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Note

Separation of inorganic isomers by thin-layer chromatography

IV. Ligand isomers of various coordination numbers

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In previous papers in this series, we described the separation by thin-layer chromatography (TLC) on silica gel of square planar non-electrolytic geometric isomers of platinum(II)[1], octahedral non-electrolytic and electrolytic geometric isomers of various metals[2], and square planar non-electrolytic and electrolytic geometric isomers of various metals[3]. In the present paper we extend our TLC separations to include compounds which are isomeric by virtue of isomerism within the ligands. Our preparation and TLC separation of the geometric and ligand isomers of *cis*- and *trans*-$[Pt(Bu_2S)_2Cl_2]$ (where Bu = *n*-, iso, *sec.*-, and *tert.*-butyl) will be described in a forthcoming separate article. Inasmuch as we demonstrated in our first article[1] that separations can be carried out quantitatively and with significant amounts of material (*ca.* 200 mg of total mixture), all the separations reported here are strictly qualitative.

EXPERIMENTAL

Isomer samples were kindly provided by the persons listed alphabetically under Acknowledgements (designated by initials in Table I). All solvents were C.P. or reagent grade. Generous samples of the adsorbents used, SilicAR® TLC-7F and TLC-7G, were provided by Mallinckrodt (St. Louis, Mo., U.S.A.). Microscope slides (75 × 25 mm) were used for all separations except for sample 12 (Table I), which required 200 × 50 mm plates to achieve separation, and for sample 9, for which an Eastman 6061 silica gel Chromatogram™ sheet, 20 × 20 mm, 100 μm thickness (Eastman, Rochester, N.Y., U.S.A.) was used.

Since sample 9 containing zerovalent tungsten was susceptible to oxidation, in this case the use of oxygen-containing solvents normally used in TLC was avoided. The solvents used were dried over sodium, and a 36 × 36 × 20 in. plastic glove bag (Instruments for Research and Industry, Cheltenham, Pa., U.S.A.) with a continuous dry nitrogen purge was used throughout the procedure.

Plates were developed by the ascending technique, and iodine vapor was used for visualization for all samples except sample 9, which was detected by infrared absorption spectra; sample 12(b), which was detected with ultraviolet light; and samples

15–18, the colors of which were so intense that no visualization was required. Further details are given in previous articles[1–3].

RESULTS AND DISCUSSION

The results obtained are summarized in Table I. R_F values 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. Coordination No. 6: MA_4B_2: 1,2,4,5; MA_3B_3: 6; $M(AA)_2B_2$: 7(partial), 8; $M(AB)C_4$: 9; Binuclear: 10(partial), 11; Coordination Nos. 6 and 5: $MA_4(BB)$ and MA_4B: 12; Coordination No. 5: $M(ABC)D_2$: 13 (partial); Coordination No. 4: MA_2B_2: 14, 15(partial); MA_3B: 16(partial); $M(AB)_2$: 18; Coordination No. 2: MAB: 20(partial). Samples 3, 17, and 19 could not be separated. For samples 18 and 19, the two isomers of each pair gave widely differing R_F values when chromatographed separately (18(a) and (b), 0.00 and 0.84, respectively; 19(a) and (b), 0.00 and 0.87, respectively), but the R_F values were much closer when the mixture was chromatographed.

In addition to the compounds shown in Table I, the following compounds could not be separated for the reasons cited. Coordination No. 6, type MA_4B_2: Ni(picoline)$_4Cl_2$, β-pic (pale green), γ-pic (pale green) (G.B.[18]) —decomposes in solution with noticeable odor of the organic ligand; [Ni(picoline)$_4(ClO_3)_2$], β-pic (blue), γ-pic (blue) (A.K.M.[19,20]) —same reason; coordination No. 4, type MA_2B_2: Ni(lutidine)$_2Cl_2$, 2,3-lut (blue), 2,4-lut (purple-blue), 2,5-lut (purple-blue) (L.B.R.[5]) —either insoluble or decompose in solvents; Cu(lutidine)$_2Cl_2$, 2,3-lut (adamantine gray), 2,5-lut (pale violet), 2,6-lut (lilac) (L.B.R.[5]) —same reason; Cu(picoline)$_2Cl_2$, α-pic (bright purple), β-pic (greenish blue), γ-pic (blue) (L.B.R.[5]) —same reason; Co(picoline)$_2Cl_2$, α-pic (brilliant dark blue), γ-pic (brilliant dark blue) (G.B.[21]) —same reason; Co(chloroaniline)$_2Cl_2$, *o*-chloro (light blue), *p*-chloro (dark blue) (G.B.[21]) —same reason; type MA_3B: [$Cr(CO)_3(CH_3C_6H_4COOCH_3)$], *o*-, *m*-, and *p*-methyl (all bright yellow) (G.K.[15]) —R_F values of the three isomers virtually identical both in methanol and in acetone–water(1:1); type M(ABC)D: Ni(*o*-carboxy-N-phenylsalicylaldimine)(picoline), α-pic (bluish yellow), β-pic (orange-yellow) (although apparently tetracovalent, these compounds have an octahedral structure, the α-pic compound probably being polymeric) (A.K.M.[13]) —insoluble in water and most organic solvents; type $M(AB)_2$: bis[N-substituted 2-acetiminobis(5,5-dimethyl-1,3-cyclohexanedionato)]nickel(II), *o*-$C_6H_4CH_3$ (red-brown), *p*-$C_6H_4CH_3$ (orange) (E.P.D.[22]) —when chromatographed separately in dichloromethane the isomers differed in R_F values (0.18 and 0.31, respectively), but the mixture was not separable; [Ag(II)(pyridinecarboxylate)$_2$], 2-carboxylate (picolinate) (brown), 4-carboxylate (nicotinate) (light brown, actually a polymer with the ligand being a bridging group) (J.R.W.[23,24]) —totally immobile in all solvents from *n*-pentane (dielectric constant, 1.8) to formamide (dielectric constant, 109); compound A (yellow-brown) and compound B (yellow-grey) (J.R.W.[23,24]) —same reason; compound C, *n*-butyl (purple), isobutyl (light pink) (J.R.W.[25]) —streaking only; coordination No. 3, type M(ABC): [Ni{N-[2-(pyridyl)-ethyl]-1,2-diaminoethane}]Cl_2, 2-pyridyl,2H_2O (pale blue), 3-pyridyl,3H_2O (very pale blue) (D.W.[26,27]) —insoluble in suitable solvents: coordination No. 2, type

TABLE I

THIN-LAYER CHROMATOGRAPHY OF LIGAND ISOMERS

No. Isomer	*Source*	*Developing solvent*	*R_F value*	*ΔR_F*	*Type of separation*
Coordination No. 6					
Type MA_4B_2					
1 $[Co(CH_3 \cdot C_6H_4N)_4(ClO_4)_2]$	W.E.B.[4]	CH_2Cl_2			
(a) 3-Me (pink)			0.00 (3-Me)	0.24	Complete
(b) 4-Me (pink)			0.24 (4-Me)		
2 $[Co(C_7H_9N)_4(ClO_4)_2]$	W.E.B.[4]	CH_2Cl_2			
(a) $4\text{-}C_2H_5 \cdot C_5H_4N$ (pink)			0.64 (4-Et)	0.36	Complete
(b) $3,5\text{-}(CH_3)_2 \cdot C_5H_3N$ (pink)			1.00 ($3,5\text{-Me}_2$)		
3 $[Co(C_9H_{11}N)_4(ClO_4)_2]$	W.E.B.[4]	CH_2Cl_2–$(CH_3)_2CO$ (9:1)			
(a) 4-iso-Pr·C_6H_4N (pink)			0.00, *0.40**, 0.78, 1.0		None, but possible purifications
(b) 4-*n*-Pr·C_6H_4N (pink)			*0.44**, 0.89, 1.0		of the individual compounds
(c) 3-Et,4-Me·C_6H_3N (pink)			0.00, *0.44**, 0.87, 1.0		(a), (b), and (c)
4 $Cu(lutidine)_4Cl_2$	L.B.R.[5]	EtOAc			
(a) 3,4-lutidine (bright blue)			0.55 (3,4-lut)	0.05	Partial
(b) 3,5-lutidine (pale blue)			0.60 (3,5-lut)		
		Et_2O	0.35 (3,4-lut)	0.10	Complete
			0.45 (3,5-lut)		
5 $[CuL(NO_3)_2]_n$ (octahedral with bridging L and NO_3^- groups)	W.J.G.[6]				
(a) L I = 1,2-di(2-pyridyl)-ethylene (mauve)		Dissolved in H_2O, developed in EtOH	0.66 (L II)	0.21	Complete
			0.87 (L I)		
(b) L II = 1,2-di(4-pyridyl)-ethylene (green)		CH_3OH	0.60 (L III)	0.17	Complete
			0.77 (L I)		
(c) L III = 1-(2-pyridyl)-2-(3-pyridyl)ethylene (purple-blue)		Dissolved in H_2O, developed in $(CH_3)_2CO$	0.08 (L II)	0.18	Complete
			0.26 (L III)		
Type MA_3B_3					
6 $Rh(O\text{–}As)_3Cl_3$, where (O–As) = methoxyphenyl-dimethylarsine	L.V.[7]	CH_2Cl_2			
(a) *p*-(O–As) (bright orange-yellow)			0.53 (*p*-O–As)	0.12	Complete
			0.65 (*m*-O–As)		

	(b) *m*-(O–As) (dull orange-yellow)					
	Type M(AA)$_2$B$_2$ (L monodentate, non-bridging; NO_3^- bridging)					
7	$CoL_2(NO_3)_2$	W.J.G.[6]	EtOH	0.65 (L IV) 0.75 (L III)	0.10	Partial
	(a) L III = 1-(2-pyridyl)-2-(3-pyridyl)ethylene; 6-hydrate (pale pink)					
	(b) L IV = 1-(2-pyridyl)-2-(4-pyridyl)ethylene (pink)					
8	$NiL_2(NO_3)_2$	W.J.G.[6]	$(CH_3)_2CO$	0.00 (L IV) 0.40 (L IV)	0.40	Complete
	(a) L III = as above (green)					
	(b) L IV = as above (green)					
	Type M(AB)C$_4$					
9	*cis***-[W(PP)(CO)$_4$] (where PP = 2-*cis*- or *trans*-propenyldiphenylphosphine)	L.V.I.[8–10]	*n*-C_5H_{12}–C_6H_6 (1:1)	0.95 (*cis*-PP) 0.98 (*trans*-PP)	0.03	Partial
	cis-PP (yellow)		*n*-C_5H_{12}–C_6H_6 (5:1)	0.82 (*cis*-PP) 0.98 (*trans*-PP)	0.16	Complete
	trans-PP (yellow)		*n*-C_5H_{12}–C_6H_6 (15:1)	0.66 (*cis*-PP) 0.91 (*trans*-PP)	0.25	Complete
	Binuclear complexes					
10	[Fe(N-tolylsalicylidene-imine)$_2$]$_2$O*** (bidentate ligand)	B.O.W.[11]	CH_3OH	0.75 (*m*-tolyl) 0.84 (*p*-tolyl)	0.09	Partial
	(a) *m*-tolyl (reddish brown)					
	(b) *p*-tolyl (reddish brown)					
11	[Fe(N-chlorophenyl-salicylideneimine)$_2$]O*** (bidentate ligand)	B.O.W.[11]	$(CH_3)_2CO$–H_2O (1:1)	0.65 (*m*-Cl) 0.87 (*p*-Cl)	0.22	Complete

(Continued on p. 142)

TABLE 1 (*continued*)

No. Isomer	*Source*	*Developing solvent*	R_F *value*	ΔR_F	*Type of separation*
(a) *m*-chloro (orange) (b) *p*-chloro (reddish brown)					
Coordination Nos. 6 and 5 *Types* $MA_4(BB)$ *and* MA_4B					
12 $\{SnI_4[OS(CH_2CH_2)_2SO]\}$	R.C.P.[12]	$(CH_3)_2CO$–H_2O (1:3)	0.33 (a) 1.00 (b)	0.66	Complete
(a) *trans*-1,4-dithian 1,4-dioxide (bidentate) (coord. no. 6) (yellow-orange) (b) *cis*-1,4-dithian 1,4-dioxide (monodentate) (coord. no. 5) (yellow-orange)					
Coordination No. 5 (Apparent only, actually octahedral) *Type* $M(ABC)D_2$					
13 $Ni(C_{14}H_9O_3N)(picoline)_2$ (where $C_{14}H_9O_3N$ = *o*-carboxy-N-phenylsalicylaldimine) (a) α-picoline (black) (b) γ-picoline (deep orange)	A.K.M.[13]	Dissolved in $CHCl_3$, developed in $(CH_3)_2CO$–$CHCl_3$ (2:1)	0.59 (α-pic) 0.66 (γ-pic)	0.07	Partial (impurities detected at R_F = 0.39 for both isomers)
Coordination No. 4 *Type* MA_2B_2					
14 $Cu(lutidine)_2Cl_2$	L.B.R.[5]	EtOAc	0.25 (3,4-lut) 0.35 (3,5-lut)	0.10	Complete
(a) 3,4-lutidine (pale blue) (b) 3,5-lutidine (pale blue)					
15 $Cu(picoline)_2(NCS)_2$ (with Cu–NCS bonding)	S.S.[14]	$(CH_3)_2CO$	0.48 (γ-pic) 0.62 (β-pic)	0.14	Partial

(a) β-picoline (green)
(b) γ-picoline (green)

Type MA_3B

16	$[Cr(CO)_3(ClC_6H_4COOCH_3)]$	G.K.[15]	$(CH_3)_2CO$–H_2O (1:1)	0.57 (*p*-Cl) 0.75 (*m*-Cl)	0.18	Partial

(a) *p*-chloro (orange)
(b) *m*-chloro (orange)

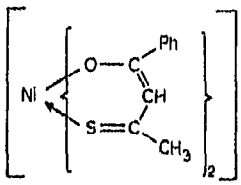
17	$[Cr(CO)_3(CH_3OC_6H_4$-$COOCH_3)]$	G.K.[15]	$(CH_3)_2CO$–H_2O (1:1)	0.73 (*p*-MeO) 0.78 (*o*-MeO)	0.05	None

(a) *p*-methoxy (yellow)
(b) *o*-methoxy (yellow)

Type $M(AB)_2$

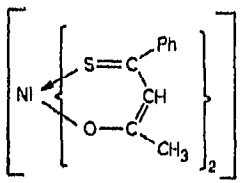
18	$[Ni(C_{10}H_9OS)_2]$	E.U.[16,17]	Dissolved in $(CH_3)_2CO$, developed in CH_3OH	0.21–0.61 (a), tailing 0.71 (b)	0.10	Complete

(a) Bis(benzoylthio-acetonato)nickel(II)



(purple-brown)

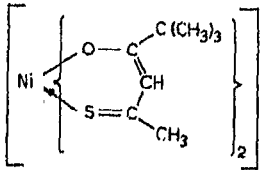
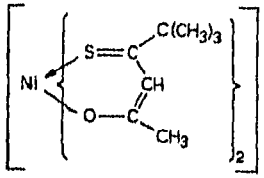
(b) Bis(thiobenzoyl-acetonato)nickel(II)



(brown)

(Continued on p. 144)

TABLE I (*continued*)

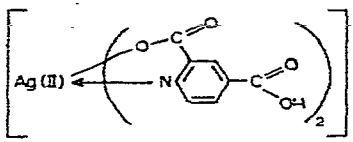
No.	*Isomer*	*Source*	*Developing solvent*	R_F *value*	ΔR_F	*Type of separation*
19	$[Ni(C_8H_{13}OS)_2]$	E.U.[16,17]	Dissolved in $(CH_3)_2CO$, developed in CH_3OH	0.78 (a) 0.78 (b)	0.00	None
	(a) Bis(pivaloylthio-acetonato)nickel(II)					
						
	(chocolate brown)					
	(b) Bis(thiopivaloyl-acetonato)nickel(II)					
						
	(brown)					
	Coordination No. 2					
	Type MAB					
20	Cu(I)(SCN)(picoline)[§] (with Cu–SCN bonding)	S.S.[14]	C_2H_5OH			
	(a) α-pic (white)			0.62 (α-pic) 0.70 (β-pic)	0.08	Partial
	(b) β-pic (yellowish white)			0.54 (γ-pic) 0.60 (α-pic)	0.06	Partial
	(c) γ-pic (white)			0.56 (γ-pic) 0.68 (β-pic)	0.12	Partial

* These compounds either were impure or were decomposed into several products by the solvent system. The R_F value for the most intense spot is italicized.

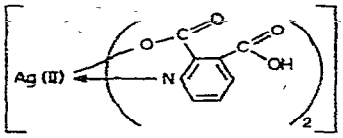
** In both ligand isomers the bidentate ligand PP is coordinated at adjacent (*cis*) positions on the octahedron.

*** In mixtures the R_F values were found to be lower than those of the individual isomers.

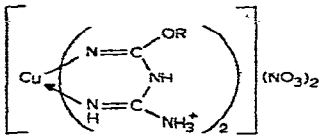
§ In C_2H_5OH–$(CH_3)_2CO$ (1:1), R_F values for the three isomers were found to be 0.70 (α-pic), 0.67 (β-pic), and 0.65 (γ-pic), and a separation of all three isomers was not attempted.



compound A



compound B



compound C

MAB: [$Ph_3P \cdot Au \cdot SC(S)OR$], *n*-propyl (yellow), isopropyl (yellow) (J.M.S.[28]) —very similar R_F values for all solvents used.

CONCLUSIONS

The advantages of TLC in the separation of inorganic isomers have been discussed in previous articles[1,2]. In the present paper we have extended the method to a more subtle type of isomerism and have separated a number of non-electrolytic ligand isomers of various metals, Co(II), Cu(I) and (II), Rh(III), Ni(II), W(0), Fe(III), Cr(0), and Sn(IV), with various coordination numbers containing a variety of ligands of various types. The method may be applied to air-sensitive materials (a complex of zerovalent tungsten) provided that adequate precautions are taken. Because of the wide differences in the structures of the isomers and the ligands involved, no generalizations can be made concerning R_F values.

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