/(i_d - i)$ vs. $E_{1/2}$ plots [27]. This yields 0.81 and 0.63 for the numbers of protons associated with first and the second reduction wave, respectively. These fractional values and the low value of αn (0.85, 0.822) suggests the occurence of a heterogeneous proton transfer [28].

The electro-reduction process of the free ligand was examined by the logarithmic analysis [i.e. $\log(I/I_d - I)$ and $E(V)$] at different *pH* values. Straight lines for all *pH*-values are found and αn show that the electrode processes are electrochemically irreversible [29].

Table 3. Effect of pH on $E_{1/2}$ vs. SCE, I_d "diffusion constant" and αn of benzaldehyde triazine (*BHT*), in 50% dioxane-water

pH	$E_{1/2}/V$	$I_d/\mu A$	αn^a	αn^b	$\frac{\partial \log I_d}{\partial \log h}$
In universal buffer					
2.0 1st	−0.48	8.12	1.23	0.86	0.48
2nd	−1.08	9.74	–	0.74	–
3.0 1st	−0.57	6.4	0.97	0.86	0.55
2nd	−1.07	7.22	0.38	0.80	0.53
4.0 1st	−0.62	5.42	0.75	0.86	0.55
2nd	−1.10	5.85	0.41	0.80	0.53
5.0 1st	−0.68	5.53	0.90	0.61	0.52
2nd	−1.14	5.20	0.39	0.74	0.51
6.0 1st	−0.74	5.63	0.85	0.86	0.48
2nd	−1.20	5.20	0.41	0.74	0.45
7.0 1st	−0.79	5.63	0.91	0.74	0.50
2nd	−1.25	4.04	–	1.03	0.46
8.0	−0.86	5.42	0.91	0.94	0.47
9.0	−0.92	5.20	0.54	0.80	0.48
10.0	−0.97	3.47	0.64	0.86	0.51
11.0	−1.03	5.42	0.07	0.86	0.38
12.0	−1.06	5.42	0.48	0.74	0.50
In acetate buffer					
3.0	−0.54	7.04	1.00	0.74	0.51
4.0	−0.59	7.03	1.06	0.74	0.56
5.0 1st	−0.66	6.94	1.18	0.57	0.57
2nd	−1.14	5.42	0.29	0.74	0.46
6.0 1st	−0.76	6.83	0.54	0.65	0.52
2nd	−1.20	4.34	0.21	0.94	0.49

[a] From slope analysis

[b] From Tomas-method

For the Cu-complex the logarithm of the mercury height (h) vs. $\log I_d$ yields a straight line with a slope of 0.518, i.e. the electro-reduction of the Cu(II)-*BHT* complex is diffusion controlled on the mercury electrode. Analysis of $\log(I/I_d - I)$ vs. E(V) yields straight lines with a slope of 0.141 for the 1:1-species. This emphasises the irreversibility of the electro-reduction of the Cu(II)-*BHT* complex. A mean value of αn of 0.62 was obtained from slope analysis and the Tomas equation.

The effect of changing *BHT* ligand concentrations on the polarographic behaviour of Cu(II) was investigated in acetate buffer solution at $pH = 5.40$ which is most favourable for complex formation. Free copper(II) shows a half-wave potential −0.05 V vs. SCE. By increasing the concentration of the ligand, the half-wave potential shifts towards more negative values reflecting complex forma-

Table 4. Effect of concentration of *BHT* on I_d and $E_{1/2}$ vs. SCE of Cu(II) ($2.5\cdot 10^{-5}$ *M*) in 50% (*v*/*v*) dioxane-water, $pH = 5.40$

$[L]\times 10^5/M$	$[L]/[Cu^{2+}]$	$-E_{1/2}/V$	$I_d/\mu A$	$(E_{3/4}-E_{1/4})/V$
0	–	0.05	0.42	0.03
0.532	0.213	0.07	0.29	0.09
1.06	0.420	0.15	0.27	0.08
1.259	0.507	0.175	0.26	0.08
1.587	0.635	0.20	0.16	0.06
2.11	0.844	0.22	0.24	0.05
2.50	1.0	0.22	0.33	0.06
3.02	1.21	0.22	0.21	0.06
3.729	1.50	0.22	0.192	0.05
4.89	2.0	0.21	0.18	0.06
6.09	2.50	0.22	0.185	0.05
7.27	3.00	0.20	0.195	0.06

tion. Plotting the ratio $[L]/[M]$ vs. $E_{1/2}$ Fig. 5 is obtained. A constant reduction potential is found after complete formation of the 1:1 complex.

The stability constant of the Cu^{2+}-*BHT* complex was calculated using Bierant's method for irreversible electrode reactions [30]. Inserting the spectrophotometrically measured $pK_a = 13.42$ and the used $pH = 5.4$, a stability constant for the 1:1 Cu(II)-*BHT* complex formation of 13.38 is obtained. The value of $\log K_1$ of Cu(II)-*BHT* is larger than the corresponding *pH*-metric and spectrophotometric values, a fact previously reported and discussed by Moussa et al. [31].

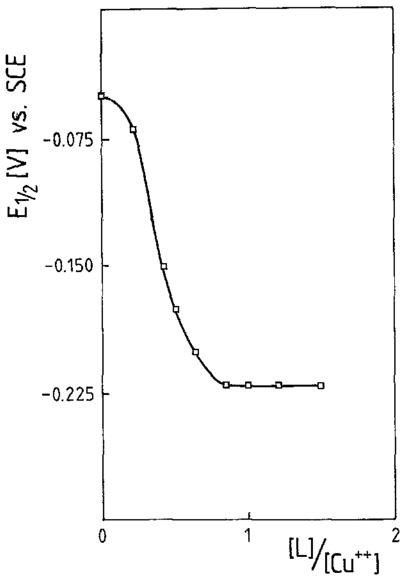
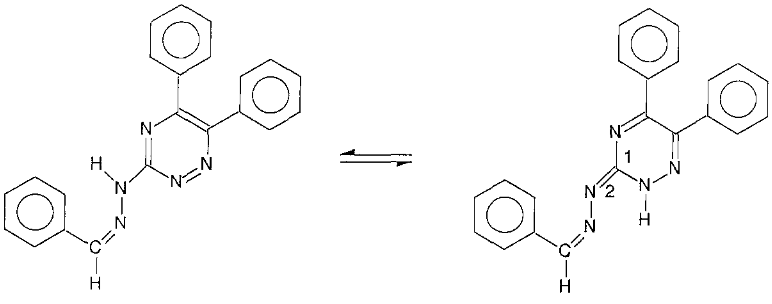


Fig. 5. Relation between $E_{1/2}$ vs. $[L]/[Cu^{2+}]$ in 50% (*v*/*v*) dioxane-water at $pH = 5.40$ (acetate buffer)

Discussion

BHT is a mono-basic ligand. Its structure can be considered as consisting of an a-triazine hydrazo group condensed with benzaldehyde represented by two tautomeric forms **I** and **II**.

It is difficult to decide from the infra red spectra whether the hydrazo hydrogen atom is mainly located on the hydrazo group or on the triazine nitrogen atom. The ultraviolet spectrum shows the presence of two intense bands assigned to a π-π^* and n-π^* transition, respectively. The molar absorptivity for the first transition is more than twice the value reported [11] for two aromatic rings conjugated like in structure **I**. This enhanced transition can be explained in terms of further conjugation in the aliphatic chain linking the aromatic groups. This is supported by the ^{1}H-NMR spectra, where the chemical shift of the NH signal indicates the migration of a proton from the aliphatic chain to the triazine ring as shown in the form II.



I II

Scheme 1

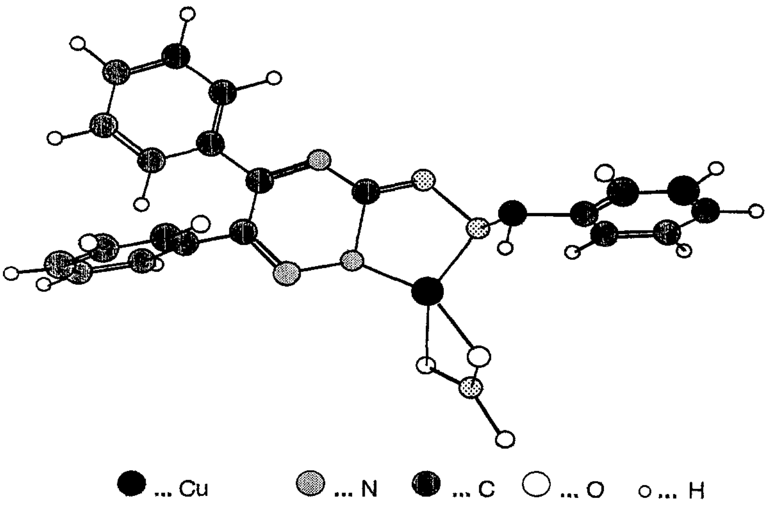


Fig. 6. MM2-optimized structure of 3-(α-phenyl)ethylidene-hydrozino-5,6-diphenyl-1,2,4-tetrazine-copper(II)-nitrate (formal charges are ommited and the π-electron system is given in a simplified form)

Only one ionizable proton with the value of $\log K^{H}$ is present in the ligand. Ligands containing the group Ar–NH–N=C < R_2 are normally ionized in moderately alkaline media, and have pK_a values ranging within 6 and 9 [32, 33]. This high basicity suggests that the proton of the hydrazo group is most likely attached to the triazine ring nitrogen atom, where it is less ionizable [34].

Cu(II) is capable of forming 1:1 and 1:2 complexes (as shown from pH-metric studies). A comparison of the stepwise formation constants might raise doubts about the extent of participation of all particular donor sites in the bonding. The K_{ML}/K_{ML2} ratio obtained is probably too small to be accounted for by appreciable steric hindrance [35]. On the basis of the presented results and on the basis of a MM2-geometry optimization we suggest that the complex occurs in the form shown in Fig. 6. The tetragonal surrounding of the Cu-coordination center and the drilled positions of the phenyl-substituents are in agreement with the UV-, IR- and ^{1}H-NMR spectra. The calculations give lower energies for a coordination of the copper-central ion to the N_2-atom in triazine than to the N_4-atom. This confirms the stronger basicity of N_2 compared with that one of N_4-atom, which is due to their chemical surroundings.

Acknowledgements

Thanks for financial support are due to the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project 8795).

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Received February 25, 1992. Revised May 11, 1992. Accepted June 12, 1992