

CHROM. 8584

PARTITION PAPER CHROMATOGRAPHY OF INORGANIC IONS

XXI. PAPER CHROMATOGRAPHY OF MIXED COBALT(III) COMPLEXES

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(Received July 15th, 1975)

SUMMARY

The partition paper chromatography of a series of ethylenediamine, dipyridyl and *ortho*-phenanthroline complexes of cobalt(III) has been studied with butanol-acid-water solvent mixtures. The rather unusual properties of tris(propylenediamine)-cobalt(III) are discussed.

INTRODUCTION

One of the most important of the early applications of paper chromatography to the chemistry of metal complexes is the work by Dwyer *et al.*¹ on the separation of mixed propylenediamine-ethylenediamine complexes of cobalt(III) and on the separation of various optical isomers of tris(propylenediamine)cobalt(III) complexes. R_F values of other cobalt(III) complexes have been reported^{2,3} in solvents such as butanol-hydrochloric acid-water, but there has not been a survey of the relation between the complexing group and chromatographic mobility. Recently, several mixed complexes of the type $[\text{Co}(\text{en})_2(o\text{-phen})]^{3+}$ have been synthesized* for work on outer-sphere complexing and paper electrophoresis⁴ and it was felt that it would be interesting to study their chromatographic behaviour in partition solvents.

EXPERIMENTAL

The following complexes were prepared according to the literature methods: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (ref. 5); $[\text{Co}(\text{en})_3]\text{Cl}_3$ and $[\text{Co}(\text{pn})_3]\text{Cl}_3$ (ref. 6) and $[\text{Co}(\text{dip})_3]\text{Cl}_3$, $[\text{Co}(o\text{-phen})_3]\text{Cl}_3$, $[\text{Co}(\text{en})(o\text{-phen})_2]\text{Cl}_3$, $[\text{Co}(\text{en})_2(o\text{-phen})]\text{Cl}_3$, $[\text{Co}(\text{dip})_2(o\text{-phen})]\text{Cl}_3$ and $[\text{Co}(\text{dip})(o\text{-phen})_2]\text{Cl}_3$ (ref. 4).

Chromatography was carried out overnight on Whatman No. 3MM paper by the ascending technique in cylindrical glass jars with ground-glass-sealed covers. The room temperature was 20–22°. The spots were detected by spraying the chromatograms with ammonium polysulphide.

* The following abbreviations are used; en = ethylenediamine; pn = propylenediamine; dip = dipyridyl; *o*-phen = *ortho*-phenanthroline.

RESULTS AND DISCUSSION

Fig. 1a shows the chromatogram obtained with butanol-hydrochloric acid-water (6:1:3), the solvent used by Dwyer *et al.*¹, and indicates also why it was felt that other solvent systems should be investigated. Here $[\text{Co}(\text{NH}_3)_6]^{3+}$ moves slower than $[\text{Co}(\text{en})_3]^{3+}$ which is slower than $[\text{Co}(\text{pn})_3]^{3+}$. The latter ion, which has numerous

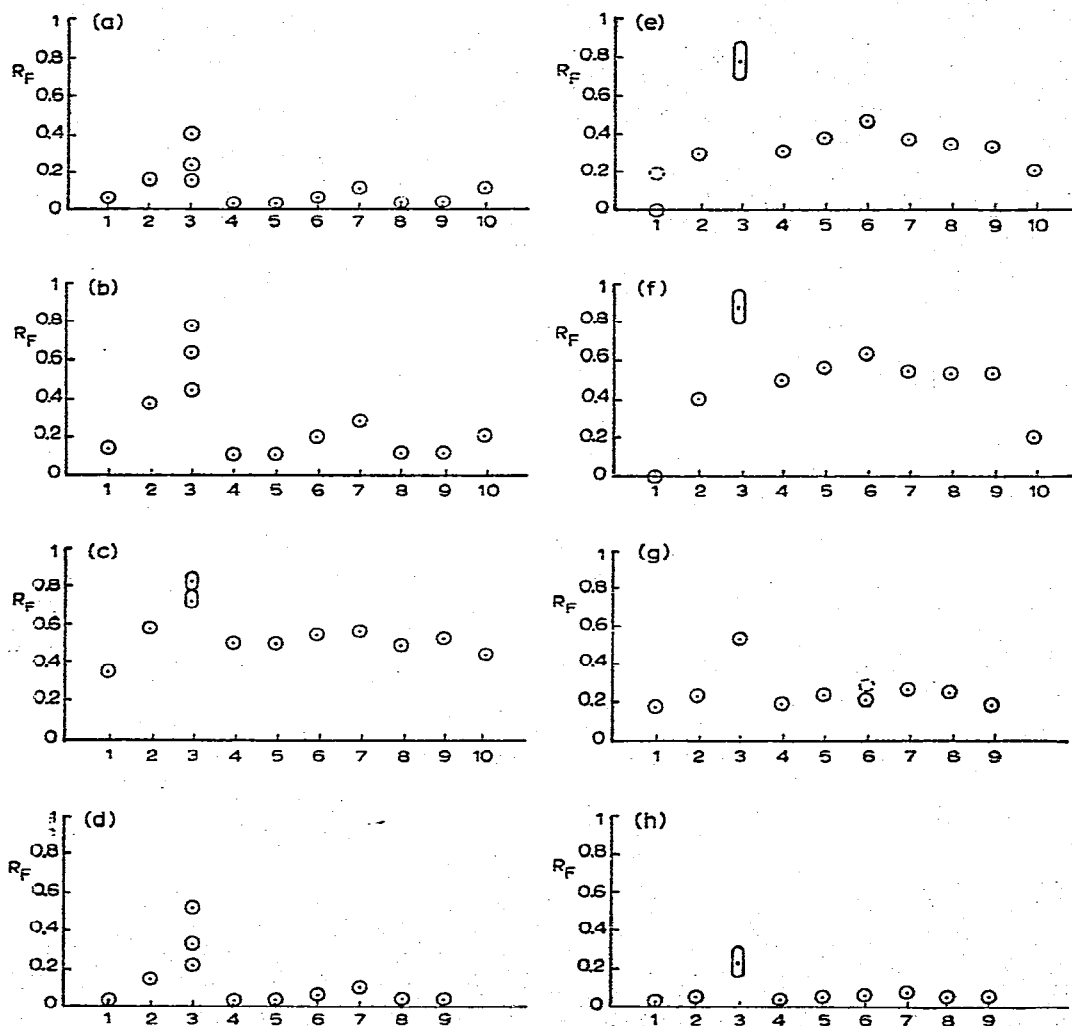


Fig. 1. Schematic chromatograms of Co(III) complexes. On all chromatograms the following compounds were run: 1 = $[\text{Co}(\text{NH}_3)_6]^{3+}$; 2 = $[\text{Co}(\text{en})_3]^{3+}$; 3 = $[\text{Co}(\text{pn})_3]^{3+}$; 4 = $[\text{Co}(\text{dip})_3]^{3+}$; 5 = $[\text{Co}(\text{o-phen})_3]^{3+}$; 6 = $[\text{Co}(\text{en})(\text{o-phen})_2]^{3+}$; 7 = $[\text{Co}(\text{en})_2(\text{o-phen})]^{3+}$; 8 = $[\text{Co}(\text{dip})_2(\text{o-phen})]^{3+}$; 9 = $[\text{Co}(\text{dip})(\text{o-phen})_2]^{3+}$ and 10 = Co^{2+} . Solvents: a-c, Butanol-hydrochloric acid-water (6:1:3, 4:1:1 and 4:3:1, respectively); d, butanol-hydrobromic acid-water (5:1:4); e-f, butanol-perchloric acid-water (7:1:2 and 4:1:1, respectively); g, butanol-1 *N* perchloric acid (1:1) and h, butanol-nitric acid-water (10:1:9). Chromatograms obtained overnight on Whatman No. 3MM paper by the ascending technique at a room temperature of 20–22°.

isomers⁷, has already been reported⁸ as separating into three spots of which the fastest was identified as the racemic pair *D*-[Co{(+)pn}₃]Cl₃ and *L*-[Co{(-)pn}₃]Cl₃. Thus the additional presence of three symmetrically spaced methyl groups on the surface of the complex caused the R_F value to increase from 0.18 to 0.42. All the other ions studied moved slower than [Co(en)₃]³⁺ in spite of the fact that the bulk or "hydrophobicity" of the chelating groups should be much higher than with [Co(pn)₃]³⁺.

Figs. 1b and 1c show the general trend in R_F values is not changed on increasing the proportion of hydrochloric acid and/or water in the solvent.

The two solvent mixtures used here were employed previously by Aprile *et al.*⁹ to separate some cobalt(III) dipyriddy complexes. It is also interesting that with the first solvent there are again three well separated spots for [Co(pn)₃]³⁺, while with the second only two may be discerned. This is probably due to the very high R_F values of the spots. In Figs. 1a and 1b the values of R_F increase regularly in the series [Co(*o*-phen)₃]³⁺, [Co(en)(*o*-phen)₂]³⁺, [Co(en)₂(*o*-phen)]³⁺ and [Co(en)₃]³⁺ and curiously there is no difference in R_F between [Co(dip)₃]³⁺, [Co(dip)₂(*o*-phen)]³⁺, [Co(dip)(*o*-phen)₂]³⁺ and [Co(*o*-phen)₃]³⁺. Thus not even the asymmetry of the mixed complexes due to the difference between dip and *o*-phen causes a measurable difference in the R_F values. Fig. 1d shows that the behaviour is essentially the same in butanol-hydrobromic acid-water (5:1:4). The use of another solvent employed by Dwyer *et al.*¹, namely butanol-water-perchloric acid (7:2:1) is shown in Fig. 1e. The most remarkable difference from the solvents containing hydrochloric acid is that [Co(pn)₃]³⁺ moves as a single, although elongated, spot. The differences between [Co(en)(*o*-phen)₂]³⁺ and [Co(en)₂(*o*-phen)]³⁺ are of the same order as in Figs. 1a and 1b; however, both [Co(en)₃]³⁺ and [Co(dip)₃]³⁺ move less than the mixed complexes. Thus one cannot regard this effect as due to gradual substitution but rather to the asymmetry of the complex. The same sequences were observed for a solvent mixture richer in water and perchloric acid (Fig. 1f) where the R_F values are higher. [Co(NH₃)₆]³⁺ has $R_F = 0$ in both solvents containing perchloric acid because its perchlorate is precipitated at the start. When the solvents contained little perchloric or nitric acid (Figs. 1g and 1h), [Co(NH₃)₆]³⁺ was not precipitated, but the sequences of all the other complexes was essentially the same.

In butanol-sulphuric acid-water (10:1:9) all the complexes had $R_F = 0$ except [Co(pn)₃]³⁺ which moved slightly ($R_F = 0.03$). Butanol-trichloroacetic acid-water gave rather elongated spots which were unsuitable for separation purposes. Butanol-acetic acid-water mixtures gave compact spots with forward comets. To the data presented above may be added R_F values calculated from a chromatogram of Dwyer *et al.*¹ for the separation of a mixture of [Co(en)₃]³⁺, [Co(en)₂(pn)]³⁺, [Co(en)(pn)₂]³⁺ and [Co(pn)₃]³⁺ where the optical form of pn is (-). These R_F values are 0.14, 0.22, 0.32 and 0.42 (using the present results for [Co(en)₃]³⁺ and [Co(pn)₃]³⁺ to calculate R_F values for the other two spots).

In Fig. 2 R_M values of this series and of [Co(en)_x(dip)_y]³⁺ in the same solvent are plotted against the number of en groups in the complex. The above results thus pose a series of problems: why does a methyl group on the en group cause an increase in extraction (*i.e.* in R_F value) while a larger increment in size of the chelating group produces a decrease of about the same order, why does the difference between the dip and *o*-phen groups produce no measurable differences in R_F value with any of the solvent mixtures examined and why are the three spots of

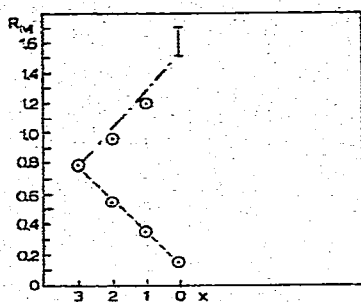


Fig. 2. Graph of R_M against the number of en groups in the series $[\text{Co}(\text{en})_x(\text{pn})_3]^{3+}$ (---) and $[\text{Co}(\text{en})_x(\text{dip})_3]^{3+}$ (-.-) for the solvent butanol-hydrochloric acid-water (6:1:3).

$[\text{Co}(\text{pn})_3]^{3+}$ separated in butanol-hydrochloric acid and butanol-hydrobromic acid mixtures but not in butanol-perchloric acid or butanol-nitric acid?

The three forms of $[\text{Co}(\text{pn})_3]^{3+}$ separated in butanol-hydrochloric acid were studied by Dywer *et al.*⁸ who concluded that each spot is due to a racemic mixture of isomers containing various optical forms of propylenediamine, *viz.*: fastest, D- $[\text{Co}\{(+)\text{pn}\}_3]\text{Cl}_3$ and L- $[\text{Co}\{(-)\text{pn}\}_3]\text{Cl}_3$; intermediate, D- $[\text{Co}\{(+)\text{pn}\}_2\{(-)\text{pn}\}]\text{Cl}_3$ and L- $[\text{Co}\{(-)\text{pn}\}_2\{(+)\text{pn}\}]\text{Cl}_3$ and slowest, D- $[\text{Co}\{(+)\text{pn}\}\{(-)\text{pn}\}_2]\text{Cl}_3$, L- $[\text{Co}\{(-)\text{pn}\}\{(+)\text{pn}\}_2]\text{Cl}_3$, D- $[\text{Co}\{(-)\text{pn}\}_3]\text{Cl}_3$ and L- $[\text{Co}\{(+)\text{pn}\}_3]\text{Cl}_3$. MacDermott⁷ extended this work pointing out that all possible forms of isomerism (optical, position, geometric and conformational) could yield 2^{10} isomers for $[\text{Co}(\text{pn})_3]^{3+}$, and separated the *trans* and *cis* forms by crystallization from the "fastest" chromatographic fraction. Whichever of the isomers is present in each fraction, the separation represents a chromatographic phenomenon if one compares it with the movement of the other Co(III) complexes.

Calculated ΔR_M values for the three solvent systems which give good separations of the three fractions are given in Table I. In each case the ΔR_M value is between 0.2 and 0.4, *i.e.*, a rather large difference compared with the series shown in Fig. 2. Thus a small difference in configuration, providing it is of the right type can have an enormous effect on the partition equilibria, while much larger differences need not have any effect at all!

TABLE I

ΔR_M VALUES OF THE THREE SPOTS OBTAINED FROM $[\text{Co}(\text{pn})_3]^{3+}$

Butanol-hydrochloric acid-water (6:3:1)			Butanol-hydrochloric acid-water (4:1:1)			Butanol-hydrobromic acid- water (5:1:4)		
R_F	R_M	ΔR_M	R_F	R_M	ΔR_M	R_F	R_M	ΔR_M
0.16	0.72	0.22	0.43	0.12	0.37	0.22	0.55	0.26
0.24	0.50	0.36	0.64	-0.25	0.30	0.34	0.29	0.34
0.42	0.14		0.78	-0.55		0.53	-0.05	

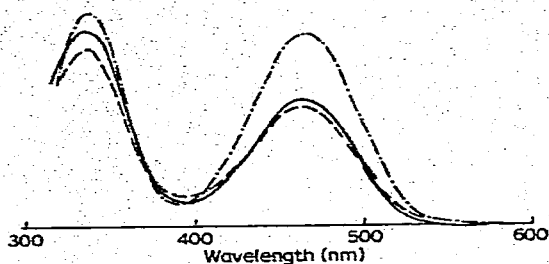


Fig. 3. Visible-region spectra of the three fractions obtained from $[\text{Co}(\text{pn})_3]^{3+}$ in butanol-hydrochloric acid-water (6:1:3). — — —, First fraction; - · -, second fraction; ———, third fraction.

We have done some additional work on $[\text{Co}(\text{pn})_3]^{3+}$ because Jenkins and Monk⁶ measured conductivities which are now widely quoted. Approximately 30 mg of each fraction were prepared by applying larger amounts of $[\text{Co}(\text{pn})_3]^{3+}$ to a Whatman No. 3MM sheet, cutting out the visible yellow bands and eluting them with water. All of the three fractions had no measurable optical rotation. Their spectra in the visible region had the same peaks but the peak height ratios were different for the three samples as shown in Fig. 3. In paper electrophoresis the three fractions had identical mobilities in dilute perchloric and hydrochloric acids. The mobilities of the original mixture (one spot only) as well as of the other complexes are given in Table II.

In dilute sodium sulphate, $[\text{Co}(\text{pn})_3]^{3+}$ separated into three fractions. This is presumably due to differences in outer-sphere complexing (see ref. 3). The three fractions isolated in butanol-hydrochloric acid partition chromatography correspond to these three fractions as shown in Fig. 4. Thus two very different separation principles cause the complex to separate into the same three fractions.

The above results are evidence that the conductivity values obtained by Jenkins and Monk⁶ are satisfactory since all of the separable isomers present in their complex move with identical velocities in dilute hydrochloric or perchloric acid. How-

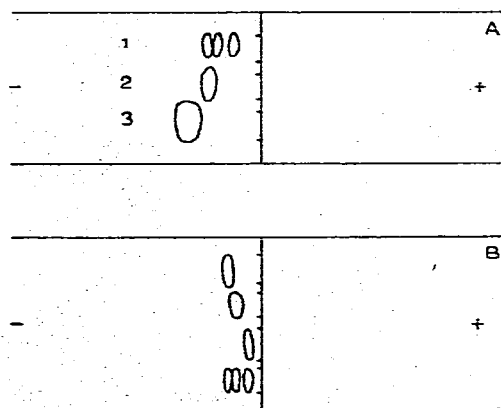


Fig. 4. Electropherograms of A, $[\text{Co}(\text{pn})_3]^{3+}$ (1), $[\text{Co}(\text{en})_3]^{3+}$ (2) and $[\text{Co}(\text{NH}_3)_6]^{3+}$ (3) in 0.05 *N* sodium sulphate at 1500 V for 30 min on Whatman No. 1 paper at 8°; B, $[\text{Co}(\text{pn})_3]^{3+}$ and its three fractions (separated by partition chromatography with butanol-hydrochloric acid-water) in 0.1 *N* sodium sulphate at 300 V for 15 min on Whatman No. 1 paper at 8°.

TABLE II
ELECTROPHORETIC MOBILITIES OF Co(III) COMPLEXES

Paper, Whatman No. 1; apparatus, Shandon high-voltage electrophoresis; temperature, 8°.

Electrolyte	Concentration of electrolyte (N)	Voltage (V)	Time (min)	Mobility (mm)	$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$	$[Co(pn)_3]^{3+}$ *	$[Co(dip)_3]^{3+}$	$[Co(o-phen)_3]^{3+}$
Perchloric acid	1	1000	60	95	62	47	10	0	0
	0.5	1500	45	136	89	68	24	0	0
	0.1	1500	45	118	80	65	37	0	0
Hydrochloric acid	1.0	1000	60	97	52	36	45	40	40
	0.5	1500	45	121	70	53	56	51	51
	0.1	1500	45	130	87	70	69	62	62

* Always a single spot.

ever, their extrapolated conductivity value for the ion-pair $[\text{Co}(\text{pn})_3]\text{SO}_4$ is actually an average value for three species whose conductivities differ by as much as 100% from each other in sulphate concentrations as low as 0.05 *N*.

In conclusion, a larger range of complexes than had been reported before has been examined in a series of butanol-acid-water mixtures. The usual additivity rules for organic molecules cannot be applied to series of Co(III) complexes of 3+ charge because rather small differences in structure may produce large changes in R_F values and quite large differences in structure can, on the other hand, have no effect at all.

ACKNOWLEDGEMENT

Thanks are due to V. Cardaci and A. Cristalli for technical assistance.

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