Synthesis nano-Cooper via bis-thiourea derivatives

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Abstract

The applications of copper nanoparticles (CuNPs) have generated an interest in recent years due to catalytic and microbial properties. The literature reviewed methods of obtaining CuNPs by chemical techniques can be generalized as the reduction of copper (II) inorganic salts in the presence of surfactants (in 10-30-fold excess) [1]. In present study we present the method for preparation of CuNPs by using the Cu^{2+} complex compounds with ligands (L_1, L_2) containing non-substituted amino groups suitable for the reduction of Cu^{2+} cation. Synthesis of $Cu(L_1)_2$ and $Cu(L_2)_2$ complexes was performed at room temperature. The production of $Cu(L_1)_2$ and $Cu(L_2)_2$ complexes in the reaction mixture is accompanied with formation of a certain amount of CuNPs as it was observed in [2]. Obtained CuNPs were characterized by UV-Vis and IR spectroscopy. The elaborated method allows the synthesis of CuNPs without using additional reducers and surfactants.

Keywords: *Copper nanoparticles*, *Bis-thiourea derivatives*, *5-Amino-1,2,4-triazol-3-thione derivatives, Green technologies*

Introduction

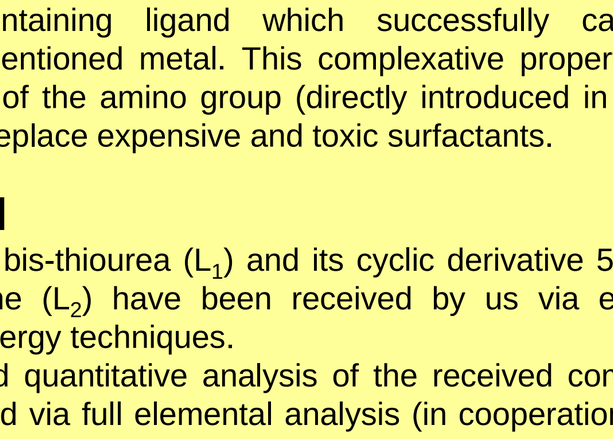
The literature reviewed methods of obtaining CuNPs by chemical techniques can be generalized as the reduction of copper (II) inorganic salts in the presence of a large excess of surfactants. We also have reviewed an information about known triazole-containing ligand which successfully can be used for complexation of mentioned metal. This complexative property, as well as the reductive property of the amino group (directly introduced in the complex), we planned to use to replace expensive and toxic surfactants.

Experimental

The initial benzoyl bis-thiourea (L_1) and its cyclic derivative 5-amino-4-benzoyl-1,2,4-triazol-3-thione (L_2) have been received by us via elaborated original simple and safe-energy techniques.

The qualitative and quantitative analysis of the received compounds (L1) and (L_2) were performed via full elemental analysis (in cooperation of analytical unit of Uzhhorod university), LC/MS – liquid chromatography (Dionex UltiMate 3000 Quarternary Analytical LC System connected with a Varian 310-MS, Preshov university), spectral characteristics: NMR spectra (in cooperation with Institute of Organic Chemistry NASU, Kyiv, Ukraine); infrared spectroscopy (Shimadzu FTIR Prestige 21 with ATR accessory), UV-Vis spectroscopy (Shimadzu UV-1800); the control the purity of the resulting products was carried out via LC/MS – liquid chromatography (Dionex UltiMate 3000 Quarternary Analytical LC System connected with a Varian 310-MS, Presov university).

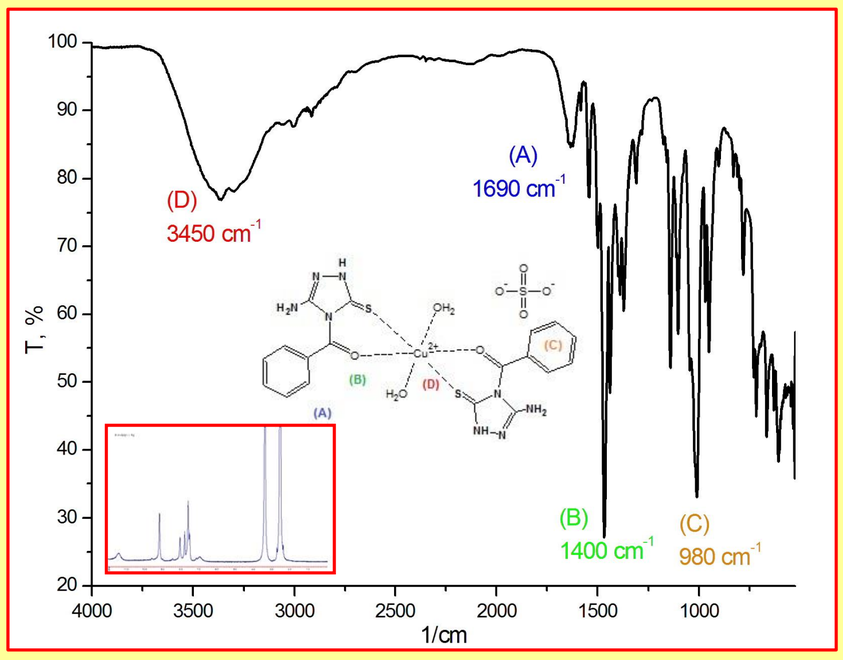
General route to access of cooper nanoparticles



Results and discussion

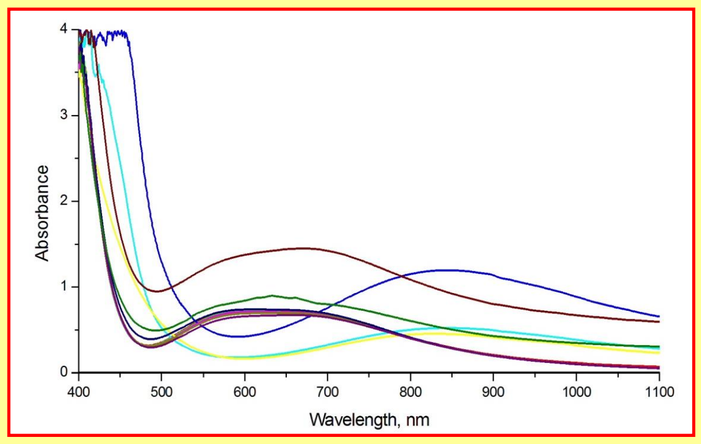
We have elaborated a simple and safe-energy techniques for production of benzoyl bis-thiourea and its cyclic derivative (5-amino-4-benzoyl-1,2,4-triazol-3-thione) starting from thiourea and benzoyl chloride. It must be noted that usage of Rotary Evaporator (instrument: Rotavapor Buchi R-3 for organic solvent's utilization) allows to increase the yields of target compounds. The composition & structure of last were confirmed via full elemental analysis and spectral data.

Investigation of the possibility of complexation of Copper (II) with received triazole (4) and its liner derivative (3) was tested in different medium at room temperature: 1) heterogenic reaction in water; 2) heterogenic reaction in ethyl alcohol; 3) homogenic reaction in system: DMSO – ethyl alcohol (1:2). The homogenic reaction was optimal. Then optimal conditions for these reactions have been found.



As can be seen after spectral evolution the full structure of triazole complex (example on triazole complex with Cooper sulfate) contains not only Cooper and triazole moieties but also residue of correspondent inorganic acid (we have used $CuSO_4$ and $CuCl_2$) and water.

Dynamics of the complexation of Cu(II) & urea (L_1)

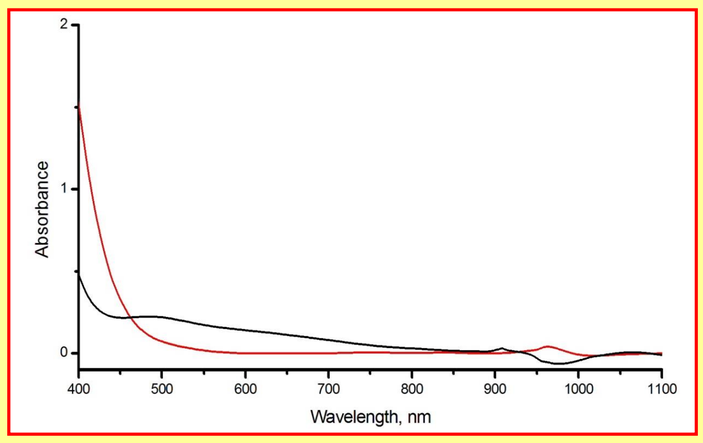


The production of complexes $Cu(L_1)_2$ and $Cu(L_2)_2$ in the reaction mixture is accompanied by formation of a small amount of nanoparticles of copper, which according to the literature UV-data have a size of 2-20 nm. Control has been performed by UV-Vis and IR spectroscopy. It is noted that while maintaining the reaction mixture for several days or with moderate heating latter – the shifting of the equilibrium toward the formation of CuNPs has been observed.

We have attempted to replace surfactants by organic ligands that can be used for complexation of transition metal cations. That is why the behavior of isolated complexes was studied more details. For example as can be seen from UV spectrum the Cooper complex with bis-thiourea (3) gives small amount of Cu-NPs after its mixing in ethanol medium during 1 hour at room temperature.

The same results we have also received after mixing $Cu(L_1)_2$ in reducing environment (Glyoxal) in water medium at room temperature.

As results we can concluded that the elaborated protocol allows the synthesis of the CuNP without adding of reducers and surfactants avoiding long term heating.



Conclusions

In result of above-described research the newest methods of investigation of the implementation of green chemistry approach to the synthesis of Cu-complexes with bis-thiourea and amino-1,2,4-triazol-3-thione has been carried out. The original green technique of CuNPs chemical producing has been elaborated.

Acknowledgment

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References

1. Gawande, M.B., Goswami, A., Felpin, F.-X. et al. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis // Chem Rev.-2016.116, N 6,-P. 3722-3811.

2. J. Khatouri, M. Mostafavi, J. Amblard and J. Belloni. Radiation-induced copper aggregates and oligomers // Chem Phys Lett.-1992.-191, N 4.-P. 351356.