

# THE PAPER CHROMATOGRAPHIC SEPARATION OF COBALT(II) CHLORIDE AND SOME AMMINE AND ETHYLENEDIAMINE COMPLEXES OF COBALT(III)

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## INTRODUCTION

In the paper-chromatographic separation of metal-ammine complexes, the metal can either be converted to the complex by using an ammoniacal solvent system, or it can be applied to the paper as a prepared complex.

ERDEM AND ERLÉNMEYER<sup>1</sup> have studied the behaviour of cadmium acetate in ammoniacal solvents, and interpret the triple spotting of cadmium as indicating the separation of different ammine complexes. A few separations of trivalent cobalt complexes have been described. YAMAMOTO *et al.*<sup>2</sup> and LEDERER<sup>3</sup> have investigated some ammine complexes; STEFANOVIĆ AND JANJIĆ<sup>4</sup> have separated the geometric isomers of three ethylenediamine complexes.

Since the work described here was completed, SINGH AND DEY<sup>5</sup> have obtained separations of the amines of copper, silver, cadmium, nickel and cobalt, using 50% ethanol as eluting solvent. Further, AGRINIER<sup>6</sup>, in a study of the application of paper chromatography to the determination of certain elements in minerals, has separated silver, lead, selenium, zinc and copper by elution with concentrated ammonia.

It has now been found possible to separate copper, cobalt and nickel, and zinc from cadmium using a selected ternary solvent system of methanol-water-ammonia, which does not give double-spotting with cadmium. The behaviour of 14 ammine and ethylenediamine complexes in: acetone-aqueous hydrochloric acid, methanol-aqueous hydrochloric acid, and ether-methanol-aqueous hydrochloric acid has been investigated in some detail, and a number of new separations are described. Brief mention of some of this work has been made elsewhere<sup>7</sup>.

## EXPERIMENTAL

### *Preparation of the solutions*

0.1 *N* solutions of copper, cobalt, nickel, zinc and cadmium acetates were used for spotting the chromatograms described in Section A. The complexes  $\text{Co(en)}_3\text{Cl}_3^*$ ,  $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ , and  $[\text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3$  were prepared as follows:

\* en = ethylenediamine.

(a) *Tris(ethylenediamine) cobalt(III) chloride*<sup>8</sup>,  $\text{Co(en)}_3\text{Cl}_3$ . This was prepared by the aerial oxidation (3 hours) of aqueous cobaltous chloride (24 g:75 ml  $\text{H}_2\text{O}$ ) in the presence of 30% ethylenediamine (61 g) and 6 N HCl (17 ml). After evaporation to a small volume on a steam bath, the complex crystallized in orange-yellow needles, easily soluble in water.

(b) *trans-Dichlorobis(ethylenediamine) cobalt(III) chloride*<sup>9</sup>,  $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ . Prolonged aerial oxidation (approx. 10–12 h) of aqueous cobaltous chloride (160 g:500 ml) and 10% ethylenediamine (600 g) was carried out. Excess concentrated HCl (350 ml) was added followed by evaporation to approx. 750 ml when the bright green plate-like crystals of the hydrochloride of the base were deposited.

(c) *trans-Diaquobis(ethylenediamine) cobalt(III) chloride*,  $[\text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3$ . The green *trans*-isomer from (b) was converted to the red *cis*-isomer by evaporation in aqueous solution. This complex (2 g) was converted to the *cis*-dibromo-complex by cautious warming with  $\text{NH}_3$  (10 ml;  $d = 0.880$ ) followed by trituration with solid NaBr. The dibromo-complex crystallized in red needles, and was purified from a little  $\text{H}_2\text{O}$  by reprecipitation with NaBr<sup>10</sup>. It was converted to the *cis*-diaquo-complex by cautious warming with the equivalent amount of conc. HCl<sup>11</sup>.

The aqueous solutions each contained 10  $\mu\text{g}$  cation/ $\mu\text{l}$ . The other cobalt(III) solutions were of a similar concentration (except where stated otherwise). The preparation of these complexes is now described:

(d) *Hexammino-cobalt(III) chloride*<sup>12</sup>,  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ . A mixture of cobaltous chloride (18 g) dissolved in ammonium chloride (12 g in 25 ml  $\text{H}_2\text{O}$ ) was mixed with  $\text{NH}_3$  (40 ml;  $d = 0.880$ ) and oxidised in the cold with "20 volume" hydrogen peroxide (35 ml). On warming to 60° the required complex was formed in golden-brown crystals.

(e) *Ammonium tetranitro-diammino-cobaltate. Erdmann's salt*,  $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ . Ammonium chloride (20 g) and sodium nitrite (27 g) were dissolved in  $\text{H}_2\text{O}$  (150 ml). After filtration, the filtrate was mixed with cobaltous chloride (18 g in 50 ml  $\text{H}_2\text{O}$ ) and 20% aqueous ammonia (5 ml) and aerial oxidation carried out for 1½ h. On spontaneous evaporation, brown crystals of the required complex were formed.

(f) *Trinitro-triammino-cobalt(III)*<sup>12</sup>,  $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ . Cobalt carbonate (7 g) was dissolved in a mixture of water (40 ml) and glacial acetic acid (10 ml), and added to a solution of sodium nitrite (15 g) in  $\text{NH}_3$  (70 ml;  $d = 0.880$ ). The mixture was oxidised in the cold with "20 volume" hydrogen peroxide (20 ml). On warming the mustard-yellow complex was produced, and was recrystallized from very dilute acetic acid.

(g) *cis-Dinitrotetrammine cobalt(III) chloride*, 1:2  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ . Carbonato-tetrammine cobaltic nitrate (5 g) was dissolved in water (50 ml) and conc. nitric acid (3 ml), treated with sodium nitrite (10 g), warmed for 10 min, cooled and acidified with 6 N nitric acid (65 ml). After standing for 24 h the precipitate of mixed acid and neutral flavonitrate was removed and recrystallized from very dilute acetic acid. It was converted to the required chloride form by dissolution in water (1 g in 30 ml)

followed by treatment with ammonium chloride (2 g), the complex being precipitated by the gradual addition of methylated spirit (100 ml).

(h) *trans-Dinitrotetrammine cobalt(III) chloride*,  $1:6[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ . To a cold filtered solution of ammonium chloride (4 g) and sodium nitrite (5.5 g) in water (30 ml) was added 2 N ammonia (10 ml) and cobaltous chloride (3.5 g in 10 ml  $\text{H}_2\text{O}$ ). Aerial oxidation was carried out for 4 h, and after standing for 24 h the required complex was filtered off. It was purified by dissolution in very dilute acetic acid and reprecipitation with concentrated ammonium chloride solution.

(i) *Chloro-pentammine cobalt(III) chloride*,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . Conc. HCl (4.5 ml) was added to a solution of carbonatotetrammine cobaltic nitrate (3 g in 40 ml  $\text{H}_2\text{O}$ ). After removal of all  $\text{CO}_2$  the solution was made slightly ammoniacal, and an excess of  $\text{NH}_3$  (5 ml;  $d = 0.880$ ) added. The solution was heated for  $\frac{3}{4}$  h, cooled, and conc. HCl (50 ml) added. After further warming for 1 h, the solution was allowed to cool, when it deposited violet-red crystals of the required complex.

(j) *Sodium cobaltinitrite*<sup>12</sup>,  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ . Cobaltous nitrate (10 g) was dissolved in a warm solution of sodium nitrite (30 g in 30 ml  $\text{H}_2\text{O}$ ), and 50% acetic acid (10 ml) gradually added with good stirring. After aerial oxidation for  $\frac{1}{2}$  h, ethanol (50 ml) was added at  $0^\circ$  with good stirring; the orange-coloured crystals were filtered and washed with ethanol.

(k) *Potassium trioxalato-cobaltate*<sup>12</sup>,  $\text{K}_3[\text{Co}(\text{Ox})_3] \cdot 3\frac{1}{2} \text{H}_2\text{O}$ . Oxalic acid dihydrate (12.6 g), potassium oxalate (36.8 g), and cobalt carbonate (12 g) were dissolved in boiling water (250 ml). After cooling the solution to  $30^\circ$ , finely divided lead dioxide (30 g) was slowly added with good stirring, followed by a uniform mixture of glacial acetic acid (12.5 ml) and water (12.5 ml), the addition of which should take not less than  $\frac{1}{2}$  h. After spontaneous oxidation (with stirring) for 1 h, and removal by filtration of excess dioxide, the complex was precipitated as dark green crystals by slow addition of ethanol (250 ml).

(l) *Ammonium diammino-dinitro-oxalato-cobaltate*,  $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{Ox}]$ . Erdmann's salt (5 g) was dissolved in warm water (25 ml) and oxalic acid (2.5 g in 12.5 ml  $\text{H}_2\text{O}$ ) added at  $50^\circ$ . After standing for 24 h, the crystalline precipitate was filtered off (A). To the filtrate (B) was added 2.5 g ammonium chloride as saturated solution; this precipitated the complex  $[\text{Co}_4(\text{NO}_2)_6(\text{C}_2\text{O}_4)_3(\text{NH}_3)_6]\text{NH}_4 \cdot 6\text{H}_2\text{O}$ , and the solution after filtration of this complex was found to contain the required ammonium salt of  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{Ox}]^-$ . This complex was also found in the filtrate obtained by dissolving the crystals (A) in water, and precipitating the complex  $[\text{Co}_4(\text{NO}_2)_6(\text{Ox})_3(\text{NH}_3)_6]\text{NH}_4$  as above.

### *Descending elution technique*

*Section A.* The all-glass apparatus<sup>13</sup> consisted of two troughs (24 cm long and 2.5 cm in diameter) supported by a glass stand contained in a tank (23 cm  $\times$  28 cm  $\times$  52 cm deep) covered with a ground-glass plate drilled with two holes located one over each of the two troughs. The purpose of the holes was to permit solvent to be admitted

into the trough without removing the glass cover-plate, and so disturbing the equilibration of the tank.

Sheets of Whatman No. 1 paper 10 cm  $\times$  40 cm were used for the chromatograms, with the starting line marked 8 cm from the upper narrow edge. Two creases, 4 cm and 6 cm above the starting line produced a V-shaped fold which could then be placed in the glass trough. The paper strip was held in position with a piece of glass rod fitted with a central side arm to allow easy removal after elution. 0.5 cm spots of the solutions were placed 2 cm apart on the starting line and allowed to dry. The paper was placed in a trough in the tank; a second trough was filled with solvent and equilibration of tank and paper allowed to proceed overnight. A quantity of the eluting solvent was placed in the empty trough, and elution allowed to proceed for 2-3 h, the temperature being maintained at  $18^\circ \pm 2^\circ$ . The length of run was 25-40 cm. The chromatogram was then removed, dried and sprayed as follows.

Rubeanic acid<sup>14</sup> was used to detect the copper, cobalt and nickel, and 8-hydroxyquinoline<sup>15</sup> revealed the positions of the zinc and cadmium.

*Section C.* The apparatus was smaller than that used in Section A, the tank being 10 cm  $\times$  16.5 cm  $\times$  31 cm deep. Equilibration of the tank was carried out for 24 h, and of the paper for 45 min. The length of run was 20 cm on Whatman No. 1 paper. Other conditions were similar to those above.

#### *Ascending elution technique*

*Section B.* The apparatus consisted of a gas-jar (30 cm high  $\times$  8 cm diameter), the top of which was accurately ground flat and greased with vaseline. 100 ml of solvent was introduced into the jar, which was then sealed by two flat glass plates, (14 cm  $\times$  5 cm), ground flat on the 14 cm sides. A cover plate (14 cm  $\times$  9 cm) was placed over these two slides, and held in position by two rubber bands. Before elution was commenced, the apparatus was equilibrated for 1 h. The cover plate was then removed, the slides were gently displaced sideways and the paper strip inserted until the lower edge just touched the solvent surface. The protruding upper end of the strip was folded to lie flat along the surface of the slides, which were then pushed tightly together and again held in position by the cover plate and rubber bands.

Whatman No. 1 paper, cut perpendicularly to the machine direction into strips 6  $\times$  30 cm, was used for the chromatograms. The length of run was  $15.0 \pm 0.2$  cm at  $18^\circ \pm 2^\circ$ . The size of the spots was standardised at 1.5  $\mu$ l using a calibrated capillary dropper<sup>17</sup>.

#### *Section A. The separation of copper, cobalt and nickel, and zinc from cadmium*

Preliminary experiments showed that as the ammonia concentration increased above 15 ml, the spot compactness improved. The solvent mixtures given in Table I were next investigated.

At 15 ml water (interpolating from the results at 10 and 20 ml water where necessary) an increase in the volume of conc. ammonia from 10 to 40 ml resulted in

TABLE I

Solvent number	1	2	3	4	5	6	7	8	9	10
Volume methanol	70	65	55	60	55	45	60	55	50	40
Volume water	5	10	20	10	15	25	0	5	10	20
Volume ammonia, $d = 0.88$	25	25	25	30	30	30	40	40	40	40

the elevation of all  $R_F$  values. Copper and nickel gradually "pulled away" from the cobalt (which never completely left the starting line) so that at 30 ml conc. ammonia a good separation of copper, cobalt and nickel was achieved. The blue colour of the copper spot during elution showed that it moved as the ammine. The separation of zinc and cadmium was also at its best with this solvent mixture. Above 30 ml ammonia, the spots became distended and the separations inferior.

Variations in the water concentration, with the conc. ammonia maintained at 30 ml, confirmed that the optimum solvent composition for the separations Cu-Co-Ni and Zn-Cd, was: 55 ml methanol + 15 ml water + 30 ml conc. ammonia.  $R_F$  values were: Co 0-0.3 (bulk at very low  $R_F$ ), Cu 0.35-0.50, Ni 0.55-0.70, Zn 0.34-0.53, and Cd 0.70-0.79.

The forward tailing of cobalt was presumably due to the atmospheric oxidation of cobalt(II) at the starting line to cobalt(III), which then moves to  $R_F$  0.30. In many of the solvents investigated, cadmium produced two spots on the chromatogram. This was attributed *either* to the effect of sharp solvent composition gradients along the paper (*e.g.* a water front) *or* to the separation of two amines of cadmium (*cf.* ref<sup>1</sup>). The former is considered to be the more likely, and compares with the double spot phenomenon observed for certain organic molecules<sup>18</sup>.

A number of ternary mixtures taken from the solvent systems:  $\text{CH}_3(\text{CH}_2)_2\text{OH}-\text{H}_2\text{O}-\text{NH}_3$ ,  $(\text{CH}_3)_2\text{CHOH}-\text{H}_2\text{O}-\text{NH}_3$ , and  $(\text{CH}_3)_2\text{CO}-\text{H}_2\text{O}-\text{NH}_3$  showed no appreciable improvement on the results obtained with the methanol solvent just described. However,  $(\text{CH}_3)_2\text{CHOH}-\text{H}_2\text{O}-\text{conc. ammonia}$  (40:30:30, v/v) produced an excellent separation of copper ( $R_F$  0.3-0.6) and nickel ( $R_F$  0.7-0.8).

#### Section B. The separation of cobalt(II) chloride from some cobalt(III) ethylenediamine complexes

The solvent systems  $(\text{CH}_3)_2\text{CO}-\text{H}_2\text{O}-\text{HCl}$  and  $\text{CH}_3\text{OH}-\text{H}_2\text{O}-\text{HCl}$  were investigated over wide ranges of composition (Table II) for the separation of  $\text{CoCl}_2$  from  $\text{Co}(\text{en})_3\text{Cl}_3$ ,  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ , and  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}_3$ .

The complexes always remained very close together on the chromatogram with no separation of the adjacent extremities of the spots. In the acetone solvents maximum separation of  $\text{CoCl}_2$  from the nearest complex was obtained with  $(\text{CH}_3)_2\text{CO}-\text{H}_2\text{O}-\text{conc. HCl}$  (sp. gr. = 1.18), 88:6:6 (v/v), with an  $R_F$  separation of 0.15 of the adjacent extremities of the spots of  $\text{CoCl}_2$  and  $\text{Co}(\text{en})_3\text{Cl}_3$ . The  $R_F$  values of the centres of gravity of the spots were:  $\text{CoCl}_2 = 0.32$ , complexes = 0.05-0.06.

TABLE II

Solvent numbers	11	12	13	14	15	16	17	18	19	20	21
	22	23	24	25	26	27	28	29	30	31	32
Volume methanol* or acetone**	92	90	88	90	88	86	84	86	84	82	80
Volume water	6	6	6	8	8	8	8	10	10	10	10
Volume conc. HCl	2	4	6	2	4	6	8	4	6	8	10

\* Solvents 11-21.

\*\* Solvents 22-32.

The system methanol-aqueous hydrochloric acid produced greater centre of gravity  $R_F$  separation of  $\text{CoCl}_2$  from the complexes, but unfortunately the spot size was greater than with the acetone solvents. At the optimum solvent composition, methanol-water-conc. HCl, 92:6:2(v/v), the  $R_F$  values were:  $\text{CoCl}_2 = 0.70$ , complexes = 0.18-0.23.

*The separation of  $\text{Co(en)}_3\text{Cl}_3$  from  $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$  and  $[\text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3$*

With solvents 33-37, all the solutes moved very little or not at all. With solvents 38-41, the spots were very compact and moved some way from the starting line. However, with the two remaining solvents (42 and 43) the spots became much larger, resulting in considerable overlapping.

TABLE III

Solvent number	33	34	35	36	37	38	39	40	41	42	43
Volume ether	81.3	78.9	78.1	77.6	76.7	55.8	53.0	52.0	50.9	49.2	47.5
Volume methanol	16.3	16.8	15.6	15.5	15.3	34.5	31.8	31.2	30.6	29.5	28.5
Volume water	0.0	3.2	4.8	6.1	8.0	0.0	5.4	7.8	10.2	17.3	24.0
Volume conc. HCl	2.4	2.1	1.5	0.8	0.0	10.7	9.9	9.1	8.3	4.0	0.0

Without the ether, solvents 38-41 gave a slight  $R_F$  separation at a high  $R_F$  value, but with some overlapping. The addition of ether resulted in a "pulling back" of the spots to lower  $R_F$  values, but the *distance* of separation did not decrease commensurately with the fall in  $R_F$ . Consequently, solvents 38-41 were re-investigated by descending elution using the same procedure as adopted in Section C. It was found that the increase in the length of the run more than offset the effect of the added ether. In fact a separation of  $\text{Co(en)}_3\text{Cl}_3$  from  $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$  and  $[\text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3$  was obtained, typical  $R_F$  values being those for solvent number 40:

$\text{CoCl}_2 = 0.16$ ,  $\text{Co(en)}_3\text{Cl}_3 = 0.16$ ,  $[\text{Co(en)}_2\text{Cl}_2]\text{Cl} = 0.09$ ,  $[\text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3 = 0.095$ . The acid front in this solvent was at  $R_F 0.70$ .

There was some slight reduction of the dichloro-complex to  $\text{Co(II)}$ , but this was so slight as to be hardly detectable. Further, there was a very faint spot at  $R_F = 0.12$  in the  $[\text{Co(en)}_2(\text{H}_2\text{O})_2]\text{Cl}_3$  "lane" which did not correspond to any of the other

solutes on the chromatogram. It appears that this is due to a product of an equilibrium reaction on the chromatogram, possibly  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ . This could quite easily be produced by the equilibrium:



particularly in the presence of an HCl-containing solvent and reactive cellulose.

### Section C. The separation of some cobalt(III) complexes

It has already been reported in a preliminary communication<sup>7</sup> that the solvent system: ether-methanol-water-conc. HCl, 50:30:20:2 (v/v), is extremely valuable for the separation of some ammine complexes of cobalt(III). Full details are now given in Table IV and the appended remarks.

TABLE IV

Solute	$R_F$ values mean tailing limits		Remarks
1 $\text{CoCl}_2$	0.43	(0.35-0.49)	Compact spot
2 $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{Ox}]$	0.74	(0.73-0.75)	Slight tailing to $R_F$ 0.35*
3 $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	0.31	(0.28-0.33)	Some tailing to $R_F$ 0
4 $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$	0.08	(0.05-0.11) and	
	0.34	(0.30-0.38)	
5 <i>cis</i> - $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$	0.23	(0.18-0.27)	Faint tailing to $R_F$ 0.10
6 <i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$	0.74	(0.73-0.75)	Slight tailing to $R_F$ 0**
7 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	0.14	(0.11-0.17)***	
8 $\text{Co}(\text{NH}_3)_6\text{Cl}_3$	0†, and		Main spot at $R_F$ 0, but a little at 0.15
	0.15	(0.11-0.20)	
9 $\text{Na}_3\text{Co}(\text{NO}_2)_6$	0.43	(0.35-0.49)	Some tailing to 0.70. Main spot = Co(II) (due to rapid conversion of the complex during elution)
10 $\text{K}_3\text{CoOx}_3$	0.66	(0.62-0.70)	Some tailing to 0.35 (due to decomposition)
11 <i>cis</i> - or <i>trans</i> - $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	0.27	(0.19-0.33)	Compact spot

The  $R_F$  value of the acid front was 0.75. Ox =  $(\text{COO})_2^{-2}$ . en = ethylenediamine.

\* The tailing back to  $R_F$  0.35 indicates decomposition to Co(II) during elution.

\*\* There was some tailing between spots, and back to  $R_F$  0. The double-spotting suggests either a *cis-trans* separation, or a separation of the nitro- and nitrate-isomers.

\*\*\* An intensification of the tailing at  $R_F$  0.34 suggests decomposition to one of the components present in the spot of  $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ . The original solution contained solid chloro-pentamminocobaltic chloride (purpureo cobaltic chloride) dissolved in the eluting solvent.

† The spot at  $R_F$  0 was very probably due to hydrolysis at the starting line.

### SUMMARY

By use of an eluting solvent containing ammonia dissolved in aqueous methanol, it has been found possible to separate by paper chromatography copper, cobalt and nickel, and zinc from cadmium.

Certain new separations of a variety of ammine and ethylenediamine complexes of cobalt(III) are described, the eluting solvents used being ternary and quaternary mixtures of ether, methanol, water and concentrated hydrochloric acid.

References p. 379.

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