ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 3, pp. 368–371. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.Yu. Gusev, A.V. Radushev, G.S. Bogomazova, T.D. Batueva, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 3, pp. 385–388.

Extraction and Complexation of Cu(II) with Undecanoic Acid *N,N*-Diethylhydrazide

V. Yu. Gusev, A. V. Radushev, G. S. Bogomazova, and T. D. Batueva

Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences,
ul. Koroleva 3, Perm, 614013 Russia
e-mail: cheminst@mpm.ru

Received July 24, 2007

Abstract—A new reagent, undecanoic acid *N,N*-diethylhydrazide, was synthesized, and its pK_{a1} was determined. The reagent recovers Cu(II) to 99–100% from solutions whose acidity ranges from pH 6 to 1 M NH_3. Copper(II) is extracted in the form of a neutral complex of the composition Cu(II):reagent = 1:2. The reagent is incorporated in the complex in the deprotonated form. An equation for the extraction of Cu(II) from ammonia solutions was suggested. The extraction isotherm was constructred. Ammonium salts, when present in solution, considerably decrease the degree of copper extraction. The reagent is less efficient extractant of copper than *N,N*-diethylbenzhydrazide.

DOI: 10.1134/S1070363208030055

Complexation and extraction of Cu(II) with unsubstituted hydrazides of aliphatic carboxylic acids were studied previously [1]. We found no data in the literature on the extraction of copper with *N,N*-dialkylsubstituted hydrazides of aliphatic carboxylic acids.

It is interesting to examine the effect exerted by *N,N*-alkylation of hydrazides on their complexing andextractive properties with respect to Cu(II). The subject of this study is undecanoic acid *N,N*-diethylhydrazide **I**.

Acid–base equilibria in solutions of *N,N*-dialkylhydrazides are similar to those in solutions of unsubstituted hydrazides [2] and are quantitatively characterized by the dissociation constants pK_{a1} and pK_{a2}:

$$H_2L^+ \xrightleftharpoons{-H^+;\ pK_{a1}} HL \xrightleftharpoons{-H^+;\ pK_{a2}} L^-. \qquad (1)$$

where HL is the neutral form of the reagent and H_2L^+ and L^- are its protonated and deprotonated forms, respectively. The pK_{a1} value was determined spectrophotometrically [3] under the following conditions: λ 205 nm; C_I 1.2×10^{-3} M; *l* 2 cm; *I* 0.1 (KCl); solvent H_2O–EtOH, 1:1. pK_{a1} = 3.45±0.05 (*n* 7; P 0.95).

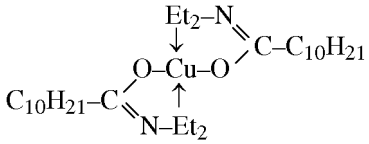
Deprotonation of the reagent starts at an alkali concentration exceeding 3 M. At such alkali concentrations aqueous-alcoholic solutions used for the measurements undergo phase separation, which makes the determination of pK_{a2} impossible.

The results of extraction of $CuSO_4$ with a solution of **I** in hexane are shown in Fig. 1. The extraction of Cu(II) starts at pH > 1 and increases to 99–100% with an increase in pH from 1 to 6. Although at pH > 5 the reagent virtually completely transforms from the protonated to neutral form, the recovery *R* reaches a maximum only at pH 6 when copper hydroxide and basic salts are formed, and an increase in *R* is associated with their precipitation. In an ammonia solution, the precipitate dissolves with the formation of the ammine complex, and the extraction is observed again, remaining high up to 1 M concentration of NH_3. As the NH_3 concentration is increased further to 3 M, the recovery decreases to 85%. The range of efficient extraction of Cu(II) with reagent **I** (from pH 6 to 1 M NH_3) is narrower, compared to *N,N*-dihexylbenzhydrazide (efficient extraction in the range from pH 4.5 to 1 M NH_3).

It is well known that carboxylic acid hydrazides form with metal ions complexes of two types: cationic (type I) and neutral (type II), in which the ligands are incorporated in the neutral and deprotonated forms, respectively [5]. Copper(II) is extracted with a solution of **I** in hexane in the form of a red complex. Its

composition was determined by methods of isomolar series (Fig. 2) and molar ratios (Fig. 3) [6]. Figure 2 shows that, in the intersection point of the straight lines, [Cu(II)]:[**I**] = 1:2. In Fig. 3, the straight lines intersect in the point corresponding to the same ratio.

Thus, the extractable complex has the composition [Cu(II)]:[**I**] = 1:2. When passed through a bed of KU-2-8gS cation exchanger in the Na^+ form, the extract retained its color, which suggests that the complex bears no positive charge, i.e., is electrically neutral (type II). To confirm the structure of the complex, we recorded the IR spectra of a solution of **I** in hexane and of the extract of its copper complex. The spectrum of the reagent contains the stretching vibration bands of the following groups (cm^{-1}): 3190, N–H; 1692, C=O free; 1672, C=O bound. In the spectrum of the complex in solution, these bands are absent, but a new band corresponding to stretching vibrations of the C=N group appears at 1570 cm^{-1}.



Thus, the IR spectra confirm the assumption that the reagent molecule is incorporated in the complex in the deprotonated form. In the spectrum of the extract, the bands of stretching vibrations of the NH_3 molecule at 3200–3400 cm^{-1} are absent, which indicates that the complex contains no ammonia. Thus, the structure of the copper complex with **I** can be described by the following formula:

$$Cu(NH_3)^{2+}_{4(a)} + 2\,C_{10}H_{21}CONHNEt_{2(o)}$$

$$\rightleftarrows Cu(C_{10}H_{21}CONNEt_2)_{2(o)} + 2\,NH^+_{4(a)} + 2\,NH_{3(a)}.$$

The extraction of Cu(II) with **I** from ammonia solutions can be described by the equation

The extraction isotherm is shown in Fig. 4. Its steep ascent suggests the efficiency of **I** as a Cu(II) extractant. The capacity for Cu(II) of a 2.5×10^{-3} M solution of the reagent in hexane is 1.13×10^{-3} M, which is close to limiting saturation of the organic phase at the ratio [Cu(II)]:[**I**] = 1:2.

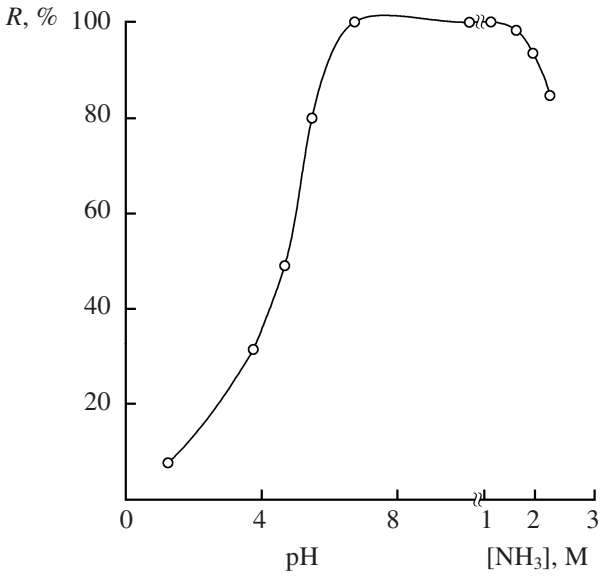


Fig. 1. Degree R of copper recovery from a $CuSO_4$ solution with a solution of **I** in hexane as a function of the solution acidity. $C_{\mathbf{I}}$ 2.5×10^{-2} M, $C(CuSO_4)$ 5×10^{-3} M; V_o:V_a 1:10; τ 3 min.

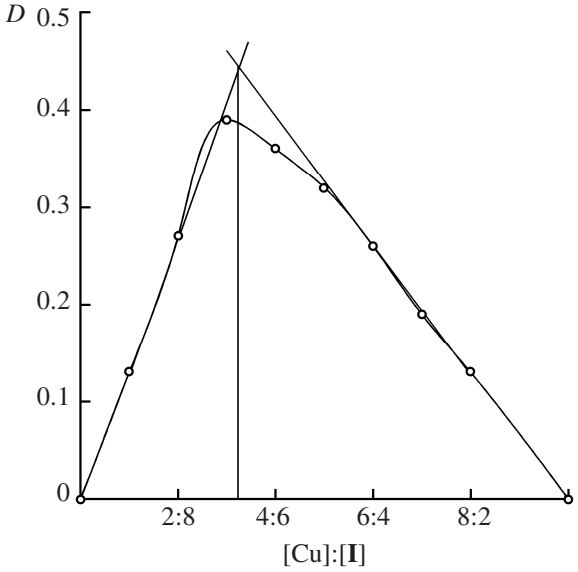


Fig. 2. Isomolar series in the extraction of copper from a $CuSO_4$ solution with a solution of **I** in hexane. $C(CuSO_4)$ = $C_{\mathbf{I}}$ = 0.01 M; V_o:V_a 1:1; λ 440 nm; l 1 cm; $C(NH_3)$ 0.2 M; τ 3 min.

Because copper-containing ammonia solutions usually contain ammonium salts, we examined their effect on the extraction of Cu(II). Data illustrating the effect of NH_4Cl and $(NH_4)_2SO_4$ on the extraction of Cu (II) with **I** from ammonia solution are given in Table 1. It can be seen that these salts suppress the extraction.

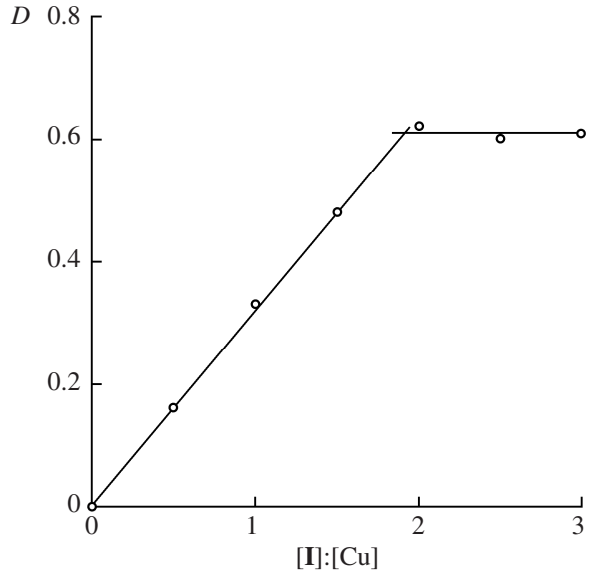


Fig. 3. Method of molar ratios in the extraction of copper from a $CuSO_4$ solution with a solution of **I** in hexane. $CCuSO_4$ 2.5×10^{-3} M; CNH_3 0.2 M; I 0.1 (KCl); V_o:V_a 1:2; λ 440 nm; l 1 cm; τ 3 min.

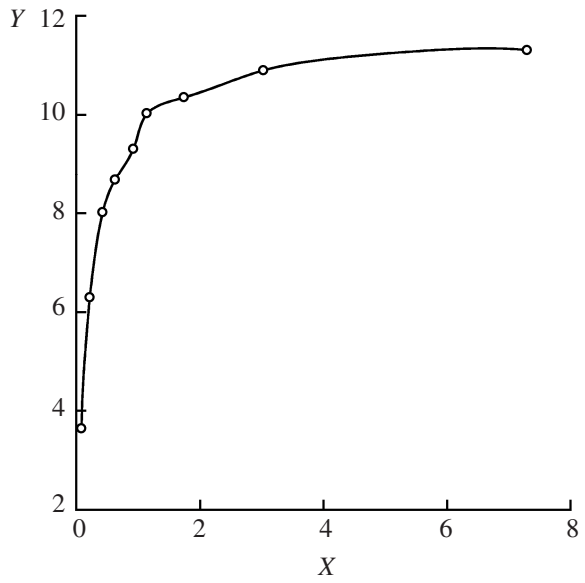


Fig. 4. Isotherm of copper extraction from a $CuSO_4$ solution with a 2.5×10^{-3} M solution of **I** in hexane. V_o:V_a 1:1; CNH_3 0.5 M; I 0.1 (KCl). (X, Y) [Cu(II)] in the aqueous and organic phases, respectively, $\times10^4$ M.

Table 1. Influence of NH_4Cl and $(NH_4)_2SO_4$ on the degree of extraction R of Cu(II) with **I**. $C_{Cu(II)}$ 5×10^{-3} M; C_I 2.5×10^{-2} M; V_o:V_a 1:10

NH_4Cl			$(NH_4)_2SO_4$		
$C(NH_4)Cl$, M	R, % (0.1 M NH_3)	R, % (1 M NH_3)	$C(NH_4)_2SO_4$, M	R, % (0.1 M NH_3)	R, % (1 M NH_3)
0	100	98	0	100	98
0.05		77.6	0.05		34
0.1		65.3	0.1	75.2	1.2
0.2	91.9	16.1	0.2	42.1	
0.3	56.8	14.5			
0.5	32	7.5	0.5	6.9	

The degree of Cu(II) recovery decreases with an increase in the concentration of not only ammonium salts but also of ammonia. Ammonium sulfate suppresses the copper extraction more strongly than does NH_4Cl at equal molar concentration, because the former contains the double amount of ammonium ions.

It was interesting to compare our data on the effect of ammonium salts on the extraction of copper with **I** with the data obtained for *N,N*-diethylhydrazide of an aromatic acid in order to reveal the effect of the structure of the hydrocarbon radical on the process.

We chose *N,N*-diethylbenzhydrazide **II**. The data on the effect of ammonium salts on the extraction of copper with this reagent are given in Table 2. Comparison of Tables 1 and 2 shows that, in the case

Table 2. Influence of NH_4Cl, $(NH_4)_2SO_4$, and $(NH_4)_2CO_3$ on the degree of extraction (R) of Cu(II) with compound **II**. $C_{Cu(II)}$ 5×10^{-3} M; C_{II} 5×10^{-2} M; V_o:V_a 1:2

NH_4Cl			$(NH_4)_2SO_4$			$(NH_4)_2CO_3$		
$C(NH_4Cl)$, M	R, % (0.3 M NH_3)	R, % (0.5 M NH_3)	$C(NH_4)_2SO_4$, M	R, % (0.3 M NH_3)	R, % (0.5 M NH_3)	$C(NH_4)_2CO_3$, M	R, % (0.3 M NH_3)	R, % (0.5 M NH_3)
0	98	97				0	98	97
0.5	87.5	80.4	0.5	79.7	56.3	0.5	80.6	70
1.0	64.6	53.2	1.0	57.8	45.9	0.8	67	48.3

of **II**, the effect of ammonium salts on the extraction of copper is considerably weaker than in the case of **I**. This difference is apparently due to the fact that compound **I** forms a less strong complex with copper.

EXPERIMENTAL

The ^{1}H NMR spectrum was recorded on a Mercuryplus300 spectrometer (300 MHz) from a $CDCl_3$ solution, internal reference HMDS. The IR spectra were taken on a Specord M80 spectrometer. The UV spectra and the optical densities of solutions were measured on a Specord M40 spectrophotometer. The pH values were measured with an I-160M pH meter equipped with glass and silver chloride electrodes.

Conductomeric titration was performed with an OK-102/1 conductometer. Thin-layer chromatography was performed on Silufol plates in the system *m*-xylene–BuOH (2:1). The spots were visualized with phosphomolybdic acid. Elemental analysis was performed with a CHNS-932 analyzer. The Cu(II) concentration in solution was determined photometrically with sodium diethyldithiocarbamate [7].

$$C_{10}H_{21}CONHNH_2 + 2\,EtBr \rightarrow C_{10}H_{21}CONHNEt_2 + 2\,HBr.$$

The reagent was prepared by alkylation of the corresponding hydrazide with alkyl halide [8], using instead of sodium metal easier-to-handle KOH:

Synthesis of I. To a solution of 20 g of undecanoic acid *N,N*-diethylhydrazide in 90 ml of *i*-PrOH, 15 ml of EtBr was added, and then a solution of 11.2 g of KOH in 70 ml of *i*-PrOH was added dropwise with stirring. The mixture was heated until it became neutral (~3 h), after which it was filtered and the solvent was distilled off. Hexane (50 ml) was added to the residue, the mixture was stirred, and the undissolved residue was filtered off. The solvent was distilled off from the mother liquor, and the residue was recrystallized from acetone–water (2:1). Yield of **I** 6 g (23%), mp 68–69°C, R_f 0.64. Found, %: C 70.23; H 12.59; N 10.75. $C_{15}H_{32}N_2O$. Calculated, %: C 70.31; H 12.50; N 10.94. IR spectrum (mineral oil), ν, cm^{-1}: 3224 (N–H); 1662 (amide **I**); 1556 (amide **II**). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.68 s (1H, NH); 2.81 q (*J* 7.2), 2.77 q (*J* 7.2) (3H, CH_2N, *E* isomer); 2.40–2.52 m (2.5H, CH_2N, *Z* isomer, CH_2CO, *E* isomer); 2.14 t (0.5H, CH_2CO, Z isomer, *J* 7.8); 1.57–1.66 m (2H, CH_2CH_2CO); 1.28, 1.24 both br.s (14H, CH_2); 1.09 t (*J* 7.2), 1.06 t (*J* 7.2) (6H, CH_3CH_2N); 0.86 t (3H, CH3, *J* 6.6). Double set of the proton signals from the NH_2 and CH_2CO fragments is due to *Z,E* isomerism arising from hindered rotation around the C–N bond [9]. The presence of two quartets of the CH_2N protons at 2.81 and 2.77 ppm is apparently due to hindered rotation around the N–N bond. The main substance content determined by conductometric titration with an acid [10] was 97%.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Federation President's program for support of leading scientific schools (project no. 2020.03.3) and by the program of the Presidium of the Russian Academy of Sciences "Directed Synthesis of Substances with Preset Properties and Development of Functional Materials Based on Them."

REFERENCES

1. Gusev, V.Yu., Radushev, A.V., and Bogomazova, G.S., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 12, p. 2108.
2. Gusev, V.Yu., Radushev, A.V., Chernova, G.V., Lesnov, A.E., and Karmanov, V.I., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 10, p. 1674.
3. Bernshtein, I.Ya. and Kaminskii, Yu.L., *Spektrofotometricheskii analiz v organicheskoi khimii* (Spectrophotometric Analysis in Organic Chemistry), Leningrad: Khimiya, 1975.
4. Radushev, A.V., Gusev, V.Yu., Batueva, T.D., Bogomazova, G.S., Shabalina, L.S., Tyryshkina, V.N., and Karmanov, V.I., *Zh. Neorg. Khim.*, 2006, vol. 51, no. 12, p. 2096.
5. Machkhoshvili, R.I., *Coordination Compounds of Metals with Hydrazides*, Doctoral Dissertation, Moscow: Inst. of General and Inorganic Chemistry, 1983.
6. Zolotov, Yu.A., Ekstraktsiya *vnutrikompleksnykh soedinenii* (Extraction of Chelates), Moscow: Nauka, 1968.
7. Podchainova, V.N. and Simonova, P.N., *Analiticheskaya khimiya elementov. Med*' (Analytical Chemistry of Elements. Copper), Moscow: Nauka, 1990.
8. Hinman, R.L. and Flores Minerva, C., *J. Org. Chem.*, 1959, vol. 24, May, p. 660.
9. Bouchet, Ph., Elguero, J., Jacquier, R., and Pereillo, J.-M., *Bull. Soc. Chim. Fr.*, 1972, no. 6, p. 2264.
10. Radushev, A.V., Chekanova, L.G, Gusev, V.Yu., and Sazonova, E.A., *Zh. Anal. Khim.*, 2000, vol. 55, no. 5, p. 496.