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TECHNICAL NOTE

*Electrolytic preparation of an isomer pair of cobalt (III) mixed complexes**

L. CAMPANELLA AND V. CARUNCHIO

Institute of Analytical Chemistry, University, Rome, Italy

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The electrolytic preparation of some coordination compounds of cobalt (III), such as the amino-, sulphato- and acetato-complexes, had already been described [1-5]: the presence of the ligand in the electrolysed solution stabilizes the +3 oxidation state of cobalt, which is generated anodically. All the cobalt (III) complexes prepared up to date by electrochemical methods contain various numbers of the same ligand group, without having regard to the coordinated water molecules. In this note we deal with the electrolytic preparation of two mixed complexes of cobalt (III), *cis*- and *trans*-[Co en_2 $(OCOCH_3)_2]ClO_4$, where en = ethylenediamine.

The oxidation was performed in a cell with the anode and cathode compartments separated by a porous fritted disk and an agar-$NaNO_3$ layer. The electrodes were in turn (1) both of platinum, (2) a platinum cathode and a cobalt anode (supplied by 'Johnson & Matthey, London', as spectrographically pure: Fe 5 ppm, Si 5 ppm, Mg 5 ppm, Al 1 ppm, Ca 1 ppm, Cu 1 ppm, Ag 1 ppm), (3) both of graphite. The catholyte was always 0·1 M $HClO_4$ solution. The anolyte varied according to the used electrodes: in the cases (1) and (3), it was a solution containing cobalt (II) perchlorate, ethylenediamine and acetic acid, whilst in case (2) cobalt (II) perchlorate was absent, since cobalt (III) was generated directly from the cobalt anode.

The operating value of the anodic potential was determined following an examination of the appropriate polarization curves. The experiments were performed at 25 or 60°C, depending on which geometrical isomer had to be prepared [6]. Immediately after the anodic oxidation, the electrolysed solutions were analysed by visible spectrophotometry and polarography based on the different behaviour of cobalt compounds according to the oxidation state and the isomeric configuration [7, 8, 9] and by paper and ion-exchange chromatography by which we showed that it was possible experimentally to differentiate the prepared complexes of cobalt (III) from the compounds of cobalt (II).

Under the same experimental conditions, the use of a platinum anode gave less satisfactory results, as the solution after electrolysis still contained a percentage of cobalt (II) higher than in the other cases (anode of platinum or of graphite). The higher cobalt (III) yield obtained with graphite anodes can presumably be ascribed to the catalytic properties of this material in respect of the oxidation process Co (II)→Co (III) [10]. However, the highest yields were obtained when a cobalt anode was employed. This result may be due to the different anolyte, not containing cobalt (II) perchlorate, in contact with the cobalt anode: also it was observed that, by prolonging the electrolysis time at the same oxidation potential between electrodes of platinum or of graphite, the degree of conversion of cobalt (II) to cobalt (III) could not be increased above a certain limit. This supports the hypothesis

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that, on proceeding electrolysis, the current efficiency of the cobalt oxidation process decreases because of the marked influence of other electrolytic processes, such as water oxidation.

These results can be explained by assuming that the anodic oxidation of cobalt (0) to cobalt (II) and then to cobalt (III) occurs in two steps, the second of which is faster than the first, so that the formation of cobalt (II) complexes is prevented. In addition, the presence of the ligand species inhibits the formation of $[Co\ (H_2O)_6]^{3+}$. Consequently solutions containing the cobalt (III) compounds as predominant species are obtained and the solid compounds which can be crystallized from these solutions are characterized by high purities. When a platinum or a graphite anode is employed, cobalt (II) complexes are already formed in the solution before the oxidation of the central metal; but by operating at more positive potentials and for more prolonged times, very pure compounds can also be obtained with these anode materials. Although the results described above show that the cobalt anode is to be preferred to the other two, nevertheless the low oxygen overpotential on cobalt, the high cost of the metal and the greater amount of electricity needed for the oxidation of cobalt (0) to cobalt (III), can lead one to use graphite electrodes.

The examined solutions were also evaporated to dryness. The isolated compounds, after they were washed with ethanol and successively with ether and dried under aspiration, were characterized by elemental analysis and by the visible spectra of their aqueous solutions, the results of which agreed in indicating as *cis*- and *trans*- $[Co\ en_2\ (OCOCH_3)_2]ClO_4$ the residues of the solutions electrolysed respectively at 25 and 60°C. Elemental analysis: *cis*-isomer, found %: Co 15·0, C 24·0, H 5·9, N 14·8—calculated %: Co 14·8, C 24·2, H 5·5, N 14·1; *trans*-isomer, found %: Co 15·1, C 24·0, H 5·2, N 14·5—calculated, as for *cis*.

In conclusion, the described electrochemical method allows us to prepare *cis*- and *trans*- $[Co\ en_2\ (OCOCH_3)_2]ClO_4$ with better yields and in shorter times than the usual methods. It must be emphasized that the obtained compounds are characterized by degrees of high purity that are directly related to the nature of the preparation technique, which is based on a direct synthesis rather than on a substitution reaction, as in most chemical methods.

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