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Chromatographic Studies of Metal Complexes.
Part IV. Thin Layer Chromatographic Separation of *cis* from *trans* Isomers of Cobalt(III) Mixed Ligand Complexes

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Abstract

With acidic mixed solvents (40:60:0.2 formamide: methanol:acetic acid or 40:60:0.25 *N,N*-dimethylformamide:methanol:perchloric acid) cationic *cis* and *trans* isomers of cobalt(III) mixed chelates were successfully separated by thin layer chromatography (TLC) using silica gel H adsorbent. The mechanism of separation is based on an ion-exchange process. R_F values of *cis* complexes were found to be greater than those of the *trans* complexes. In addition to other factors, solubilities of the complexes have a profound effect on the R_F values of these cationic complexes.

Introduction

The separation of *cis* from *trans* isomers has always been a challenging problem for the coordination chemist. Adsorption chromatography [1,2] and thin layer chromatography (TLC) [3–8] are valuable techniques that have been applied to the solution of this problem. The pioneers in this area were probably Linhard *et al.* [9], who separated *cis* from *trans* isomers of the $[Co(N_3)_2(NH_3)_4]^+$ ion on an alumina column. From TLC studies on silica gel Seiler *et al.* [10], Tsunoda *et al.* [11], and later Druding and Hagel [12,13] successfully separated *cis* from *trans* isomers of different cobalt(III) complexes by using either acidic, basic, or buffer solutions as eluents.

Overwhelming evidence shows that for octahedral complexes, developed with an acidic or water-containing solvent, the *trans* isomer is more mobile than the corresponding *cis* isomer. This generalization, along with other evidence, led to the assignment of the *trans* configuration to $[CoF(en)_2(H_2O)]^{2+}$ [14]. According to Burwell *et al.* [15] the *cis* isomer can be retained more strongly on silica gel or on a resin bed than the *trans* isomer since the former can have two points of attachment to the silanol sites of the silica gel or to the acidic sites of an ion exchange resin, whereas the *trans* groups, being on opposite sites of the complex, can attach at only one point. If the mechanism is one of adsorption rather than of ion exchange, then this trend should also prevail since the *cis* isomer would be more polarized than the *trans* isomer.

This mechanism is supported by Kyuno's experiments [16] for the separation of $[Co(CO_3)(NO_2)_2(NH_3)_2]^-$ and $[Co(NO_2)_2(C_2O_4)(NH_3)_2]^-$ ions on an alumina column. In both cases the elution order of the three possible geometric isomers was: *trans*-NO_2, *trans*-NH_3, and *cis* isomer, i.e. the least polarized ion was the most mobile. However, contrary to the above line of argument, the reverse order of R_F values has also appeared in the literature [17–21].

In the present article we report the successful separation of five pairs of *cis-trans* isomers of cobalt(III), using two different solvents on silica gel adsorbent (Table 1). We found that the *cis* isomers always show higher R_F values than the corresponding *trans* isomers in both the developers (I and II) used.

Experimental

Materials

All isomers were prepared according to published procedures [22,23]. Samples were purified by repeated recrystallization until the spectra agreed with the reported values and/or until the thin-layer chromatograms showed that no impurities were present. The isomers were also identified by infrared spectroscopy (Fig. 1). The solution spectra of all

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TABLE 1. Colors, electronic spectra and R_F values of cobalt(III) complexes with developer I (40:60:0.2) formamide:methanol: acetic acid) and developer II (40:60:0.25 *N,N*-dimethylformamide:methanol:perchloric acid)

Complex^a	Color	Electronic spectra in methanol, developer I and developer II		R_F	
		Band II (cm^{-1}) (ϵ)	Band I (cm^{-1}) (ϵ)	Developer I	Developer II
cis-$[Co(NO_2)_2(AMUH)_2]NO_2$	brownish red	30000 (6430)	21700–21300 (435)	0.61	0.57
trans-$[Co(NO_2)_2(AMUH)_2]NO_2$	dark red	30000 (6425)	21650–21300 (420)	0.55	0.52
cis-$[Co(NO_2)_2(AEUH)_2]NO_2$	brownish red	30000 (6430)	21700–21300 (435)	0.64	0.60
trans-$[Co(NO_2)_2(AEUH)_2]NO_2$	orange	30000 (6420)	21700–21300 (425)	0.60	0.52
cis-$[Co(NO_2)_2(AP^iUH)_2]NO_2$	brownish red	30000 (6425)	21600–21300 (435)	0.69	0.63
trans-$[Co(NO_2)_2(AP^iUH)_2]NO_2 \cdot 2H_2O$	orange	30000 (6410)	21700–21300 (430)	0.64	0.60
cis-$[Co(NO_2)_2(AB^nUH)_2]NO_2$	brownish red	30000 (6400)	21700–21300 (430)	0.74	0.70
trans-$[Co(NO_2)_2(AB^nUH)_2]NO_2$	orange	30000 (6400)	21500–21300 (452)	0.67	0.63
cis-$[Co(NO_2)_2(AB^iUH)_2]NO_2$	brownish red	30000 (5660)	22700–21300 (508)	0.79	0.73
trans-$[Co(NO_2)_2(AB^iUH)_2]NO_2$	orange	30000 (4100)	21700–21300 (336)	0.75	0.70
cis-$[Co(NO_2)_2(AA^iUH)_2]NO_2$	brownish red	30000 (5640)	22700–21700 (416)	0.85	0.80
trans-$[Co(NO_2)_2(AA^iUH)_2]NO_2$	orange	30000 (5560)	21700–21300 (376)	0.77	0.73
cis-$[Co(NH_2)_2(bigH)_2](SO_4)_{1.5}$	red		20200 (120)	0.25	0.19
trans-$[Co(NH_3)_2(bigH)_2](SO_4)_{1.5}$	red–violet		20200 (80)	0.32	0.27

^{a}AA^{i}UH = 1-amidino-*O*-isoamylurea; AA^{n}UH = 1-amidino-*O*-n-amylurea; AMUH = 1-amidino-*O*-methylurea; AEUH = 1-amidino-*O*-ethylurea; AB^{i}UH = 1-amidino-*O*-isobutylurea; AB^{n}UH = 1-amidino-*O*-n-butylurea; AP^{i}UH = 1-amidino-*O*-isopropylurea; bigH = biguanide; DMSO = dimethyl sulfoxide.

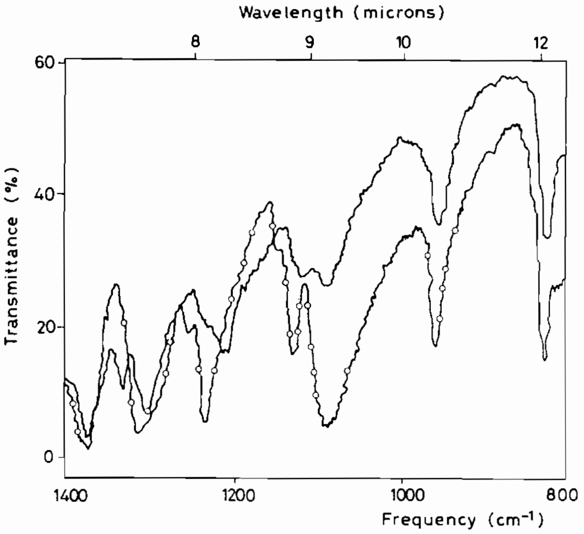

Fig. 1. Infrared spectra of *cis*-$[Co(NO_2)_2(AMUH)_2]NO_2$ (brownish red) (——) and of *trans*-$[Co(NO_2)_2(AMUH)_2]NO_2$ (red) (–o–).

cobalt(III) complexes were recorded by using a Hilger Uvispec spectrophotometer over the range of 300–550 nm. Infrared spectra were recorded at CDRI, Lucknow, India.

Procedure

The adsorbent (Merck silica gel H) was slurried with distilled water (two parts of water to one part of adsorbent) and sprayed on glass plates of thickness 0.25 mm with the aid of a Moving Spreader apparatus. The plates were dried in air for 20 min, heated at 105–110 °C for 1 h and stored in a desiccator as prescribed by Stahl [24]. The chromatographic chambers were saturated with the developers for at least two days, and development was carried out at room temperature. The developer was allowed to travel 13–14 cm from the point of application of the samples. R_F values were reproducible to within ±0.02 R_F unit. All the cobalt(III) complexes were detected by spraying with an aqueous solution of Na_2S, which colors the spots black.

Results and Discussion

The existence of two different crystalline modifications of each cobalt(III) complex has been established by electronic spectra [22, 23] (Table 1). All the complexes exhibit two absorption bands, one located at around 335 nm and the other a broad absorption band at 440–480 nm (Table 1, Fig. 2). The *cis* complexes were expected to exhibit higher intensity bands than the corresponding *trans* species (Fig. 1). Both isomers showed the presence of strong bands at ~810–830 cm^{-1}, but the red compound obtained by the air oxidation method revealed only the strong absorption band at 1315 cm^{-1}, whereas the brownish red one revealed two bands located at 1310 and 1335 cm^{-1} (Fig. 1).

When all the cationic complexes were developed with water, they remained at the point of application

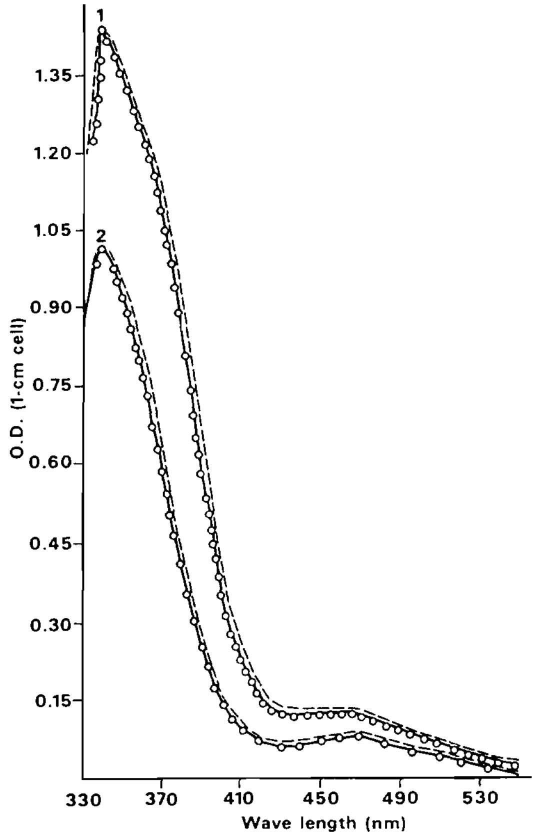

Fig. 2. Electronic absorption spectra in a methanol solution, in developer I (----) and in developer II (–○–): (1) *cis*-$[Co(NO_2)_2(AB^iUH)_2]NO_2$ (0.00025 M), (2) *trans*-$[Co(NO_2)_2(AB^iUH)_2]NO_2$ (0.00025 M).

since silica gel (≡Si–OH) is charged negatively in contact with water [25, 26]. By using developers containing neutral salts such as NaCl, KCl, Na_2SO_4, K_2SO_4, etc. separation of *cis* from *trans* isomers could not be accomplished, although the cationic complexes moved and exhibited high R_F values. With solvents I or II, however, successful separation of *cis* from *trans* isomers was accomplished. The acid present in the mixed solvents (developers I or II) helped to resist any possible hydrolytic reactions.

A perusal of Table 1 shows that the *cis*-$[Co(NO_2)_2(AAUH)_2]^+$ cation (AAUH = 1-amidino-*O*-alkylurea) always shows higher R_F values than that of the *trans* isomer. These differences in R_F values for *cis* and *trans* isomers may originate in the differences in dipole moments, solubilities, ion-pair formation between the complex cation and the anion present in the developer, stability of the complexes, steric hindrance, adsorptivity and symmetry [26–33]. We believe that the higher R_F values of the *cis*-$[Co(NO_2)_2(AAUH)_2]^+$ complexes in the present study are due mainly to the higher solubilities of the *cis* isomers than those of the corresponding *trans* isomers [22]. Our results confirmed those of Stefanović and Janjić and others [18–21], who observed that *cis* isomers always show higher R_F values than the corresponding *trans* isomers.

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