Polish J. Chem., **77**, 895–902 (2003) **PHYSICAL CHEMISTRY**

Electrochemical Behaviour of Chloride and Bromide Complexes of Palladium(II) with 4-Amino-6-methyl-3-thio–3,4-dihydro-1,2,4-triazin-5(2H)-one in Dimethylformamide at Glassy Carbon Electrode

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The electrochemical behaviour of palladium(II) complexes of $PdCl_2L$ (I) and $PdBr_2L$ (II) (L = 4-amino-6-methyl-3-thio–3,4-dihydro-1,2,4-triazin-5(2H)-one) has been investigated in dimethylformamide at glassy carbon electrode. Under cyclic voltammetric conditions, complex $PdCl_2L$ is found to undergo a one-electron oxidation at 1.27 V with a prewave, which is similar to oxidation of ligand L. The oxidation of ligand shows an oxidation wave at 1.25 V with EC mechanism. In the chemical reaction following the one electron irreversible oxidation of ligand, the electrochemical-generated cation radical forms a dimer, which is reduced at reverse scan at –0.66 V to reproduce the monomer. Thus, the nature of oxidation of both complexes I and II suggests a ligand-centered oxidation, because their oxidation behaviour is similar to oxidation of ligand L. However, the reduction of both complexes I and II shows a reduction peak at –1.31 V and –1.33 V respectively, which is related to reduction of metal center of complexes, Pd (II) to Pd (I).

Key words: palladium(II), triazine, electrochemistry, oxidation, reduction

Interest in the synthesis and electrochemical behaviour of donor groups attached to thioheterocyclic compounds and their metal complexes has considerably increased in recent years, because such molecules can function as structural and functional models to stabilize the unique oxidation state of particular metal ions. As thio- compounds are easily oxidized and greatly complicate the characterization of their complexes, the behaviour of such compounds as donors in transition metal complexes has not been the subject of such detailed study as the other donor groups. However, an important focus of thioheterocyclic coordination chemistry has been the platinum group metal ions, because of the unusual properties that their complexes demonstrate and their theoretical interest and biological important [1–3]. The coordination chemistry of palladium with these ligands has received a good deal of attention, because of the ability of soft thio ligands to bind very effectively to the soft metal ion and unusual stereochemical, spectroscopic, and electrochemical properties exhibited by thio complexes [4]. Due to its electronic requirement, palladium(II) typically forms square

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planar complexes, which are characterized by a yellow-orange color and limited electrochemical behaviour.

More recently, interest has turned to related systems with nitrogen and sulfur as donor atoms [5,6]. As a continuation of our studies of platinum group metal ions [7,8] and the thiotriazine ligands [9,10], this article describes the electrochemical behaviour of palladium(II) complexes of $PdCl_2L$ (I) and $PdBr_2L$ (II) (L = 4-amino-6-methyl-3-thio-3,4-dihydro-1,2,4-triazin-5(2H)-one), in which these complexes have a similar ligand but different halid atoms.

EXPERIMENTAL

Chemicals and reagents: The two-thiotriazine complexes, $PdCl_2L$ (I) and $PdBr_2L$ (II) were prepared by procedure reported previously [11,12]. Dimethylformamide (DMF), tetrabutylammonium perchlorate (TBAP) and $PdCl_2$ obtained from Merck were used without further purification. Solution concentrations were 10^{-3} M in complexes (yellow-orange color) and ligands and 0.10 M in TBAP as supporting electrolyte, which were stable under such conditions.

Instrumentation: All experiments were carried out under a nitrogen atmosphere at room temperature by using a Metrohm model 746 VA Trace Analyzer Connected to a 747 VA Stand. Controlled potential coulometry was performed using an EG & G PAR model 173 potentiostat/galvanostat. Voltammograms were recorded in DMF by using a glassy carbon electrode (2 mm in diameter) as working electrode that was pre-polished by Al_2O_3 (10 μm gril size), rinsed with doubly distilled water, and repeated scan in the range of potential 1.40 to –1.40 V in 0.10 M $NaHCO_3$.

RESULTS AND DISCUSSION

Electrochemistry of ligand L: The cyclic voltammogram of L shows a main irreversible anodic peak at 1.25 V with a prepeak, which appears at a high scan rate (Fig. 1). Then the negative scans of potential after appearance of anodic peak shows a cathodic peak at –0.66 V, which is related to reduction of oxidation product at positive

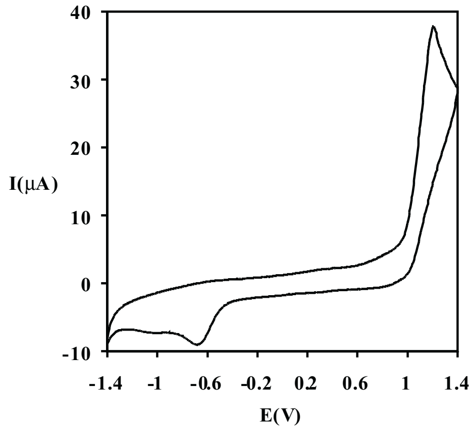

Figure 1. The cyclic voltammogram of ligand L, 10^{-3} M L, scan rates 200 mV s^{-1}, 0.10 M TBAP.

potential. The height of less positive peak increases by increasing concentration and then becomes constant, but the height of the main anodic peak is a linear function of concentration. The above results confirm that the first peak has an adsorptive character, due to adsorption of the product and the second one is diffusion-controlled.

The cyclic voltammograms of ligand L recorded at different scan rates (ν) are shown in Fig. 2a. The linear dependence of the main anodic peak current with $\nu^{1/2}$ shows that the oxidation is diffusion-controlled. The decrease of its current function ($I_a/\nu^{1/2}$) with increasing scan rate (Fig. 2b) shows a coupled chemical reaction, which follows the electron transfer (EC mechanism) [13]. Coulometric experiments at potential more positive than the oxidation peak show an overall number of about 1.0±0.10 electron per one molecule. The EC mechanism occurs quite frequently in organic compounds, which undergoe electrochemical oxidation and produces a reaction species (radicals) that tend to dimerize [13]. The same mechanism for most thiol

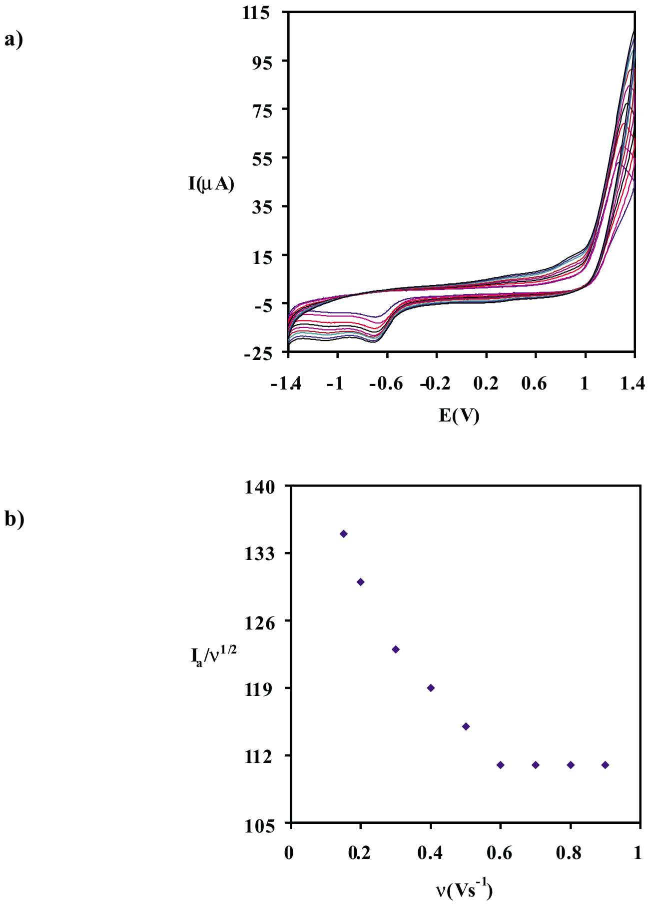

Figure 2. a) The cyclic voltammograms of L at different scan rates: 150, 200, 300, 400, 500, 600, 700, 800 and 900 mV s^{-1}, 10^{-3} M L, 0.10 M TBAP. b) The plot of current function ($I_a/\nu^{1/2}$) *vs.* scan rate for ligand L.

compounds [14] and some thiotriazines [10] was reported, in which the generated radical cations dimerized after one irreversible electron oxidation to form RSSR. Thus, from the above results it can be concluded that the oxidation of ligands L at 1.25 V is due to the oxidation of the ligand to the radical. Then two radicals can dimerize to a dimer in a coupled chemical reaction, which reduces to their monomers at negative scan at –0.66 V, according to the scheme:

$$2RSH \longrightarrow 2RS^{\circ} + 2H^{+} + 2e^{-};$$

$$2RS^{\circ} \longrightarrow RSSR;$$

$$RSSR + 2H^{+} + 2e^{-} \longrightarrow 2RSH$$

In order to obtain information on the rate determining step, b was determined using the following equation, valid for a totally irreversible diffusion controlled process [13]

$$E_P = (b/2) \log \upsilon + \text{const}$$

On the basis of this equation, the slope of E_a *vs* log υ plot is b/2, where b indicates the Tafel slope. The slope of the plot of E_a *vs* log υ for ligand L was found to be 0.0606 V and b = 2(0.0606) V. This slope indicates the transfer coefficient $\alpha = 0.48$ for L.

Electrochemistry of $PdCl_2L$: The cyclic voltammogram of 10^{-3} M $PdCl_2L$ in dimethylformamide containing 0.10 M tetrabutylammonium perchlorate shows a main irreversible anodic peak at 1.27 V with a prepeak at 0.98 V (Fig. 3a). At reverse scan, two cathodic peaks appear at $E_{c1} = –0.73$ and $E_{c2} = –1.31$ V. The height of all cathodic and anodic peaks increases with increasing of concentration, which indicates that the electron transfers are diffusion controlled.

Fig. 3b shows the cyclic voltammogram of complex (I) at a negative scan. As can be seen from the figure, only one cathodic peak is observed at –1.31 V. Two anodic peaks at positive potentials are similar to the oxidation of ligand L. The cyclic voltammograms of complex $PdCl_2L$ at different scan rates are shown in Fig. 4a. The current peak is linear with $\nu^{1/2}$ (r = 0.99). The decreasing anodic current function ($I_a/\nu^{1/2}$) with increasing scan rate (Fig. 4b) indicates the EC mechanism similar to ligand L. Coulometry at potential more positive than the anodic wave shows one electron oxidation per one molecule. Recording the cyclic voltammograms after coulometry shows a decreasing anodic current at 1.27 V and an increasing cathodic peak at –0.73 V, which is due to reduction of the dimer to the monomer. Thus, from the above results it can be concluded that the oxidation of complex (I) at positive potential is a ligand-centered reaction.

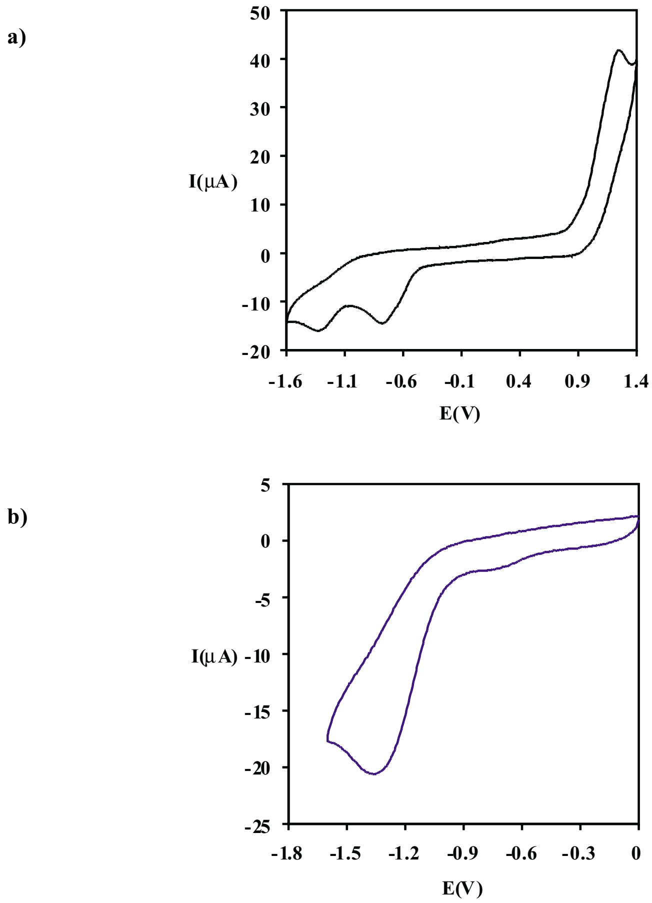

Figure 3. a) The cyclic voltammogram of complex (I). b) The cyclic voltammogram of complex (I) at negative scan, starting potential from 0.00 V to –1.60 V, 10^{-3} M $PdCl_2L$, 0.10 M TBAP, scan rate 200 mV s^{-1}.

Scanning potential from 0.00 V in cathodic direction shows only one reduction peak at –1.31 V (E_{c2}) (Fig. 3b), which confirms that the first cathodic peak at –0.73 V (E_{c1}) is due to reduction of the product of oxidation peak at 1.27 V. Thus, the more negative cathodic peak potential, E_{c2}, is related to reduction of metal ion, Pd(II). The cyclic voltammogram of $PdCl_2$ at negative potentials shows a broad peak at –1.20 V, which is similar to the reduction peak (E_{c2}) of complex $PdCl_2L$. The cyclic voltammograms of complex at various scan rates also show the linear dependence of cathodic peak with $\nu^{1/2}$. The plot of cathodic current function ($I_{c2}/\upsilon^{1/2}$) *vs* scan rate is independent of scan rate, which shows the electron transfer without any coupled chemical reaction (E mechanism). Coulometry at potentials more negative than this cathodic peak shows one electron reduction per one molecule, in which the height of the peak decreases during the coulometry. The above results show, that the reduction peak at

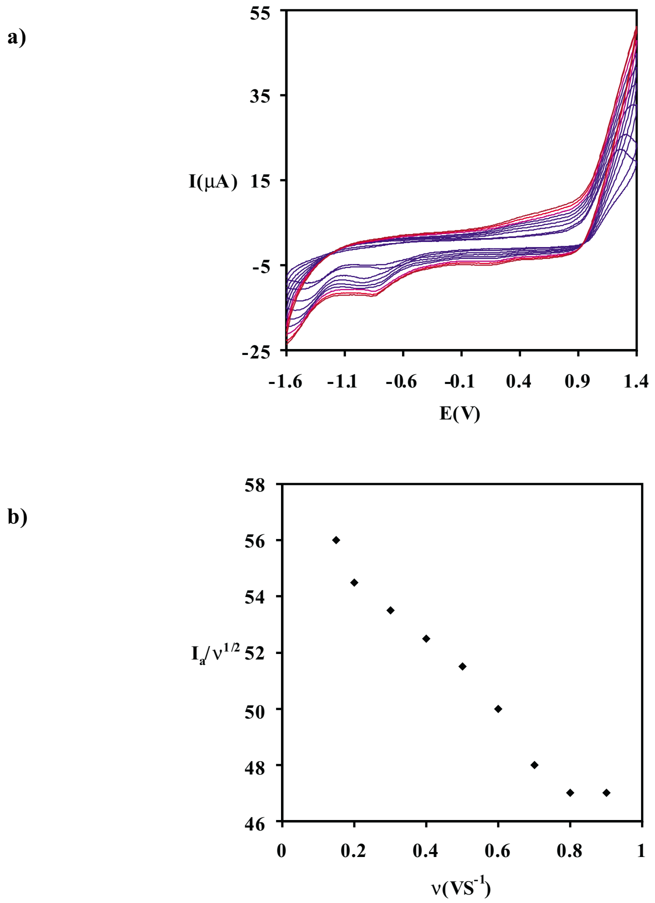

Figure 4. a) The cyclic voltammograms of complex (I) at different scan rates: 150, 200, 300, 400, 500, 600, 700, 800 and 900 mV s^{-1}, 10^{-3} M PdCl$_2$L, 0.10 M TBAP. b) The plot of current function (I$_a$/$\nu^{1/2}$) *vs*. scan rate for complex I.

–1.31 V is due to one electron reduction of Pd (II) to Pd (I). Thus, the reduction of complex (I) is metal-centered both in long-time and short time scale.

Electrochemistry of complex PdBr$_2$L: The cyclic voltammogram of complex PdBr$_2$L is shown in Fig. 5.The cathodic scan shows only one reduction peak at E$_{c2}$ = –1.33 V, and in the reverse anodic scan, an oxidation peak is observed at 1.05 V. Again in reverse cathodic scan, two cathodic peaks in addition to cathodic peak at –1.33 V are observed at –0.26 V (small) and at –0.74 V. The concentration effect again shows that all peaks are diffusion-controlled (linear dependence of I$_p$ on concentration). The decreasing current function with increasing scan rate (EC mechanism) and obtaining one electron per one molecule shows again that the anodic peak is due to oxidation of ligand L. Thus, the oxidation of complex (II), similar to complex (I), is ligand-centered. The cathodic peak at –1.33 V is again related to reduction of Pd (II) to Pd (I). The coulometry at potentials more negative than this cathodic peak shows one electron re-

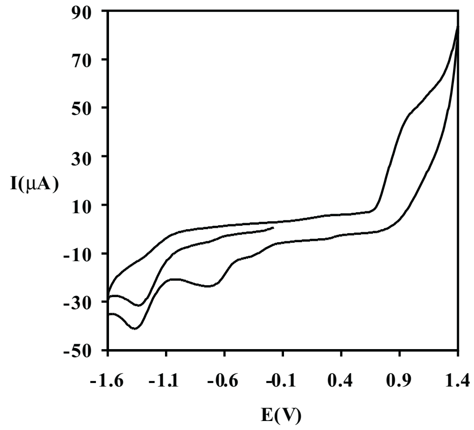

Figure 5. The cyclic voltammogram of complex (II). Starting potential at negative scan from –0.10 V to –1.60 V. Then reversing potential to 1.40 V and reversing potential at negative potential to –1.60 V, 10^{-3} M $PdBr_2L$, 0.10 M TBAP, scan rate 200 mV s^{-1}.

duction per one molecule. The scan rate effect shows that the current function ($I_{c2}/v^{1/2}$) for more negative peak is independent of scan rate (E mechanism). Again the reduction peak at –1.33 V of complex $PdBr_2L$ is metal-centered. The electrochemical data for ligand L and both complexes I and II are given in Table 1.

Table 1. Electrochemical data of complexes and ligand.

Compound	E_a (V)	E_{c1} (V)	E_{c2} (V)
L	+1.25[a]	–0.66	–
$PdCl_2L$	+1.27[a]	–0.73	–1.31
$PdBr_2L$[b]	+1.05	–0.74	–1.33

[a]with a prepeak; [b]with one cathodic peak at –0.26 V.

CONCLUSIONS

From our results we can conclude that ligand L can be oxidized irreversibly by EC mechanism. The cation radical generated at one electron oxidation of ligand can dimerize, in which in a negative scan reduces to its monomer. The oxidation of both complexes of I and II, which differ in its halid atoms, shows one main anodic peak at 1.27 and 1.05 V, with a reduction peak at reverse scan –0.73 and –0.74 V, respectively. Thus, both complexes show a similar oxidation behaviour such as ligand L (ligand-centered oxidation). The more positive oxidation peak of complex I with respect to complex II shows that complex II more easily oxidizes than I, due to the difference of halid ions. It seems that the electron withdrawing of chloride ion is greater than bromide ion, in which the ligand oxidation in complex II occurs at less positive potential. The reduction of both complexes are metal-centered and relates to reduction of Pd(II) to Pd(I). It can be concluded that the kind of halid ion does not affect the reduction of the complex and the presence of thiotriazine ligand stabilizes the oxidation state of Pd(I).

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