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Short Communication

Abrasive Voltammetry of Trinuclear Cobalt-Benzoato Complex with *iso*-Nicotinamide at a Carbon Paste Electrode

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A voltammetric study of $[Co_3(\mu\text{-}bz)_4(bz)_2(inca)_2]$ complex (insoluble in aqueous media) using carbon paste electrode is presented. The electrochemical behaviour of the complex was investigated in various media (sodium hydroxide, sulphuric acid and perchloric acid). In acidic media a reduction of *iso*-nicotinamide ligand was observed whereas in alkaline media a reversible oxidation of its Co(II) centre occurs.

Keywords: cobalt(II) organocomplex compound, cyclic voltammetry, carbon paste electrode, abrasive voltammetry

1. INTRODUCTION

Carbon paste electrodes (CPEs) are inherent part of electroanalytical chemistry due to their unique properties such easy surface renewing or applicability in inorganic, organic and biological analysis [1]. One of the special chapters where CPEs are also involved is the electrochemical analysis of solids [2]. Carbon pastes can easily be modified by addition of a solid compound and then, they are called “modified CPEs”. In their very first work, Kuwana and French [3] used modified CPEs for electrochemical studies of poorly soluble organic compounds. This new field of research expanded after introduction of abrasive stripping voltammetry by Scholtz et al. [4]; such a technique was primarily used for electrochemical studies of inorganic salts [5].

As regards *iso*-nicotinamide (*inca*), it is a pyridine derivative containing an amido group in the γ-position and, as known, it meets pharmaceutical importance since it possesses antitubercular, antipyretic and antibacterial activity. However, metal complexes of such biologically important ligands are sometimes more effective than free ligands and thus, their mixed salts are often applied in pharmaceutical preparations [6-8]. For example, electrochemical behaviour of the cobalt dipicolinate complexes with *iso*-nicotinamide in non aqueous solution of dimethylsulfoxide was studied [9].

Recently, a title compound – trinuclear cobalt-benzoato complex with *iso*-nicotinamide, $[Co_3(\mu\text{-}bz)_4(bz)_2(inca)_2]$ (where *bz* means benzoate; for its molecular structure see Fig. 1) – was synthesized and subjected to its structural, spectral and magnetic studies [10]. In this contribution, abrasive voltammetry at CPEs was used to complete the overall characterization of the compound.

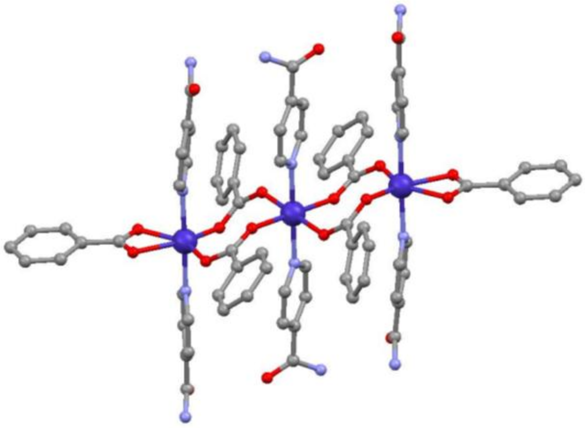

Figure 1. Molecular structure of $[Co_3(\mu\text{-}bz)_4(bz)_2(inca)_2]$. For clarity, hydrogen atoms are omitted.

2. EXPERIMENTAL

2.1. Chemical and Reagents

All chemicals used in this work were of analytical grade (Merck or Sigma Aldrich). Stock solutions of perchloric or sulphuric acids as well as sodium hydroxide were used as supporting electrolytes. Before use, they were diluted appropriately.

2.2. Apparatus and Working Electrodes

All measurements were performed with a computer-controlled electrochemical analyser (model PGSTAT 30; Metrohm Autolab, Utrecht) operated via the NOVA 1.8 software (ibid). A three-electrode cell consisting of a working (CPE), reference (Ag/AgCl/3 M KCl) and counter (Pt plate) electrodes was used.

Concerning working electrodes, the bare carbon paste one was prepared by mixing 0.375 g of graphite powder (product "CR-5", with average particle size of 5μm; Maziva/Týn nad Vltavou) and 0.125 g of paraffin oil (Merck); the mixture obtained was thoroughly homogenized. The resultant carbon paste was packed into a piston-driven electrode holder [11]. The modified CPE was prepared in the same way as the previous electrode, the only difference was that 50 mg of the studied cobalt organocomplex were added. The electrode surface was renewed by smoothing on wet filter paper or before starting a new set of experiments. For comparative measurements in non-aqueous media, a glassy carbon disc (2 mm in diameter) was used.

3. RESULTS AND DISCUSSION

Electrochemical behaviour of the [Co_3(μ-*bz*)$_4$(*bz*)$_2$(*inca*)$_2$] complex in aqueous media was studied by cyclic voltammetry. Since the complex is not soluble in water, it was mixed with the carbon paste material which enabled to study its redox behaviour in solid state at supporting electrolytes.

In acidic media ($HClO_4$), the only redox process observed was an irreversible reduction of the *iso*-nicotinamide ligand in the complex at -0.871 V (see Fig. 2). Measurements were always compared with cyclic voltammograms of 1 mM *iso*-nicotinamide solution in the same supporting electrolyte using a bare CPE, and the irreversible reduction peak at -0.867 V of the same shape as in case of the complex was observed; it should be mentioned that such reduction of *iso*-nicotinamide was already described in detail [12]. Furthermore, the complex was subjected to a test in 0.1 M H_2SO_4 in which a reduction peak at -0.764 V was observed again. The slight shift (about 100 mV) of the peak potential towards more positive potential can be attributed to protonation of the ligand which plays a key role in its reduction mechanism. Moreover, the peak potential was also influenced by the scan rate, when the polarization speed varied from 20 – to 500 mV s^{-1}); the peak potential was shifted towards more negative values which is typical for kinetically controlled irreversible electrode reactions.

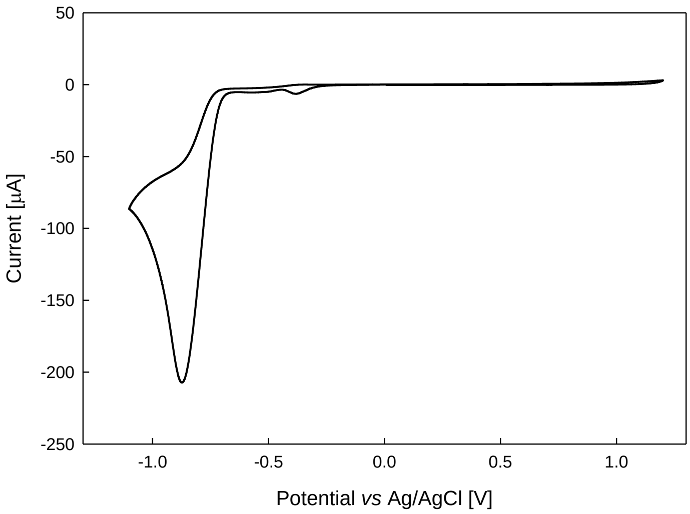

Figure 2. Cyclic voltammogram of [Co_3(μ-*bz*)$_4$(*bz*)$_2$(*inca*)$_2$] in 0.1 M $HClO_4$; scan rate 50 mV s^{-1}; modified CPE.

In alkaline media (0.1 M NaOH), the reduction of *iso*-nicotinamide ligand in the complex compound disappeared and contrarily, the reversible redox process at 0.135 V appeared (Fig. 3). While the reversible one-electron redox process was characterised by anodic-cathodic peak separation of 59 mV (ΔEp = Ep$_a$ – Ep$_c$), in case of the redox reaction of the complex with a ΔEp width = 19 mV was observed. This indicates that three electrons are involved within one redox step, hence it can be expected that probably all three Co(II) centres in the complex studied are reversibly oxidized to Co(III).

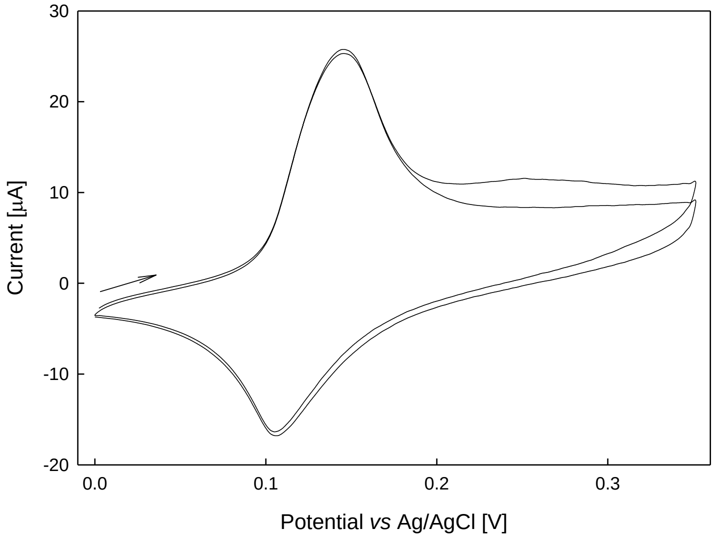

Figure 3. Cyclic voltammogram of [Co_3(μ-*bz*)$_4$(*bz*)$_2$(*inca*)$_2$] in 0.1 M NaOH; scan rate 50 mV s^{-1}; modified CPE.

Marginally, electrochemical behaviour of the title complex compound was studied in non-aqueous media (acetonitrile) using the glassy carbon electrode (GCE).

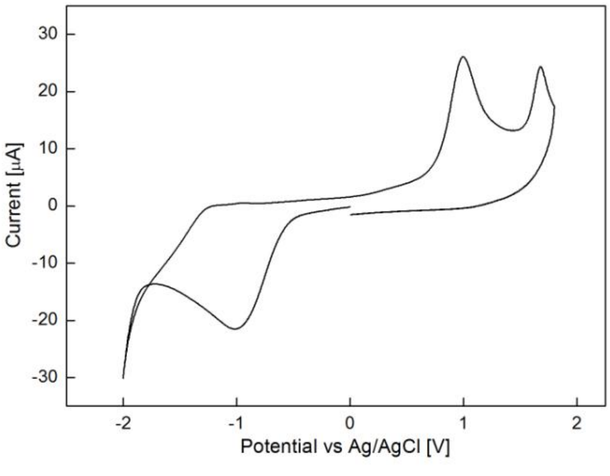

Figure 4. Cyclic voltammogram of [Co_3(μ-*bz*)$_4$(*bz*)$_2$(*inca*)$_2$] in acetonitrile containing 0.1 M $LiClO_4$; scan rate 50 mV s^{-1}; GCE.

As can clearly be seen from Fig. 4, a corresponding CV record in acetonitrile is completely different from that presented above. Two oxidation peaks with E_p = 1.0 V and 1.7 V, and a reduction one at E_p= -0.96 V were found. It can be concluded that within the given potential window, all the redox reactions are irreversible. It should be mentioned that measurements in such media often involve formations of cation or anion radicals. Hence, in our case, it is not clear if the Co(II) centre plays any role in the redox process and so, further discussion would be disputable. Thus, in order to explain the complex behaviour in non-aqueous media, further experiments (e. g., electrochemical studies within series of the complex structure variation) are inevitable.

4. CONCLUSION

As shown in this article, the method of abrasive voltammetry with a carbon paste electrode acquitted well to characterize electrochemical behaviour of the $[Co_3(\mu\text{-}bz)_4(bz)_2(inca)_2]$ complex. It should be pointed out that this approach – a direct modification of the paste with a compound of interest – offers an effective tool for studying metal complexes similar to that presented in this article.

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