

Note

Separation of cobalt(III) complexes with mixed ethylenediamine-trimethylenediamine coordination spheres

ALDO ARBUSTI and MICHAEL LEDERER

Laboratorio di Cromatografia del C.N.R., Via Romagnosi 18A, Rome (Italy)

(Received December 28th, 1978)

In general, thin-layer chromatography (TLC) has replaced paper chromatography in most fields, the main reasons being that TLC is faster and gives better separations. There are, however, some separations where paper chromatography has been retained as a result of advantages such as ease of handling in work with radioactive isotopes and in small-scale preparative work in the complex chemistry of metals, mainly cobalt(III) complexes. In the latter field it is used routinely for separating mixtures on the scale of about 30–100 mg on a sheet of thick paper.

We recently had to repeat one of these separations, the separation of a mixture of $[\text{Co}(\text{en}_2\text{tn})]^{3+}$ and $[\text{Co}(\text{entn}_2)]^{3+}$, and found the published method¹ to give low R_F values and poor separations (Fig. 1). We decided that this separation would be a good occasion to review a number of variables for this type of separation, and we report our results below.

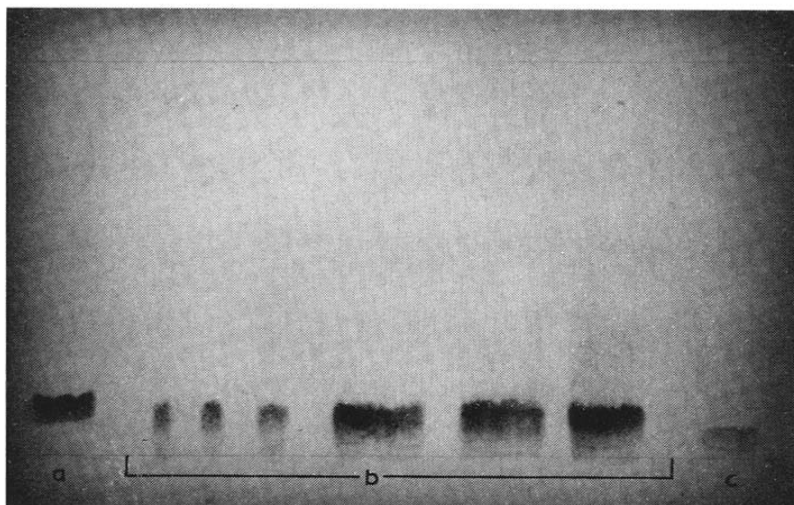


Fig. 1. Separation of mixed en–tn complexes of Co(III) according to Bang *et al.*¹. Paper: Whatman No. 3MM. Solvent: *n*-butanol–acetone–phenol–pyridine–benzene–water–acetic acid (14:14:30:14:14:4:7). Development by the ascending technique overnight. a = $[\text{Co}(\text{tn})_3]^{3+}$; b = several spots of the crude reaction mixture containing $[\text{Co}(\text{en})_3]^{3+}$ and mixed en–tn complexes; c = $[\text{Co}(\text{en})_3]^{3+}$.

EXPERIMENTAL AND RESULTS

The mixture studied was prepared as described by Bang *et al.*¹ by oxidising cobalt(II) with a stream of air in a solution containing ethylenediamine (en) and trimethylenediamine (tn).

Solvent system

The solvent system used by Bang *et al.*¹ seemed rather complex and also it contained unpleasant constituents (phenol and pyridine), so we decided to try various solvents based on *n*-butanol. In preliminary trials we noted (as also did Bang *et al.*¹) that the R_F differences between $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{en}_2\text{tn})]^{3+}$, $[\text{Co}(\text{entn}_2)]^{3+}$ and $[\text{Co}(\text{tn})_3]^{3+}$ were about equal and in order to obtain the best separation it was sufficient to find the largest R_F difference between $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{tn})_3]^{3+}$.

The results are summarized in Table I. *n*-Butanol-water mixtures containing hydrochloric, hydrobromic, nitric or trichloroacetic acid gave much poorer separations than *n*-butanol-perchloric acid-water mixtures.

TABLE I

R_F VALUES OF $[\text{Co}(\text{en})_3]^{3+}$ AND $[\text{Co}(\text{tn})_3]^{3+}$ IN VARIOUS *n*-BUTANOL-WATER-ACID MIXTURES

Paper: Whatman No. 3MM. Development: ascending for 22 h.

Solvent	R_F values		ΔR_F
	$[\text{Co}(\text{en})_3]^{3+}$	$[\text{Co}(\text{tn})_3]^{3+}$	
<i>n</i> -Butanol-water-HCl (7:2:1)	0.20	0.23	0.03
<i>n</i> -Butanol-water-HNO ₃ (7:2:1)	0.09	0.17	0.08
<i>n</i> -Butanol-water-HBr (7:2:1)	0.21	0.23	0.02
<i>n</i> -Butanol-water-CCl ₃ COOH (7:2:1)	0.46	0.62	0.16
<i>n</i> -Butanol-water-HClO ₄ (7:2:1)	0.33	0.53	0.20
<i>n</i> -Butanol-water-HClO ₄ (6.5:2.5:1)	0.41	0.55	0.14
<i>n</i> -Butanol-water-HClO ₄ (6:3:1)	0.41	0.56	0.15
<i>n</i> -Butanol-water-HClO ₄ (5.5:3.5:1)	0.45	0.55	0.10
<i>n</i> -Butanol-water-HClO ₄ (7:1:2)	0.38	0.61	0.23
<i>n</i> -Butanol-water-HClO ₄ (6:2:2)	0.49	0.71	0.22

In the latter mixtures an increase in the water concentration lowered the R_F difference and an increase in perchloric acid concentration increased it, but the spot shape was poorer at high perchloric acid concentrations. The mixture *n*-butanol-perchloric acid-water (7:2:1) was found to be the optimal composition. However, it gives an R_F difference of only 0.20; thus a separation of the four substances would have optimally an R_F difference of 0.066 between each pair of spots, which is small as it is generally considered necessary to have an R_F difference of more than 0.1 for a complete separation in paper chromatography and 0.05 in TLC.

Supports

In our search for an adequate preparative separation, we compared Whatman papers of several thicknesses: Nos. 1, 3MM and 17. The results are shown in Fig. 2.

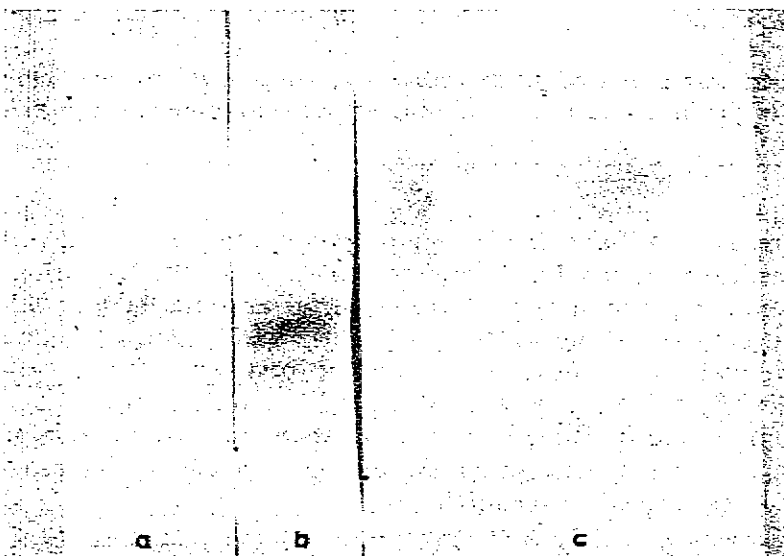


Fig. 2. Chromatograms of mixed en-tn complexes of Co(III) on various papers. Solvent: *n*-butanol-water-perchloric acid (7:2:1). Development by the ascending technique overnight. Paper: (a) Whatman No. 1; (b) Whatman No. 3MM; (c) Whatman No. 17. The chromatograms show the separation obtained with a solution of the crude reaction mixture. The lowest spot in (b) is an impurity (perhaps Co^{2+}). The next spot is $\text{Co}(\text{en})_3^{3+}$ and the two adjacent higher spots are $[\text{Co}(\text{en},\text{tn})]^{3+}$ and $[\text{Co}(\text{entn})]^{3+}$.

It is surprising that the 3MM paper gives such superior separations. In this work it is, of course, understood that we compared "the best" conditions for a separation.

A comparison of two cellulose thin layers is shown in Figs. 3 and 4. Curiously, the "better" layer, Cel 400, gave poorer separations, but this is mainly due to the poorer spots that could be applied. Whereas Cel 400 absorbed the solution quickly and thus gave large spots, Cel 300 allowed fine lines to be placed on the layer from a capillary. As it is now fashionable to express the quality of separation in terms of the number of plates achieved, we decided to compare the best systems in this manner using the simple equations proposed by Delley²:

$$E = \frac{\text{distance moved by zone}}{\text{zone width}}$$

and

$$n = 16E^2$$

where E is the efficiency of the chromatogram and n is the number of theoretical plates achieved by the zone. The results from a few chromatograms are given in Table II, from which it appears that on Whatman 3MM paper about half the number of plates are achieved compared with a cellulose thin layer.

Time factor in the separation

One aspect of TLC and especially high-performance TLC (HPTLC) that is being stressed continuously is that separations performed quickly are much superior to slower separations as the band spreading due to diffusion cancels the advantage of

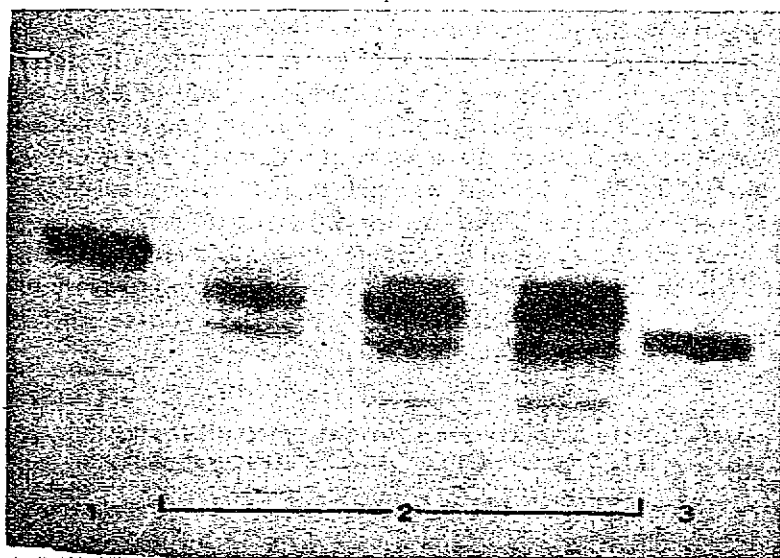


Fig. 3. Separation of mixed en-tn complexes of Co(III) on Polygram Cel 300 thin layers. Solvent: *n*-butanol-water-perchloric acid (7:2:1). 1 = $[\text{Co}(\text{tn})_3]^{3+}$ (showing two minor bands also); 2 = three samples (various amounts) of the reaction mixture containing $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{en}_2\text{tn})]^{3+}$ and $[\text{Co}(\text{en}\text{tn}_2)]^{3+}$ (note also a slow-moving impurity, probably Co^{2+}); 3 = $[\text{Co}(\text{en})_3]^{3+}$.

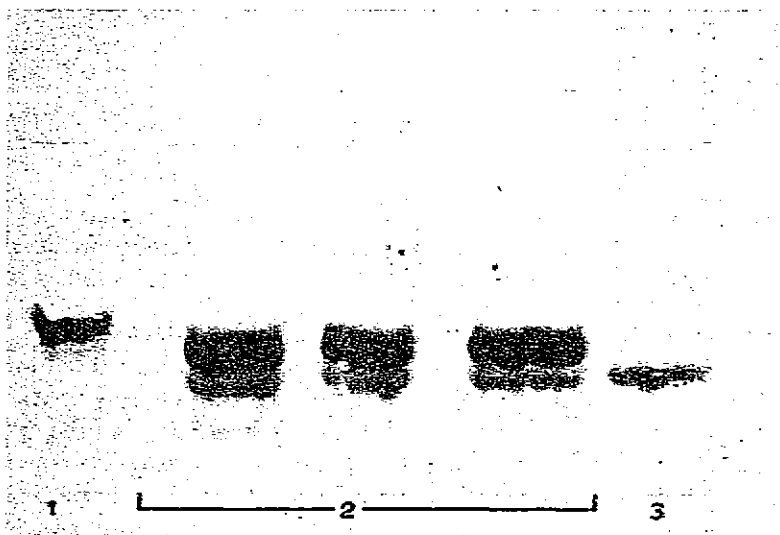


Fig. 4. Separation of mixed en-tn complexes of Co(III) on Polygram Cel 406 thin layers. Conditions and samples as in Fig. 3. Note the incomplete separation of $[\text{Co}(\text{en}_2\text{tn})]^{3+}$ and $[\text{Co}(\text{en}\text{tn}_2)]^{3+}$, which is due mainly to the poor spots produced during the spotting of the samples.

the larger distance moved. Thus it had been concluded that optimal separations on thin layers are obtained with a movement of the solvent front of 100 mm and in HPTLC of 40 mm (with development times of 3 h and 20 min, respectively). If this were so, we felt that much poorer separations should be obtained in an overnight development on Whatman 3MM paper. In order to examine this question, we chose

TABLE II
EFFICIENCY AND PLATES NUMBERS OF SOME COBALT(III) COMPLEXES ON CELLULOSE PAPER AND THIN LAYERS
Solvent: *n*-butanol-water-perchloric acid (7:2:1).

Layer or paper	Distance moved by the spot (mm)			Band width (mm)	Efficiency			Number of theoretical plates		
	$[\text{Co}(\text{en})_3]^{3+}$	$[\text{Co}(\text{m})_3]^{3+}$	$[\text{Co}(\text{en})_3]^{3+}$		$[\text{Co}(\text{en})_3]^{3+}$	$[\text{Co}(\text{m})_3]^{3+}$	$[\text{Co}(\text{en})_3]^{3+}$	$[\text{Co}(\text{m})_3]^{3+}$	$[\text{Co}(\text{en})_3]^{3+}$	$[\text{Co}(\text{m})_3]^{3+}$
Polygram Cel 300 thin layer developed for 3 h	42	62	5	6	10.3	8.4	6.2	1060	1700	
Polygram Cel 400 thin layer developed for 3 h	33	46	6	5	9.2	6.2	6.2	620	1300	
Whatman No. 3MM paper developed for 22 h	87	141	20	20	7	4.3	4.3	310	800	

another separation that we use routinely for preparative purposes, namely the separation of three isomers of $\text{Co}(\text{pn})_3^{3+}$ with *n*-butanol–water–hydrochloric acid, first described by Dwyer *et al.*³, which yields three well separated spots. The thin layers were developed either for the optimum of 10 cm or left overnight for the same time as the paper chromatogram. An unexpected result was obtained: the number of theoretical plates did not decrease by more than 20% on going from a 3-h to a 22-h development. Further, the thin layers showed two other well separated bands [presumably other $\text{Co}(\text{pn})_3^{3+}$ isomers], which did not occur on the paper chromatograms. We have extended this work to developments at regular intervals from 3 h onwards, and the results are given in Table III.

TABLE III

PLATE NUMBERS OF THE THREE BANDS OBTAINED FROM $[\text{Co}(\text{pn})_3]^{3+}$ WITH *n*-BUTANOL–WATER–HYDROCHLORIC ACID (6:3:1) WITH VARIOUS DEVELOPMENT TIMES

Layer or paper	Development time (h)	Distance moved by the solvent (mm)	Theoretical plate numbers		
			Band 1	Band 2	Band 3
Polygram Cel 300	1	8	800	320	256
	2	80	1300	784	720
	3	120	2050	1024	1200
	4	128	2544	1072	1232
	6	154	3100	864	1152
	10	180*	3600	1472	1440
	15	180	1650	2080	1600
	24	180	2200	784	924
Whatman No. 3MM paper	6	146	304	—	—
	15	246	928	224	160
	22	296	800	336	192

* Here the solvent reached the top of the plate; there was a slight movement of the spots due to some evaporation even after they reached the top.

Whatman 3MM paper achieved one third to half of the plate numbers obtained on thin layers, even under conditions where the diffusion times were the same. Hence one can conclude that the lower plate number is due to the poor and erratic "packing" (the convective mixing term of the Van Deemter equation) and larger "particle size" of the paper in comparison with the more homogeneous "packing" and smaller "particle size" of the thin layer. The time factor is secondary. Table III shows another unexpected effect, namely that the plate number does not decrease after reaching a maximum with a development of about 100 mm but remains more or less constant from then to about 15 h of development. Probably one of the factors contributing to this plateau is a self-sharpening effect due to evaporation during development, similar to that produced artificially by Perry⁴.

It is, of course, tempting to use these results to draw general conclusions. However, for this we would have had to standardize the spot applied, which was of little use to us as we wished only to achieve a good preparative separation (*i.e.*, with large loads). However, it can be concluded that paper chromatography is not inferior because of its slowness but rather because of the poor quality of the paper.

Also, on examining illustrations in some books on chromatography, it became clear that the systems studied here are far from representative, and some sugar spots on overflowing paper chromatograms achieve as many as 8000 theoretical plates, *i.e.*, about a 10-fold greater efficiency than that obtained here with cobalt(III) complexes.

REFERENCES

- 1 O. Bang, A. Engberg, K. Rasmussen and F. Woldbye, *Acta Chem. Scand.*, 29 (1975) 749.
- 2 R. Delley, *Chromatographia*, 9 (1976) 10.
- 3 F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Amer. Chem. Soc.*, 85 (1963) 2913.
- 4 J. A. Perry, *J. Chromatogr.*, 113 (1975) 267.