

CHROM. 9017

Note

Separation of inorganic isomers by thin-layer chromatography

V. Structural, linkage, geometric, and conformational isomers of various coordination numbers

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(Received January 12th, 1976)

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 metals², square planar non-electrolytic and electrolytic geometric isomers of various metals³, and ligand isomers of various coordination numbers⁴. In the present paper we extend our TLC separations to include structural, linkage, and conformational isomers as well as geometric isomers of coordination number five. Inasmuch as we have demonstrated in our first article¹ that TLC separations can be carried out on a semiquantitative preparative scale (with *ca.* 200 mg of total mixtures), all the separations reported here are strictly qualitative.


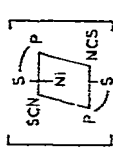
EXPERIMENTAL

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 the Mallinckrodt Chemical Works, St. Louis, Mo., U.S.A. Microscope slides (75 mm × 25 mm) were used for plates and were developed by the ascending technique. Iodine vapor was used for visualizing all samples except for samples No. 2, No. 3, and No. 8, the colors of which were so intense that no visualization was required. Further details are given in previous articles¹⁻⁴.

RESULTS AND DISCUSSION

The results obtained are summarized in Table I. R_f values were reproducible to ± 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_3B , sample No. 1 (partial); $M(ABBA)(CD)$, samples No. 2 and No. 3; Coordination Nos. 6 and 4 — $M(AB)_2C_2$ and MA_2B_2 , sample No. 4; Coordination No. 5 — $M(AB)_2C$, sample No.

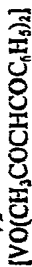
TABLE I
THIN-LAYER CHROMATOGRAPHY OF MISCELLANEOUS ISOMERS

No.	Isomer	Source	Developing solvent	R_F	AR_F	Type of separation
<i>Coordination No. 6</i>						
<i>Type MA₂B (linkage isomers)</i>						
1	[Ir(NH ₃) ₂ NCS or SCN](ClO ₄) ₂ (a) Ir-SCN (deep yellow) (b) Ir-NCS (bright yellow)	H-HS ⁵	acetone acetone-water (1:1)	0.31 (Ir-S) 0.60 (Ir-S)	0.38 (Ir-N) (streaking) 0.73 (Ir-N) (streaking)	partial partial
<i>Type M(ABBA)(CD)</i>						
2	<i>cis</i> -[Co(trien)(L-alaninate)]I ₂ ·H ₂ O, where trien = tridentate triethylenetetramine (a) β ₁ (pink) (b) β ₂ (RR + SS) (orange) (c) β ₂ (RS) (pink-orange)	BED ⁶	water	0.44 (a) 0.00 (c)	0.68 (b) 0.45 (a)	complete complete
3	<i>cis</i> -[Co(trien)(L-prolinate)]I ₂ ·H ₂ O (a) β ₁ (brick red) (b) β ₂ (brick red)	BED ⁶	water	0.16 (b)	0.75 (a)	complete
<i>Coordination Nos. 6 and 4</i>						
<i>Types M(AB)₂C₂ and MA₂B₂</i>						
4	<i>trans</i> -[Ni(DPES) ₂ (NCS) ₂] ⁺ , where DPES = 2-diethylphosphinoethyl ethyl sulfide, (C ₂ H ₅) ₂ PC ₂ H ₄ S(C ₂ H ₅)	JFS ⁷				
	(a)  (yellow)		dissolved in acetone developed in methanol	0.05	0.78	complete ⁷
	(b)  (olive) (not available)		dissolved in acetone developed in water	0.17	1.00	complete ⁷

NOTES

NOTES

Coordination No. 5

Type $M(AB)_2C$ (a) *cis* (olive crystals) (sample No. 1)(b) *cis* (green powder) (sample No. 2)RLB⁹dichloromethane
dichloromethane0.16 (*trans*?)
0.90 (minor
constituent)0.60 (*cis*?)
0.78 (*cis*)0.44 partial?
0.78 none

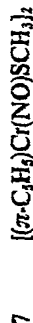
Binuclear complexes

RET^{9,10}

methanol-water (1:1)

0.10, 0.85,
1.00 (b)

— partial?

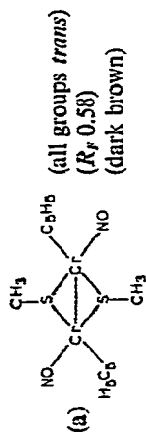
(purple)¹¹(brown)¹⁰GRK^{12,13}dissolved in dichloro-
methane
developed in ethanol

0.90 (b)

0.12

complete

(Five isomers possible)



(Continued on p. 398)

TABLE I (continued)

No.	Isomer	Source	Developing solvent	R_f	ΔR_f	Type of separation
	(b) Mixture of four possible isomers based on planar (C ₁ -S) ₂ cycle (brown) (R_f 0.88)					
	Type M (ABA)C (linkage isomers)					
8	[Pd(Et ₂ dien)NCSe or SeCN][B(C ₆ H ₅) ₃], where Et ₂ dien = tridentate ligand N ₁ N ₂ N ₃ ,N ₄ -tetramethyldiethylenetriamine	JLB ^{14,15}	acetone	0.02 (a)	0.96 (b)	complete
	(a) Pd-NCSe (pale yellow)					
	(b) Pd-SeCN (bright yellow)					

* This compound exists in two isomeric forms—an olive, paramagnetic, octahedral form in which DPES is bidentate with both P- and S-bonding and a yellow diamagnetic, square planar form in which DPES is monodentate with only P-bonding. Although the olive complex reportedly isomerizes to the yellow isomer in acetone solution, while the reverse isomerization is not reported, when the yellow isomer, which was the only sample provided, was chromatographed, two distinct spots were obtained. The spots could not be identified isomerically.

5 (partial); Binuclear complexes, sample No. 6 (partial), sample No. 7; M(ABA)C, sample No. 8. Samples No. 2 and No. 3 contained impurities which were visualized on the plates with iodine vapor. The separations of samples No. 4 and No. 6 are questionable for the reasons cited in Table I. With regard to sample No. 5, only *cis*-[VO(benzac)₂] is known in the pure state, while solutions prepared from the solid *cis* isomer presumably contain a mixture of *cis*- and *trans*-[VO(benzac)₂]¹⁶. Although two spots were obtained on chromatographing sample No. 5a, which would seem to confirm this presumption, only one spot (with a minor constituent at the origin) was obtained on chromatographing sample No. 5b, leading us to believe that sample No. 5a may have contained impurities and that therefore its separation into *cis* and *trans* isomers is doubtful. For sample No. 7, although the *trans* isomer (sample No. 7a) could be separated completely from sample No. 7b, the latter, supposedly a mixture of four possible isomers, could not be separated into these four isomers.

In addition to the isomers shown in Table I, separations were attempted with the following isomers (listed by type), but were unsuccessful for the reasons cited.

Coordination No. 6 —M(ABBA)(CD), *cis*-[Co(trien)(H₂NCH₂COO)]I₂·H₂O: β₁ (pink-orange), β₂ (RR + SS) (reddish orange), β₂ (RS) (pink-orange) (BED)⁶; same R_F values.

Coordination Nos. 6 and 4 —M(AA)₂B₂, [Co(2,2'-bipyridine)Cl₂]: α (octahedral polymer, light blue), β (tetrahedral monomer, royal blue) (JK)^{17,18}; R_F = 0 for both forms in dichloromethane.

Coordination No. 5 —Binuclear complexes, (π-C₅H₅)₂Fe₂(CO)₃P(OR)₃, where R = OCH₃, OC₂H₅ and OC₆H₅ (RJH)¹⁹; on the basis of IR spectroscopic evidence, each of these three dark red compounds is believed to exist as a mixture of geometric isomers in solution, yet in dichloromethane no chromatographic separations were obtained.

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 include the separation of various types of structural isomers²⁰, such as linkage isomers (samples No. 1 and No. 8), and coordination number isomers (sample No. 4), as well as conformational isomers of Coordination No. 6 (samples No. 2 and No. 3) and geometric isomers of Coordination No. 5 (sample No. 7). Samples No. 6a and No. 6b are also diastereoisomers. The metals represented in this paper are Ir(III), Co(III), Ni(II), Sn(IV), V(IV), Cr(III), and Pd(II). Because of the wide differences in the structures of the isomers and of the ligands involved, no generalizations can be made concerning R_F values.

ACKNOWLEDGEMENTS

We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 1152-B), the National Science Foundation (Undergraduate Research Participation Program Grants GY 2607 and GY 9916), and the California State University, Fresno Research Committee, for support of this research. We also wish to thank Ralph R. Calder, Richard A. Houghten,

Jr., Shan Yaw Lee, and Robert K. Masters for experimental assistance and the following persons, listed in alphabetical order, for kindly providing experimental samples of isomers: R. Linn Belford, John L. Burmeister, Bodie E. Douglas, R. J. Haines, Michael A. Hitchman, Jacob Kleinberg, Graham R. Knox, Hans-Herbert Schmidtke, John F. Sieckhaus, and Robert E. Tapscott.

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