Inorganica Chimica Acta, 53 (1981) L201–L203
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Electrochemical Synthesis of the N,N′-ethylenebis(monothioacetylacetoniminato)cobalt(II), copper(II), nickel(II) and zinc(II) Complexes

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Received November 20, 1980

Introduction

The complexes N,N′-ethylenebis(monothioacetylacetoniminato)cobalt(II), copper(II), nickel(II) and zinc(II) ([M{(sacac)$_2$en}] with M = Co, Cu, Ni and Zn) [1, 2] are of interest from many points of view in particular the cobalt compound is a synthetic model of oxygen carriers [3]. Their electrochemical properties [4–6], as well as their structures [7–9] show several interesting features.

With the aim of extending capabilities of electrochemical preparative methods in choice to the chemical ones, this paper deals with the electrochemical synthesis of the above listed complexes.

Experimental

Chemicals and Reagents

Na[ClO$_4$] supporting electrolyte and acetonitrile (MeCN) solvent were prepared and/or purified as described in ref. 4.

The synthesis of the N,N′-ethylenebis(monothioacetylacetonimine) ligand, H$_2$[(sacac)$_2$en], was performed according to ref. 2.

Anhydrous sodium acetate was obtained by heating $NaC_2H_3O_2 \cdot 3H_2O$ (C. Erba) at 120 °C up to constant theoretical weight.

Foils and wires of cobalt, copper, nickel and zinc were Alpha Products.

Apparatus and Procedure

Both voltammetric tests and preparative electrolyses were carried out in an H-shaped cell with anodic and cathodic compartments separated by a sintered glass disk. The reference electrode was always an aqueous saturated calomel electrode (S.C.E.), connected to the cell *via* a salt bridge. Microelectrodes of the different metals were thin wires, partially covered with paraffin to reduce their area. The macroelectrodes used in the preparative electrolyses were foils with an apparent area of about 10 cm^2. The counter electrode was always a mercury pool. The electrolysis cell was equipped with a condenser.

In all the preparative electrolyses the ligand amount was about 32 mg (0.125 mmol) in a volume of 25 cm^3. A stoichiometric amount of sodium acetate was added to promote the deprotonation of the H$_2$[(sacac)$_2$en] species.

The polarizing units were either a PAR Model 170 Electrochemistry System or an Amel potentiostat Model 551. The recording device was a Linseis Model 1800 XY recorder. An Amel integrator Model 558 was used as coulometer.

IR spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer, by employing KBr pellet technique, in the wavenumber range 4000–400 cm^{-1}.

Visible spectra were performed on a Perkin-Elmer Model 575 spectrophotometer, by using 1 cm thickness optical cells.

In order to recover the electrolysis products, MeCN solvent was removed under reduced pressure;

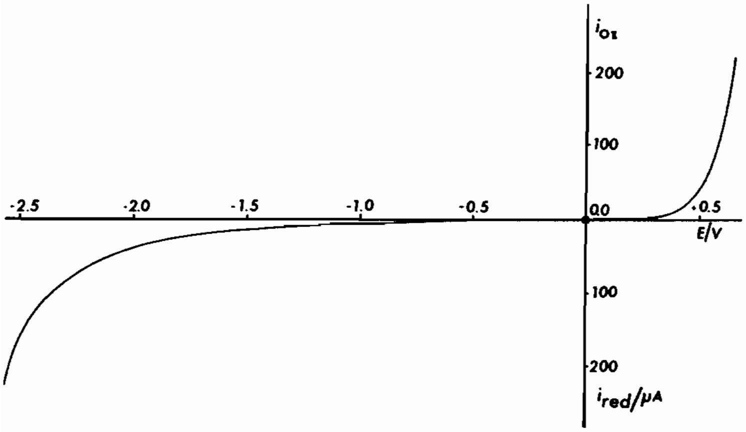

Fig. 1. Single sweep voltammograms showing the available potential range with a cobalt microelectrode in a 0.1 *M* Na[ClO$_4$], MeCN solution. Scan rate 0.2 V s^{-1}; (●) starting potential for both anodic and cathodic scans.

TABLE I. Experimental Conditions for the Electrochemical Syntheses.

Complex	Working Potential (V)	Temperature (°C)	Yield (%)	
			Electrolysis Solution	Recrystallized Solid
$[Co\{(sacac)_2en\}]$	+0.20	60	85 ± 5	70
$[Cu\{(sacac)_2en\}]$	−0.30	75	90 ± 5[a]	75[a]
$[Ni\{(sacac)_2en\}]$	+0.25	60	77 ± 3	63
$[Zn\{(sacac)_2en\}]$	−0.60	75	–	40[a]

[a] By waiting for one hour after completion of the electrolysis.

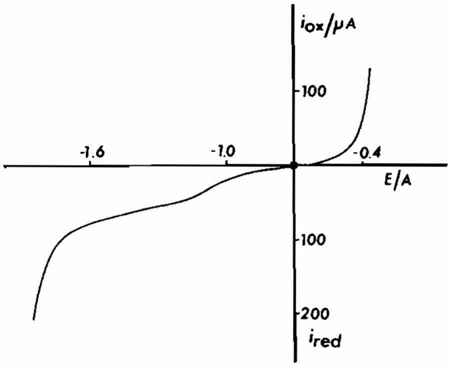

Fig. 2. Single sweep voltammograms showing the available potential range with a copper microelectrode in a 0.1 *M* $Na[ClO_4]$, MeCN solution. Scan rate 0.2 V s^{-1}; (●) starting potential for both anodic and cathodic scans.

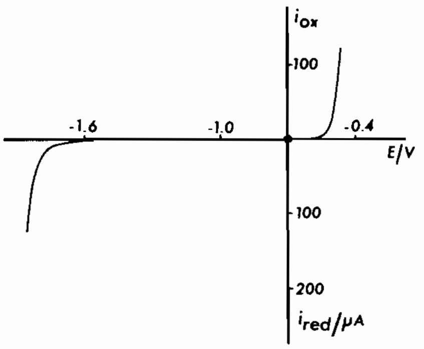

Fig. 3. Single sweep voltammograms showing the available potential range with a zinc microelectrode in a 0.1 *M* $Na[ClO_4]$, MeCN solution. Scan rate 0.2 V s^{-1}; (●) starting potential for both anodic and cathodic scans.

the obtained solid was shaken with anhydrous benzene to separate ionic species. The crude products were recrystallized from acetone.

Results and Discussion

$[Co\{(sacac)_2en\}]$

Figure 1 shows linear sweep voltammograms obtained with a cobalt microelectrode in a MeCN solution containing 0.1 *M* $Na[ClO_4]$ as supporting electrolyte. The addition of both $H_2[(sacac)_2en]$ and $NaC_2H_3O_2$ does not significantly affect this voltammetric picture. Accordingly, by polarizing the cobalt macroelectrode at a potential of +0.2 V up to a consumption of a number of Faradays twice that of ligand moles, the yield in cobalt complex, evaluated just at the end of the electrolysis, is rather low (about 25%); it slowly increases in the long run. In agreement with the experimental conditions followed in the conventional chemical synthesis [1], the electrolyses have been performed at a temperature of about 60 °C. During the electrolyses ultrapure argon is bubbled through, owing to the very high reactivity of $[Co\{(sacac)_2en\}]$ towards oxygen. The nature of the forming product has been established on the basis of cyclic voltammograms on electrolyzed solutions [6]. At the end of the electrolyses a first evaluation of the amount of complex formed is accomplished by measuring the height of the anodic peak relative to the oxidation of the complex $[Co\{(sacac)_2en\}]$ recorded with a platinum working microelectrode, and fitting its value on a calibration curve drawn out in the same experimental conditions. The yield results of 85 ± 5% if referred to the starting ligand amount. Quantitative determinations by visible spectrophotometric measurements at a $\lambda = 415$ nm lead to at all coincident results.

By recrystallization the complex is obtained in a yield of 70%. Its nature is checked by IR spectroscopy: the spectrum perfectly overlaps that recorded on the completely characterized product, chemically prepared according to ref. 2.

$[Cu\{(sacac)_2en\}]$, $[Ni\{(sacac)_2en\}]$, $[Zn\{(sacac)_2en\}]$

In Figs. 2 and 3 linear sweep voltammograms recorded with copper and zinc microelectrodes in

$Na[ClO_4]$ 0.1 *M*, MeCN solution, are shown. The corresponding voltammogram with a nickel electrode has been already reported in literature [10].

Also in these cases the voltammetric pictures are almost unaffected by the addition to the solution of $H_2[(sacac)_2en]$ and/or $NaC_2H_3O_2$.

By anodizing the macroelectrodes at room temperature in the presence of free ligand and acetate, only a very small amount of the complexes is formed, even on waiting some time after the end of the electrolyses; the reaction takes place only by heating the solutions. In Table I the operative conditions for the synthesis of all the studied complexes are reported. In particular, the synthesis is more difficult for copper and zinc complexes: after the completion of the electrolysis carried out at 75 °C, the solution has to be maintained at this temperature for about one hour. On the other hand, the nickel complex forms, with an high yield, just during the electrolyses performed at 60 °C.

It should be noted that the yield in zinc complex formed in solution has been not evaluated, as by UV-visible spectra no reliable measurement on this compound can be made in the presence of a comparable amount of free ligand. Analogously, the presence of free ligand does not allow the performing of any voltammetric determinations, because of electrode poisoning leading to irreproducible responses.

In conclusion, the proposed electrochemical synthesis method is a notably valuable one in the case of the cobalt complex, in view of the high yield obtained; for the other complexes the validity of the method is at least comparable with that of the chemical one.

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