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Note

Separation of inorganic isomers by thin-layer chromatography

II. Octahedral geometric isomers

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Although thin-layer chromatography (TLC) has been applied mostly to the separation of organic and biological materials, recent years have seen its increased application to inorganic separations. Syntheses of coordination compounds frequently produce more than one isomer, and rapid, efficient, and reliable methods for separating the resulting mixtures are desirable. Therefore, the growing number of separations of isomeric complexes by TLC[1–9] is especially welcome.

In a previous publication in this series[4], we have applied silica gel G (Kensington Scientific, Oakland, Calif., U.S.A.) to the TLC separation of six non-electrolytic geometric isomers of platinum(II), for two of which separation by column chromatography had proven unsuccessful[10]. In an effort to prove the general applicability of the method, we have extended our studies to include geometric isomers of various metals with coordination number six. Inasmuch as we demonstrated in our first article[4] that TLC separations can be carried out on a semi-quantitative preparative scale (with *ca.* 200 mg of total mixtures), all the separations reported here are strictly qualitative. In addition to using mixtures prepared from pure isomers, we also applied the method to materials that should theoretically exist in more than one isomeric form.

EXPERIMENTAL

Materials

Isomer samples were either prepared and characterized in this laboratory (designated GBK in Table I) or were kindly provided by the persons listed alphabetically under Acknowledgements (designated by initials in Table I). All solvents were C.P. or reagent grade. The adsorbent used was silica gel TLC sorbent (SilicAR® TLC-7G or TLC-7F, Mallinckrodt, St. Louis, Mo., U.S.A.), which was generously furnished by the manufacturer. We are also indebted to Englehard Industries (Newark, N.J., U.S.A.) for experimental samples of platinum sponge.

Procedure

Microscope slides (75 × 25 cm) were thoroughly cleaned with detergent, rinsed with distilled water, and coated with a slurry consisting of one part of adsorbent in

three parts of a 1:1 (v/v) mixture of methanol and redistilled methylene chloride. The plates were air-dried for 10–20 min and activated by drying for 1 h at 110° just prior to use. Isomers and mixtures were applied as saturated solutions in the appropriate solvent or solvent mixture, and the plate was air-dried and developed by the ascending technique[11]. After air-drying the plates, the isomers were detected as intense yellow-brown spots with iodine vapor. Thiocyanate complexes could be visualized with iron(III) chloride solution, and in the case of highly colored compounds no visualization was required. Separated isomers were identified by comparison with R_F values obtained for the pure isomers when available or by mixed melting point measurements or other characterization techniques. Further details are given in previous articles[4,10].

RESULTS AND DISCUSSION

The results obtained are summarized in Table I. The R_F values reported were reproducible to $\pm$ 0.03. Although many developing solvents and mixtures were evaluated, only the most successful combinations, *i.e.*, those resulting in maximum differences between R_F values and minimum tailing, are shown. The following samples, listed by type and number, were successfully separated: MA_2B_4: 1–3 (partial); $M(AA)_2B_2$: 4, 5 (partial); $M(AA)_2BC$: 6, 7, 10; 8, 9, and 11 (partial); $M(AB)_2C_2$: 12 (partial); MA_3B_3: 13, 14; MA_3B_2C: 19, 20; $M(AA)(BC)_2$: 23 (partial); $M(AB)_3$: 24–27; M(AAA)(BBC): 28 (partial); $M(AA)B_2C_2$: 29. The remaining samples could not be separated. In many cases (samples 15–18, 21, and 22), unsuccessful separations do not necessarily imply failure; the materials chromatographed were only theoretically capable of existing in two isomeric forms. In fact, samples 15–17 were later found to consist exclusively of the *cis* form[26]. The results obtained for samples 14–18, 21, and 22 agreed with those obtained by column chromatography[57]. Samples 1, 2, 14, and 19 were also previously separated by column chromatography[57]. Sample 20, which could not be separated by column chromatography because of limited solubility[38], was separated completely by TLC.

In some cases, complete separations were precluded by isomerization (sample 3, *trans* isomer stable only in the solid state[14,39]) or decomposition (sample 3, odor of isonitrile noticeable on dissolution; samples 8–11, hydrolysis or aquation) known to occur. Samples 4, 5, 8–12, and 24–28 represent the first electrolytes that we have separated by either column chromatography or TLC, although we have separated *cis*-$[Ir(Et_2S)_3Cl_3]$ from *trans*-$[Ir(Et_2S)_4Cl_2]$–*trans*-$[Ir(Et_2S)_2Cl_4]$ (originally believed to be *trans*-$[Ir(Et_2S)_3Cl_3]$)[38,40]. Sample 28 was previously separated into three isomers by column chromatography[37]. It constitutes the first compound that we have separated into more than two isomers. For all separations obtained, R_F *cis* $< R_F$ *trans*, except for samples 6, 7, 12, and 29. For samples 6 and 7 Boucher's TLC results[18] agree with ours.

In addition to the isomers shown in Table I, separations were attempted with the following isomers (classified by type) but were unsuccessful for the reasons cited. MA_2B_4: *cis* (blue-black)- and *trans* (blue)-$Rb_2[IrCl_2Br_4]$, *cis* (pigeon blue)- and *trans* (blue)-$Cs_2[OsI_2Cl_4]$, *cis* (orange)- and *trans* (yellow)-$Rb_2[OsBr_2Cl_4]$ (WP)[41] —insolubility in suitable solvents, decomposition in the solvent (water); $M(AA)_2B_2$: *cis* (dark brownish orange)- and *trans* (light brownish orange)-$[Cotn_2(NO_2)_2]NO_2$, *cis*

TABLE I

TLC OF HEXACOORDINATE GEOMETRIC ISOMERS

No.	Isomer	Source	Developing solvent	R_F		ΔR_F	Type of separation
				cis	*trans*		
	Type MA_2B_4						
1	$[Pt(Et_2S)_2Cl_4]$* *trans* (lemon yellow) *cis* (bright yellow)	GBK[12]	C_6H_6	0.00	0.56	0.56	Complete
2	$[Pt(n\text{-}Bu_3P)_2Cl_4]$* *trans* (golden yellow) *cis* (greenish yellow)	GBK[13,**]	C_6H_6	0.00	0.90	0.90	Complete
3	$[Fe(NCC_6H_4\text{-}p\text{-}CH_3)_4Cl_2]$ *trans* (violet) *cis* (orange)	FB[14]	$(CH_3)_2CO$–CH_2Cl_2 (2:8)	0.96	1.0	0.04	Partial (isomerization in solution)
	Type $M(AA)_2B_2$						
4	$K[Cr(H_2O)_2(C_2O_4)_2]$ *trans* (3 H_2O) (purple-pink) *cis* (2 H_2O) (deep purple)	FJ[15,16]	$(CH_3)_2CO$–H_2O (1:1)	0.37	0.63	0.26	Complete
5	$[Cren_2(NCS)_2]SCN$ *trans* (2 H_2O) (orange) *cis* (orange)	EK[17]	CH_3OH	0.66	0.92	0.26	Partial
	Type $M(AA)_2BC$						
6	$[Co(acac)_2(NO_2)py]$ *trans* (brown) *cis* (red)	LJB[18]	CH_2Cl_2	0.25	0.05	0.20	Complete
7	$[Co(acac)_2(NO_2)$(4-*tert.*-butylpyridine)] *trans* (brown) *cis* (red)	LJB[18]	CH_2Cl_2	0.52	0.32	0.20	Complete
8	$[Coen_2(CH_3NH_2)Cl]Cl_2$ one form only (*cis*-*trans* mixture) (purple-pink)	SCC[19]	EtOH–H_2O (9:1)	0.32***	0.56***	0.24	Partial (considerable tailing)

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TABLE I (*continued*)

No.	Isomer	Source	Developing solvent	R_F		ΔR_F	Type of separation
				cis	*trans*		
9	$[Coen_2(EtNH_2)Cl]Cl_2$ one form only (*cis–trans* mixture) (purple-red)	SCC[19]	EtOH–H_2O (9:1)	0.00***	0.48***	0.48	Partial (considerable tailing)
10	$[Coen_2(n\text{-}C_3H_7NH_2)Cl]Cl_2$ one form only (*cis–trans* mixture) (purple-pink)	SCC[20]	EtOH–H_2O (9:1)	0.10***	0.30***	0.20	Complete
11	$[Coen_2(iso\text{-}C_3H_7NH_2)Cl]Cl_2$ one form only (*cis–trans* mixture) (pink-purple)	SCC[20]	EtOH–H_2O (9:1)	0.00***	0.51***	0.51	Partial (considerable tailing)
Type $M(AB)_2C_2$							
12	$[Cr\{(+)(-)\text{-pn}\}_2(NCS)_2]SCN$ *trans* (2 H_2O) (yellow-orange) *cis* (orange-pink)	EK[17]	CH_3OH	0.92	0.18	0.74	Partial (considerable tailing)
Type MA_3B_3							
13	$[Crpy_3Cl_3]$ one form only (*cis–trans* mixture) (light green)	HK[21]	$(CH_3)_2CO$–CH_2Cl_2 (1:1)	0.78***	0.95***	0.17	Complete
14	$[Rhpy_3Cl_3]^*$ *trans* or *mer* (1, 2, 6) (yellow) *cis* or *fac* (1, 2, 3) (red-orange)	H-HS[22–24] GW[22–24]	$(CH_3)_2CO$	0.05	0.91	0.89	Complete
15	$[Ru(Et_2S)_3Cl_3]$ one form only (*cis*) (orange)	JEF[25,26]	$CHCl_3$	0.40	–	–	None
16	$[Rh(Et_2S)_3Cl_3]$ one form only (*cis*) (red-orange)	JEF[25,26]	$CHCl_3$	0.39	–	–	None
17	$[Rh(Et_2S)_3Br_3]$ one form only (*cis*) (brown)	JEF[25,26]	$CHCl_3$	0.31	–	–	None
18	$[Rh(Ph_3P)_3Cl_3]$ one form only (incompletely characterized) (orange-red)	BWM[27,0]	$CHCl_3$	0.82	–	–	None

19	$[Ir(Ph_3P)_3HCl_2]$* α(*trans*-Cl, *mer*-Ph_3P) (yellow) β(*cis*-Cl, *mer*-Ph_3P) (pale yellow)	LV[28-30]	C_6H_6–$CHCl_3$ (9:1)	0.00	0.65	0.65	Complete
20	$[Ir(H_2O)py_2Cl_3]$ *trans* (H_2O) (orange-red) *cis* (1½ H_2O) (deep yellow)	MD[31,32]	$CHCl_3$	0.00	0.38	0.38	Complete
21	$[Ir(Ph_3P)_3H_2Cl]$ one form only (white)	BWM[27]	$CHCl_3$		0.57		None
Type MA_2B_2CD							
22	$[Ir(Ph_3P)_2HCl_2(CO)]$ one form only (white)	BWM[27]	$CHCl_3$		0.78		None
Type $M(AA)(BC)_2$							
23	[Coen(glycinate)$_2$] (a) *trans*(*o*) (reddish violet) (b) β-*cis*(*o*)c_1 (pink) (c) α-*cis*(*o*) (pink)	DWC[33]	$(CH_3)_2CO$–H_2O (1:1)	(a) 0.55 (a) 0.71 (b) 0.71	(b) 0.70 (c) 0.71 (c) 0.83	0.15 0.00 0.12	Partial (tailing) None Partial (considerable tailing)
Type $M(AB)_3$							
24	[Fe{N-1-(2′-pyridyl)-ethylideneaniline}$_3$]$(ClO_4)_2$ one form only (*cis*–*trans* mixture) (dark violet)	PK[34]	Cellosolve–HCl (9:1)	0.48***	0.71***	0.23	Complete
25	[Fe{N-1-(2′-pyridyl)ethylidene-*p*-phenylenediamine}$_3$]$(ClO_4)_2$ one form only (*cis*–*trans* mixture) (violet)	PK[34]	Cellosolve–HCl (1:1)	0.51***	1.00***	0.49	Complete
26	[Fe{N-1-(2′-pyridyl)-benzylideneaniline}$_3$]$(ClO_4)_2$ one form only (*cis*–*trans* mixture) (dark violet)	PK[34]	Cellosolve–HCl (7:3)	0.66***	1.00***	0.3	Complete
27	L-$[Co\{(-)pn\}_3]Br_3$ *trans* (reddish brown) *cis* (orange)	TEM[35,36]	Dissolved in H_2O Developed in CH_3OH	0.00	0.61	0.61	Complete

(Continued on p. 460)

TABLE I (*continued*)

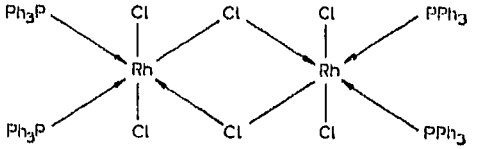
No. Isomer	*Source*	*Developing solvent*	R_F		ΔR_F	*Type of separation*
			cis	*trans*		
Type M(AAA)(BBC)						
28 [Co(diethylenetriamine)(L-aspartate)]NO_3 mixture of three isomers (s-*cis*, u′-*cis*, and u²-*cis*) (brick red)	JIL[37]	C_2H_5OH	0.00, 0.70 (brown) 0.57 (purple) 1.0 (brown)			Partial
Type M(AA)B_2C_2						
29 [$Sn(C_6H_5)_2Cl_2$·CDTD] where CDTD = *cis*-1,4-dithian 1,4-dioxide, $OS(CH_2CH_2)_2SO$ (a) *cis* (white) (b) *trans* (white)	RCP[57,58]	CH_3OH–C_2H_5OH–CH_2Cl_2 (0.50:0.15:0.35)	0.00 (*trans*)	0.80 (*cis*)	0.80	Complete

* Separated previously by column chromatography[38].

** These isomers have not been previously described.

*** Since the sample provided was a mixture and since the pure isomers were not available for reference, it is not certain which spot is due to the *cis* form and which to the *trans* form. According to Tobe[60], there is no evidence for the presence of *trans* isomers in these preparations.

◊ This compound is now believed to be a chlorine-bridged dimer such as



(brick red)- and *trans* (dark purple)-[Cotn$_2$(NCS)$_2$]SCN (tn = trimethylenediamine) (SK)[42,43]— insolubility in suitable solvents, decomposition on acidification used to increase solubility in methanol; *cis* (dull orange-yellow)- and *trans* (yellow)-[Ir(*o*-C$_6$H$_4$-{As(CH$_3$)$_2$}$_2$)$_2$Cl$_2$]Cl (LVo)[44] —both forms give R_F values of 0.00, possibly due to isomerization; MA_3B_3: *cis* or *fac* (1, 2, 3) (white)- and *trans* or *mer* (1, 2, 6) (orange)-[Rh(Et$_3$P)$_3$Cl$_3$], *cis* or *fac* (1, 2, 3) (white)- and *trans* or *mer* (1, 2, 6) (pale yellow)-[Ir(*n*-Bu$_2$PhP)$_3$Cl$_3$](SOG)[45,59]— same R_F values in acetone; $M(AB)_3$; β (*cis* or *fac*) (pink) (with 1 H$_2$O)- and α (*trans* or *mer*) (violet)-[Co(glycinate)$_3$], β (*cis* or *fac*) (pink)- and α (*trans* or *mer*) (violet)-[Co(alaninate)$_3$], β (*cis* or *fac*) (pink) (with 2 H$_2$O)- and α (*trans* or *mer*) (violet) (with 1 H$_2$O)-[Co(leucinate)$_3$] (EK)[46]— soiuble only in water or slightly soluble in acetone, R_F values either 1.00 with tailing to origin or else 0.00; the first two isomer pairs have also been found inseparable by column chromatography[38]; *cis* or *fac* (1, 2, 3) (yellow-brown)- and *trans* or *mer* (1, 2, 6) (yellow-brown)-[Cr(8-hydroxyquinolinate)$_3$] (FU)[47–49]— insolubility or limited solubility in suitable solvents, spots failed to move in any solvent; $M(AAA)_2$: *cis* or *fac* (purple)- and *trans* or *mer* (purple-black)- Na or K [Co(iminodiacetate)$_2$] (DWC)[50,51] — insolubility in suitable solvents, soluble only in aqueous acids which yielded only streaking on plates; M(AAA)(BBB): s-*cis* (brick red)-, u-*cis* (pink)-, and *trans* (brick red)-[Co(diethylenetriamine)(iminodiacetate)]ClO$_4$ (DWC)[52] — same reasons as previous isomers; $M(AAAA)B_2$: β-*cis* (RR, SS) (violet)-, *trans* (RR, SS) (green)-, and *trans* (RS) (light green)-[Co(1, 4, 8, 11-tetraazaundecane)Cl$_2$]Cl (MLT)[53,54] — insolubility in suitable solvents, chromatography in acetone–water (1:1) yielded streaks; Binuclear complex: *cis* (C_{2h}; $A_u + 2B_u$) (white)- and *trans* (C_{2h}; $A_u + 2B_u$) (yellow)-[Ru(CO)$_3$Cl$_2$]$_2$ (FGAS)[55] — possible isomerization in ethanol, similar R_F values for both isomers.

CONCLUSIONS

The use of TLC for the separation of isomeric complexes possesses a number of distinct advantages:

(1) By careful choice of a developing solvent system, a large difference in mobilities (R_F values) and consequently a sharp and complete separation can be attained. In the present study, an isomer pair (sample 20) previousiy found not amenable to column chromatography was successfully separated.

(2) In conjunction with other evidence, TLC behavior possesses some potential diagnostic value in structure proof[40]. For most of the compounds investigated, the *trans* isomer was found to be more mobile, *i.e.*, to possess a higher R_F value, than the *cis* isomer, in agreement with findings reported for electrolytic cobalt(III) complexes[5]. This greater mobility of the *trans* isomer, which would be predicted from its lower dipole moment, agrees with the results obtained by us from column chromatography[10,38]. Nevertheless, a number of exceptions to the general rule that the *trans* isomer is more mobile than the *cis* isomer are known[6,9,56], so conclusions about configuration should be drawn only with caution and should be supplemented with other data.

(3) The time required for TLC is, of course, much less than that needed for equivalent separations by column chromatography.

(4) With TLC, iodine vapor may be used as a sensitive detecting reagent, thus eliminating the necessity for specific spot tests[10,38]. We have found this reagent,

denoted as "universal" for organic compounds by Bobbitt[11], to be useful in detecting a variety of coordination compounds. Its sensitivity makes it of particular value in assessing purity or detecting solvent-induced isomerization; by its use, trace quantities of one isomer can be detected in the presence of large quantities of the other. For many colored coordination compounds no visualization is necessary.

(5) Although column chromatography is still quite advantageous for preparative separations, TLC is also adaptable for this purpose, as we have shown[4]. Furthermore, preliminary separations by TLC are convenient for rapidly determining the solvents and conditions to be used for larger-scale separations by column chromatography.

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