complex by a chromatographic method. The higher degree of resolution obtained for the dextrorotatory enantiomer (the more soluble component in this system) is in accord with the general trend found for the simple inorganic salt systems.

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# The Separation of Inorganic Stereoisomers by Adsorption Chromatography. I. Non-electrolytic Geometric Isomers of Platinum(II)[1]

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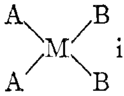
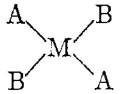
By the use of chromatographic columns of silica gel, Porocel (activated bauxite), activated alumina, and Linde Molecular Sieves, *cis–trans* isomer pairs of the mononuclear complexes dichlorobis-(tri-*n*-butylphosphine)-platinum(II), dichlorobis-(diethyl sulfide)-platinum(II), and dichlorodipyridineplatinum(II) and the binuclear complex *sym*-di-$\mu$-phenylthiodichlorobis-(tri-*n*-propylphosphine)-diplatinum(II) have been separated, the first two quantitatively and in significant amounts. In all cases, the non-polar or slightly polar *trans* isomer was first eluted with a relatively non-polar solvent (a solvent mixture in the cases of $[Pt((C_2H_5)_2S)_2Cl_2]$ and $[Pt(py)_2Cl_2]$); then the highly polar *cis* isomer was eluted with a more polar solvent. Attempts to separate *cis* from *trans* isomers of dinitrodiamminepalladium(II), dichlorodiammineplatinum(II), *sym*-di-$\mu$-ethylthiodichlorobis-(*tri-n*-propylphosphine)-diplatinum(II), and *sym*-di-$\mu$-*p*-nitrophenylthiodichlorobis-(tri-*n*-propylphosphine)-diplatinum(II) using various adsorbents were unsuccessful. Results, ideal conditions for separation, and structure-proof possibilities are discussed.

## Introduction

A general method for the preparation of inorganic *cis* and *trans* isomers has yet to be discovered; syntheses vary depending upon the particular complex. Occasionally, phenomena such as unequal solubilities or Chernyaev's *trans* effect permit isolation of one particular isomer, but in most cases isomer mixtures that require separation are obtained.[2]

Formation of a chemical bond between atoms of different electronegativities produces an unequal charge distribution. Depending upon the geometry, the resulting molecule may be polar or non-polar. Thus, for *cis* and *trans* isomers of type $MA_2B_2$ where M is a metal ion with coordination number four and square planar ($dsp^2$) configuration, the unsymmetrical *cis* isomer 

is polar, while the symmetrical *trans* isomer 

is usually non-polar.

Commercially available adsorbents that contain polar linkages often exhibit an unusually high affinity for polar molecules. Such adsorbents should strongly adsorb polar *cis* isomers, while non-polar *trans* isomers should be adsorbed to a smaller extent or not at all. The purpose of the research described in this paper was to apply this preferential adsorption to a practical separation of non-electrolytic inorganic geometric isomers.

Although adsorption chromatography has been used to separate a wide variety of isomeric organic substances, the technique has been applied to only a limited number of inorganic isomers.[3] In some of these cases diagnostic use of chromatography has been mentioned,[3f-k] and non-electrolytic geometric isomers have been chromatographically separated using non-aqueous solvents.[3o,p] Unlike paper chromatography, col-

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(1) Presented before the Division of Inorganic Chemistry at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961. The authors gratefully acknowledge the financial assistance of Research Corporation and the National Science Foundation (Grant NSF-G11241).

(2) R. G. Wilkins and M. J. G. Williams, in "Modern Coordination Chemistry" (J. Lewis and R. G. Wilkins, ed.), Interscience Publishers, Inc., New York, N. Y., 1960, pp. 197–201.

umn chromatography is not limited to small samples; the adsorbents described in this work are applicable to macroscopic separations of non-electrolytes. Solubility considerations probably will prevent the application of this technique to ionic isomers.

## Experimental

(1) **Isomers.**—All reagents were C.P. or reagent grade. Isomers were characterized by elemental analyses, melting points, physical properties, and chemical reactions. Unless noted otherwise, melting points agreed with literature values. Dipole moments were not measured, but literature values are given. Potassium tetrachloroplatinate(II) was prepared by reducing an aqueous suspension of potassium hexachloroplatinate(IV)[4] with hydrazine dihydrochloride.[5,6]

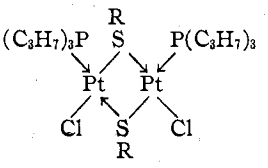
**Dichlorodiammineplatinum(II).**—The deep yellow *cis* isomer was prepared by the action of aqueous $NH_3$ on $K_2PtCl_4$[6–8]; the yellow *trans* isomer, by evaporating with 6 *M* HCl a solution of $[Pt(NH_3)_4]Cl_2$ prepared from $K_2PtCl_4$ and excess $NH_3$.[6,9–11]

**Dichlorobis-(diethyl sulfide)-platinum(II).**[12,13]—The light greenish yellow *cis* isomer was prepared by allowing excess diethyl sulfide to react with $K_2PtCl_4$; the bright yellow *trans* isomer by the reaction of diethyl sulfide with excess $K_2PtCl_4$; dipole moments,[12,14] *cis* 9.5 D.; *trans* 2.41 D.

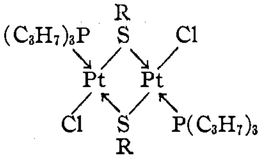
**Dichlorobis-(tri-*n*-butylphosphine)-platinum(II).**[15,16]—Both the snow white *cis* isomer and the yellow *trans* isomer were prepared by the action of tri-*n*-butylphosphine[17] on $K_2PtCl_4$. The isomers were separated by their differing solubilities; dipole moments,[15] *cis* 11.5 D.; *trans* 0 D.

**Dichlorodipyridineplatinum(II).**[18,19]—The pale yellow *cis* isomer was prepared by treating aqueous $K_2PtCl_4$ with pyridine; the very pale yellow *trans* isomer by evaporating with HCl a solution of $[Pt(py)_4]Cl_2$ prepared from the *cis* compound and excess pyridine.[11]

**Binuclear Thio-Bridged Platinum(II) Isomers.**[20]—



*cis*



*trans*

(I) *sym*-Di-*μ*-ethylthiodichlorobis-(tri-*n*-propylphosphine)-diplatinum(II), R = $C_2H_5$: dipole moments,[21] *cis* (pale yellow) 10.3 D.; *trans* (very pale yellow) *ca.* 0 D.

(II) *sym*-Di-*μ*-phenylthiodichlorobis-(tri-*n*-propylphosphine)-diplatinum(II), R = $C_6H_5$: dipole moments,[21] *cis* (pale yellow) 11.2 D.; *trans* (pale yellow) 0.75 D.

(III) *sym*-Di-*μ*-*p*-nitrophenylthiodichlorobis-(tri-*n*-propylphosphine)-diplatinum(II), R = *p*-$C_6H_4NO_2$: melting point, *cis* 84–88° (lit. value 129–131°, hence *cis* probably impure); dipole moments,[21] *cis* (yellow) 13.0 D.; *trans* (yellow) 4.68 D.

**Dinitrodiamminepalladium(II).**—The very pale yellow *cis* isomer was prepared by treating an ammoniacal $PdCl_2$ solution with a concentrated $NaNO_2$ solution[22]; the yellowish white *trans* isomer, by adding $NaNO_2$ to a $[Pd(NH_3)_4]Cl_2$ solution followed by formic acid reduction.[11,23]

(2) **Eluents.**—All eluents were C.P. or reagent grade. Eastman spectro-grade benzene (S777) and acetone (S297) were used in quantitative separations since reagent grade solvents left residues on evaporation.

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(3) **Cation exchange resins:** (a) $[Co(NH_3)_4(NO_2)_2]X$, E. L. King and R. R. Walters, *J. Am. Chem. Soc.*, **74**, 4471 (1952), M. Mori, M. Shibata, and J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955) (in Japanese), *cf. Chem. Abstr.*, **51**, 11150c (1957); (b) $[Cr(H_2O)_4(SCN)_2]X$, J. T. Hougen, K. Schug, and E. L. King, *J. Am. Chem. Soc.*, **79**, 519 (1957); (c) $[Cr(H_2O)_4Cl_2]X$, E. L. King, Sr. M. J. M. Woods, and H. S. Gates, *ibid.*, **80**, 5015 (1958); (d) $[Co(en)_2(NO_2)_2]Cl$, M. Mori, M. Shibata, and J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955)(in Japanese); *cf. Chem. Abstr.*, **51**, 11150c (1957); (e) $[Co(en)_2Cl_2]Cl$, $[Co(en)_2(SCN)_2]Cl$, M. Mori, M. Shibata, and M. Nanasawa, *Bull. Chem. Soc. Japan*, **29**, 947 (1956)(in German); (f) $K[Co(en)(C_2O_4)(NO_2)_2]$, E. Kyuno, *Nippon Kagaku Zasshi*, **80**, 981 (1959); (g) $K[Co(NH_3)_2(CO_3)(NO_2)_2]$, E. Kyuno, *ibid.*, **81**, 724 (1960); (h) $K[Co(NH_3)_2(C_2O_4)(NO_2)_2]$, E. Kyuno, *ibid.*, **81**, 728 (1960); (i) $[Ru(H_2O)_4Cl_2]X$, R. E. Connick and D. A. Fine, *J. Am. Chem. Soc.*, **82**, 4187 (1960); (j) $K[Ru(H_2O)_2Cl_4]$, R. E. Connick, in "Advances in the Chemistry of the Coordination Compounds" (S. Kirschner, ed.), The Macmillan Co., New York, N. Y., pp. 15–20; **Paper chromatography:** (k) $[Co(NH_3)_4(NO_2)_2]X$, $[Co(en)_2Y_2]X$ where Y = $NO_2$, Cl, Br, NCS, or SCN, $[Co(en)_2YCl]Cl$ or $-Cl_2$ where Y = $NO_2$, NCS, or $NH_3$, and $[Pt(NH_3)_2(py)_2]Cl_2$, G. Stefanović and T. Janjić, *Anal. Chim. Acta*, **11**, 550 (1954); **19**, 488 (1958); **Alumina:** (l) $[Co(NH_3)_4(N_3)_2]X$, M. Linhard, M. Weigel, and H. Flygare, *Z. anorg. Chem.*, **263**, 233 (1950); (m) $[Cr(en)_2(OH)_2]X$, F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958); (n) $[Co(en)_2(OH)_2]X$, $[Co(NH_3)_4(NO_2)_2]NO_3$, A. Jensen, J. Bjerrum, and F. Woldbye, *ibid.*, **12**, 1202 (1958); (o) $[Pt((C_2H_5)_3M)_2R_2]$ and $[Pt((C_2H_5)_3M)_2(R)Cl]$ where M = P or As and R = an alkyl or aryl group, J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959); (p) $[Co(trifluoroacetylacetonate)_3]$, and $[M(benzoylacetonate)_3]$ where M = Co(III), Cr(III), and Rh(III), R. C. Fay and T. S. Piper, "Abstracts of Papers, 140th National Meeting, American Chemical Society, Chicago, Ill., Sept. 3–8, 1961," p. 29-N.

(4) Prepared from 99.98+% Pt sponge purchased from Goldsmith Bros. Smelting and Refining Co., Chicago, Ill.

(5) N. G. Klyuchnikov and R. N. Savelava, *Zh. Neorgan. Khim.*, **1**, 2764 (1956).

(6) G. B. Kauffman and D. O. Cowan, *Inorg. Syn.*, **7**, in press.

(7) L. Ramberg, *Ber.*, **46**, 2362 (1913).

(8) L. Ramberg, *Z. anorg. allgem. Chem.*, **83**, 33 (1913).

(9) M. Peyrone, *Ann.*, **51**, 15 (1845).

(10) M. Peyrone, *ibid.*, **61**, 180 (1847).

(11) Dipole moments for these isomers have never been determined because of their insolubility in non-polar solvents.

(12) K. A. Jensen, *Z. anorg. allgem. Chem.*, **225**, 97, 115 (1935).

(13) G. B. Kauffman and D. O. Cowan, *Inorg. Syn.*, **6**, 211 (1960).

(14) The dipole moment of the *trans* isomer is not zero because the $C_2H_5$ groups are not coplanar with the Pt–Cl and Pt–S bonds; *cf.* ref. 12.

(15) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 225 (1936).

(16) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, in press.

(17) Prepared by a modified Grignard reaction between *n*-butylmagnesium bromide and phosphorus(III) chloride according to I. K. Jackson, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 2109 (1931) and G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **6**, 87 (1960).

(18) S. M. Jørgensen, *J. prakt. Chem.*, [2] **33**, 409 (1886).

(19) G. B. Kauffman, *Inorg. Syn.*, **7**, in press.

(20) Small samples of these isomers were kindly furnished by Drs. J. Chatt, P. G. Owston, and F. A. Hart, Imperial Chemical Industries, Ltd. For preparation and properties see J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953); 2807 (1960).

(21) The dipole moment of the *trans* isomer is not zero because the groups attached to the S atoms are not coplanar with the $PtS_2Pt$ ring; *cf.* ref. 20.

(22) F. G. Mann, D. Crowfoot, D. Gattiker, and W. Wooster, *J. Chem. Soc.*, 1642 (1935).

(23) H. B. Jonassen and N. L. Cull, *Inorg. Syn.*, **4**, 179 (1953).

(3) **Adsorbents.**—A representative selection of adsorbents of different types was used. Except when indicated otherwise, adsorbents were used directly from the original containers without activation. Samples were generously provided by the companies listed. **Molecular Sieves,**[24] Types 4A, 5A, and 13X, 1/16 in. pellets and powder (Linde Co., New York, N. Y.). **Activated carbon,** Type CAL, 12–40 mesh (Pittsburgh Coke and Chemical Co., Pittsburgh, Penna.). **Chromatopac** I-8003, acid-washed Celite, 60–100 mesh, and **magnesiated silica** I-8070, 60–100 mesh (Research Specialties Co., Berkeley, Calif.). **Sea Sorb** 53, adsorptive magnesia, 20–100 mesh (Food Machinery and Chemical Corp., New York, N. Y.). **Filtrol** 90, alumina (Filtrol Corp., Los Angeles, Calif.). **Florex** XXS, specially treated Florida fullers earth, 60–100 mesh, and **Florosil**, magnesia–silica gel, 60–100 mesh (Floridin Co., Tallahassee, Fla.). **Celite** analytical filter-aid L-665-A (Johns-Manville Corp., New York, N. Y.). Alcoa **activated alumina**, grade F-1, 14–28 mesh (Aluminum Co. of America, Chemicals Div., Pittsburgh, Penna.). **Porocel**, activated bauxite, 6% V. M., 60–140 mesh (Minerals and Chemicals Corp. of America, Menlo Park, N. J.). Davison **silica gel**, grade 15, 35–60 mesh (Davison Chemical Co., Baltimore, Md.).

(4) **Columns.**—The columns were of four types— (1) 5-ml. Mohr pipets, (2) 10-ml. and 50-ml. burets, (3) chromatographic columns modified with stopcocks for controlling flow rate (catalog no. 21502, 200 mm. long, 19 mm. i.d., Fisher Scientific Co., Pittsburgh, Penna.), and (4) chromatographic columns with Ultramax valves (no lubricant required) for controlling flow rate (catalog no. 80-G 1300, 24 in. long, 3/8 in. i.d., Fischer and Porter Co., Hatboro, Penna.). To prevent contamination of effluent, stopcocks for types 2 and 3 were lubricated with a stopcock grease insoluble in organic solvents.[25] Adsorbent was retained with glass wool plugs in types 1 and 2 and with removable Selas fritted-glass disks in types 3 and 4.[26] Qualitative experiments were performed with type 1 columns; quantitative separations, with type 2, 3, and 4 columns.

A slurry of adsorbent suspended in the equilibrating solvent, *i.e.*, the solvent used to elute the *trans* isomer, was poured into the column container; as the excess solvent was drained, the adsorbent settled, forming a bed. Care was taken never to allow the liquid level to fall below the top of the bed.

(5) **Procedure.**—By means of a long glass capillary pipet controlled with a hypodermic syringe, a concentrated, but not saturated, solution of the *trans* isomer in a solvent of low polarity was placed on the adsorbent column. In order to detect possible isomerization in the solvent, such solutions had been previously allowed to stand for an hour, evaporated to dryness at room temperature (25–30°), and the melting points of the residues determined. The solution and container washings were allowed to seep into the column. The isomer was now eluted with the same solvent at a flow rate of *ca.* 0.3–3.0 cm./min., the effluent was collected in spot plates, and "break-through" (first appearance), "peak" (maximum intensity), and "terminal" (disappearance) volumes were determined by spot-testing. If the isomer was not eluted, the procedure was repeated with eluents of increasing polarity until the isomer was detected in the effluent. The entire procedure then was repeated with the *cis* isomer.

On the basis of a number of such experiments, a pair of solvents was chosen, the first of which (low polarity) would elute the *trans* but not the *cis* isomer, while the second (higher polarity) would elute the *cis* isomer. Although in some cases, the "breakthrough," "peak," and "terminal" volumes for the *cis* and *trans* isomers with the same eluent were sufficiently different to permit a separation using only one eluent, under such conditions the *cis* isomer was eluted only slowly with extensive "trailing"; use of different eluents for *cis* and *trans* isomers resulted in more distinct and more easily controlled separations.

The actual separations were now performed using a *ca.* 1:1 by weight mixture of the *cis* and *trans* isomers; the different effluents were collected in separate containers,[27] the isomers were detected and identified, and purity was determined as described in sections 6 and 7. After all the *trans* isomer had been eluted, the flow rate could be increased for elution of the *cis* isomer. Once started, a separation was continued without interruption until completed.

(6) **Detection of Isomers in Effluent.**—For qualitative column experiments, the following spot test reagents, listed with their isomer reactions, were used. Formulas refer to both isomers unless otherwise specified. **Tin(II) chloride** (0.5 *M* in 1 *M* HCl, freshly prepared).[28]—$[Pt(NH_3)_2Cl_2]$, bright yellow-orange; binuclear Pt(II) isomers, faint yellow. **Dithioöxamide** (1 g. of rubeanic acid in 25 ml. of ethanol).—$[Pt((C_2H_5)_2S)_2Cl_2]$, deep red-violet; $[Pt(NH_3)_2Cl_2]$ and $[Pt(py)_2Cl_2]$, red (after addition of 1 drop of $HNO_3$ to effluent); binuclear Pt(II) isomers, colors varying from yellow to gray. **Oxine** (1 g. of 8-hydroxyquinoline in 25 ml. of ethanol.—$[Pt((C_2H_5)_2S)_2Cl_2]$ and *cis*-$[Pt((C_4H_9)_3P)_2Cl_2]$, yellow; binuclear Pt(II) isomers, $[Pt(py)_2Cl_2]$, and *trans*-$[Pt((C_4H_9)_3P)_2Cl_2]$, no reaction. **Dithizone** (0.1 g. of diphenylthiocarbazone in 10 ml. of methyl ethyl ketone).—$[Pt((C_2H_5)_2S)_2Cl_2]$, pink; and $[Pt((C_4H_9)_3P)_2Cl_2]$, dark brown (both after addition of 1 drop of ethanol to effluent); $[Pt(py)_2Cl_2]$ and binuclear Pt(II) isomers, no reaction. In all cases, colors were compared with eluent blanks. Low solubility rather than intrinsic stability of the pyridine isomers probably prevented them from responding to several of the tests.

(7) **Differentiation and Purity Tests for Recovered Isomers.**—Although the conditions for elution of a given isomer were known from preliminary column experiments

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[24] Hitherto Molecular Sieves have been used to separate primarily liquids and gases (*cf.* Publications No. 8605A and 8614A, Linde Air Products Co., New York, N. Y., 1956). The authors are indebted to Dr. George W. Watt, University of Texas, for suggesting their use for separating solid inorganic geometric isomers in solution.

[25] Nonaq, catalog no. 14-633, Fisher Scientific Co., Fair Lawn, N. J.

[26] Since glass wool retaining plugs allowed fine particles of some adsorbents, especially Porocel, to contaminate the effluent, columns with fritted-glass disks were used for quantitative separations.

[27] Weighed 125-ml. glass-stoppered erlenmeyer flasks were used for quantitative separations. Rotary vacuum evaporators (Model 1007-4N, Rinco Instrument Co., Greenville, Ill.) were used to evaporate effluents to constant weight at room temperature. Gentle heat was occasionally applied to prevent the solvent from freezing.

[28] G. H. Ayres and A. S. Meyer, Jr., *Anal. Chem.*, **23**, 299 (1951).

with separate isomers, the identities and purities of the isomers obtained at different points in the process were confirmed by mixed melting point and decomposition point measurements (Fisher-Johns apparatus). Both isomers of $[Pt((C_2H_5)_2S)_2Cl_2]$ have the same melting point, but a mixture gives a large melting point depression. *cis* Isomers of $[Pt((C_2H_5)_2S)_2Cl_2]$ and $[Pt((C_4H_9)_2P)_3Cl_2]$ gave immediate precipitates of AgCl with ethanolic $AgNO_3$, while the less labile *trans* isomers reacted only on long standing. The isomers of $[Pt((C_4H_9)_3P)_2Cl_2]$ also were readily differentiated by color (*cis*, white; *trans*, yellow) and by reaction with oxine (*cf*. section 6).[29]

## Results

Many eluents and eluent mixtures were evaluated, but only the most successful combinations will be given here.

(1) **$[Pt((C_4H_9)_3P)_2Cl_2]$**.—Data for qualitative separations obtained with type 13X **Molecular Sieves** are shown as item 1 in Table I. Separations can be seen more clearly and vividly if presented as in Fig. 1, but to save space, data for all qualitative separations will be presented in Table I. The melting point of the recovered *cis* isomer was only 4–5° below that of the original isomer, but the *trans* isomer was recovered as a gummy mass whose melting point could not be determined. The differentiation methods described in Experimental, section 7, confirmed the fact that a separation had indeed been accomplished. By using the size column indicated, complete separations were limited to 10–20 mg. isomer mixtures.[30]

In an attempt to "scale-up" the separations from a milligram level to a more practical level, other adsorbents were evaluated. Both qualitative (Table I) and quantitative (Table II) separations were obtained with **silica gel**[31] (Table I, item 2; Table II, item 1), **Porocel** (Table I, item 3; Table II, item 2), and **activated alumina** (Table I, item 4; Table II, item 3). If both elution of isomers and evaporation of effluent were carried out rapidly, no isomerization occurred. In contrast to the separations with Molecular Sieves, the recovered *trans* isomer was obtained in crystalline form.

However, isomerization on a silica gel column was encountered with one sample of $[Pt((C_4H_9)_3P)_2Cl_2]$ which apparently was contaminated with $(C_4H_9)_3P$ (Table II, item 4). The melting points showed that the recovered isomers were pure; the ratio of *cis* isomer to *trans* isomer had changed significantly although the *total* weight of *both* recovered isomers indicated that the separation was quantitative. Since $[Pt((C_4H_9)_3P)_2Cl_2]$ is known to isomerize in benzene solution if even traces of $(C_4H_9)_3P$ are present,[32] such behavior is not surprising.[33]

**Synthesis.**—Several attempts were made to apply the separation method to an actual synthesis. Instead of separating the isomers of $[Pt((C_4H_9)_3P)_2Cl_2]$ by differing solubilities,[15,16] the crude, waxy reaction mixture, containing occluded $K_2PtCl_4$, KCl, and $(C_4H_9)_3P$, was washed several times with water, dried with $Na_2SO_4$, and dissolved in benzene.[34] The solution was placed on a silica gel column, eluted with benzene and acetone, and the effluents evaporated. Pure *trans* isomer was recovered from the benzene effluent in good yield, but the *cis* isomer recovered from the acetone effluent was contaminated with *trans* isomer and other impurities.

(2) **$[Pt((C_2H_5)_2S)_2Cl_2]$**.—Data for a typical qualitative separation obtained with type 5A **Molecular Sieves** are shown in Table I, item 5. Type 13X gave similar results. "Overloading" effects similar to those described in connection with $[Pt((C_4H_9)_3P)_2Cl_2]$ were encountered, and therefore other adsorbents were evaluated.

Both qualitative (Table I) and quantitative (Table II) separations were obtained with **silica gel** (Table I, item 6; Table II, item 5), **Porocel** (Table I, item 7; Table II, item 6), and **activated alumina** (Table I, item 8; Table II, item 7). **Activated carbon** or **Celite** showed no isomer adsorption; isomers eluted from activated carbon were recovered as decomposed glassy masses.

(3) **$[Pt(py)_2Cl_2]$**.—Table I shows data for

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(29) Oxyphenylenetelluronium hydrogen sulfate, suggested by H. D. K. Drew, F. W. Pinkard, and E. G. Cox (*J. Chem. Soc.*, 988 (1932)) for detecting traces of *cis*-$[Pt(NH_3)_2Cl_2]$ in a large amount of *trans*-$[Pt(NH_3)_2Cl_2]$, was prepared (H. D. K. Drew, *ibid.*, 233, 3054 (1926)), but its value was found to be limited to that particular isomer pair.

(30) Use of larger samples resulted in only partial separations because of similar elution behavior of both isomers as well as extensive "trailing." This apparent "overloading" effect led us to believe that adsorption was occurring on the *surface* of the Molecular Sieves rather than in the interstices, thus utilizing only a small fraction of their potential capacity.

(31) The white color of this adsorbent permits one to observe visually the elution of colored isomers.

(32) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273, 4300 (1952); 70 (1953); 525 (1956). Jensen (ref. 15) encountered no isomerization in benzene solutions to which $(C_4H_9)_3P$ had not been added.

(33) In view of the adequate separations obtained with silica gel, Porocel, and activated alumina, the following briefly investigated adsorbents showed little promise for the reasons indicated. Activated carbon—isomers recovered as decomposed glassy masses; **Florex XXS, Sea Sorb,** and **Filtrol**—column attacked by eluents; and **Celite**—no isomer adsorption.

(34) Even before the benzene solution was placed on the column, the presence of $(C_4H_9)_3P$ caused rapid isomerization as shown by a deepening of the yellow color (*cf.* ref. 32).

TABLE I

QUALITATIVE SEPARATIONS OF *cis–trans* ISOMERS

| Isomer | Adsorbent | Column vol. = ht. × cross-sect. (cm.³ = cm. × cm.²) | Flow rate (cm./min.) | Eluent | Elution volumes (col. vols.) | | |
|---|---|---|---|---|---|---|---|
| | | | | | "Break-through" | "Peak" | "Terminal" |
| $[Pt((C_4H_9)_3P)_2Cl_2]$[a] | | | | | | | |
| (1) *trans* | 13X Molecular Sieves, 50 mesh | 5.04 = 26.5 × 0.190 | 8 | $C_6H_6$ | 0.35 | 0.40 | 0.45 |
| *cis* | | | 8 | N,N-Dimethylformamide | 0.80 | 1.01 | 1.60 |
| | | | | | (+2.00)[b] | (+2.00) | (+2.00) |
| (2) *trans* | Silica gel | 3.10 = 16.6 × 0.187 | 0.65 | $C_6H_6$ | 0.62 | 0.91 | 1.79 |
| *cis* | | | .65 | $(CH_3)_2CO$ | 0.21 | 0.47 | 1.44 |
| | | | | | (+2.12) | (+2.12) | (+2.12) |
| (3) *trans* | Porocel | 6.92 = 37.0 × 0.187 | .85 | $C_6H_6$ | 0.49 | 0.82 | 1.26 |
| *cis* | | | 1.28 | $(CH_3)_2CO$ | 0.54 | 0.85 | 1.66 |
| | | | | | (+1.76) | (+1.76) | (+1.76) |
| (4) *trans* | Activated alumina | 3.80 = 20.3 × 0.187 | 0.79 | $C_6H_6$ | 0.42 | 1.05 | 2.47 |
| *cis* | | | .86 | $(CH_3)_2CO$ | 0.48 | 0.84 | 3.05 |
| | | | | | (+3.68) | (+3.68) | (+3.68) |
| $[Pt((C_2H_5)_2S)_2Cl_2]$[a] | | | | | | | |
| (5) *trans* | 5A Molecular Sieves, 50 mesh | 5.06 = 22.0 × 0.23 | .5 | $C_6H_6$ | 0.60 | 0.80 | 1.20 |
| *cis* | | | .5 | *p*-Dioxane | 0.50 | 0.90 | 2.30 |
| | | | | | (+1.30) | (+1.30) | (+1.30) |
| (6) *trans* | Silica gel | 3.87 = 20.7 × 0.187 | .54 | $0.5(CH_3)_2CO:100C_6H_6$ | 0.25 | 1.13 | 6.16 |
| *cis* | | | .71 | $(CH_3)_2CO$ | 0.25 | 0.41 | 1.85 |
| | | | | | (+7.00) | (+7.00) | (+7.00) |
| (7) *trans* | Porocel | 3.52 = 18.8 × 0.187 | .65 | $C_6H_6$ | 0.23 | 0.69 | 1.79 |
| *cis* | | | .71 | $(CH_3)_2CO$ | 0.23 | 0.51 | 7.05 |
| | | | | | (+3.00) | (+3.00) | (+3.00) |
| (8) *trans* | Activated alumina | 3.80 = 20.3 × 0.187 | .68 | $C_6H_6$ | 0.84 | 1.89 | 4.21 |
| *cis* | | | 1.00 | $(CH_3)_2CO$ | 0.39 | 0.47 | 2.56 |
| | | | | | (+4.27) | (+4.27) | (+4.27) |
| $[Pt(py)_2Cl]$[c] | | | | | | | |
| (9) *trans* | Silica gel | 5.11 = 27.3 × 0.187 | 0.75 | $17(CH_3)_2CO:100C_6H_6$ | 1.10 | 1.49 | 3.49 |
| *cis* | | | .75 | $(CH_3)_2CO$ | 0.46 | 0.90 | 2.03 |
| | | | | | (+4.00) | (+4.00) | (+4.00) |
| (10) *trans* | Porocel | 4.09 = 21.87 × 0.187 | .52 | *p*-Dioxane | 0.42 | 0.93 | 3.17 |
| *cis* | | | .52 | $(CH_3)_2CO$ | 0.42 | Indefinite | 3.77 |
| | | | | | (+3.21) | | (+3.21) |
| (11) *trans* | Activated alumina | 3.71 = 19.8 × 0.187 | .63 | $7(CH_3)_2CO:100C_6H_6$ | 1.51 | 2.17 | 3.99 |
| *cis* | | | .63 | $(CH_3)_2CO$ | 0.70 | 1.41 | 3.83 |
| | | | | | (+4.69) | (+4.69) | (+4.69) |
| $[((C_3H_7)_3P)_2Pt_2(C_6H_5S)_2Cl_2]$[a] | | | | | | | |
| (12) *trans* | Silica gel (acetone-washed) | 2.18 = 9.30 × 0.234 | .95 | $C_6H_5CH_3$ | 0.33 | 0.75 | 4.50 |
| *cis* | | | 2.6 | $CH_3CN$ | 0.66 | 0.84 | 2.50 |
| | | | | | (+7.00) | (+7.00) | (+7.00) |

[a] Sample—*ca.* 2 mg. isomer in 1 cm.³ of *trans* eluent. [b] Numbers in parentheses indicate volume of first eluent used before switching to second eluent. [c] Sample—1 cm.³ of saturated solution.

typical qualitative separations obtained with **silica gel** (item 9), **Porocel** (item 10), and **activated alumina** (item 11). Quantitative separations were not attempted because the very low solubility of these isomers would require the use of excessively large volumes of solvent to elute a weighable amount of isomer.

**(4) $[((C_3H_7)_3P)_2Pt_2(C_6H_5S)_2Cl_2]$.**—Unlike mononuclear Pt(II) complexes of which the *cis* isomer is always much less soluble in organic solvents than is the *trans*, both *cis* and *trans* isomers of binuclear thio-bridged Pt(II) complexes are very soluble in most organic solvents. Data for a typical qualitative separation obtained with acetone-activated[35] **silica gel** are shown in Table I, item 12.[36,37]

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(35) Non-reproducible elution behavior, encountered with unactivated columns, finally was eliminated by activating the columns either by heating or by preliminary rinsing with acetone.

## Discussion

Basically, the separation depends upon the relative strengths of the attractions between isomers and eluent, isomers and adsorbent, and eluent and adsorbent. Ideal conditions for separation can thus be best summarized in terms of three variables.

(1) **Isomers.**—Ideal isomer pairs should (a) be non-electrolytes, (b) have widely differing dipole moments for *cis* and *trans* isomers, (c) be inert in order to minimize isomerization, (d) show great differences between *cis* and *trans* isomers for differentiation purposes, (e) have well established properties to facilitate identification, and (f) be soluble in both polar and non-polar solvents.[38]

(2) **Eluents.**[39]—The ideal eluent (a) should dissolve both *cis* and *trans* isomers, (b) should have a low boiling point so that the eluted isomer can be quickly recovered by evaporation of effluent at room temperature, a process which minimizes isomerization, and (c) should not interact with isomers to form oils or isomerized or decomposed products.

(3) **Adsorbents.**—The ideal adsorbent should (a) adsorb the *cis* isomer but not so strongly that it cannot be eluted by a polar solvent, (b) not cause isomerization, and (c) be inert to organic solvents.

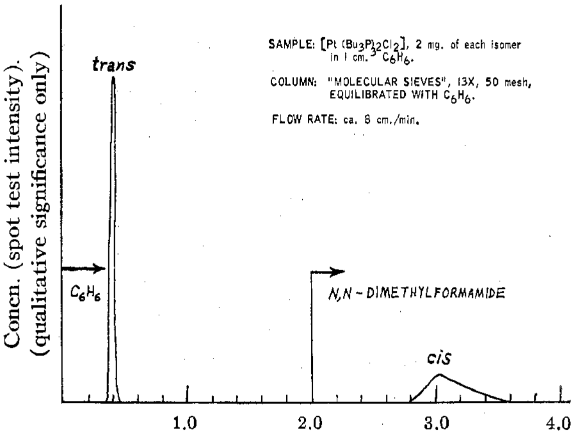

Fig. 1.—Elution profile of a typical qualitative separation of an isomer pair.

The method is presently limited by the fact that so far we have been able to satisfy only a few of the ideal conditions, but the search for more suitable isomers, eluents, and adsorbents is being continued. The most restrictive limitation is insolubility, a factor probably mainly responsible for the lack of success with $[Pd(NH_3)_2(NO_2)_2]$ and $[Pt(NH_3)_2Cl_2]$, the first isomers investigated in this work.[40] Even with complexes of platinum, which generally are regarded as stable, isomerization, the second major limitation, may occur. (see $[Pt((C_4H_9)_3P)_2Cl_2]$ above).[41] Furthermore, some adsorbents, such as activated carbon or silica gel, are known to catalyze heterogeneously isomerization in a wide variety of complexes.[42] Isomer–eluent interaction, the third major limitation, may be largely responsible for the difficulties encountered with some binuclear thio-bridged Pt(II) isomers.[43]

In all our successful separations, the first isomer to be eluted with a relatively non-polar solvent

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(36) No separations were obtained for $[((C_3H_7)_3P)_2Pt_2((C_2H_5)_2S)_2Cl_2]$ and $[((C_3H_7)_3P)_2Pt_2(p\text{-}C_6H_4NO_2S)_2Cl_2]$ on acetone-activated **silica gel** and **activated alumina** columns using eluents of widely varying polarity, including solvent mixtures as well as pure solvents. Difficulties encountered were non-adsorption or identical elution behavior of both isomers and extensive "trailing" of isomers on elution.

(37) The melting point of the recovered *trans* isomer was 165.5–166° (original isomer, 163–165°). Unfortunately, the purity of the eluted *cis* isomer could not be checked by melting point determination since it always was recovered as a yellow oil from acetone, acetonitrile, or methanol. This same oil was obtained on evaporating toluene and acetonitrile solutions during preliminary isomerization tests. Reproducible elution behavior of both separate *cis* and *trans* isomers as well as of mixtures indicated that a separation had indeed been accomplished. The limited isomer supply prevented quantitative experiments, further investigation of conditions for crystallization of the *cis* isomer, and analysis of the oils.

(38) Fulfillment of this last condition is so rare that we have been forced to work with isomers soluble in polar and *moderately polar* solvents.

(39) Although a classification of solvents based on eluting power has exact significance only for a given system under the most precise conditions, a number of workers have established several very similar elutriotropic solvent series, in which eluting power generally increases with increasing dielectric constant. These series, which served as general guides in our selection of solvents, can be found in: E. Lederer and M. Lederer, "Chromatography: A Review of Principles and Applications," Elsevier Publishing Co., Amsterdam, 2nd ed., 1957, pp. 38–41; W. Trappe, *Biochem. Z.*, **305**, 150 (1940); H. H. Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, New York, N. Y., 1942; J. Jacques and J. P. Mathieu, *Bull. soc. chim. France*, 94 (1946); and H. S. Knight and S. Groennings, *Anal. Chem.*, **26**, 1549 (1954).

(40) Equilibration ("shaking") experiments and chromatographic column experiments on various adsorbents with solutions of these isomers in N,N-dimethylformamide and water, the only common solvents in which they were soluble, showed no significant adsorption, probably due to adsorption of polar solvent in preference to the isomers.

(41) We encountered no difficulties in our separations of $[Pt((C_2H_5)_2S)_2Cl_2]$ although isomerization in both solid state and solution has been reported (*cf.* F. G. Angell, H. D. K. Drew, and W. Wardlaw, *J. Chem. Soc.*, 349 (1930); H. D. K. Drew and G. H. Wyatt, *ibid.*, 56 (1934); and J. V. Quagliano and L. Schubert, *Chem. Rev.*, **50**, 220 (1952)).

(42) R. Schwarz and W. Kronig, *Ber.*, **56**, 208 (1923); N. Shilov and B. Nekrasov, *Z. physik. Chem.*, **118**, 79 (1925); B. Nekrasov, *J. Russ. Phys. Chem. Soc.*, **58**, 207 (1926); I. I. Zhukov and O. P. Shipulina, *Kolloid-Z.*, **49**, 126 (1929); and J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(43) Since oils were obtained with the *cis*-$C_6H_5S$ and *cis*- and *trans*-*p*-$C_6H_4NO_2S$ isomers, but not with the *cis*- or *trans*-$C_2H_5S$ isomers, oil formation might be due to interaction of $\pi$ electrons on the benzene ring with eluent.

TABLE II

QUANTITATIVE SEPARATIONS OF *cis–trans* ISOMERS

| Isomer | Adsorbent | Col. vol. = ht. × cross-sect. (cm.³ = cm. × cm.²) | Flow rate (cm./min.) | Eluent and vols. (cm.³) | Wt. isomer (g.) | | M.p. isomer (°C.) | | Recovery (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Recovd. | Orig. | Recovd. | Orig. | |
| $[Pt((C_4H_9)_3P)_2Cl_2]$ | | | | | | | | | |
| (1) *trans* | Silica gel | 11.5 = 12.4 | 0.65 | $C_6H_6$ (75) | 0.1089 | 0.1101 | 60–63 | 62–65 | 98.91 |
| *cis* | | × 0.930 | .65 | $(CH_3)_2CO$ (100) | .1068 | .1045 | 140–143 | 143–144 | 102.2 |
| (2) *trans* | Porocel | 10.3 = 3.63 | .85 | $C_6H_6$ (75) | .0522 | .0525 | 61–63 | 62–65 | 98.42 |
| *cis* | | × 2.83 | 1.28 | $(CH_3)_2CO$ (100) | .0502 | .0515 | 140–141 | 143–144 | 97.47 |
| (3) *trans* | Activated | 14.2 = 5.02 | 0.79 | $C_6H_6$ (75) | .0247 | .0244 | 59–60 | 62–64 | 101.2 |
| *cis* | alumina | × 2.83 | .86 | $(CH_3)_2CO$ (100) | .0270 | .0273 | 140–144 | 143–144 | 98.90 |
| (4) *trans* | Silica gel | 12.0 = 12.9 | .39 | $C_6H_6$ (50) | .6179 | .5048 | 62–64 | 62–63 | 122.4 |
| *cis* | | × 0.930 | .50 | $(CH_3)_2CO$ (100) | .4209 | .5275 | 141–143 | 139–141 | 79.79 |
| $[Pt((C_2H_5)_2S)_2Cl_2]$ | | | | | | | | | |
| (5) *trans* | Silica gel | 12.6 = 13.5<br>× 0.930 | .54 | $0.5(CH_3)_2CO$:<br>$100C_6H_6$ (90) | .4705 | .4703 | 96–100 | 98.6 | 100.0 |
| *cis* | | | .71 | $(CH_3)_2CO$ (100) | .5168 | .5107 | 94–98 | 98.6 | 101.2 |
| (6) *trans* | Porocel | 9.82 = 3.47 | .65 | $C_6H_6$ (75) | .0270 | .0271 | 96–100 | 98.6 | 99.63 |
| *cis* | | × 2.83 | .71 | $(CH_3)_2CO$ (100) | .0297 | .0296 | 95–99 | 98.6 | 100.3 |
| (7) *trans* | Activated | 14.7 = 5.20 | .68 | $C_6H_6$ (75) | .0261 | .0259 | 94–96 | 98.6 | 100.8 |
| *cis* | alumina | × 2.83 | 1.00 | $(CH_3)_2CO$ (100) | .0277 | .0283 | 92–97 | 98.6 | 97.87 |

was the *trans* isomer; then the *cis* isomer was eluted with a more polar solvent. These experiments, however, made with a small number of isomers of one particular metal in one particular oxidation state with one particular configuration, are not sufficient to establish the generality of this behavior.[44] Extreme caution is necessary in using chromatographic elution behavior for diagnostic purposes.[45] Since final proof of configuration usually depends upon the use of as many different approaches as possible, any new method of structure-proof is always a welcome contribution to stereochemistry. Practical application of chromatography to this purpose, however, must await further successful separations of isomer pairs of other coördination numbers.[46] If the method proves to possess general validity, it might be applied not only to practical separations, syntheses, and structure-proof, but also to the separation of complexes which occur in more than two isomeric forms. Ultimately, it might even be used for the separation of isomer pairs for which isomers are theoretically possible, yet have never been isolated.

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(44) In a subsequent article, we will show that an apparent exception, found in the separation on silica gel of the hexacoördinate isomer pair $[Ir((C_2H_5)_2S)_3Cl_3]$, which exhibits the reverse behavior, probably is due to incorrect configurations. The unusual elution behavior led us to determine dipole moments, which showed the originally assigned configurations to be incorrect and demonstrated the utility of the chromatographic separation method in structure-proof.

(45) L. Zechmeister, private communication, Aug. 15, 1960.

(46) Chromatographic studies of the non-electrolytic hexacoördinate isomer pairs $[Pt(NH_3)_2Cl_4]$, $[Pt((C_2H_5)_2S)_2Cl_4]$, $[Ir((C_2H_5)_2S)_3Cl_3]$, $[Ir(py)_2Cl_4]$, $[Ir(py)_3Cl_3]$, $[Ir((C_6H_5)_3P)_3HCl_2]$, and trisglycinato-, trisalaninato-, trisvalinato-, and tristryptophanatocobalt(III) will form the basis of a subsequent article.