

fluorine resonance spectrum at -5.42 and -5.27 ppm, respectively. The nmr evidence, therefore, tends to rule out structures I-IV¹² but is entirely consistent with what one would expect for either structure V or structure VI. It should be mentioned here that it is possible that either of these two structures may also be the correct structure for compound I, but this could not be confirmed because of the solvent problem mentioned earlier. The simultaneous formation of I and II under the same experimental conditions in approximately the same amounts and the close similarity of infrared spectra lead us to suspect that these compounds may, in fact, be the two expected geometrical isomers.

It may be noted that a compound having structure V is optically inactive while one with structure VI will exist as optical isomers. A successful resolution of either compound I or II may indicate which structure is correct.

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(12) The absence of multiple peaks cannot, of course, be taken as positive proof that only a single proton environment exists. The proton peak width at half peak height is 1.3 cps, similar to other β -diketonates known to contain a single proton environment. From experience with numerous other β -diketonate complexes having nonequivalent protons, it is considered extremely unlikely that protons in dissimilar rings would have exactly the same magnetic environment. Furthermore, substitution and isomerization reactions are known to occur extremely slowly with respect to proton relaxation rates, so the existence of equilibria that would average the environments may be discounted.

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The Separation of Nonelectrolytic Geometric Isomers of Platinum(II) by Thin Layer Chromatography

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The use of thin layer chromatography as an important separative, diagnostic, and preparative technique is well established, especially in the organic and biochemical areas. Its application to inorganic compounds, however, has been much less extensive and has been limited primarily to the separation of the common cations and anions.¹⁻³

(1) J. M. Bobbitt, "Thin-Layer Chromatography," Reinhold Publishing Corp., New York, N. Y., 1963.

(2) E. Stahl, "Thin-Layer Chromatography," Academic Press Inc., New York, N. Y., 1965.

(3) E. J. Goller, *J. Chem. Educ.*, **42**, 442 (1965), and references therein.

Syntheses of coordination compounds frequently produce more than one isomer,⁴ and, consequently, rapid, efficient, and reliable methods for separating the resulting mixtures are desirable. A recent study describing the separation of a number of electrolytic geometric isomers of amines and amines of cobalt(III) by thin layer chromatography⁵ prompts us to report our results of a similar study of nonelectrolytic isomers. The present paper, then, describes the separation by thin layer chromatography of a number of nonelectrolytic geometric isomers of platinum(II) (square-planar configuration) which we had separated previously by column chromatography.⁶ In addition, the separation of two pairs of binuclear platinum(II) isomers [*sym*-di- μ -ethylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II) and *sym*-di- μ -*p*-nitrophenylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II)] for which column chromatography had proven inadequate (see footnote 36 of ref 6) is here reported.

Experimental Section

Isomers.—Dichlorobis(diethyl sulfide)platinum(II),⁷ dichlorobis(tri-*n*-butylphosphine)platinum(II),⁸ dichlorodipyridineplatinum(II),⁹ *sym*-di- μ -phenylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II),¹⁰ *sym*-di- μ -ethylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II),¹⁰ and *sym*-di- μ -*p*-nitrophenylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II)¹⁰ were prepared according to the literature references given. Both the *cis* and *trans* forms of each of these compounds were characterized by elemental analyses, melting points, physical properties, and chemical reactions.⁶

Chromatography.—Microscope slides (75 × 25 mm) were thoroughly cleaned with detergent, rinsed with distilled water, and coated with a slurry consisting of 1 part of Silica Gel G (Kensington Scientific Corp., Oakland, Calif.) in 3 parts of a 1:1 by volume mixture of methanol and redistilled methylene chloride.¹¹ The plates were air dried for 10–20 min and activated by drying for 1 hr at 110° just prior to use.

Saturated solutions of the *cis* isomer, the *trans* isomer, and a 1:1 by weight mixture of both isomers, all in redistilled methylene chloride, were applied side by side along the origin of the plate, resulting in three distinct spots. After the plate had been air dried for 2–3 min, it was placed in a small screw-cap jar containing the solvent and was developed by the ascending technique.¹ When the solvent had attained a height of ca. 6 cm, the plate was removed from the developing chamber and was air dried. The positions of the isomers were detected as intense yellow-brown spots by placing the developed and dried plate in a screw-cap jar containing a few iodine crystals.¹ The mixed samples were found to have separated into two spots. The isomers which were thus separated from the mixtures were identified by comparison with the R_f values obtained for the pure isomers.

(4) 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, p 197.

(5) L. F. Druding and R. B. Hagel, *Anal. Chem.*, **38**, 478 (1966), and references therein.

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(9) G. B. Kauffman, *ibid.*, **7**, 249 (1963).

(10) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953); 2807 (1960). Samples of these isomers were kindly furnished by Drs. J. Chatt, P. G. Owston, and F. A. Hart of Imperial Chemical Industries, Ltd.

(11) The use of a mixture of organic solvents rather than water as the slurry medium aids in maintaining a uniform suspension, yields an even layer thickness (ca. 200 μ) when poured directly onto the slides, and requires less time for evaporation of the solvent prior to activation. Separation of the various isomer pairs was shown to be independent of the slight variations in layer thickness obtained by this method.

Results

One of the few disadvantages of thin layer chromatography is that R_f values are not exactly reproducible, especially among different laboratories. Although our values were reproducible to ± 0.03 , the important consideration in the separation, as opposed to the identification, of isomers is not the specific R_f values but rather the difference between the *cis* and *trans* migrations. The reproducible ΔR_f values are indicative of the effectiveness of separation in the various systems studied. Many developing solvents and mixtures were evaluated, but only the most successful combinations, *i.e.*, those resulting in maximum differences between R_f values and minimum trailing,¹¹ are shown (Table I).

TABLE I
SOME TYPICAL QUALITATIVE SEPARATIONS OF *cis-trans* ISOMERS

Compound	Developing solvent	R_f		ΔR_f
		<i>cis</i>	<i>trans</i>	
[Pt((C ₂ H ₅) ₂ S) ₂ Cl ₂]	C ₆ H ₆	0.00	0.45	0.45
	CH ₂ Cl ₂	0.15	0.60	0.45
	C ₆ H ₆ -(CH ₃) ₂ CO (19:1)	0.20	0.65	0.45
[Pt((C ₄ H ₉) ₃ P) ₂ Cl ₂]	C ₆ H ₆	0.00	0.95	0.95
	CH ₂ Cl ₂	0.40	0.95	0.55
	C ₆ H ₆ -CH ₂ Cl ₂ (1:1)	0.15	0.95	0.80
[Pt(py) ₂ Cl ₂]	CH ₂ Cl ₂	0.00	0.20	0.20
	C ₆ H ₆ -(CH ₃) ₂ CO (5:1)	0.10	0.55	0.45
	CH ₂ Cl ₂ -(CH ₃) ₂ CO (5:1)	0.45	0.80	0.35
[(C ₂ H ₅) ₂ P] ₂ Pt ₂ (C ₆ H ₅ S) ₂ Cl ₂	C ₆ H ₆	0.05	0.45	0.40
	CH ₂ Cl ₂	0.40	0.85	0.45
[(C ₂ H ₅) ₂ P] ₂ Pt ₂ (C ₂ H ₅ S) ₂ Cl ₂	CH ₂ Cl ₂	0.40	0.80	0.40
	C ₆ H ₆ -CH ₂ Cl ₂ (1:2)	0.20	0.60	0.40
[(C ₂ H ₅) ₂ P] ₂ Pt ₂ (NO ₂ C ₆ H ₄ S) ₂ Cl ₂	C ₆ H ₆	0.00	0.30	0.30
	CH ₂ Cl ₂	0.50	0.70	0.20
	C ₆ H ₆ -(CH ₃) ₂ CO (2:1)	0.85	0.95	0.10

Separations were also achieved on a semiquantitative preparative scale. For example, two large Silica Gel G plates (200 × 100 mm) were prepared with a Kirchner-type apparatus¹ adjusted to give a layer thickness of 200 μ . A mixture of 100 mg of *cis*- and 100 mg of *trans*-dichlorobis(tri-*n*-butylphosphine)-platinum(II)¹² in redistilled methylene chloride solution was applied along the origins of the activated plates by use of a microsyringe, and the plates were developed with Eastman Spectrograde (S 777) benzene as the solvent. The silica gel containing and surrounding the band at R_f value 0.0–0.1 on each plate was then removed and eluted with Eastman Spectrograde acetone (S 297). The silica gel containing and surrounding the band at R_f 0.85–1.0 on each plate was similarly removed and eluted with redistilled methylene chloride. Evaporation of the first eluent yielded 91 mg (91% recovery) of the white, crystalline *cis* isomer, mp 140–142° (lit. value⁸ 143–144°), and evaporation of the second eluent yielded 93 mg (93% recovery) of the yellow, crystalline *trans* isomer, mp 61–63° (lit. value⁸ 62–65°). Reanalysis of the sepa-

(12) The *trans* isomer was not chromatographically pure but contained traces of *cis* isomer.

rated isomers by qualitative thin layer chromatography confirmed the fact that a complete separation without solvent-induced isomerization had been achieved. By the use of additional plates, the separation can be extended to mixtures on a larger scale.

Discussion

The use of thin layer chromatography 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, two isomers previously found not amenable to column chromatography were successfully separated.

(2) In conjunction with other evidence, thin layer chromatographic behavior possesses potential diagnostic value in structure proof.¹³ For all 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.⁶

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

(4) With thin layer chromatography, iodine vapor may be used as a sensitive detecting reagent, thus eliminating the necessity for specific spot tests.⁶ We have found this reagent, denoted as "universal" for organic compounds by Bobbitt,¹ to be useful in detecting a variety of coordination compounds of cobalt, chromium, platinum, and iridium. 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. As a case in point, a sample of *trans*-[Pt((C₄H₉)₃P)₂Cl₂] with the required melting point was found to contain traces of the *cis* isomer.

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

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(13) The value of column chromatography in this connection has already been established. Anomalous elution behavior of the supposedly *cis* and *trans* isomers of [Ir((C₂H₅)₂S)₂Cl₂] led us to question the assignment of structures to these compounds; the structure assigned by previous investigators to the *trans* isomer was subsequently shown to be incorrect: G. B. Kauffman, J. H. Tsai, R. C. Fay, and C. K. Jørgensen, *Inorg. Chem.*, **2**, 1233 (1963).

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The Solvolysis of Hexaaquochromium(III) in Dimethyl Sulfoxide

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Although several different workers have reported preparing the hexa(dimethyl sulfoxide)chromium(III) perchlorate, $\text{Cr}(\text{DMSO})_6(\text{ClO}_4)_3$, no one has reported preparing any compound containing an ion of the series $\text{Cr}(\text{H}_2\text{O})_n(\text{DMSO})_{6-n}^{3+}$, $n = 1-5$.¹ We would like to report the results of a more extensive investigation of the reaction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with DMSO. These results are (1) the position of absorption maxima as a function of the average number of DMSO ligands per chromium and (2) the average number of DMSO ligands per chromium as a function of DMSO concentration in aqueous solution.

Experimental Section

$\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ was prepared by reducing reagent grade CrO_3 with H_2O_2 in 1 *M* HClO_4 . The product was recrystallized once from hot water. The ultraviolet spectrum compared favorably with that reported by Plane.² $\text{Cr}(\text{DMSO})_6(\text{ClO}_4)_3$ was prepared by the method reported by Cotton and Francis.^{1a} The DMSO was used as received. Three separate preparations of the compound gave products with Cr:DMSO ratios ranging from 1:5.1 to 1:5.8. Recrystallizing the compound from DMSO at 100° gave a product with a Cr:DMSO ratio of 1:5.95. *Anal.* Calcd for $\text{Cr}(\text{DMSO})_6(\text{ClO}_4)_3$: Cr, 6.35; DMSO, 57.2. Found: Cr, 6.33; DMSO, 56.4. The molar absorptivities at 444 and 634 $m\mu$ were 36.3 and 33.5 $M^{-1} \text{ cm}^{-1}$, respectively. Drago reported 34.6 and 33.4, and Schläfer reported 31.6 and 30.2 $M^{-1} \text{ cm}^{-1}$ for the molar absorptivities at 444 and 634 $m\mu$.^{1b,c} The compound was analyzed for chromium by oxidizing the chromium to dichromate with peroxydisulfate in the presence of a small amount of AgNO_3 . A known excess of standard ferrous solution was added and the excess was back-titrated with standard dichromate solution. The compound was analyzed for DMSO as described elsewhere.³

The absorption spectrum as a function of the average number of DMSO ligands attached to the chromium was determined in the following manner. A number of 125-ml erlenmeyer flasks, each containing 25 ml of DMSO, were suspended in a constant-temperature bath maintained at 40.0°. A known amount of $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$, ca. 0.25 g, was added to each flask. At time intervals of about 15 min near the start and about 30 min later, flasks were removed and were quenched in a Dry Ice-acetone bath. Later each flask was warmed to room temperature, and a quantity of the solution from each flask was used to determine the

absorption spectrum from 400 to 450 $m\mu$ and from 575 to 650 $m\mu$ using a Beckman DB recording spectrophotometer. Ten milliliters of the solution from each flask was used to charge a cation-exchange column containing Dowex 50-X 8 (100-200 mesh) resin in the H^+ form. Ten bed volumes of cold water were washed through the column to clean it of the solvent DMSO. Blank experiments confirmed that this was sufficient water to wash the resin bed free of solvent DMSO. The Cr(III) species were eluted with 8 *N* H_2SO_4 . The effluent was analyzed for DMSO. The concentration of Cr(III) was determined from the initial amount of $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ used.

An attempt to isolate various $\text{Cr}(\text{H}_2\text{O})_n(\text{DMSO})_{6-n}^{3+}$ species using cation-exchange resins was made. A jacketed column was constructed from a 50-ml buret and 45-mm glass tubing. Dowex 50-X 8 (100-200 mesh) resin in the H^+ form was used to pack the column. Water at 1° was circulated through the jacket. About 3 mmoles of $\text{Cr}(\text{H}_2\text{O})_n(\text{DMSO})_{6-n}^{3+}$ where n averaged 3 as determined from Figure 1, was run into the top of the column and the column was washed with 500 ml of cold water. The column was eluted with 8 *N* H_2SO_4 at a flow rate of 1 ml/hr. No separation of the band was obtained. The absence of a second band also indicates that no appreciable formation of polymeric material had occurred.

In the experiments designed to determine the average number of DMSO ligands per chromium as a function of DMSO concentration in aqueous solution, the following procedure was employed. Solutions containing various amounts of DMSO were made by adding the calculated amount of DMSO to a volumetric flask and diluting to volume with distilled water. About 0.25 g of $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ was added to 25 ml of the desired solution and was allowed to come to equilibrium at 40.0°. The spectrum of the solution was determined using a Beckman DB spectrophotometer. The location of the absorption maxima was used along with Figure 1 in estimating the average number of DMSO molecules coordinated.

Results and Discussion

The investigation of Cr(III) in methanol and methanol-water mixtures has been reported by Jayne and King.⁴ They showed that methanol could replace water molecules in the coordination sphere; however, methanol does not compete for coordination positions nearly as well as DMSO does. Several investigators⁵ have shown that in the series of compounds $\text{Cr}(\text{H}_2\text{O})_n(\text{NH}_3)_{6-n}^{3+}$, $n = 0-6$, the absorption maximum shifts to higher energy as n decreases. This would be expected when ligands of one crystal field strength are replaced stepwise by ligands of a larger crystal field.

Figure 1 shows the relation between the wavelength of the absorption maximum of the $\text{Cr}(\text{H}_2\text{O})_n(\text{DMSO})_{6-n}^{3+}$ species and the average ligand DMSO:Cr ratio. If one makes the assumption that the stepwise rate constants for the formation of $\text{Cr}(\text{DMSO})_6^{3+}$ are all of the same order of magnitude, one must conclude that all $\text{Cr}(\text{H}_2\text{O})_n(\text{DMSO})_{6-n}^{3+}$ species exist in appreciable concentration at some time during the solvolysis of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ in DMSO. This assumption is reasonable in view of the equilibrium constants calculated for the chromium(III)-methanol species.⁴ The scatter of the points in Figure 1 is due to the expected poor precision of the analytical method involving ion-exchange separation.

From the results shown in Figure 1 it is obvious that

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