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Note

Separation of inorganic isomers by adsorption chromatography

II. Non-electrolytic octahedral and square planar geometric isomers

GEORGE B. KAUFFMAN, GARY L. ANDERSON and LARRY A. TETER
Department of Chemistry, California State University, Fresno, Calif. 93740 (U.S.A.)
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In a previous publication in this series[1], we have applied the preferential adsorption of non-electrolytic geometric isomers on selected commercially available adsorbents to the separation of mononuclear and binuclear platinum(II) isomers of coordination number four. In an effort to prove the general applicability of the method, we have extended our studies to include isomers of various metals with coordination number six and metals other than platinum with coordination number four. Inasmuch as we demonstrated in our first article[1] that separations could be carried out quantitatively and with significant amounts of material (more than a gram 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 eluents were C.P. or reagent grade. The two adsorbents used were silica gel, grade 15, 35–60 mesh (Davison Chemical, Baltimore, Md., U.S.A.) and activated alumina, 35–60 mesh (Fisher Chemical, Pittsburgh, Pa., U.S.A.). In two cases (isomers 4 and 21), the following adsorbents were also used: Celite, acid-washed, 60–100 mesh, and magnesiated silica, I-8070, 60–100 mesh (Research Specialties, Berkeley, Calif., U.S.A.); Florex XXS, 60–100 mesh, and Florosil, 60–100 mesh (Floridin, Tallahassee, Fla., U.S.A.); Norite, activated carbon (Atlas Powder, Wilmington, Del., U.S.A.); and Porocel, activated bauxite, 6% V.M., 60–140 mesh (Minerals and Chemicals Corp. of America, Menlo Park, N.J., U.S.A.). Generous samples of adsorbents were furnished by the companies listed. We are also indebted to Englehard Industries (Newark, N.J., U.S.A.) for experimental samples of platinum sponge.

Columns and procedure

Columns were of two types, *viz.*, (i) 10-ml and 50-ml burettes, and (ii) chro-

TABLE I

COLUMN CHROMATOGRAPHY OF GEOMETRIC ISOMERS

No.	Isomer	Source	Adsorbent	Column volume = height × cross-section (cm^3 = cm × cm^2)	Flow-rate (cm/min)	Eluent	Elution volumes (column volumes)			Type of separation
							"Break-through"	"Peak"	"Terminal"	
COORDINATION NO. 6										
Type MA_2B_4										
1	$[Pt(Et_2S)_2Cl_4]$	GBK[2]	SiO_2	4.35 = 18.6 × 0.234						Complete
	trans (lemon yellow)				1.60	C_6H_6	0.52	0.66	1.24	
	cis (bright yellow)				1.23	$(CH_3)_2CO$	0.62	0.71	0.93	
							(÷3.60)*	(÷3.60)	(÷3.60)	
2	$[Pt(n\text{-}Bu_3P)_2Cl_4]$	GBK[3,**]	Al_2O_3	3.54 = 15.1 × 0.234						Complete
	trans (golden yellow)				3.24	C_6H_6	0.57	0.70	0.90	
	cis (greenish yellow)				3.10	$(CH_3)_2CO$	0.46	0.67	0.87	
							(÷2.74)	(÷2.74)	(÷2.74)	
3	$[Irpy_2Cl_4]$	GBK[4]	SiO_2	1.6 = 7.5 × 0.214						Complete
	trans (violet-black)				5.0	$CHCl_3$-$(C_2H_5)_2O$ (9:1)	–	–	6.0	
	cis (violet-black)				5.0	$CHCl_3$-C_2H_5OH (1:1)	–	–	2.0	
									(÷6.5)	
4	$[Pt(NH_3)_2Cl_4]$	GBK[5]	All listed	16 = 16.0 × 0.99						None
	trans (lemon yellow)				1.0	H_2O	–	–	0.40	
	cis (lemon yellow)				1.0	H_2O	–	–	0.40	
5	$pyH[Irpy_2Cl_4]$	GBK[6]	SiO_2	1.5 = 7.0 × 0.214						None
	trans (red)				5.0	Pyridine	–	–	0.40	
	cis (orange)				5.0	Pyridine	–	–	0.40	
Type MA_3B_3										
6	$[Rhpy_3Cl_3]$		Al_2O_3	3.5 = 15 × 0.234						Complete
	trans or *mer* (1,2,6) (yellow)	H-HS[7-9]			1.50	$CHCl_3$-CCl_4 (9:1)	0.95	1.20	1.55	
	cis or *fac* (1,2,3) (red-orange)	GW[7-9]			1 50	N,N-Dimethylformamide	0.45	0.60	0.90	
							(÷3.50)	(÷3.50)	(÷3.50)	
7	"$[Ir(Et_2S)_3Cl_3]$"	GBK[10,11]	SiO_2	1.5 = 7.0 × 0.214						Complete
	cis or *fac* (1,2,3) (yellow)				5.0	$CHCl_3$	–	–	6.80	
	"*trans*" (actually *trans*-$[Ir(Et_2S)_4Cl_2]$–*trans*-$[Ir(Et_2S)_2Cl_4]$)				5.0	C_2H_5OH	–	–	2.00	
									(÷7.00)	

8	$[Ru(Et_2S)_3Cl_3]$ one form only (*cis*) (orange)	JEF[12]	Al_2O_3	3.5	=15	×0.234	0.89	$CHCl_3$	No separation; volume not recorded			None
9	$[Rh(Et_2S)_3Cl_3]$ one form only (*cis*) (red-orange)	JEF[12]	Al_2O_3	3.5	=15	×0.234	0.83	$CHCl_3$	No separation; volume not recorded			None
10	$[Rh(Et_2S)_3Br_3]$ one form only (*cis*) (brown)	JEF[12]	Al_2O_3	3.5	=15	×0.234	0.92	$CHCl_3$	No separation; volume not recorded			None
11	$[Rh(Ph_3P)_3Cl_3]$ one form only (incompletely characterized) (orange-red)	BWM[13],***	Al_2O_3	3.5	=15	×0.234	0.76	$CHCl_3$	No separation; volume not recorded			None
12	$[Irpy_3Cl_3]$	GBK[14,15]	SiO_2	1.5	=7.0	×0.214						None
	trans (1,2,6) (yellow)						5.0	$CHCl_3$-C_2H_5OH (1:1)	Too insoluble for detection			
	cis (1,2,3) (yellow)						5.0	$CHCl_3$-C_2H_5OH (1:1)	Volume not recorded			
Type MA_3B_2C												
13	$[Ir(Ph_3P)_3HCl_2]$	LV[16–18]	SiO_2	3.9	=18	×0.217						Complete
	α (*trans*-Cl, *mer*-Ph_3P) (yellow)						0.88	C_6H_6-$CHCl_3$ (9:1)	0.45	0.53	0.81	
	β (*cis*-Cl, *mer*-Ph_3P) (pale yellow)						0.88	$(CH_3)_2CO$	0.46 (+2.55)	0.51 (+2.55)	0.77 (+2.55)	
14	$[Ir(H_2O)py_2Cl_3]$	MD[19,20]	Al_2O_3	3.5	=15	×0.234						None
	trans (H_2O) (orange-red)						0.73	$(CH_3)_2CO$-CH_3OH (99:1)	0.45	–	–	
	cis ($1\frac{1}{2}H_2O$) (deep yellow)						0.73	$(CH_3)_2CO$-CH_3OH (99:1)	0.45	–	–	
15	$[Ir(Ph_3P)_3H_2Cl]$ one form only (white)	BWM[13]	Al_2O_3	3.5	=15	×0.234	0.65	$CHCl_3$	No separation; volume not recorded			None
Type MA_2B_2CD												
16	$[Ir(Ph_3P)_2HCl_2(CO)]$ one form only (white)	BWM[13]	Al_2O_3	3.5	=15	×0.234	0.70	$CHCl_3$	No separation; volume not recorded			None

(*Continued on p.468*)

TABLE I *(continued)*

No.	Isomer	Source	Adsorbent	*Column volume = height × cross-section (cm^3 = cm × cm^2)*	*Flow-rate (cm/min)*	*Eluent*	*Elution volumes (columes volumes)*			*Type of separation*
							"Break-through"	*"Peak"*	*"Terminal"*	
Type M($\overline{AB}$)$_3$, tris(unsymmetrical chelate)										
17	[Cr($C_6H_5CO{\cdot}CH{\cdot}CO{\cdot}CH_3$)$_3$]	JPC[21]	Al_2O_3	$3.3 = 14 \times 0.234$						Complete
	one form (*cis–trans* mixture?) (olive drab)				0.76	C_6H_6	0.57	0.65	0.75	
					0.76	$CHCl_3$	0.71 (+0.8)	0.78 (+0.8)	0.89 (+0.8)	
					1.45	N,N-Dimethyl-formamide	0.45 (+0.8 +1.0)	0.50 (+0.8 +1.0)	0.56 (+0.8 +1.0)	
18	[Cr($C_2H_5O{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CH_3$)$_3$] one form (crude) (brown)	JPC[21]	Al_2O_3	$3.3 = 14 \times 0.234$	0.72	C_6H_6	No separation; volume not recorded			None
19	[Cr($CH_3{\cdot}CO{\cdot}CH{\cdot}C(CH_3)N$(*p*-$CH_3C_6H_4$))$_3$]	JPC[22,23]	Al_2O_3	$3.3 = 14 \times 0.234$	0.70	$CHCl_3$	No separation; volume not recorded			None
	one form (*cis–trans* mixture) (purplish brown)				0.70	C_6H_6	Two bands on column, but could not be eluted			None
20	[Cr($CF_3{\cdot}CO{\cdot}CH{\cdot}CO$(2-thiophenyl))$_3$]	JPC[21]	Al_2O_3	$3.5 = 15 \times 0.234$	0.65	C_6H_6	No separation; volume not recorded			None
	one form (*cis–trans* mixture?) (yellowish brown)				0.65	Cyclohexane	No separation; volume not recorded			None
21	[Co($OOCCH_2NH_2$)$_3$]	GBK[24]	All listed	$16 = 16.0 \times 0.99$						None
	β (*cis* or *fac* (1,2,3)) (pink)				1.0	H_2O or 3 *M* H_2SO_4	—	—	0.40	
	α (*trans* or *mer* (1,2,6)) (violet)				1.0	H_2O or 3 *M* H_2SO_4	—	—	0.40§	
22	[Co((+)(−)-alaninate)$_3$]	VC[25,26]	SiO_2, Al_2O_3	$17 = 17.0 \times 0.99$						None
	β (*cis* or *fac* (1,2,3)) (red)				1.1	H_2O	No separation; volume not recorded			
	α (*trans* or *mer* (1,2,6)) (violet)				1.1	H_2O	No separation; volume not recorded			

23	[Co((+)(−)-valinate)$_3$]	VC[25,26]	SiO$_2$, Al$_2$O$_3$	17 =17.0×0.99						None
	β (*cis* or *fac* (1,2,3)) (red)				1.1	H$_2$O	No separation; volume not recorded			
	α (*trans* or *mer* (1,2,6)) (violet)				1.1	H$_2$O	No separation; volume not recorded			
24	[Co((+)(−)-tryptophanate)$_3$]	JB[27]	SiO$_2$, Al$_2$O$_3$	17 =17.0×0.99						None
	cis? (brown)				1.1	H$_2$O	No separation; volume not recorded			
	trans? (reddish brown)				1.1	H$_2$O	No separation; volume not recorded			
COORDINATION NO. 4										
Type MA$_2$BC										
25	[Ir(Ph$_3$P)$_2$(CO)Cl]	BWM[13]	Al$_2$O$_3$	3.0 =13 ×0.234						Complete
	one form (lemon yellow)				0.65	C$_6$H$_6$	1.00	1.33	2.50	
					0.65	CHCl$_3$	1.00 (+5.00)	1.21 (+5.00)	1.56 (+5.00)	
Type M(AB)$_2$										
26	[Ni{(CH$_3$)$_2$N·CH$_2$C(=NOH)C(CH$_3$)=NO}$_2$]	EU[28]								
	cis–trans mixture		SiO$_2$	3.25=15.2×0.214	0.51	Various solvents	Never eluted			None
	trans? (orange)		Al$_2$O$_3$	3.33=14.2×0.234	0.67	CHCl$_3$	0.74	1.06	∞	Partial
	cis? (red)		Al$_2$O$_3$	3.33=14.2×0.234	0.78	CHCl$_3$	2.03	2.50	∞	
Binuclear complexes										
27	[π-C$_5$H$_5$Fe{As(CF$_3$)$_2$}(CO)]$_2$	RGH[29,30]	Al$_2$O$_3$	4.2 =18 ×0.234	0.50	*n*-Hexane	2.9	–	7.1	Partial
	cis–trans mixture (yellow-brown)									
28	[CH$_3$SFe(CO)$_3$]$_2$ mixture (*ca.* 25% *syn(cis)* and *ca.* 75% *anti(trans)*) (red)	RBK[31,32]	Al$_2$O$_3$	4.2 =18 ×0.234	0.75	*n*-Hexane	No separation; volume not recorded			None

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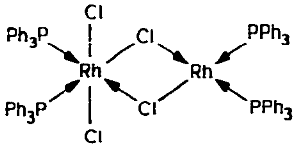
[*] Numbers in parentheses indicate the volume of the first eulent used before switching to second eluent.

[**] These isomers have not been previously described.

[***] This compound is now believed to be a chlorine-bridged dimer such as



[§] With an activated charcoal column and saturated Cl$_2$ water as eluent, the *α* isomer was still not eluted after 1000 column volumes or else it had been eluted so slowly that it had not been detected.

matographic columns modified with stopcocks for controlling flow-rate (Fisher Scientific, Pittsburgh, Pa., U.S.A.). Isomers were detected in the effluent by either color, IR-5, or the following spot test reagents: tin(II) chloride (0.5 *M* in 1 *M* HCl, freshly prepared), dithiooxamide (1 g of rubeanic acid in 25 ml of ethanol), oxine (1 g of 8-hydroxyquinoline in 25 ml of ethanol), or dithizone (0.1 g of diphenylthiocarbazone in 10 ml of methyl ethyl ketone or carbon tetrachloride). Although the conditions for elution of a given isomer were known from preliminary column experiments with separate isomers, when these were available, the identities and purities of the separated isomers were confirmed either by mixed melting point and decomposition point measurements (Fisher-Johns apparatus), by reaction or lack of reaction with ethanolic silver nitrate, or by IR-5 measurements. Further details are given in the previous article[1].

RESULTS AND DISCUSSION

The results obtained are summarized in Table I. The following samples, listed by type and number, were successfully separated: MA_2B_4: 1, 2, 3; MA_3B_3: 6, 7; MA_3B_2C: 13; $M(\overline{AB})_3$: 17; MA_2BC: 25, 26 (partial); Binuclear Coord. No. 4 : 27 (partial). The remaining samples could not be separated. In many cases (samples 8–11, 15, 16, 18, and 25), unsuccessful separations do not necessarily imply failure; the materials chromatographed were only theoretically capable of existing in two isomeric forms. In the case of samples 4, 5, 12, 14, and 21–24, limited solubility in non-polar or even moderately polar solvents required the use of strongly polar solvents, which were adsorbed by the columns in preference to the isomers, thus precluding successful separations.

In some cases (samples 1 and 13), purification was achieved in the course of separation; the eluted, separated isomers possessed higher melting points than the original samples. In one case (sample 17), the material was split into three successive fractions, containing *ca.* 75, 5, and 20% of the original material, respectively. With sample 19, separation into two bands on the column was observed, but the material was always eluted as one fraction. With sample 26, *cis–trans* isomerization occurred on dissolving and even more strongly on the column so that a complete separation could not be accomplished. With sample 27, although only one band was eluted, IR-5 measurements on the effluent showed that the leading edge adsorbed at a lower wavenumber than the trailing edge. Samples 21 and 28 have been separated by other workers using TLC[33] and column chromatography[31,32,34], respectively.

Our successful application of thin-layer chromatography (TLC) to the separation of non-electrolytic geometric isomers of platinum(II)[35] for which column chromatography was unsuccessful prompted us to apply this method to the samples employed in the present article except for samples 3–5, 7, and 18–24. In all cases, the TLC results agreed with the results obtained by column chromatography, and the *trans* isomers were found to be more mobile, *i.e.*, to possess higher R_F values than the *cis* isomers. Also, in the case of sample 14, for which column chromatography was unsuccessful, a separation was obtained by TLC. The TLC separation of these isomers as well as of electrolytic (cationic and anionic) isomers, ligand isomers, linkage isomers, and isomers of non-metals (*e.g.*, carboranes and phosphonitriles) will form the basis of a subsequent article.

CONCLUSIONS

Column chromatography is applicable to the separation of geometric isomers of different structure and type, provided suitable isomers, eluents, and adsorbents are available. Ideal isomer pairs should be soluble in both polar and non-polar or moderately polar solvents, should differ widely in polarity, and should not isomerize in the eluent or on the adsorbent. The ideal eluent should have a low boiling point so that the eluted isomer can be quickly evaporated at room temperature in order to minimize possible isomerization. The ideal adsorbent should adsorb the more polar isomer but not so strongly that it cannot be eluted by a polar solvent. The limited solubility of isomers in non-polar or moderately polar solvents seems to be the most restrictive limitation, followed by isomerization.

In cases where the configurations of the isomers were known, successful separations always involved elution of the *trans* isomer first, followed by the *cis* isomer, a behavior which has diagnostic value in proof of configuration. Thus, an apparent exception to this behavior encountered with "isomer" pair 7 suggested that the configuration assigned by the original investigators[36] merely on the basis of color might be incorrect. A subsequent study of configuration by a number of diverse methods[11] showed the yellow form of $[\mathrm{Ir(Et_2S)_3Cl_3}]$ to be the *cis* or *fac* (1, 2, 3) isomer and the red form to be a "polymerization" isomer, *trans*-$[\mathrm{Ir(Et_2S)_4Cl_2}]$-*trans*-$[\mathrm{Ir(Et_2S)_2Cl_4}]$, which, being an electrolyte, would naturally be expected to be adsorbed more strongly than the nonelectrolytic *cis* isomer. However, a few exceptions to the general rule that the *trans* isomer is more mobile than the *cis* isomer are known[37].

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