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# Preparation and Characterization of Cobalt(III)Bipyridine and Phenanthroline Complexes

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In connection with the studies carried out in this laboratory on solid–solid thermal reactions [1–2], outer-sphere complexes [3], resolution of racemic compounds [4], we undertook the preparation of the following series of complexes: [Co(AA)$_3$]X$_3$, [Co(AA)$_2$(BB)]X$_3$ and [Co(AA)(BB)$_2$]X$_3$, were AA = *o*-phenanthroline (*o*-phen) or 2,2′-bipyridine (bipy); BB = ethylenediamine (en); X = Cl$^-$, NO$_3^-$. For these experiments, the compounds have to be chromatographically pure and, for the thermal reactions, in the chloride and nitrate forms.

The coordination complexes [Co(bipy)$_2$(en)]Cl$_3$, [Co(bipy)$_2$(en)](NO$_3$)$_3$ and [Co(*o*-phen)$_3$](NO$_3$)$_3$ apparently have not been previously reported. We report here the synthesis and characterization of these complexes.

Furthermore, although several synthetic routes to prepare [Co(*o*-phen)$_3$]Cl$_3$ [5–6], [Co(bipy)$_3$]Cl$_3$ [6–8], [Co(*o*-phen)$_2$(en)]Cl$_3$ [9] and [Co(bipy)(en)$_2$]Cl$_3$ [3] have been reported, in our experience, yield and purity by these methods are often unsatisfactory. In this paper some new routes of synthesis or some modification to the published methods are proposed. The purity of the prepared complexes was checked by high voltage paper electrophoresis (HVPE) [3] and chromatography (TLC).

## Experimental

High voltage paper electrophoresis and thin layer chromatography separations were carried out as described in previous papers [3, 2].

TLC experiments were performed on precoated silica gel plates (5 × 5 cm) by using sat. aqueous LiCl–EtOH (1:2) as eluent. R$_f$ values found: Co(bipy)$_3^{3+}$, 0.04; Co(bipy)$_2$(en)$^{3+}$, 0.20; *cis*-Co(bipy)$_2$Cl$_2^+$, 0.31; Co(bipy)(en)$_2^{3+}$, 0.60; Co(en)$_3^{3+}$, 0.87; cobalt(II) at the liquid front. Cobalt(II) and the free ligands, *o*-phenanthroline and 2,2′-bipyridine, were detected as previously described [10].

Visible spectra were measured with a Beckman DK-2A spectrophotometer, using 1 cm cells.

### *Preparation of Complexes*

Published methods are used to prepare the following complexes : [Co(*o*-phen)(en)$_2$]Cl$_3$ [3], [Co(en)$_3$]Cl$_3$ [11], *cis*[Co(*o*-phen)$_2$Cl$_2$]Cl [10] and *cis*-[Co(bipy)$_2$Cl$_2$]Cl [7]. [Co(*o*-phen)$_2$Cl$_2$]NO$_3$ and [Co(bipy)$_2$Cl$_2$]NO$_3$ were obtained by dissolving the corresponding chlorides in EtOH and by adding a mixture of conc. HNO$_3$–EtOH (1:4).

### *[Co(bipy)$_2$(en)]Cl$_3$ and [Co(bipy)$_2$(en)](NO$_3$)$_3$*

To a suspension of 2g (0.0039 mol) of *cis*-[Co(bipy)$_2$Cl$_2$]Cl in 10 ml of water ethylenediamine chloridrate (3.5 ml of 10% aqueous solution; 0.0052 mol) was added dropwise with stirring. To the resulting yellow solution, 60–70 ml of EtOH and then about 150 ml of acetone were added until a copious yellow-orange precipitate was obtained. Before filtration, the mixture was stored overnight at about 0 °C. At least one recrystallization from H$_2$O–EtOH (1:10) was necessary to give a compound free from the possible coproduct, Co(bipy)(en)$_2^{3+}$. Obtained 1.4 g of recrystallized product (62%). For [Co(bipy)$_2$(en)]Cl$_3$·2H$_2$O found% (calcd%): Co 10.1 (10.27), C 46.9 (46.05), H 4.67 (4.93), N 14.4 (14.64).

The [Co(bipy)$_2$(en)](NO$_3$)$_3$ was obtained by dissolving the corresponding chloride (1 g) in 10 ml of water; excess of solid LiNO$_3$ was added. A yellow-orange crystalline precipitate formed immediately, which was filtered off and washed with EtOH and ethyl ether. Yield: 0.98 g (81%).

### *[Co(o-phen)$_3$](NO$_3$)$_3$*

An excess (2 g, 0.01 mol) of *o*-phenanthroline monohydrate was slowly added to a stirred solution of *cis*-[Co(*o*-phen)$_2$Cl$_2$]NO$_3$ (2.8 g; 0.0045 mol) in 150 ml of N,N-dimethylformamide. The solution changed very slowly from violet to yellow; after two days at room temperature, 300 ml of acetone–ethyl ether (10:1) were added. A orange-yellow crystalline precipitate separated which was filtered off and washed with acetone–ethyl ether (5:1), until the washings did not contain free *o*-phenanthroline (test with ferrous chloride). The yield is 2.2 g (65%).

### *[Co(o-phen)$_3$]Cl$_3$ and [Co(bipy)$_3$]Cl$_3$*

2 g (0.0035 mol) of *cis*-[Co(*o*-phen)$_2$Cl$_2$]Cl were dissolved in 10 ml of water by heating for few minutes at 60 °C. To the pink-violet solution excess of *o*-phenanthroline monohydrate (1.6 g, 0.008 mol) was added with stirring and the solution left to cool. During the addition of *o*-phenanthroline the solution turned to yellow. Acetone was added and an oil was

obtained. A crystalline precipitate was obtained by "grinding" the oil in a mortar with acetone. The precipitate was washed a several times with acetone until the washings did not contain free *o*-phenanthroline. The yield is 2.1 g (75%).

$[Co(bipy)_3]Cl_3$ was prepared in a similar manner to the corresponding *tris*-phenanthroline complex above described (85%).

*$[Co(o\text{-}phen)_2(en)]Cl_3$*

The method of Palade [9] modified as follows, was used to prepare this complex. A 1.87 g (0.0032 mol) amount of *cis*-$[Co(o\text{-}phen)_2Cl_2]Cl$ was suspended in EtOH (100 ml) at room temperature and the mixture vigorously stirred. The complex slowly dissolved during the reaction with 16.5 ml of 1% in EtOH ethylenediamine (0.0031 mol) and the addition of 50 ml of abs. EtOH in 10 ml portions. A yellow crystalline precipitate of $[Co(o\text{-}phen)_2(en)]Cl_3$ separated and was filtered off, then washed very carefully and for many times with abs. EtOH and ethyl ether. (Yield: 1.3 g; 71%).

*$[Co(bipy)(en)_2]Cl_3$*

4.28 g (0.014 mol) of *cis*-$[Co(en)_2Cl_2]Cl$ and 2.35 g of 2,2'-bipyridine (0.015 mol), dissolved in 20 ml of distilled water, were heated on the water-bath at 100 °C for 30 min. The cooled reddish-yellow solution was treated with 70 ml of EtOH and then stored at 0 °C overnight. A precipitate separated out which was identified by electrophoresis as $[Co(en)_3]Cl_3$. To the mother liquor were added 200 ml of acetone and two hours after a precipitate formed which was filtered off and dried: the electropherogram shows it to be a mixture of the two asymmetric complexes $[Co(bipy)(en)_2]Cl_3$ and $[Co(bipy)_2(en)]Cl_3$. The former complex was obtained by dissolution of the precipitate in 10 ml cold water and reprecipitation with 100 ml EtOH. Yield: 3.96 g (64%).

## Results and Discussion

It was reported [9] that *o*-phenanthroline readily enters the inner coordination sphere of dichloro- or of diaquo-*bis*-(ethylenediamine) complexes of cobalt(III): a rapid substitution of the chloride or aquo groups occurs to give a mixed *bis*-ethylenediamine-phenanthroline complex, $Co(en)_2(o\text{-}phen)^{3+}$. We have found that analogous behaviour is shown by the corresponding $[Co(bipy)_2Cl_2]Cl$: in the presence of ethylenediamine, a similar substitution reaction occurs, to give $[Co(bipy)_2(en)]Cl_3$. Strictly controlled experimental conditions provide a good yield (62%) of a chromatographically pure compound, whose visible spectrum is shown in Fig. 1.

In Fig. 2 an electropherogram of the $[Co(bipy)_3]Cl_3$, $[Co(bipy)_2(en)]Cl_3$, $[Co(bipy)(en)_2]Cl_3$ and $[Co(en)_3]Cl_3$ complexes, alone and in mixture, is shown. As expected, in this case too the sequence of migration is related to the ligands [3] and the synthetized complex by us, $Co(bipy)_2(en)^{3+}$, moves between $Co(bipy)_3^{3+}$ and $Co(bipy)(en)_2^{3+}$. The same sequence was found in TLC, as results from the $R_f$ values reported in the Experimental part.

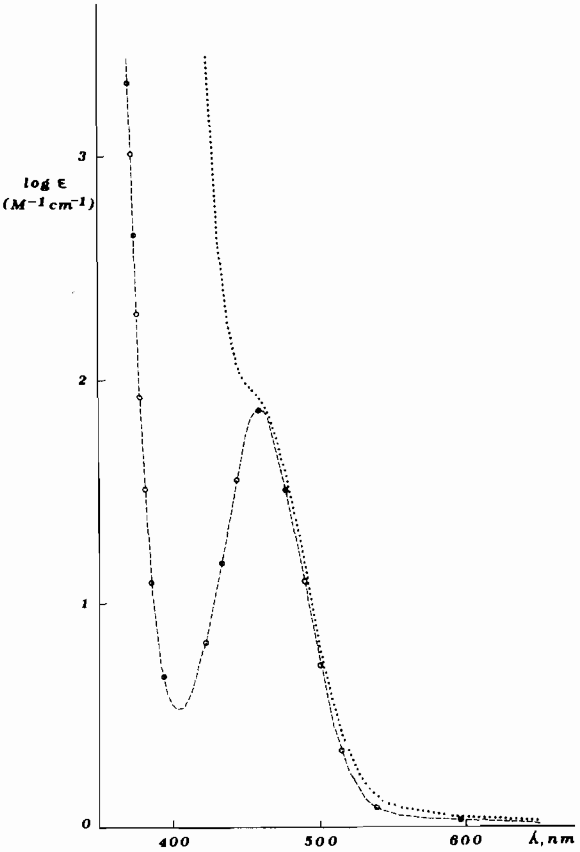

Fig. 1. Absorption spectra in aqueous solution (0.005 *M*) for $[Co(bipy)_2(en)]Cl_3$ (– – – –) and $[Co(o\text{-}phen)_3](NO_3)_3$ (.......).

Different methods are reported for the preparation of $[Co(o\text{-}phen)_3]Cl_3$ as: solid–solid thermal reaction between $[Co(NH_3)_5Cl]Cl_2$ and *o*-phenanthroline hydrate [5]; oxidation, both anodic [6] or by chlorine [5] of the corresponding *tris*-(*o*-phenanthroline)cobalt(II) complex. $[Co(bipy)_3]Cl_3$ was prepared similarly [6–8]. By using in these preparations as starting material *cis*-$[Co(o\text{-}phen)_2Cl_2]Cl$ or *cis*-$[Co(bipy)_2Cl_2]Cl$, high yields and a simple route were available for the synthesis of $[Co(o\text{-}phen)_3]Cl_3$ and $[Co(bipy)_3]Cl_3$, respectively. Attempts to prepare $[Co(o\text{-}phen)_3](NO_3)_3$ from the corresponding chloride by adding dil. $HNO_3$ or $LiNO_3$ in various solvent media, as in the case of many complexes of this type, were unsuccessfull. Good results were achieved following the procedure pointed out for the preparation of $[Co(o\text{-}phen)_3]Cl_3$. *cis*-[Co(*o*-

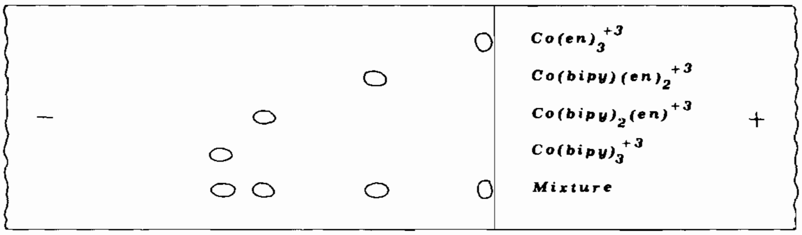

Fig. 2. Paper electropherogram of 2,2′-bipyridine-ethylenediaminecobalt(III) complexes. Paper, Whatman No. 1; Camag high voltage apparatus; electrolyte 0.25 *M* $Na_2SO_4$; 2000 V at 2.5 °C for 30 min.

phen)$_2$Cl$_2$]NO$_3$ resulted not soluble to a suitable extent in many organic solvents. Satisfactory results were obtained by using N,N-dimethylformamide as solvent. In Fig. 1 the absorption spectrum of these complexes is shown. It compared well with the spectrum reported for the corresponding chloride [9].

In the methods of preparation reported here, *cis*-Co(*o*-phen)$_2$Cl$_2^+$ or *cis*-Co(bipy)$_2$Cl$_2^+$ are the starting materials. In our opinion a careful control of the purity for both these complexes is necessary in order to avoid the formation of undesirable byproducts. These dichloro complexes hydrolise readily in aqueous solvents and could be present in the chromatograms as long tails, masking eventually other species. Numerous and different chromatographic systems have been tried. No hydrolysis reaction seemed to occur in saturated aqueous LiCl–EtOH (1:2) and HCl 1N–EtOH (1:5) as solvent.

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