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Robert B. Hagel[a]; Leonard F. Druding[a]
[a] Department of Chemistry, Rutgers University, Newark, New Jersey

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Separation of Cobalt(III) Amine Complexes by Thin-Layer Chromatography: II. The Separation of Higher-Charged Cobalt(III) Complexes

ROBERT B. HAGEL and LEONARD F. DRUDING*
DEPARTMENT OF CHEMISTRY
RUTGERS UNIVERSITY
NEWARK, NEW JERSEY

Summary

A solvent system of formamide–methanol–glacial acetic acid has been found to be particularly useful in the separation of the geometrical isomers of di- and tripositive cobalt(III) amine complexes from each other. Best separations are obtained for the various aquo complexes, so that this method may be of value in the study of hydrolysis or solvolysis reactions of these complexes.

INTRODUCTION

In recent years, a large number of thin-layer chromatographic systems have been developed for the separation of inorganic complexes (*2*, *3*, *4*, *5*). In our previous investigations (*1*), excellent separations were obtained for cobalt(III) amine complexes that differed from one another in charge, as well as for the separation of the geometrical isomers of the unipositively charged ions. However, separation of the di- and tripositively charged ions was very poor, often resulting in closely spaced or overlapping bands on the plates. This observation appears to be true of the other systems reported to date. There has been a need for an effective and reliable separation of the geometrical isomers of the higher charged complex ions for such purposes as following the product forma-

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* To whom correspondence should be addressed.

tion in hydrolysis and solvolysis reactions, and for the rapid identification of reaction products. The previous work suggested that the silica gel used as the adsorbant was behaving as a weak cation exchanger in which the higher-charged species are retained more tenaciously. Under these circumstances, the differences in polarity between the *cis* and *trans* isomers are small compared to the attractive force between the silica gel and the +2 or +3 ion. Two alternatives are possible: to choose an adsorbant with a weaker retention power for the higher-charged complexes, or to choose a solvent system more capable of either solvating or displacing the higher-charged ions.

EXPERIMENTAL

As before, the cobalt(III) amine complexes were prepared according to methods described in such literature as the periodical *Inorganic Syntheses*. The purity criteria used for the various preparations were their thin-layer chromatograms.

The thin-layer plates used for these separations were commercially precoated silica gel plates (Type Q-I, Quantum Industries, Fairfield, N. J.). These plates were used as supplied by the manufacturer. The 50 × 200 mm plates gave more uniform results that did the 200 × 200 mm plates. Extremely small volumes of samples were applied (0.4 λ of approximately 0.05 *M* solutions). The chromatograms were developed by the ascending technique in a large tank. The time required for 120 mm of total solvent travel was about 100 min. Use of a sandwich-type developing chamber produced no change in developing time. Apparently, the fineness of the silica gel particles and the type of binder used on these plates deter fast solvent travel.

Attempts were made to use plates coated with Silica Gel H (Brinkman Instruments, Westbury, N. Y.). While the development times for these plates was about 45 min for the same solvent travel, the faster time resulted in lower R_F values and much poorer resolution of the different complexes.

Detection of the complexes was accomplished by spraying the plates with an aqueous solution of nitroso-R salt (Fisher Scientific, Fair Lawn, N. J.), which produced a bright orange spot against a pale yellow to green background.

R_F values were reproducible to within ±0.02 R_F units. The R_F values were not only determined from pure compounds, but also from analysis of the products of acid and base hydrolysis reactions.

RESULTS

The best solvent system found for the separation of the geometric isomers of the higher-charged cobalt(III) amine complexes was a mixture of formamide–methanol–glacial acetic acid in the ratio of 40:60:0.1. Table 1 compares the R_F values in this solvent system with the values previously reported for the dimethyl sulfoxide–methanol–perchloric acid system (*1*). In most cases, the R_F values are larger for the present solvent system than the former one.

Table 2 lists the R_F values of some substituted pentamminecobalt(III) complexes, while Table 3 gives the R_F values of some selected *cis-* and *trans*-diacidobis(ethylenediamine)cobalt(III) complexes and their hydrolysis products.

TABLE 1

Comparison of R_F Values of Some Cobalt(III) Amine Complexes on Silica Gel Using Different Solvents

	DMSO-MeOH-HClO$_4$[a]		HCONH$_2$-MeOH-HOAc[b]	
Complex	*trans*	*cis*	*trans*	*cis*
$[Co(en)_2(OAc)_2]^+$	0.65	—	0.63	—
$[Co(en)_2(N_3)_2]^+$	0.80	0.61	0.85	0.77
$[Co(en)_2(N_3)(NCS)]^+$	0.89	0.85	0.92	0.85
$[Co(en)_2(N_3)(NO_2)]^+$	0.77	0.68	0.81	—
$[Co(en)_2Br_2]^+$	0.79	0.60	0.84	0.77
$[Co(en)_2Cl_2]^+$	0.75	0.57	0.80	0.77
$[Co(en)_2Cl(NCS)]^+$	0.82	0.68	0.94	0.85
$[Co(en)_2Cl(NO_2)]^+$	0.73	0.69	0.80	0.75
$[Co(en)_2F_2]^+$	0.73	0.53	0.82	0.78
$[Co(en)_2(NCS)_2]^+$	0.84	—	0.95	—
$[Co(en)_2(NCS)(NO_2)]^+$	0.91	0.82	—	0.78
$[Co(en)_2(H_2O)(OAc)]^{2+}$	—	—	0.57	—
$[Co(en)_2(H_2O)Br]^{2+}$	0.16	—	0.58	0.36
$[Co(en)_2(H_2O)Cl]^{2+}$	0.24	0.18	0.64	0.55
$[Co(en)_2(H_2O)F]^{2+}$	0.35	0.17	0.63	0.41
$[Co(en)_2(H_2O)(NCS)]^{2+}$	0.56	0.54	0.70	0.43
$[Co(en)_2(H_2O)(NO_2)]^{2+}$	0.50	0.48	0.57	0.34
$[Co(en)_2(H_2O)_2]^{3+}$	0.36	0.17	0.19	0.12
$[Co(NH_3)_4(H_2O)Cl]^{2+}$	0.20	—	0.63	—
$[Co(NH_3)_4(H_2O)(NO_2)]^{2+}$	0.19	—	0.72	0.65
$[Co(NH_3)_4(H_2O)_2]^{3+}$	—	0.29	0.25	0.11

[a] L. F. Druding and R. B. Hagel, *Anal. Chem.*, **38**, 478 (1966).

[b] This work.

TABLE 2

R_F Values of Some Substituted Pentammine–Cobalt(III) Complexes

Complex	R_F
$[Co(NH_3)_5N_3]^{2+}$	0.60
$[Co(NH_3)_5Br]^{2+}$	0.68
$[Co(NH_3)_5Cl]^{2+}$	0.67
$[Co(NH_3)_5(CN)]^{2+}$	0.55
$[Co(NH_3)_5F]^{2+}$	0.59
$[Co(NH_3)_5(NO_2)]^{2+}$	0.62
$[Co(NH_3)_6]^{3+}$	0.62
Co^{2+}	1.00 + tail to origin

As in the previous report, an acidic solvent was chosen to repress the hydrolysis of the complexes during the elution and to provide an ionic medium whereby the proton could displace the adsorbed complexes. Glacial acetic acid was found to give slightly better separation of the dipositive complexes than perchloric acid. That no hydrolysis took place during elution was evident by the lack of tailing of the complexes on the plate.

This solvent system yielded separations that were entirely analogous with previous results for silica gel adsorbant, except that resolution of the geometrical isomers of the higher-charged complexes was greatly improved. Anionic and neutral complexes move with or near the solvent

TABLE 3

Selected R_F Values of $[Co(en)_2AB]^+$ and Their Hydrolysis Products

Complex	R_F	Complex	R_F
trans-Cl_2	0.80	*trans*-NO_2-Cl	0.80
cis-Cl_2	0.77	*cis*-NO_2-Cl	0.75
trans-Cl-H_2O	0.64	*trans*-NO_2-H_2O	0.57
cis-Cl-H_2O	0.55	*cis*-NO_2-H_2O	0.34
trans-$(H_2O)_2$	0.19	*trans*-$(H_2O)_2$	0.19
cis-$(H_2O)_2$	0.11	*cis*-$(H_2O)_2$	0.11
trans-Br_2	0.84	*trans*-NCS-Cl	0.94
cis-Br_2	0.77	*cis*-NCS-Cl	0.85
trans-Br-H_2O	0.58	*trans*-NCS-H_2O	0.70
cis-Br-H_2O	0.36	*cis*-NCS-H_2O	0.43
trans-$(H_2O)_2$	0.19	*trans*-$(H_2O)_2$	0.19
cis-$(H_2O)_2$	0.11	*cis*-$(H_2O)_2$	0.11

front. *Trans* complexes are more mobile than the *cis* isomers, as expected for the postulated ion exchange mechanism.

While separation of the *cis* and *trans* isomers of the complexes of the types $[Co(en)_2(A)(H_2O)]^{2+}$, $[Co(NH_3)_4(A)(H_2O)]^{2+}$, $[Co(en)_2(H_2O)_2]^{3+}$, and $[Co(NH_3)_4(H_2O)_2]^{3+}$ (where A is an anionic ligand) were quite good, separations of the various complexes of the type $[Co(NH_3)_5A]^{2+}$ were not as good.

In general, it was found that the acidopentamminecobalt(III) complexes had higher R_F values than the acidoaquotetramminecobalt(III) complexes, although the ionic charge on the two types of complexes are the same. The R_F values for $[Co(NH_3)_5Cl]^{2+}$ and *trans*- and *cis*-$[Co(NH_3)_4(H_2O)Cl]^{2+}$ are 0.47, 0.42, and 0.32, respectively. A possible explanation is that the aquo group is quite similar to the silanol sites of the silica gel, so that a substitution reaction could take place where the silanol group substitutes for the aquo group in the coordination sphere of cobalt(III). Such a substitution could conceivably take place without rupturing the cobalt–oxygen bond. Burwell et al. (*6*) have shown that the silanol group of silica gel can replace chloride in $[Co(en)_2Cl_2]^+$. By this type of mechanism of silanol substitution into the coordination sphere of cobalt(III), a stronger bond can be developed than in the case where the ionic complex, with its coordination sphere intact, is exchanged for one of the silanol protons. The tripositive *cis*-diaquotetraamine complexes $[Co(en)_2(H_2O)_2]^{3+}$ and $[Co(NH_3)_4(H_2O)_2]^{3+}$ are always retained more strongly than any other cobalt(III) complex; these two complexes have their aquo groups located so that both may bond to the silica gel. Although other tripositive complexes such as $[Co(NH_3)_6]^{3+}$ and *trans*-$[Co(en)_2(H_2O)_2]^{3+}$ may be displaced by hydronium ion, the *cis*-diaquo complexes are not so displaced.

Use of this solvent system along with the previously reported dimethyl sulfoxide–methanol solvent system should enable the inorganic chemist to completely separate all of the possible products of solvolysis reactions.

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