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Note

Thin-layer chromatographic detection of some impurities in cobalt(III) complexes

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In the preparation of *trans*-[Coen₂Cl₂]Cl⁺ (ref. 1), the presence of impurities such as Co²⁺ and Coen₃³⁺ were noted^{2,3}. As this complex is used as a starting material for the preparation of several other complexes, it is necessary to check its purity. It is well known that cobalt(II), in the presence of acetone or ethanol, reacts with CNS⁻ ions to give green-blue complexes with different colours and compositions depending on the Co²⁺ : CNS⁻ ratio⁴.

In this paper, we report the results obtained using an ammonium thiocyanate-water-ethanol mixture as eluent in thin-layer chromatography (TLC). We wanted to see whether, by choosing suitable conditions, it would be possible to detect and estimate roughly the Co²⁺ ions that are present as impurities in some cobalt(III) complexes prepared from a cobalt(II) salt. The following complexes were tested: *trans*-[Coen₂Cl₂]Cl, [Coen₃]Cl₃, [Co(NH₃)₆]Cl₃, [Cotn₃]Cl₃, *cis*-[Cophen₂Cl₂]Cl, [Cophen₃]Cl₃ and [Codyp₃]Cl₃.

In addition, a very simple chromatographic method has been worked out for detecting the unreacted ligands in [Cophen₃]Cl₃ and [Codyp₃]Cl₃ preparations.

EXPERIMENTAL

Preparations

Published methods were used to prepare the complexes: *trans*-[Coen₂Cl₂]Cl (ref. 1), [Coen₃]Cl₃ (ref. 5), [Cotn₃]Cl₃ (ref. 6), [Co(NH₃)₆]Cl₃ (ref. 7), [Cophen₃]Cl₃ (ref. 8) and [Codyp₃]Cl₃ (ref. 9).

The method of Prosperi *et al.*⁸, modified as follows, was used to prepare *cis*-[Cophen₂Cl₂]Cl. A 3.96-g (0.02-mole) amount of 1,10-phenanthroline hydrate was added slowly to a vigorously stirred solution of 2.38 g (0.01 mole) of CoCl₂·6H₂O in 4 ml of 4 N hydrochloric acid. To the pink slurry formed were added activated carbon and, dropwise with constant stirring, 2 ml of 30% hydrogen peroxide solution. The slurry gradually turned pale brown and was grey-violet after about half an hour. After about 4 h the precipitate was washed with portions of 2 N hydrochloric acid

* Abbreviations used: en = ethylenediamine; tn = 1,3-diaminopropane; phen = 1,10-phenanthroline; dyp = α,α' -dipyridyl. In the figures the complexes are abbreviated as follows: [Cophen₃]Cl₃ = phen₃, [Coen₃]Cl₃ = en₃, etc.

until the washings were colourless and then with acetone, in which 1,10-phenanthroline is soluble. A 3.7-g amount of grey-violet product was obtained, corresponding to a yield of *ca.* 60%.

Chromatography

The separations were effected by TLC on 5×10 cm pre-coated silica gel plates (Merck, Darmstadt, G.F.R.) using the following mobile phases: (E_1) ammonium thiocyanate (50 g in 50 ml of water)-ethanol (1:5); (E_2) ammonium thiocyanate (10 g in 50 ml of water)-ethanol (1:5); (E_3) water-ethanol (1:5).

Portions (4–25 μ l) of solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in water, of complexes in ethanol-water or in water, and of 1,10-phenanthroline or α, α' -dipyridyl in ethanol, were applied to the plates and development was carried out in small glass jars (10 cm high, diameter 7 cm) at room temperature. Ascending development to a height of 6–7 cm was normally complete in 20–25 min. The spot corresponding to cobalt(II) is easily visible, owing to its blue colour. The spots corresponding to the complexes or to 1,10-phenanthroline and α, α' -dipyridyl were detected by spraying with ammonium sulphide or iron(II) sulphate solution, respectively.

RESULTS AND DISCUSSION

Sensitivity of the reaction

On a thin layer of pre-coated silica gel, solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were chromatographed with aqueous solutions of ammonium thiocyanate and ethanol in different proportions. The best results were obtained with eluent E_1 . With this eluent, after a few minutes of elution, a blue spot appeared, which moved near to the solvent front. In Fig. 1 the results obtained by chromatography of 4- μ l samples of 10^{-3} , $8 \cdot 10^{-4}$, $2 \cdot 10^{-4}$ and 10^{-4} M Co^{2+} solution are shown; the size of the spot depends on the amount of Co^{2+} present.

The lowest cobalt concentration detectable was $2 \cdot 10^{-4}$ M; the sensitivity limit was 0.05 μ g and the dilution limit 1:100,000. This sensitivity limit is about 10 times greater than that reported by Feigl⁴.

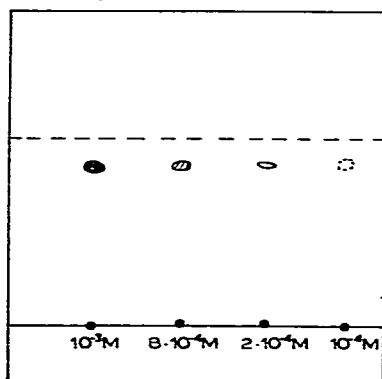


Fig. 1. Chromatograms of Co^{2+} solutions (4 μ l) at decreasing concentrations (mole/l). Eluent: E_1 . The shading indicates the intensity of the spots, from right to left: very weak; readily visible; strong; very strong.

trans-[Coen₂Cl₂]Cl

In order to decrease the possibility of hydrolysis reactions, *trans*-[Coen₂Cl₂]Cl was dissolved in ethanol-water (5:1) and fresh solutions were always employed. Preliminary experiments showed that, under our chromatographic conditions, no reaction occurs between the complex and CNS⁻ ions, although Coen₂(NCS)₂⁺ is prepared from *trans*-Coen₂Cl₂⁺ (ref. 10). This is probably due to the temperature used in the chromatographic run (about 20°) and to the short time of development. With eluent E₁, the complex gave an elonged green spot, which started from the point of application. The separation from the spot corresponding to Co²⁺ was excellent (Fig. 2).

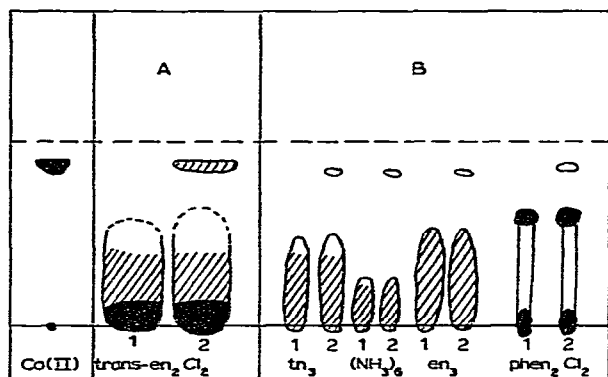


Fig. 2. Chromatograms of some cobalt(III) complexes: (1) pure compound; (2) pure compound + Co²⁺. Shading as in Fig. 1. (A) 20 μ l of a solution $4 \cdot 10^{-2}$ M for the complex and $4 \cdot 10^{-5}$ M for cobalt (II); eluent, E₁. (B) 5 μ l of a solution of 0.05 g in 0.5 ml of water for the complex and $5 \cdot 10^{-4}$ M for cobalt(II); eluent, E₂.

To test the sensitivity of the method, samples of 0.06 g of *trans*-[Coen₂Cl₂]Cl were dissolved in several ethanol-water mixtures (5 ml), each containing from $4 \cdot 10^{-4}$ to $4 \cdot 10^{-5}$ mole of CoCl₂·6H₂O; 20- μ l portions of these solutions were chromatographed as described above. The lowest concentration that could be detected was $4 \cdot 10^{-5}$ M, which corresponds to 1 part of Co(II) in 5000 parts of the complex (*i.e.*, 0.02%).

The method was applied to check the purity of a sample of crude material obtained from the preparation method reported in the literature¹. This sample was chromatographed together with a recrystallized sample of chromatographically pure *trans*-[Coen₂Cl₂]Cl to which had been added a known amount of Co²⁺ ions. From the comparison of the size of the spots corresponding to Co²⁺, the crude material contained about 0.04% of Co²⁺. This does not seem an excessive amount; however, for some physicochemical data, very pure samples were required and this technique was found to be very useful¹¹. Moreover, the importance of trace of impurities in exchange studies has often been reported¹².

[Coen₃]Cl₃, [Cotn₃]Cl₃ and [Co(NH₃)₆]Cl₃

These complexes, chromatographed as described above for *trans*-[Coen₂Cl₂]Cl, did not react noticeably with the eluent. Amounts of 0.05 g of these complexes were

dissolved in 0.5 ml of water and 5 μ l of the solutions obtained were chromatographed with eluent E₂. As shown in Fig. 2, a good separation from cobalt(II) ($5 \cdot 10^{-4}$ M) could be obtained. In this instance the ratio of the concentrations of the complex to that of Co²⁺ is about 3500:1.

cis-[Cophen₂Cl₂]Cl

A 0.025-g amount of this complex was dissolved in 0.5 ml of ethanol-water (5:1) and 5 μ l of the solution obtained were chromatographed with eluent E₂. As shown in Fig. 2, two spots were visible, joined by a tail. The spot near to the point of application is probably due to the starting complex, *cis*-Cophen₂Cl₂⁺, while that with $R_F = 0.61$ probably results from the substitution of chlorine ligands by CNS⁻ ions. This compound could thus be the species Cophen₂(NCS)₂⁺, which in preparative methods is obtained from *cis*-[Cophen₂Cl₂]Cl and potassium thiocyanate¹³.

However, even when this reaction takes place it is still possible to detect Co²⁺. A sample with a complex to Co²⁺ ratio of 3500:1 is shown in Fig. 2.

[Cophen₃]Cl₃ and [Codyp₃]Cl₃

Three 5- μ l portions of a $1.2 \cdot 10^{-1}$ M [Cophen₃]Cl₃ solution to which $4 \cdot 10^{-2}$, $8 \cdot 10^{-2}$ and $2.5 \cdot 10^{-1}$ M CoCl₂·6H₂O had been added were chromatographed with eluent E₁.

The blue spot corresponding to the Co²⁺ ion is not visible in the first chromatogram (Fig. 3), although the amount of Co²⁺ present is about 100 times the sensitivity limit of the Co²⁺-CNS⁻ reaction in an organic solvent. An explanation could be that, in the presence of Co(II) and/or in the eluent used, the [Cophen₃]Cl₃ becomes labile¹²: one molecule of the base, 1,10-phenanthroline, may be freed and may react with Co²⁺ ions, masking the presence of the latter. Chromatography showed the presence of 1,10-phenanthroline in the solution: in the first chromatogram in Fig. 3, a pink spot ($R_F = 0.7$) appeared, presumably due to the reaction between 1,10-phenanthroline and the iron(II) present as an impurity in the pre-coated silica gel layers. On spraying the plate with iron(II) sulphate the spot became deep red, as reported in the literature¹⁴. As is also shown in Fig. 3, the size of this spot decreases

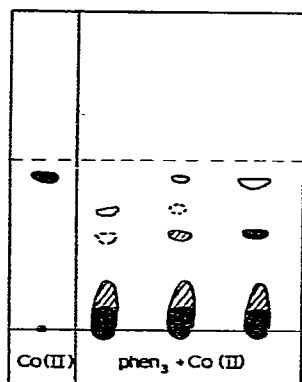


Fig. 3. Chromatograms of 5 μ l of a $1.2 \cdot 10^{-1}$ M solution of [Cophen₃]Cl₃ containing increasing amounts of cobalt(II) from left to right: $4 \cdot 10^{-2}$, $8 \cdot 10^{-2}$ and $2.5 \cdot 10^{-1}$ M. Eluent: E₁. Shading as in Fig. 1.

as the concentration of Co^{2+} increases and disappears in the last chromatogram. At the same time, another spot ($R_F = 0.55$) appears, probably due to the reaction between liberated 1,10-phenanthroline and Co^{2+} ions. The size and the intensity of this spot increase with increasing concentration of Co^{2+} . Thus, in the complex $[\text{Cophen}_3]\text{Cl}_3$, the presence of Co^{2+} as an impurity could be detected by the formation of the blue spot only if it is present in a large amount (ca. 4%). Also with the complex $[\text{Co}(\text{dyp})_3]\text{Cl}_3$, α, α' -dipyridyl appeared to be freed from the complex and Co^{2+} ions could be detected only if present in amounts greater than 4–5%.

We also wanted to test whether the complexes $[\text{Cophen}_3]\text{Cl}_3$ and $[\text{Codyp}_3]\text{Cl}_3$ were free from non-complexed ligands (1,10-phenanthroline or α, α' -dipyridyl). On pre-coated silica gel layers, in eluent E_3 , Cophen_3^{3+} and Codyp_3^{3+} remained at the point of application and the ligands moved near the solvent front. In Fig. 4 are reported the results obtained by chromatography of 25 and 20 μl of solutions of 1,10-phenanthroline and α, α' -dipyridyl, respectively, at decreasing concentrations: 2, 0.5, 0.2 and 0.1 mg/ml. For 1,10-phenanthroline it was possible to see the spot corresponding to the 0.2 mg/ml solution and for α, α' -dipyridyl that corresponding to the 0.1 mg/ml solution. In this way, 5 μg of 1,10-phenanthroline and 2 μg of α, α' -dipyridyl can be detected. With this chromatographic procedure, $[\text{Cophen}_3]\text{Cl}_3$ and $[\text{Codyp}_3]\text{Cl}_3$ samples, tested for Co^{2+} , were found to be free from ligands.

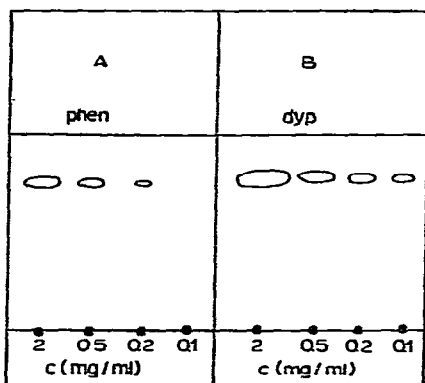


Fig. 4. Chromatograms of ethanolic solutions of (A) 1,10-phenanthroline (25 μl) and (B) α, α' -dipyridyl (20 μl) at decreasing concentrations. Eluent: E_3 .

CONCLUSION

The complexes investigated can be divided into two groups:

(1) *trans*- $[\text{Coen}_2\text{Cl}_2]\text{Cl}$, $[\text{Coen}_3]\text{Cl}_3$, $[\text{Cotn}_3]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$: no reaction seems to occur between these complexes and the ammonium thiocyanate–water–ethanol mixture used as the eluent. The Co^{2+} ions, present as impurities in these complexes, can be detected up to the limit of sensitivity of the cobalt(II)–CNS⁻ reaction in ethanolic solution.

(2) *cis*- $[\text{Cophen}_2\text{Cl}_2]\text{Cl}$, $[\text{Cophen}_3]\text{Cl}_3$ and $[\text{Codyp}_3]\text{Cl}_3$: these complexes, under our experimental conditions, react with the eluent. Nevertheless, with *cis*- $[\text{Cophen}_2\text{Cl}_2]\text{Cl}$ even small amounts of Co^{2+} ions can be detected. With $[\text{Cophen}_3]\text{Cl}_3$

and $[\text{Co}(\text{dyp}_3)\text{Cl}_3]$, however, the ligands are released from the complexes and form almost stable complexes with Co^{2+} ions, masking the presence of the latter. The presence of Co^{2+} as an impurity can be detected only if its concentration is about 4–5% of that of the complex under examination.

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