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Extraction and Complexation of Copper(II) with *para-tert*-Butylbenzhydrazide and Its *N'*,*N'*-Dimethyl Derivative

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Abstract—The extraction of copper(II) with the *para-tert*-butylbenzoic acid hydrazide and related *N'*,*N'*-dimethyl derivative was studied. The composition and structure of the extracted complexes were determined, the mechanism of extraction of copper(II) in different media was suggested, the extraction constant was calculated. The copper(II) complex compounds with these reagents were isolated.

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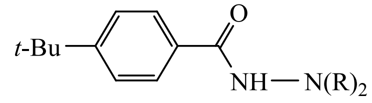
The hydrazide group is specific with respect to the copper(II) cation. A lot of copper complexes with aliphatic and aromatic acids hydrazides were obtained [1–6]. Complexes of copper(II) with the *N'*,*N'*-dialkyl hydrazides derivatives with long hydrocarbon radicals are soluble in organic solvents, which allows using these compounds for copper extraction. The extraction of copper(II) with octanoic acid hydrazide (HL) was investigated [7] and it was shown that this compound extracted copper from slightly acidic media as the cationic complex $[Cu(HL)_3]^{2+}$. The benzoic acid *N'*,*N'*-dialkylhydrazides (HL) extract copper(II) from the ammonia medium as the electrically neutral inner-complexes of the general formula CuL_2, where L is deprotonated form of the reagent [8, 9]. The extraction of copper(II) with substituted benzoic acid hydrazides containing a hydrocarbon substituent in the benzene ring, and their *N'*,*N'*-dialkyl derivatives has not been studied. Such moiety exhibits the +*I*-effect and can affect the extraction properties of the reagents, as well as the composition and structure of the formed copper(II) complex. Therefore it is interesting to investigate the extraction of copper(II) with these compounds, to compare the results with the properties of compounds containing no substituent in the benzene ring, and to determine its effect on the copper(II) extraction, the composition and structure of extracted complexes, and to isolate the copper(II) complexes with these compounds. For the study we selected *para-tert*-butylbenzoic acid hydrazide (**I**) and its *N'*,*N'*-dimethyl derivative (**II**).



R = H (**I**), CH_3 (**II**).

Table 1 lists the solubility of the reagents. As seen, the solubility of compounds in organic media increases with increasing dielectric constant (ε) of the solvent. Water falls out from this series: its dipole moment μ = 1.84, [10], which slightly increases the solubility of these compounds; the latter are also polar substances.

Figure 1 illustrates the extraction properties of compounds **I** and **II** toward copper(II). The character of the copper extraction with these substances is

Table 1. Solubility of reagents at t = 20±1°C

Solvent (ε) [10]	Solubility, g l^{-1} (M)	
	compound **I**	compound **II**
Water (1.01)	1.0 (0.005)	0.85 (0.0039)
Hexane (1.90)	0.2 (0.001)	0.18 (0.0008)
o-Xylene (2.51)	8.6 (0.045)	0.85 (0.0039)
i-AmOH (14.7)	52.0 (0.270)	157.1 (0.7141)

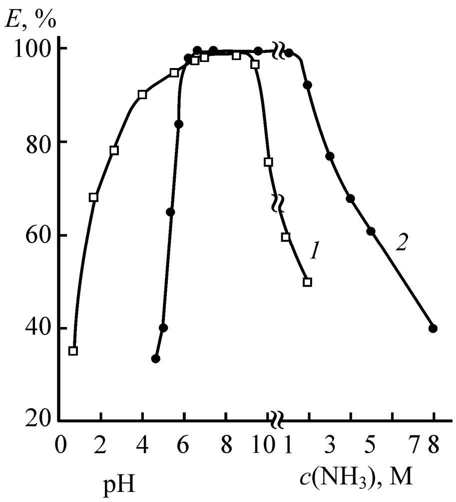


Fig. 1. Dependence of extraction of copper(II) with 0.05 M solutions of compounds **I** and **II** in *i*-AmOH on pH and concentrations of NH_3. $c_{Cu(II)} = 0.005$ M, $V_o:V_w = 1:2$, $\tau = 3$ min. (*1*) compound **I,** (*2*) compound **II**.

different. Compound **I** reacts with copper(II) in acidic medium to form a blue extractable complex. In the pH range of 0.8–6 the degree of extraction increases from 35 to 95%. It reaches 98% at pH 7 and remains constant up to pH 9. The color of the extract changes to a dirty green. With a further increase of pH the degree of extraction decreases rapidly, and at the NH_3 concentration 1 M falls to 60%. The organic phase becomes brown. Change in the color of the extract suggests that at different pH values different complexes are extracted.

Compound **II** with copper(II) forms a violet extractable complex over the entire studied range of pH values and NH_3 concentrations. It begins to extract copper(II) at higher pH values than compound **I**. In the pH range 4.8–6.7 the degree of extraction increases from 32% to 98% and remains the same until $c(NH_3)$ ~1 M. At an increase in the ammonia concentration to 5 M it falls to 60%. Thus, the introduction of two *N*',*N*'-methyl radicals to the molecule **I** shifts the region of maximum extraction of copper(II) to higher pH values and ammonia concentration. The presence of *para-tert*-butyl radical in the benzene ring has no effect on the region of maximum of the copper(II) extraction with compound **II** compared with the benzoic acid *N*',*N*'-dialkylhydrazides [8, 9].

It is known from the literature that hydrazides form two types of complexes: positively charged complexes of the general formula $[M(HL)_m]^{n+}$, where HL is the hydrazide molecule, and neutral chelate compounds of the general formula ML_n, where L is the deprotonated form of the hydrazide [11]. To determine the types of extractable complexes we used the method of ion exchange. By passing colored extracts of the complexes through the cationite KU-2-8rC in Na^+ form we established that compound **I** formed a charged complex at pH < 6 while at pH > 6 the complex was not charged. Compound **II** forms only an uncharged complex in the entire investigated range of pH and NH_3 concentrations.

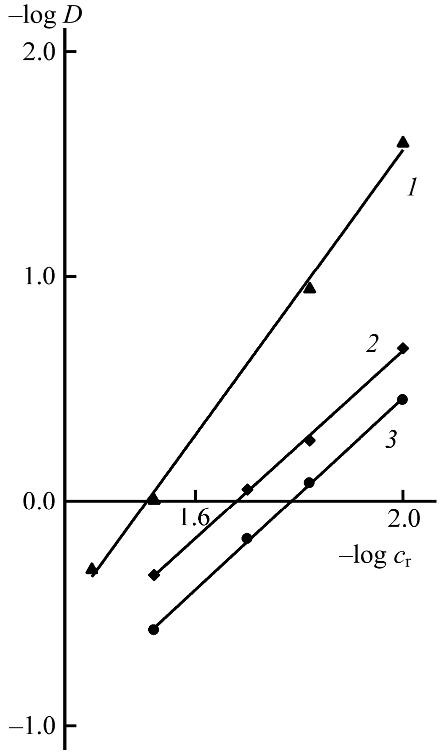


Fig. 2. Dependence of the partition coefficient logarithm (log *D*) of copper(II) vs. the reagent concentration logarithm (log c_R) at $V_o:V_w = 1:1$. (*1*) compound **I**, $c_{Cu(II)} = 0.002$ M, pH = 1.22–1.30, $\tau = 3$ min. (*2*) compound **I,** $c_{Cu(II)} = 0.005$ M, pH = 10.3 (ammonia buffer), $\tau = 5$ min., (*3*) compound **II,** $c_{Cu(II)} = 0.005$ M, pH = 10.3 (ammonia buffer), $\tau = 5$ min.

Compound **I** was established by the method of the shifting equilibrium to form at pH < 6 the extractable complex with a ratio of [Cu(II)]:[reagent] = 1:3 (Fig. 2, curve *1*) we used the method of shifting the equilibrium. At pH > 6 a complex is formed with a component ratio [Cu(II)]:[ligand] = 1:2 (Fig. 2, curve *2*). Compound **II** forms an extractable complex with a ratio of components [Cu(II)]:[ligand] = 1:2 (Fig. 2, curve *3*).

Based on these data, the process of copper(II) extraction with these compounds from weakly acidic medium can be represented by the following equations:

$$\text{Compound } \mathbf{I}\text{: } Cu^{2+}_{(w)} + 3HL_{(o)} \rightleftarrows [Cu(HL)_3]^{2+}_{(o)}, \qquad (1)$$

$$\text{Compound } \mathbf{II}\text{: } Cu^{2+}_{(w)} + 2HL_{(o)} \rightleftarrows CuL_{2(o)}. \qquad (2)$$

Here HL are the molecules of the corresponding reagents. Subscripts (w) and (o) denote the aqueous and the organic phases respectively.

The comparison of extraction properties of compound **I** and octanoic acid hydrazide (the data for the benzoic acid hydrazide are absent due to its poor solubility in organic solvents) shows that these compounds form the extractable copper complexes of the same composition and structure. They extract copper(II) more efficiently from the slightly acidic media.

Compound **II** forms with copper(II) the extractable complex, which is similar to the complexes formed with the benzoic acid *N'*,*N'*-dialkylhydrazides. Compound **II,** like these reagents, which are its structural analogs, extracts copper(II) from ammonia rather more efficiently than from acidic medium.

The IR spectrum of the Cu(II) complex with compound **II** extracted from ammonia medium does not contain the absorption bands of ammonia in the region 3200–3400 cm^{-1} (Table 5), that is, ammonia is not included in its composition. Thus, the structure of the extracted complex can be represented by the general formula CuL_2. These findings are consistent with the results of [8] that in the IR spectra of the copper(II) extract obtained with the benzoic acid *N'*,*N'*-dihexylhydrazide from the ammonia medium these bands are also absent. Since the formation of chelate compounds according to Eq. (2) proceeds with the release of protons, in the ammonium medium they will interact with ammonia to form ammonium cations. Therefore, the process of extraction of copper(II) with compound **II** in this medium can be described by the following equation:

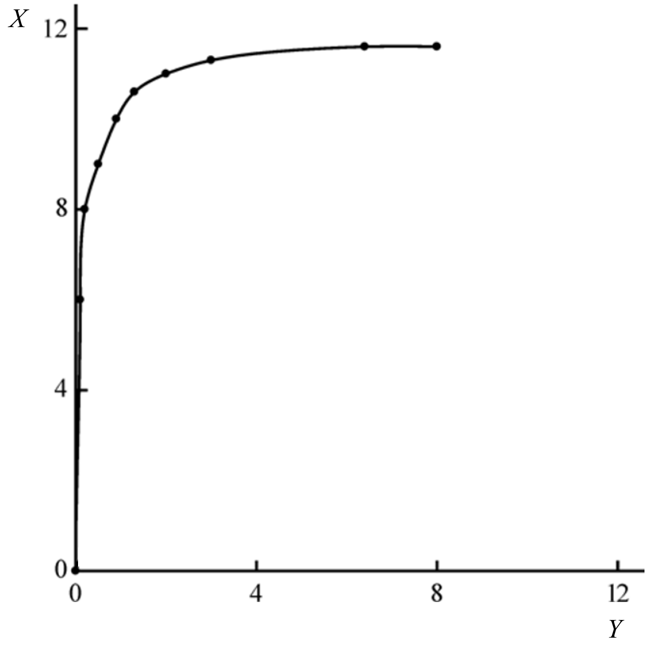


Fig. 3. The Cu(II) extraction isotherm from ammonium media with solution of compound **II** in *i*-AmOH. $V_o:V_w$ = 1:1, c_{HL} = 0.025 M, $c(NH_3)$ = 0.2 M, τ_1 = 25 min. X is $c_{Cu(II)}$ in the organic phase (mM); Y is $c_{Cu(II)}$ in the aqueous phase (mM).

$$[Cu(NH_3)_4]^{2+}_{(w)} + 2HL_{org} \leftrightarrows CuL_{2org} + 2NH_{3(w)} + 2NH^{+}_{4(w)}. \qquad (3)$$

Hence, the expression for the extraction constant is:

$$K_{ex} = \frac{[CuL_2][NH_4^+]^2[NH_3]^2}{[Cu(NH_3^{2+})_4][HL]^2}\ . \qquad (4)$$

Table 2. The calculation of the extraction constant of copper(II) with compound **II**[a]

$[Cu(NH_3)_4^{2+}]\times 10^{3}$, M	$[CuL_2]\times 10^3$, M	$[HL]^2\times 10^4$, M	$[NH_4^+]^2\times 10^3$, M	$K_{ex}\times 10^3$	log K_{ex}
0.1	7.9	0.85	0.7	0.63	2.80
0.9	10.0	0.25	0.9	0.47	2.67
1.3	10.7	0.13	1.2	0.76	2.88
1.9	10.9	0.10	1.4	0.80	2.90
2.9	11.2	0.07	1.2	0.68	2.83

[a] log K_{ex} 2.82±0.06 (P = 0.95, n = 5).

The constant was calculated using the data of the extraction isotherm of copper(II) (Fig. 3) in accordance with [12]. Table 2 shows the calculation of the constants of copper(II) extraction.

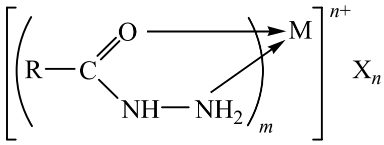
In the case of **I,** in ammonia medium a complex of unknown structure is formed.

Thus, *tert*-butyl radical in the *para* position of benzene ring has no effect on the extraction properties towards copper(II) of both substituted benzoic acid hydrazide and its *N*',*N*'-dimethyl derivative. This can be attributed to its remoteness from the functional group. The factor that dramatically changes the extraction properties of hydrazides is *N*',*N*'-alkylation of the molecules, because in this case the alkyl groups are directly attached to the hydrazide group and affect its coordination-chemical behavior.

Table 3 shows the results of elemental analysis of the obtained copper(II) complexes. Although the compound **I** forms with copper(II) the positively charged extractable complex of the composition [Cu]:[**I**] = 1:3, in the crystalline state the complex of the composition [Cu]:[**I**] = 1:2 was isolated. A similar difference in the complexes of copper(II) in solution and in solid state was also observed for ther hydrazides [5]. Shman'ko et al. attributed this difference to the Jahn–Teller effect. In the crystal the copper complex loses its degenerated state due to the change in its geometry at the removal of one ligand molecule. In solution, the stabilization occurs due to its solvation by the solvent molecules.

The uncharged complex with compound **II** is readily soluble in aliphatic hydrocarbons and chloroform, poorly in acetone, and is virtually insoluble in water. The cationic complexes of both compounds are soluble in alcohol, acetone, slightly soluble in chloroform, *o*-xylene, and insoluble in water and hydrocarbon solvents.

It is known that hydrazides and *N*',*N*'-dialkylhydrazides coordinate metals by the oxygen and terminal nitrogen atoms, forming a five-membered metallocycle [13, 14]. The structure of the resulting charged and uncharged complexes can be represented by the following general formulas:



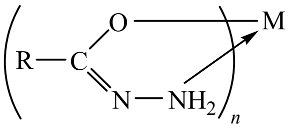


Table 4 shows the frequencies of stretching vibrations of these groups in the obtained complex compounds of copper(II) and the studied reagents. In the spectrum of the complex $[Cu(HL)_2]SO_4{\cdot}2H_2O$ with compound **I** the vibration frequency of NH_2 group is shifted by about ~100 cm^{-1} to the low-frequency region compared to the original reagent. The C=O vibration frequency (amide **I**) is shifted by 13 cm^{-1} to the low-frequency region compared with the position of this band in the solution of **I** in CCl_4 (1678 cm^{-1}). This indicates the participation of these groups in the coordination with the copper atom. The amide-**I** band of compound **I** in vaselibe oil (~1624 cm^{-1}) is shifted to the low frequency compared to the usual position in compounds of this type (~1640–1660 cm^{-1}) [15, 16]. This is due to the formation of stronger hydrogen bonds.

Table 3. Elemental analysis of the copper(II) complexes

Complexes	Complex color	Found, %				Formula	Calculated %			
		C	H	N	Cu(II)		C	H	N	Cu(II)
$[Cu(HL)_2]SO_4{\cdot}2H_2O$	Blue	45.75	6.43	9.27	10.90	$C_{22}H_{36}N_4O_8SCu$	45.56	6.21	9.66	10.96
$[Cu(HR)]Cl_2$	Green	45.02	5.55	7.69	17.97	$C_{13}H_{20}Cl_2N_2OCu$	44.01	5.64	7.89	17.91
$[Cu(HR)_2]SO_4{\cdot}2H_2O$	Bright blue	51.18	6.93	9.03	9.71	$C_{26}H_{44}N_4O_8SCu$	49.10	6.92	8.81	9.99
CuR_2	Pink	62.30	7.68	11.12	12.70	$C_{26}H_{38}N_4O_2Cu$	62.21	7.58	11.17	12.66

In the spectra of the charged complexes of compound **II** the frequency of the amide-I band is reduced by 40–50 cm^{-1} compared with the original reagent. Although the N–H group is not involved directly in the complex formation, its stretching vibration frequency is also reduced by ~20–60 cm^{-1}, due to the influence of the neighboring nitrogen atom coordinated to the metal.

The IR spectrum of the uncharged complex of general formula CuL_2 with compound **II** also does not contain the bands of stretching vibrations of ν(N–H) and ν(C=O), and there are bands of stretching vibrations of ν(C–O) and ν(C=N) at 1361 and 1538 cm^{-1}, respectively. This confirms the fact that the ligand has undergone structural changes and is involved in the complex in the deprotonated form.

Table 4. Stretching vibration frequencies (cm^{-1}) in the IR spectra of compounds **I** and **II** and their complexes with copper(II)

Compound	ν(N–H)	ν(C=O)	ν(C=N)	ν(C–O)
I (HL)	3348, 3252	1624, 1678[a]	–	–
$[Cu(HL)_2]SO_4·2H_2O$	3147	1665	–	–
II (HR)	3198	1644	–	–
$[Cu(HR)]Cl_2$	3141	1595	–	–
$[Cu(HR)_2]SO_4·2H_2O$	3178	1605	–	–
CuR_2	–	–	1538	1361

[a] Solution in CCl_4.

EXPERIMENTAL

^1H NMR spectra were recorded on a MERCURYplus300 spectrometer (Varian, USA) in $CDCl_3$, internal standard HMDS. The IR spectra were obtained on a Fourier spectrometer IFS-66 (Bruker, Germany) from pastes in vaseline oil. The pH values were measured on an I-160M ionomer (ANTEH, Belarus) with glass and silver chloride electrodes. The main compound content was deter-mined by conductometric titration with a conductivity meter OK-102/1 (Radelkis, Hungary). Elemental analysis was performed on a CHNS-932 analyzer (LECO Corporation, USA). Reagents *i*-AmOH, H_2SO_4, $CuSO_4·5H_2O$, $CuCl_2·2H_2O$ are of analytical grade, aqueous ammonia corresponds to GOST 3760-79 “2.”

para-*tert*-Butylbenzoic acid hydrazide **I** was obtained by reacting *n*-propyl *tert*-butylbenzoate with hydrazine hydrate, mp 127.5–129.5°C (lit. 126–128°C [17]).

***p*-*tert*-Butylbenzoic acid *N'*,*N'*-dimethylhydrazide (II).** 45.5 ml (0.6 mol) of 1,1-dimethylhydrazine was dissolved in 250 ml of hexane and cooled with a mixture of snow and salt. A cooled solution of 58 ml (0.29 mol) of *para*-*tert*-butylbenzoyl chloride in 100 ml of hexane was added dropwise while cooling to this solution. The reaction mixture was left overnight. Next day the formed precipitate was filtered off, dissolved in 200 ml of chloroform, and the insoluble part was filtered out. After distilling off chloroform the residue was recrystallized from a mixture of water–*i*-PrOH (3:1). Yield 57%, mp 143–144°C. IR spectrum, ν, cm^{-1}: 3209 (NH); 1644 (amide **I**); 1550 (amide **II**). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.38 s (9H, *t*-C_4H_9), 2.68 s (6H, $2NCH_3$), 7.04–7.10 s (1H, NH, *Z*- and *E*-isomers), 7.40 d (*J* 8.4) (2H, C_6H_4), 7.67 d (*J* 8.1) (2H, C_6H_4). Purity 99%. Found, %: C 70.82, 70.76, H 9.03, 9.07; N 12.70, 12.69. $C_{13}H_{20}N_2O$. Calculated, %: C 70.87; H 9.15; N 12.72.

Method of studying the extraction equilibria. The copper(II) solution was placed, then H_2SO_4 or NH_3 solution In a 50 ml separating funnel was added for obtaining the necessary pH-value, and water to 10 ml volume. 5 ml of 0.05 M reagent solution in *i*-AmOH was added, and the mixture was shaken for 3 min. Phase separation took about 10 minutes. After the complete phase separation, the aqueous layer was separated and the pH_{eq} was measured. The residual content of Cu(II) was determined photometrically [18]. The concentration of metal ions in the organic phase was calculated from the material balance.

Method of obtaining the copper(II) complex compounds. To obtain the cationic complexes with copper(II), the aqueous solutions of metal salt and ethanol solutions of hydrazide equals (molar ratio metal salt:hydrazide 1:1 or 1:2) were mixed and stirred with a magnetic stirrer for 20 min, the precipitate formed was filtered off and washed with cold ethanol and water.

The neutral complex was prepared by mixing solutions of copper(II) ammoniate and compound **II** in ethanol (a molar ratio metal salt: hydrazide = 1:2), followed by stirring for 30 min. The precipitate formed was filtered off, washed with water and cold ethanol.

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