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SEPARATION OF INORGANIC ISOMERS BY THIN-LAYER CHROMATOGRAPHY

VII. SYNTHESIS AND SEPARATION OF THE GEOMETRIC AND LIGAND ISOMERS OF DICHLOROBIS(DIBUTYL SULFIDE)PLATINUM(II)

GEORGE B. KAUFFMAN and ROBERT K. MASTERS

Department of Chemistry, California State University, Fresno, Calif. 93740 (U.S.A.)

and

JOHN C. BAILAR, Jr., PAUL R. SCHABINGER and MICHAEL J. SINWELL

William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Ill. 61801 (U.S.A.)

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SUMMARY

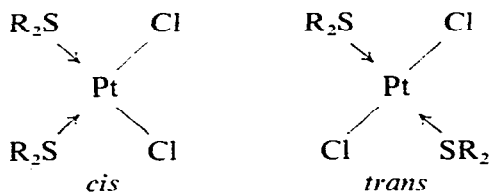
The eight possible isomers of dichlorobis(dibutyl sulfide)platinum(II) have been prepared and characterized, six of them in a pure state (*cis*- and *trans*-*n*; *cis*- and *trans*-*iso*; and *cis*- and *trans*-*sec*.). We have separated some of the geometric isomers from each other, some of the ligand isomers from each other, and some of both types from each other by thin-layer chromatography.

INTRODUCTION

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; ligand isomers of various coordination numbers⁴; structural, linkage, geometric, and conformational isomers of various coordination numbers⁵; and isomers of the non-metals boron, phosphorus, and silicon⁶. In the present article we extend our TLC separations to a compound occurring in both ligand and geometric isomer forms, and we simultaneously report reproducible syntheses for isomers of this compound, which has not been investigated since 1935.

Alkyl sulfides (thioethers) are good ligands because of the polarizability and nucleophilicity of the sulfur atom, and as early as 1888 Blomstrand⁷, together with his students Weibull, Enebuske, Rudelius, and Löhndahl, discovered two isomeric series of dialkyl sulfide-platinum(II) complexes of formula $[\text{Pt}(\text{R}_2\text{S})_2\text{X}_2]$ ($\text{R} = \text{CH}_3$, C_2H_5 , *n*- and *iso*- C_3H_7 , and *n*-, *iso*-, and *sec*- C_4H_9) by reaction of the alkyl sulfide with potassium tetrachloroplatinate(II)⁸. In 1935 Jensen⁹ measured the dipole moments of several of Blomstrand's non-electrolytic isomers, which are among the relatively few

platinum complexes freely soluble in benzene, in order to refute the view, held as late as 1930¹⁰, that these compounds were structural isomers containing tetrahedral platinum. Instead, he showed them to be true stereoisomers, in agreement with Werner's prediction^{11,12} of a square planar configuration for tetravalent platinum(II):



As is the case with most platinum(II) isomers of the PtA_2B_2 type, the unsymmetrical *cis* isomer is polar. The symmetrical *trans* isomer, on the other hand, while of lower polarity, does not possess a dipole moment of zero, for the four alkyl groups lie on the same side of the plane containing the platinum, chlorine, and sulfur atoms. Kauffman and co-workers have devised reproducible syntheses for *cis*- and *trans*- $[\text{Pt}\{(\text{C}_2\text{H}_5)_2\text{S}\}_2\text{Cl}_2]$ ¹³ and have utilized their solubility in organic solvents and differences in dipole moments to separate these isomers qualitatively and quantitatively by both column¹⁴ and thin-layer¹ chromatography.

Inasmuch as dibutyl sulfide exists in four isomeric forms (*n*, *iso*, *sec.*, and *tert.*) and for each form a *cis* and *trans* isomer of type $[\text{Pt}(\text{R}_2\text{S})_2\text{X}_2]$ is possible, a total of eight isomers of the compound $[\text{Pt}\{(\text{C}_4\text{H}_9)_2\text{S}\}_2\text{Cl}_2]$ is theoretically possible: (1) *cis-n*, (2) *trans-n*, (3) *cis-iso*, (4) *trans-iso*, (5) *cis-sec.*, (6) *trans-sec.*, (7) *cis-tert.*, and (8) *trans-tert.* Of this series, Jensen⁹ was able to prepare compounds (1), (2), (3), (4), and (6), but he did not attempt to synthesize any isomers containing *tert.*-dibutyl sulfide. We have re-investigated Jensen's work, some of which is fragmentary and inconclusive, we have devised reproducible syntheses for his isomers and the remaining three isomers, and we have separated some of the geometric isomers from each other, some of the ligand isomers from each other, and some of both types from each other by TLC.

EXPERIMENTAL

All reagents and solvents were C.P. or reagent grade. Isomers were characterized by elemental analyses (see Table I), melting points, physical properties, and chemical reactions. Unless noted otherwise, melting points (Fischer-Johns apparatus) agreed with literature values. Even traces of impurities lower the melting points considerably, but TLC verified the purity of the products. Dipole moments were not measured, but literature values⁹ are given when available. Potassium tetrachloroplatinate(II) was prepared by reducing an aqueous suspension of potassium hexachloroplatinate(IV)—which was prepared¹⁵ from samples of >99.98% Pt sponge (graciously provided by Engelhard Industries, Newark, N.J., U.S.A.)—with either hydrazine dihydrochloride^{13,16}, hydrazine sulfate¹⁷, or sulfur dioxide¹⁸. Excess hydrazine salt should be avoided to prevent formation of hydrazine complexes or reduction to platinum metal.

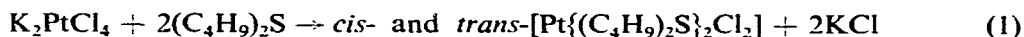
TABLE I

ANALYSES OF $[\text{Pt}\{(\text{C}_4\text{H}_9)_2\text{S}\}_2\text{Cl}_2]$ ISOMERS

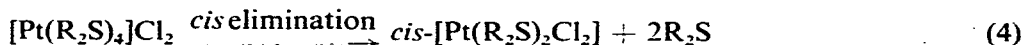
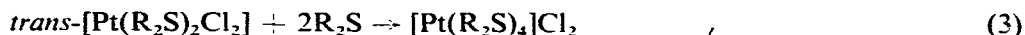
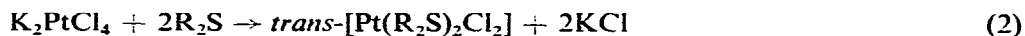
Analyses performed by Microanalytical Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Ill., U.S.A.

	C (%)	H (%)	Pt (%)
Calculated for $\text{PtC}_{16}\text{H}_{36}\text{S}_2\text{Cl}_2$	34.44	6.50	34.92
Found for <i>cis-n</i>	34.04	6.52	—
Found for <i>trans-n</i>	34.29	6.58	—
Found for <i>cis-iso</i>	34.67	6.56	—
Found for <i>trans-iso</i>	34.57	6.64	—
Found for <i>cis-sec.</i>	34.76	6.54	34.84
Found for <i>trans-sec.</i>	34.71	6.64	34.67

The overall reaction for the preparation of the dichlorobis(dibutyl sulfide)-platinum(II) isomers is:



Blomstrand⁸ suggested the following steps for this reaction in the case of the diethyl and di-*n*-propyl sulfide compounds:



The isomers are formed as a mixture; the less polar *trans* isomer is separated from the more polar *cis* isomer by extracting with light petroleum (b.p. 30°–60°). Since formation of the *cis* isomer is generally favored (except for the di-*tert.*-butyl sulfide isomers), if both isomers are desired, conditions should be chosen for maximum yields of *trans* isomer, *viz.*, avoidance of excess dibutyl sulfide ($\text{R}_2\text{S}:\text{K}_2\text{PtCl}_4 = 2:1$), use of ethanol to obtain homogeneity between the immiscible water- R_2S phases, and slow, dropwise addition of R_2S to the aqueous K_2PtCl_4 solution. The reverse conditions, *viz.*, excess dibutyl sulfide ($\text{R}_2\text{S}:\text{K}_2\text{PtCl}_4 = 4:1$), no ethanol, and addition of R_2S to the K_2PtCl_4 solution all at once, favor formation of the *cis* isomer.

Dichlorobis(di-n-butyl sulfide)platinum(II)

The *trans* isomer of this compound is very difficult to obtain pure because of isomerization to the *cis* compound. The slightest amount of impurity results in oil formation, which renders subsequent recrystallization difficult. Jensen⁹ obtained the *trans* isomer by metathesis of AgCl with *trans-}[\text{Pt}\{(\text{C}_4\text{H}_9)_2\text{S}\}_2\text{Br}_2] rather than by the general reaction discussed above, which we used. Quantitative TLC was found useful in purifying this isomer.*

A solution of 1.8 ml (0.010 mole) of *n*-(C_4H_9)₂S in 6 ml of ethanol was added with stirring to a 150-ml Erlenmeyer flask containing 2.07 g (0.005 mole) of K_2PtCl_4 in 50 ml of water (if reddish brown K_2PtCl_4 precipitates because of its insolubility in ethanol, more water should be added). The flask was stoppered, and the reaction mixture was vigorously stirred magnetically for 48 h. The oily mixture was then evaporated at room temperature (Hood!) in a 150-ml beaker. When dry, it was washed

with water on a Büchner funnel to remove any unreacted K_2PtCl_4 . The residue was dissolved in a minimum volume of acetone, and the solution was filtered and evaporated at room temperature (Hood!). The residue was extracted with several 15-ml portions of light petroleum until the washings were colorless.

After the liquid was decanted, the *cis* isomer was recrystallized from the residue with minimum boiling ethanol and an ice-salt bath. Since both isomers are soluble in ethanol at room temperature, the product was suction filtered *immediately* after removal from the ice-salt bath. The same precaution was observed with the *trans* isomer (see below).

The light petroleum extracts were evaporated (Hood!) at room temperature, and the oily, bright yellow-gold residue of crude *trans* isomer was extracted with light petroleum, decanted, and evaporated. The residue was then recrystallized from ethanol in the same manner as the *cis* isomer. A total yield of 1.61–1.89 g for both isomers (60–70% based on K_2PtCl_4) was obtained. With both isomers, better yields can be obtained by evaporating the mother liquor and recrystallizing. The *trans* isomer was dried in a desiccator for a day since the slightest amount of moisture causes isomerization to the *cis* isomer.

The greenish yellow *cis* isomer, $\mu = 9.2$ D, gave a m.p. of 82.0–83.5°. The scaly yellow *trans* isomer, $\mu = 2.35$ D, gave a m.p. of 52.0–54.0° (Jensen⁹ reported 61–62°) and was easily soluble in organic solvents.

Dichlorobis(di-iso-butyl sulfide)platinum(II)

The procedure was identical to that used for the *n*-butyl compounds with substitution of *iso*-butyl sulfide for *n*-butyl sulfide. The *trans* isomer, which is more stable than its *n*-butyl analogue, was obtained in greater yield. The *iso*-butyl isomers were the easiest of all the isomers with which to work. The yield of flaky, greenish yellow *cis* isomer, m.p. 135–139° (Jensen⁹ reported 138.5–139°), $\mu = 9.0$ D, was 1.7 g (63.1%); the compound is insoluble in light petroleum and less soluble in ethanol and diethyl ether than is the *trans* compound. The yield of yellow *trans* isomer, m.p. 105–106° (Jensen⁹ reported 110.5–111.0°), $\mu = 2.41$ D, was 0.5 g (18.6%). The total yield of both isomers was 2.20 g (81.7%).

Dichlorobis(di-sec.-butyl sulfide)platinum(II)

For this compound Jensen⁹ obtained only one form — the *trans* isomer. He ascribed the nonexistence of a *cis* form to steric hindrance caused by the bulky *sec*-butyl groups situated *cis* to each other. Our procedure was identical to that used for the *n*-butyl compounds with substitution of *sec*-butyl sulfide for *n*-butyl sulfide, a reaction time of 120 h for one of 48 h, and extractions with diethyl ether for those with light petroleum, in which both isomers have similar solubilities. A minimum volume of diethyl ether should be used since the *cis* isomer is somewhat soluble in it.

The previously unreported white *cis* isomer melts at 108–111°, while the scaly yellow *trans* isomer, $\mu = 2.39$ D, gave a m.p. of 86–89° (Jensen⁹ reported 109–110°). The total yield of both isomers was *ca.* 1.9 g (70%).

Dichlorobis(di-tert.-butyl sulfide)platinum(II)

The procedure was similar to that used for the *n*-butyl compounds with substitution of 3.6 ml (0.020 mole) of *tert*-butyl sulfide for the *n*-butyl sulfide with

omission of ethanol which causes reduction to platinum metal with time, and with omission of the extraction with light petroleum, which, in this case, causes isomerization of the *trans* isomer to *cis* isomer, as shown by TLC of the "*trans*" product (actually containing about 20% of the *cis* isomer) obtained in this way. Instead, the evaporated and washed reaction mixture was dissolved in a minimum volume (20 ml) of boiling acetone and was decanted into a 150-ml beaker containing 100 ml of hot water, whereupon a light brown precipitate formed. The acetone was allowed to evaporate, the product was collected by suction filtration, the acetone-water purification process was repeated, and the purified product (yield *ca.* 2.3 g or *ca.* 85%) was dried in a desiccator.

Attempts to separate the *cis* and *trans* isomers from this purified reaction mixture (*ca.* 80% *trans* isomer, 20% *cis* isomer) were only partially successful. Column chromatography on Merck alumina using benzene eluent separated the two isomers, but TLC experiments with these isomers with polar solvents or even nonpolar solvents such as benzene showed that isomerization occurred. Evaporation of light petroleum extracts of the purified reaction mixture at room temperature, on a steam bath, and in a refrigerator showed that although higher temperatures enhance isomerization, a moderately high temperature can be used because it apparently removes the solvent more quickly. The optimum temperature was found to be *ca.* 50°. Evaporation of the light petroleum extract with a rotary vacuum evaporator (Model 1007-4N, Rinco Instrument Co., Greenville, Ill., U.S.A.) gave a yellow residue, indicative of the *trans* isomer, but, when collected, it became reddish because of isomerization (the *cis* isomer is brown). The isomerization appears to be catalyzed by light, for reactions carried out in the dark gave reddish-brown reaction mixtures containing more *trans* isomer than the dark brown reaction mixtures resulting from reactions carried out in the light. Neither of the isomers possesses a definite melting point; the golden-yellow *trans* isomer became red at 150°, brown at 160°, and dark brown (similar in appearance to the *cis* isomer) at 175°. Between 230° and 240° both isomers decompose gradually, yielding a black residue.

Infrared spectra

Infrared spectra in potassium bromide pellets were obtained (Perkin-Elmer 467 or 521) for the six isomers obtained in a pure state, *i.e.*, *n*, *iso*, and *sec.* compounds. In all cases, water was absorbed during the measurements, resulting in absorptions at 3500 cm^{-1} , broad and variable (*w-m*), and at 1650 cm^{-1} , broad and weak. For each pair of isomers, the spectra of the *cis* and *trans* isomers were virtually identical. However, small but clear differences in transmittance between *cis* and *trans* isomers were found between 470 and 440 cm^{-1} :

- cis-n*: increase from 74% (470 cm^{-1}) to 76% (440 cm^{-1});
- trans-n*: decrease from 78% (470 cm^{-1}) to 76% (440 cm^{-1});
- cis-iso*: increase from 73% (470 cm^{-1}) to 75% (440 cm^{-1});
- trans-iso*: decrease from 80% (470 cm^{-1}) to 76% (440 cm^{-1});
- cis-sec.*: increase from 73% (470 cm^{-1}) to 76% (430 cm^{-1});
- trans-sec.*: decrease from 65% (470 cm^{-1}) to 62% (430 cm^{-1}).

Infrared spectra for both isomers of each of the three platinum complexes show the following characteristic absorption peaks:

n: 2960 (s), 2940 (s), 2880 (s), 2870 (sh), 1470 (m), 1460 (sh), 1425 (m), 1380 (w); 1315 (broad, w), 1285 (broad, w), 925 (m), 750 (broad, w), and 730 cm^{-1} (broad, w).

iso: 2960 (s), 2940 (s), 2920 (sh), 2900 (sh), 2880 (s), 1470 (s), 1455 (sh), 1420 (m), 1385 (m), 1370 (m), 1340 (w), 1335 (w), 1325 (w), 1265 (m), 1240 (w), 1220 (w), 1170 (m), 1125 (w), 1090 (s), 950 (w), 930 (w), and 870 cm^{-1} (m).

sec.: 2980 (s), 2940 (s), 2880 (s), 1465 (s), 1390 (sh), 1380 (m), 1340 (w), 1330 (w), 1270 (m), 1240 (s), 1230 (sh), 1150 (m), 1135 (sh), 1110 (w), 1060 (s), 1020 (m), 990 (w), 960 (m), 780 (m), and 340 cm^{-1} (m).

For the six isomers, the strong absorptions in the 2800–3000 cm^{-1} region can be attributed to the alkane structures, the absorptions in the 700–1700 cm^{-1} region can be attributed to the particular alkane isomer, and the low region absorptions under 700 cm^{-1} can be attributed to Pt–Cl bonding and to the potassium bromide pellet.

Thin-layer chromatography

The adsorbent used was silica gel TLC sorbent (SilicAR[®] TLC-7GF; Mallinckrodt, St. Louis, Mo., U.S.A.), which was generously donated by the manufacturer. Microscope slides (75 × 25 mm) were used for plates in all separations except for the di-*tert.*-butyl sulfide isomers and for the overall separation, both of which required 200 × 100 mm plates to achieve separation. Multiple pass development with nonpolar solvents (ref. 19, Ch. 6) was used for the ligand isomer separations, and this technique and stepwise development (ref. 19, p. 72; ref. 20) was used for the overall separation. Plates were developed by the ascending technique, and iodine vapor was used for visualizing all compounds except for the di-*sec.*-butyl sulfide isomers, for which tin(II) chloride spray (0.5 M in 1 M hydrochloric acid, freshly prepared)²¹ was used. When mixtures were chromatographed, "reading" spots were applied alongside the mixture to identify the component spots of the mixture (ref. 19, p. 81). Separated isomers were identified by R_F values, mixed melting point measurements, or other characterization techniques. Further details are given in previous articles in this series^{1–6}.

RESULTS AND DISCUSSION

The results obtained are summarized in Table II. R_F values were reproducible to ± 0.03 except for those obtained by multiple pass development and stepwise development, which are only approximate values. 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.

Among the separations of geometric isomers (Nos. 1, 2, and 4), those of the *n*, *iso*, and *tert.* complexes were completely successful. As expected, the more polar *cis* isomers possessed lower R_F values than the less polar *trans* isomers. Samples of the *cis-sec.* isomer were not available for chromatographic studies, but from the R_F values of all the remaining isomers, complete separation of the *cis* isomer from the *trans* isomer appears feasible for the *sec.* compound. For the *tert.* isomers, separations were as expected with nonpolar developers, but polar developers caused the *trans* isomer to split into three fractions.

In general, R_F values appear to decrease in the order *tert.* < *sec.* < *iso* < *n*, both for the *cis* and *trans* isomers. Among ligand isomer separations (Nos. 5, 6, and

TABLE II

THIN-LAYER CHROMATOGRAPHY OF [Pt{(C₄H₉)₂S}₂Cl₂] ISOMERS

Separation of all isomers was complete except for 3 [Pt{(sec.-C₄H₉)₂S}₂Cl₂] where there was no separation with any of the solvents.

Isomer	Developing solvent	R _F		ΔR _F
		<i>cis</i>	<i>trans</i>	
<i>Geometric isomer separations</i>				
1 [Pt{(n-C ₄ H ₉) ₂ S} ₂ Cl ₂]	Benzene	0.00	0.65	0.65
	Methylene chloride	0.45	0.90	0.45
	Chloroform	0.45	0.90–0.95	0.45–0.50
	Chloroform–benzene (1:1)	0.05	0.70	0.65
2 [Pt{(iso-C ₄ H ₉) ₂ S} ₂ Cl ₂]	Benzene	0.00	0.60	0.60
	Chloroform	0.40	0.90	0.50
	Toluene	0.00	0.65	0.65
	Methylene chloride	0.50	0.85	0.35
3 [Pt{(sec.-C ₄ H ₉) ₂ S} ₂ Cl ₂]	Chloroform–benzene (1:1)	0.05–0.10	0.70	0.60–0.65
	Methylene chloride	—	0.90	—
	Chloroform	—	0.90	—
	Benzene	—	0.55	—
4 [Pt{(tert.-C ₄ H ₉) ₂ S} ₂ Cl ₂]	Toluene	—	0.57	—
	Benzene	0.00	0.20	0.20
	Toluene	0.00	0.22	0.22
	Methylene chloride	0.00	0.48 trace 0.60 larger 0.67 largest	0.48 0.60 0.67
	Tetrahydrofuran– carbon tetrachloride (1:19)	0.00	0.45 0.60 0.70	0.45 0.60 0.70
<i>Ligand isomer separations</i>				
5 (a) <i>trans-n</i> <i>trans-tert.</i>	Benzene		0.68	
			0.13	0.55
6 (a) <i>trans-iso</i> (b) <i>trans-tert.</i>	Benzene		0.65	
			0.12	0.53
7 (a) <i>trans-n</i> and <i>trans-iso</i> (inseparable mixture) (b) <i>trans-sec.</i> (c) <i>trans-tert.</i>	Multiple pass technique: carbon tetrachloride followed by benzene		0.55	
			0.40	0.15
			0.15	0.25
<i>Overall separation</i>				
8 (a) <i>trans-n</i> and <i>trans-iso</i> (inseparable mixture) (b) <i>trans-sec.</i> (c) <i>trans-tert.</i> (d) <i>cis-n</i> and <i>cis-iso</i> (inseparable mixture) (e) <i>cis-tert.</i>	Stepwise development with methylene chloride followed by multiple pass technique with benzene and then carbon tetrachloride		0.70	
			0.60	0.10
			0.40	0.20
			0.10	0.30
			0.00	0.10

7). *R_F* values for the *trans-n* and *trans-iso* were too similar to permit any separation although multiple pass development with nonpolar solvents, stepwise development, continuous development with filter paper extension, and use of different adsorbents were employed. Multiple pass technique (carbon tetrachloride followed by benzene)

permitted complete separation of *trans-sec.* and *trans-tert.* from each other and from an inseparable mixture of *trans-n* and *trans-iso* isomers.

In the overall separation (No. 8), stepwise development, devised by Stahl for separating a group of similar nonpolar substances from a group of similar polar substances, was employed. The chromatogram was developed about halfway with methylenechloride, which deposited the less polar *trans* compounds (a, b, and c) at the solvent front about halfway up the plate and resolved the more polar *cis* isomers (d and e) at the bottom half of the chromatogram, which was then dried and developed with benzene. After drying, development with carbon tetrachloride completed the resolution.

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