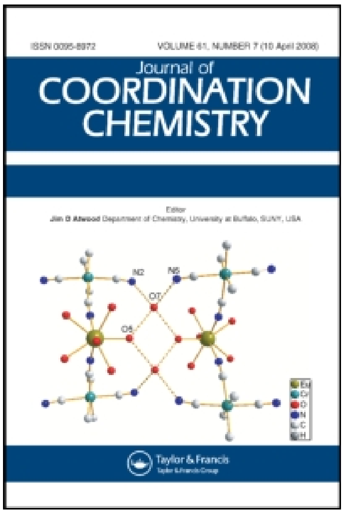

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DIRECT SYNTHESIS OF COPPER DIMETHYLDITHIOCARBAMATE DERIVATIVES: AN OPTIMIZATION USING ULTRASONIC TREATMENT

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A comparison of the synthetic approaches for copper dimethyldithiocarbamate complexes by oxidative and electrochemical dissolution of metallic copper in different non-aqueous solvents is reported. The influence of ultrasound on the synthesized products and on the reaction yields is also studied. The results show the influence of solvent on the structure and on the increase in rate of metal dissolution from simultaneous ultrasonic treatment.

Keywords: Copper; ultrasonic; carbamate; oxidative dissolution

INTRODUCTION

a. Dissolution and Activation of Metals

Oxidative dissolution (OD) of metals in a liquid phase is a type of direct synthesis of coordination and organometallic compounds starting from zero-valent metals and (in)organic ligands. It is a many-electron process, determined by the stabilization of a metal ion in solution. The type of metal and oxidant influence the kinetics of the oxidation process.[1–5]

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In a direct synthesis, the metal atoms could have different oxidation numbers in the formed products (for example, in the complexes of Fe or Cu).[1,3] The peculiarity of direct synthesis is the possibility of stabilization of non-standard oxidation states of transition metals.[3] Thus, together with Cu(I) and Cu(II), diamagnetic complexes of Cu(III),[6] were obtained in the system Cu-DMSO-CI_4-tetramethylthiuram disulfide (TMU). The use of the same system for Pd leads to formation of intermediate complexes of Pd(I).[7] Coordination compounds of Cu(III) and Pd(I) are comparatively rare.[8]

Electrosynthesis (ES) is another approach to direct synthesis,[2,3,5,9–12,13] based on the use of a sacrificial anode or cathode in solutions of substrates. This method has the following advantages: the absence of oxidants or reductants, the possibility of regulation of the process by controlling voltage and current, soft conditions of synthesis and high yields.[3,12] Electrosyntheses with copper as an anode gave coordination and organometallic compounds containing Cu(I), Cu(II) or their mixtures.[14–22]

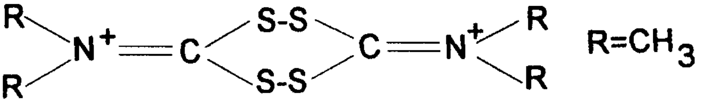
Use of ultrasonic (US) treatment in reactions between bulk metals and organic substrates[23,24] or electrosynthesis[25] is an additional factor, accelerating metal dissolution in non-aqueous solution, eliminating the formed product layer from the metal surface which enhances the posterior dissolution of metal, and, in case of the electrosynthesis, stabilizing the current.[25] Transition metals behave differently under ultrasonic treatment with their resistance depending on the metallic structure and the bond energy in the bulk metal. For example, elemental nickel is more resistant than metallic copper to ultrasonic treatment in reaction between these metals and azomethinic ligands,[24] i.e. the yields of the Ni complexes are considerably less than Cu complexes during the same reaction time.

b. Transition Metal Complexes with Dialkyldithiocarbamate Derivatives

Metal complexes with dialkyldithiocarbamates have been intensively studied and reviewed.[8] Recent publications are: (1) the review of Larin[26] on Ni complexes with thioligands, their study by EPR spectroscopy, and the determination of their magnetic properties, (2) the paper of Sharma *et al.*,[27] on heterocyclic dithiocarbamate complexes of triorganotin(IV) and (3) the work of Chinese authors (Refs. 28–35 and references therein) on X-ray diffraction of transition metal complexes (Ni, Cr) having $Ni^{II}S_4N_2$ or $Cr^{III}S_6$ coordination.

It is known[8,26] that sulfur-containing ligands stabilize unusual oxidation states of metals. Thus, interaction of copper with non-aqueous solutions of TMU in presence of CI_4 and bipy has been studied in detail.[6] The formed compounds have the general formula $[Cu_nI_m(Me_2NSC_2)_l] \cdot A$, where $n = 1-3$, $m = 0, 1, 2, 4$, $l = 1-3, 5$, $A = H_2O$, Cu_2S and CHI_3, containing Cu(I), Cu(II), or rare Cu(III), according to the magnetic data. However, it should be emphasized that diamagnetic properties of the complex are not sufficient to propose an oxidation state +3 for copper, since there are Cu(III) paramagnetic compounds.[7] The Cu^{3+} ion, as Ni^{2+}, has a d^8-configuration.

Oxidation of copper in these systems takes place through successive stages. Thus,[6] one-electron oxidation of Cu^0 by a two-component system (for example, formamide + bipy, DMF(DMSO) + CI_4), one-electron oxidation of copper(I) to copper(II) by the thiuram (or its dication)



and, for the system DMSO + CI_4 + TMU, one-electron oxidation from Cu(II) to Cu(III) takes place with participation of CI_4 or $I_2 + Me_2S{\cdot}I_2$, formed in the system.

Electrochemical dissolution of copper and other metals in non-aqueous solutions (acetone and acetonitrile) of TMU and its analogues was first carried out by Tuck *et al.*[36] Complexes with general formula $M(R_2NCS_2)_n$ are formed in good yields in these conditions. The proposed mechanism of successive complex formation in these systems includes the electrochemical step (1) followed by oxidative addition (2):[36]

$$\begin{aligned} \text{Cathode}: &\quad (R_2NCS_2)_2 + 2e \rightarrow 2(R_2NCS_2)^- \\ \text{Anode}: &\quad (R_2NCS_2)^- + Cu \rightarrow Cu^I(R_2NCS_2) + e \end{aligned} \tag{1}$$

$$Cu(R_2NCS_2) + 0.5(R_2NCS_2)_2 \rightarrow Cu^{II}(R_2NCS_2)_2 \tag{2}$$

Thus, copper can be dissolved chemically,[6] or electrochemically[36] in non-aqueous solutions of TMU. The rates of the processes are reasonable, so this interaction could serve as a *perfect model* to study the influence of simultaneous application of ultrasonic treatment on the syntheses of transition metal complexes in different non-aqueous solutions by several techniques. The present work is devoted to the study of the combination of both conventional chemical and electrochemical dissolution of copper in TMU solutions with simultaneous ultrasonic treatment.

EXPERIMENTAL

Materials

Solvents (acetonitrile, toluene, ethanol, DMSO and DMF) were dried by conventional procedures. TMU and metallic copper (both from Aldrich) were used as supplied. Metals were purified by previous treatment by concentrated HCl to remove the oxide layer. A stream of dry nitrogen was passed through the solutions during the syntheses.

Analysis and Spectroscopy

The metal content was determined by atomic absorption spectroscopy. Infrared spectra were recorded on Perkin-Elmer equipment.

Oxidative Dissolution of Copper

Sheets of copper (1 g) were placed into 100 mL of the TMU solutions during 2 h with weak agitation (the same velocity in all cases). The obtained products were filtered, washed several times by small amounts of dried acetonitrile and dried in air. The experimental conditions of the syntheses are presented in Table I.

Electrochemical Dissolution of Copper

The electrochemical synthesis was carried out according to the technique described by Tuck *et al.*[36] The electrochemical cell was a 100 mL tall-form

TABLE I Experimental conditions for the oxidative and electrochemical dissolution of copper in non-aqueous solutions of TMU

Exper.		*TMU* (g)	*Solvent*	*Use of ultrasound*	*Voltage,*[c] (V)
Ch.[a]	*El.*[b]			*Ch. or El.*	*El.*
A	I	1.25	AN	–	37
B	J	1.25	AN	+	33
C	K	1.25	EtOH+tol.	–	28
D	L	1.25	EtOH+tol.	+	31
E	M	1.30	DMF	–	35
F	N	1.30	DMF	+	33
G	O	1.30	DMSO	–	25
H	P	1.30	DMSO	+	29

[a]Chemical synthesis (oxidative dissolution); [b]Electrochemical synthesis; [c]To produce initial current of 20 mA. In all experiments: Copper, 1 g ($mCu_{init.}$); solvent volume, 100 mL; Agitation, 40 rev/min. Duration of the experiments was 2 h.

beaker. The anode was a copper sheet (1 g) and the cathode was a platinum foil. The electrolytic process was applied during 2 h in each case. n-Bu_4NBr ($\sim$0.05 g) was used as the supporting electrolyte for acetonitrile and EtOH–toluene solutions. The experimental conditions are presented in Table I. The isolated products were treated as described above.

Application of Ultrasound

The simultaneous ultrasonic treatment of solutions of TMU using a weak source of ultrasound (ultrasonic cleaner BRANSONIC 12) was made during the synthetic processes (Table I). Stronger sources of ultrasound were not used to prevent too rapid metal dissolution, turbulent processes and superheating of the reaction zone.

RESULTS AND DISCUSSION

As reported in Tables I and II, the brown and black products were obtained by oxidative and electrochemical dissolution of metallic copper in non-aqueous solvents of TMU. The complexes are stable until 260–325°C, then melt with partial decomposition.

TABLE II Results obtained in the syntheses

Exper.	*Solid*		*Cu* (f/c)[a] (%)	$mCu_{diss.}$, (g)	$mCu_{diss.}/mCu_{init.}$ (× 100%)
	Color	*m.p.* (°C)			
A	Brown	262	20.31/20.91	0.040	4.0
B	Brown	265	20.42/20.91	0.123	12.3
C	Brown	260	19.98/20.91	0.048	4.8
D	Brown	263	20.17/20.91	0.149	14.9
E	Black	320	13.62/14.11	0.053	5.3
F	Black	323	13.55/14.11	0.138	13.8
G	Black	327	13.38/13.81	0.045	4.5
H	Black	325	13.40/13.81	0.150	15.0
I	Brown	260	20.17/20.91	0.062	6.2
J	Brown	262	20.03/20.91	0.180	18.0
K	Brown	264	20.14/20.91	0.070	7.0
L	Brown	261	19.90/20.91	0.171	17.1
M	Black	323	13.70/14.11	0.064	6.4
N	Black	325	13.59/14.11	0.175	17.5
O	Black	327	13.29/13.81	0.081	8.1
P	Black	327	13.35/13.81	0.195	19.5

[a] f, found; c, calculated.

According to the elemental analysis data and IR spectra (Table II), no solvated acetonitrile and ethanol were observed in the formed compounds A–L.[37] The IR spectra of these compounds, obtained by chemical electrochemical dissolution of copper, or by combination of both methods with simultaneous ultrasonic treatment, do not significantly differ. The frequencies ν(C–N) 1530–1525 cm^{-1} and ν(C=S) 1251, 1150 and 1049 cm^{-1} are typical for dicarbamate derivatives of Cu(II). The well-known compound $\mathrm{Cu(Me_2NCS_2)_2}$ is formed in these cases.[36]

In the presence of polar, coordinating solvents, DMSO and DMF (their donor numbers are 29.8 and 27, respectively), compounds E–H and M–P with the composition $\mathrm{Cu(Me_2NCS_2)_2 \cdot 2Solv}$ are formed. The characteristic absorption bands of the coordinated solvents are in the IR spectra of synthesized compounds: DMSO – 1450–1400 and 1050 cm^{-1} (ν(S=O)), DMF – 1680 (ν(C=O)) and 1390 cm^{-1} (ν(C–N)).

Destruction of the S–S bonds could take place as a result of the interaction between metallic copper[3,6,36] (as by chemical dissolution of copper and electrochemical cleavage of the S–S bond) and non-aqueous solutions of TMU. Complexes with MS_n coordination could usually be formed as a result of such reactions, for example, electrochemical cleavage of S–S bonds in some Schiff bases.[38] Solvent molecules could also participate as ligands, coordinating to the MS_n kernel, depending on their donor numbers and steric factors.[39]

According to the literature[26,28–35] for analogous complexes having the $\mathrm{MS_4L_2}$ (L – coordinated ligand) coordination it is possible to attribute distorted octahedral structures $\mathrm{Cu(Me_2NCS_2)_2 \cdot 2Solv}$ for these compounds, where the coordination of DMSO or DMF molecules takes place through the oxygen atom. In the case of DMSO, where coordination could take place through an oxygen or a sulfur atom, the decrease in frequency of the S=O band from 1050 cm^{-1} in free DMSO to 1044–1038 cm^{-1} in its coordinated molecule[39–43] confirms oxygen coordination. The magnetic moments for these complexes at room temperature are 1.84 (DMF complex) and 1.71 B.M. (DMSO complex) corresponding to the Cu(II) state.

Comparing the rates of dissolution of copper in the experiments (Cu-solution, Cu-solution-ultrasound, Cu-solution-electrolysis, Cu-solution-electrolysis-ultrasound), the simultaneous ultrasonic treatment accelerates the process considerably (Table II). When both chemical and electrochemical dissolution of metal take place simultaneously, a maximum rate is obtained. It is difficult to evaluate metal weight dissolved only electrochemically however, a significant role of ultrasound in copper dissolution is evident with the major part dissolved due to the ultrasonic action.

Moreover, in some cases without ultrasonic treatment it is necessary to stop the electrolysis periodically in order to remove the formed product from the surface. Use of ultrasonic treatment helps to avoid this problem and to stabilize voltage.

Experiments with various metals and nitrogen- and sulfur-containing ligands without use of ultrasonic treatment indicates that deterioration of electrosynthesis conditions (unstable voltage) depends on the nature of the ligand (and, consequently, on the properties of the formed product on the metal surface) and, less important on the nature of the solvent (acetonitrile, ethanol, methanol or their mixtures with toluene).[25,44,45] Comparing copper and nickel, it has been established that, using the same ligands and solvents, electrochemical dissolution of nickel is more easily carried out (more stable voltage); evidently, this is due to the higher solubility of its complexes in comparison to the corresponding copper compounds. The use of simultaneous ultrasonic treatment permits leveling of such differences between metals such that electrosynthesis can be performed without the difficulties described above.

CONCLUSIONS

The copper dimethyldithiocarbamate complexes have the same standard compositions independent of the synthetic procedure (chemical or electrochemical). On the other hand, tetramethylthiuram disulfide (and, probably, some of its derivatives) and metallic copper could be used as a useful "standard" pair "metal–ligand" in non-aqueous solvents to study the influence of ultrasonic treatment on the oxidative (or electrochemical) dissolution of metals. From the presented results and those reported earlier,[25,44] simultaneous ultrasonic treatment accelerates considerably the rate of metal dissolution; moreover, combination with electrosynthesis improves greatly this relatively new synthetic technique. Thus for it is difficult to establish any quantitative dependence between solvent properties and rate of metal dissolution.

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