

Electrochemical properties of copper(I) halides and substituted thiourea complexes

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ABSTRACT: The complexes between copper(I) halides and *N,N'*-diphenylthiourea have been investigated by cyclic voltammetry to compare their structure and behaviour in solid state with those in solution. The halides under investigation include chloride, bromide, and iodide. Chloride and bromide complexes did not show the redox reaction, suggesting that they formed the strongest bond with the metal and hence the oxidation was inhibited. In contrast, iodide behaved differently because of the two peaks of halide and trihalide oxidations. One peak disappeared, leaving the other halide-oxidized peak shifted to a more positive voltage due to the bonding with the metal. In solution, all complexes of *N,N'*-diphenylthiourea were derived from the oxidation process and exhibited oxidation potentials shifted to positive values.

KEYWORDS: *N,N'*-diphenylthiourea, cyclic voltammetry, copper(I) complexes

INTRODUCTION

In recent years, there has been increasing interest in the electrochemical behaviour of thiourea (H_2NHNCSH) and substituted thiourea at different metal electrodes due to their various structures and applications as additives for metal electrodeposition and its ability to inhibit the corrosion process^{1–3}. The compounds have been reported to be catalysts for the electroreduction of cations such as zinc⁴ or cadmium⁵. Thiourea and substituted thiourea are able to realize different complexation mechanisms such as chelate and guest-host complexes formation⁶. Generally, catalysts change the kinetics and the mechanism according to the strength of metal-thiol interactions that are favoured by the tautomeric form of thiourea which, in turn, depends on the solution composition and the strength of the electric field at the metal-solution interface⁷. One of the metals of interest in this area is copper which has been widely used in various applications. It was found that the metal can form complexes very well with thiourea and substituted thiourea. Some of those complexes have been synthesized and studied by X-ray diffraction^{8–10}. However, the electrochemical properties have not been thoroughly studied. The results from electrochemical studies can help in understanding the mechanism of their reactions. In this work, the electrochemical properties of complexes between copper(I) halides and *N,N'*-diphenylthiourea (DPTU) (Fig. 1) were investigated by cyclic voltammetry.

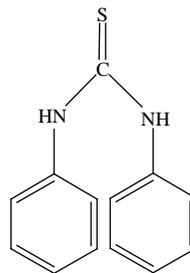


Fig. 1 The structure of the ligand *N,N'*-diphenylthiourea.

MATERIALS AND METHODS

Synthesis of complexes

DPTU was dissolved in acetonitrile at 60 °C. Then CuX ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) was slowly added with continuous stirring for 3 h. Then, the solution was filtered and the filtrate was left at room temperature. Slow evaporation of this solution yielded crystals. They were isolated by suction filtration and washed with acetone before drying in a vacuum desiccator.

Electrochemistry

A Metrohm AUTOLAB PGSTAT 100 with conventional three-electrode electrochemical glass cell was used. A glassy carbon electrode was used as a working electrode, a platinum wire electrode was used as an auxiliary electrode, and a Ag/AgCl electrode was used as a reference electrode. Acetonitrile (CH_3CN) and 0.1 M tetrabutylammonium hexafluorophosphate

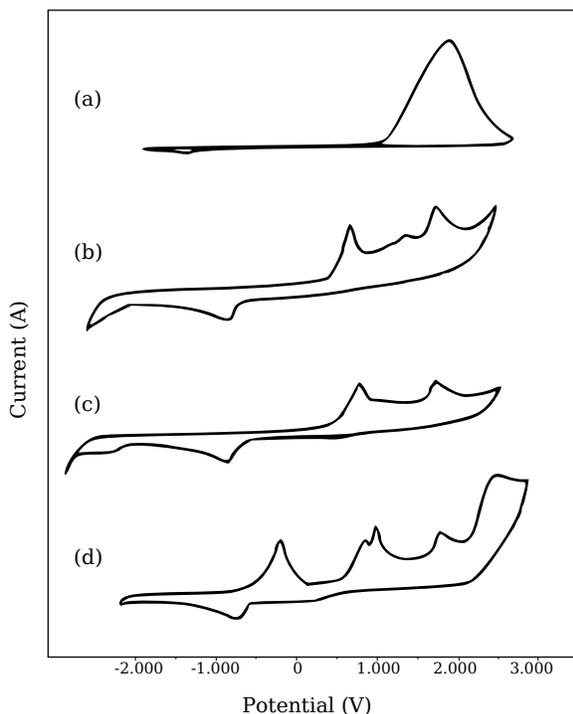


Fig. 2 Cyclic voltammogram of (a) 0.1 M DPTU, (b) 0.01 M $[\text{Cu}(\text{DPTU})_2\text{Cl}]$, (c) 0.01 M $[\text{Cu}(\text{DPTU})_2\text{Br}]$, (d) 0.01 M $[\text{Cu}(\text{DPTU})_2\text{I}]$ in 25 ml CH_3CN solution with 0.1 M TBAP as a supporting electrolyte at the glassy carbon electrode at a scan rate of 100 mV/s.

(TBAP) were used as both a solvent and a supporting electrolyte. The concentration of the complexes was 0.01 M. Nitrogen gas was used to purge the setup to eliminate interfering oxygen. All potentials were reported against Ag/AgCl .

RESULTS AND DISCUSSION

The electrochemical behaviour of N,N' -diphenylthiourea ligand

The cyclic voltammogram of the DPTU ligand reveals a redox reaction in acetonitrile as shown in Fig. 2a. The oxidation peak occurs at $\Delta E_{\text{pa}} = 1.745$ V with $I_{\text{pa}} = 1.5$ mA and the reduction peak occurs at $\Delta E_{\text{pc}} = -1.385$ V with $I_{\text{pc}} = 58.4$ μA against Ag/AgCl . This redox peak is electrochemically quasi-reversible.

The oxidation of DPTU is purely diffusion controlled; it exhibits a linear relationship between peak currents and the square root of the scan rate. In contrast, the reduction of DPTU is not controlled by diffusion and exhibits a nonlinear relationship between peak current and the square root of the scan rate. The redox reaction of DPTU is due to the

oxidation of the amino group, but the high oxidation peak current (I_{pa}) observed may have resulted from an overlap between the peak of sulphur and that of the amino group.

Electrochemical behaviour of DPTU complexes

All complexes exhibited redox peaks corresponding to the copper(I)/(0) process. The shift in potential to more negative values (for reduction) and more positive values (for oxidation) suggests that the redox reactions have a lower tendency to occur. As the copper atom binds two sulphur atoms, the electron density over the metal ion increases¹¹. In the case of $[\text{Cu}(\text{DPTU})_2\text{Cl}]$ and $[\text{Cu}(\text{DPTU})_2\text{Br}]$, the complexes with copper yield a more positive oxidation potential than the complexes with iodide. In addition, the redox peaks of chloride and bromide disappear, suggesting a stronger bond with copper. Intramolecular hydrogen bonds of the type $\text{NH}\cdots\text{Cl}$ type may also be assumed to contribute to stabilizing the Cu(I) complex¹⁰. In the case of the $[\text{Cu}(\text{DPTU})_2\text{I}]$ complex, the reaction peak corresponding to iodide does occur, but the reduction peaks appear incomplete. A plausible explanation could be the lower affinity of Cu(I) for iodide, as the bond distances of copper with iodide are longer than that of copper with chloride or bromide¹². In addition, since the intramolecular hydrogen bond distance of $\text{NH}\cdots\text{I}$ is larger than that of chloride and bromide, the copper(I) complex stability decreases with increasing atomic number of the halide. Such behaviour is in good agreement with the results of electrochemistry. This demonstrates that the iodide in the complex functions to balance the charge. In the cyclic voltammogram the oxidation peak of the DPTU ligand appears in all cases, and the oxidation potential (1.718, 1.758, and 1.738 V) and the shape of peak is varies with the composition of the complex (Figs. 2b–2d).

The complexes of copper(I) halides and substituted thiourea exhibit distinctive electrochemical behaviours. This finding forms an important basis for the description of reactions involving the formation of complexes. The preliminary electrochemical results confer good prospects for the substituted thiourea complexes which could lead to the discovery of new modifiers, such as amine and sulphur, for the determination of the copper ion.

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