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Thin-Layer Chromatography of Some Inorganic Complexes Using Microcrystalline Cellulose as the Separation Medium

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Summary

Microcrystalline cellulose as an adsorbent in inorganic thin-layer chromatography has been successfully applied to the separation of several cobalt complexes in a variety of solvent systems. The analogy between paper, ion-exchange, and silica-gel chromatographic separations is discussed.

Since King and Walter have separated $[Co(NH_3)_4(NO_2)_2]^+$ by ion-exchange chromatography (*1*), the use of chromatographic methods has greatly contributed to the study of inorganic complexes. Successful separations of cobalt, chromium, rhodium, and platinum complexes have been chromatographed on paper, ion exchange, and silica gel–starch (*2*). The last adsorbent has had wide acceptance in inorganic thin-layer chromatography (*3*). We wish to make known another TLC separation medium suitable for the separation and identification of inorganic complexes.

Recently we have reported on the separation of most of the cations in the classical qualitative analysis scheme by using Avicel, a form of microcrystalline cellulose as the adsorbent (*4*). A literature survey reveals that this adsorbent in inorganic TLC has been restricted to the separation of some B-trichloroborazines (*5*) and several of the anions and cations commonly encountered in water analysis (*6,7*). The present work was undertaken to study the TLC

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behavior of several geometrical (*cis-trans*) isomers of cobalt using microcrystalline cellulose as the adsorbent.

EXPERIMENTAL

Complex-Ion Preparation

The complex ions studied were the *cis* and *trans* isomers of $[Co(en)_2Cl_2]Cl_2$, $[Co(en)_2(NO_2)_2]NO_3$, and $[Co(NH_3)_4(NO_2)_2]NO_3$. They were prepared according to the procedures outlined by Schlesinger (*8*). The infrared spectra of these compounds at 6 and 12 μ agreed with published values (9).

Plate Preparation

A rather fluid slurry of the adsorbent was prepared by blending 50 g of microcrystalline cellulose (technical grade, Avicel Sales Division, FMC Corp., Marcus Hook, Pa.) with 212 ml of water in a Waring blender for 15–30 sec at low speed and for a few seconds at high speed. Air bubbles were removed from the slurry by gentle shaking and pumping with a water aspirator for about 2 min. The mixture was spread on 20 × 5 cm glass plates at a thickness of 0.75 mm. The plates were allowed to dry overnight and then were placed in a desiccator over sodium hydroxide until ready for use.

Mixing time varied slightly since it was observed that different lots of microcrystalline cellulose gave different consistencies to the slurry. It was found that uniform plates could best be prepared from a rather fluid slurry. Thus the departure from the mixing time originally suggested by Wolfrom et al. (*10*) became a function of the fluidity of the slurry.

Solution Preparation and Application

Aqueous solutions of the various complex ions were prepared in concentrations ranging from 0.2 to 1.0% (w/v). The *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ was dissolved in a minimum amount of water, and then the solution was brought up to volume with methyl alcohol. Mixtures of the isomers were prepared by combining equal volumes of the solutions delivered from a pipet. All solutions were applied to the microcrystalline cellulose-coated glass by capillary syringes and were allowed to dry before insertion into the chromatographic tanks. Due to the instability of these ions in solution, fresh solutions were prepared every few hours.

Solvent Systems

Redistilled or reagent-grade chemicals were used in the solvent systems. These solvent systems were made up to a total volume of 100 ml. Fresh solutions were used for duplicate runs. The development time for all the solvent systems was about 1 hr. The solvent systems are listed in Table 1.

Detection

Mixtures of the geometric isomers of the cobalt(III) complexes were detected by spraying with a 1% (w/v) aqueous solution of the disodium salt of 1-nitroso-2-naphthol-3,6-disulfonic acid. This detection reagent imparted an orange color to the complexes on a yellow background. Heating the plates at 60–100°C was found to heighten the colors of the bands.

TABLE 1

List of TLC Solvent Systems Using Microcrystalline Cellulose

No.	Solvent system
1	65 ml acetone–30 ml water–5 ml conc. nitric acid
2	70 ml acetone–20 ml water–10 ml conc. hydrochloric acid
3	60 ml methyl alcohol–40 ml dimethylformamide–10 drops perchloric acid
4	60 ml methyl alcohol–40 ml dimethylformamide–10 drops formic acid
5	60 ml methyl alcohol–40 ml dimethylsulfoxide–10 drops perchloric acid
6	60 ml methyl alcohol–40 ml dimethylsulfoxide–10 drops formic acid
7	100 ml methyl alcohol–10 drops perchloric acid
8	100 ml methyl alcohol–10 drops formic acid
9	70 ml methyl alcohol–30 ml propionaldehyde–10 drops perchloric acid
10	70 ml methyl alcohol alcohol–30 ml nitromethane–10 drops perchloric acid
11	50 ml alcohol–50 ml nitromethane–10 drops perchloric acid
12	50 ml methyl alcohol–50 ml propionaldehyde–10 drops perchloric acid
13	70 ml methyl alcohol–30 ml propionitrile–10 drops perchloric acid
14	100 ml propionaldehyde–2 g pyridine N-oxide–10 drops perchloric acid
15	50 ml methyl alcohol–50 ml *n*-butyronitrile–10 drops perchloric acid
16	70 ml methyl alcohol–30 ml *n*-butyronitrile–10 drops perchloric acid
17	70 ml methyl alcohol–30 ml tetrahydrofuran–10 drops perchloric acid
18	70 ml methyl alcohol–30 ml acrylonitrile–10 drops perchloric acid
19	50 ml methyl alcohol–50 ml acrylonitrile–10 drops perchloric acid

RESULTS

Solvents systems 1 and 2 for the separations of these complexes on Whatman's paper have been reported previously (2). Solvent systems 3 to 19 are novel and it indicates that inorganic complexes can be successfully separated in a variety of solvent mixtures. The R_F values reported in Table 2 are consistent to ±0.05 R_F units. It is to be noted that in all separations the R_F values of the *cis* complex was greater than the *trans*.

In a solvent system composed of methyl alcohol, pyridine N-oxide, and perchloric acid, a reversal of the general trend for the *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ was observed. It seems probable that solvent interaction is responsible for this result. No reproducible separations for the geometric isomers of $[Co(en)_2(SCN)$-

TABLE 2

R_F Values of Some *Cis*- and *Trans*-Co(III) Complexes by TLC Using Microcrystalline Cellulose

Solvent system	$[Co(en)_2Cl_2]Cl$		$[Co(en)_2(NO_2)_2]NO_3$		$[Co(NH_3)_4(NO_2)_2]NO_3$	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
1	—	—	0.75	0.45	0.40	0.13
2	0.52	0.21	—	—	—	—
3	—	—	0.75	0.37	—	—
4	—	—	—	—	—	—
5	0.73	0.27	0.74	0.59	—	—
6	—	—	0.14	0.09	—	—
7	—	—	0.45	0.11	—	—
8	0.50	0.34	0.36	0.15	—	—
9	—	—	—	—	0.16	0.06
10	—	—	—	—	0.44	0.20
11	—	—	—	—	0.47	0.15
12	—	—	0.31	0.15	0.17	0.03
13	—	—	—	—	0.35	0.14
14	—	—	—	—	0.13	0.03
15	—	—	0.72	0.07	0.25	0.09
16	—	—	0.53	0.08	0.30	0.09
17	—	—	—	—	0.25	0.13
18	—	—	0.59	0.42	0.27	0.11
19	—	—	—	—	0.34	0.10

Cl]Cl were obtained in the reported solvent systems. Again, destruction of the original complex by the solvent is a reasonable explanation.

DISCUSSION

All data reported in this paper and our earlier communication (*4*) support the analogy between microcrystalline cellulose TLC and paper chromatography. Using Whatman's No. 1 paper (ascending), these same cobalt(III) complexes have been separated using a solvent system composed of acetone, water, and acid (*11*). The general order of *cis* greater than *trans* for the R_F values is also reported for these separations. On an ion-exchange resin, *trans*-$[Co(NH_3)_4(NO_2)]^+$ and *trans*-$[Co(en)_2(NO_2)_2]^+$ are reported to be more adsorbed on the column than their corresponding *cis* isomers (*12,13*). By the thin-layer technique using silica gel, $[Co(en)_2Cl_2]^+$ has also been separated (*14*). The *trans* complex is reported to be more mobile than the *cis* form. A more extensive investigation of TLC–silica-gel separations of some cobalt(III) amine complexes (*15*) has also shown that *trans* isomers are more mobile than their *cis* isomers. The authors suggest that the *cis* isomer with their acid groups adjacent would have two linkages to the silica gel, while the *trans* isomer with the acido group on the opposite side of the ion would be able to form only one linkage to the silica gel. Druding and Hagel claim this results in a more tightly held *cis* isomer. Kauffman (*16*) has shown a similar behavior in the separation of some iridium complexes on silica gel.

It may be concluded that for geometric isomers separated on paper and microcrystalline cellulose TLC, the *cis* isomer, because of its larger dipole moment, is more mobile than the *trans* isomer. Silica gel with a surface consisting of silanol groups (Si–OH) operates very effectively as a weak acid ion exchanger in the same manner as a cation-exchange resin. Indeed, anion and neutral complexes have no retention on silica gel (*15*). Thus the reversal of the separation order of *cis* and *trans* cation complexes from paper and microcrystalline cellulose is to be expected.

From the data cited in Table 2, no simple quantitative relationship exists between the dipole moment of the complex and the R_F value. Qualitatively, it is observed that the solvent systems containing a constituent of high dipole moment, like dimethylsulfoxide-3,9-nitromethane-3,5-propionitrile (4.05) and butyronitrile (4.07), gave a larger difference in the R_F values of the *cis* and *trans* isomers.

In a mixture of the ions, mobilities were found to vary only slightly from the values obtained when they were taken individually. Acid concentration was also found to have a marked effect on R_F values. A band of some trace impurity was present on all the chromatograms, despite the fact that the compounds were purified by the usual techniques. Since the preparations seemed otherwise pure, this bears out the sensitivity of this method for testing isomeric purity. Seiler et al. (*14*) have also observed a trace of *cis*-$[Co(NH_3)_3(NO_2)_3]$ in their silica-gel–starch separation of *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$.

The applicability of this method to the resolution of inorganic optical isomers is at present under study.

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