the oxidation–reduction quantum yield shows the decrease with increasing wave length of irradiating light that seems characteristic of Co(III) complexes,[5] and to minimize complications from this process the retention of configuration studies were confined to the longer wave length region, where aquation was dominant. To exemplify the type of effect found, in the case of the run given by the third line of Table VI, the 34% photoaquation that occurred should have been accompanied by an increase of 0.09° in optical rotation, if entirely stereospecific, and by a decrease of 0.17°, if entirely non-stereospecific. We observe a decrease of 0.01°, corresponding to 62% retention of configuration.

It was not possible entirely to disentangle the above interpretation from the alternative ones that (a) some direct photoracemization occurs in the parent complex, that (b) the product $[Co(en)_2(H_2O)Cl]^{2+}$ is easily photoracemized or isomerized, or that (c) it photoaquates readily.

As noted in Table VI, however, a separate run with 1-*cis*-$[Co(en)_2(H_2O)Cl]^{2+}$ did give a fairly high quantum yield for loss of activity, although it was not ascertained whether this was due to process (b) or (c). We conclude, therefore, that the photoaquation of *cis*-$[Co(en)_2Cl_2]^+$ may be entirely stereospecific, and is at least partially so. It would be of interest to pursue this or related systems somewhat further, particularly to the point of determining whether the stereospecificity of photoaquation processes is at all wave length dependent. We suspect that it will be.

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The Application of Zone Melting Techniques to the Resolution of Two-Component Inorganic Salt Systems and Racemic Mixtures of Optically Active Compounds and their Diastereoisomers

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Evidence is presented that zone melting techniques are applicable to the partial resolution of two-component inorganic salt systems in aqueous solution as well as of diastereoisomeric mixtures of optically active compounds and racemic mixtures of asymmetric complexes. Resolution is achieved when one of the components is more soluble than the other and/or when the rates of dissolution at the solid–liquid interface of the two components are unequal. Unsaturated aqueous solutions containing two components which differ in solubility were subjected to the zone melting process, and the degree of resolution with respect to solubility differences was determined. In addition, partial resolution of diastereoisomeric mixtures of optically active compounds as well as enantiomeric mixtures of an inner complex in an asymmetric environment were achieved.

Discussion

Since the first papers on zone melting by Pfann[1] were published, several others have appeared which deal with various aspects of the subject, most being concerned with metals and alloys and the purification of these and other substances.[2] Pepinsky[3] suggested the use of zone melting for the separation of solutes which differ in solubility (especially diastereoisomers) from solutions which are liquid at room temperature. Essentially, the method described here consists of freezing a solution which contains two components and then causing a molten zone to traverse the frozen charge *via* the techniques presented.

It was considered of interest to study the factors responsible for the resolution of these systems since they are somewhat different from the usual zone melting situations in that rather than separating small quantities of impurities from a solvent, this method attempts to separate two components present in relatively large and ap-

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[1] W. G. Pfann, *Trans. AIME*, **194**, 747 (1952).

[2] N. L. Parr, "Zone Refining and Allied Techniques," G. Newnes, Ltd., London, 1960.

[3] R. Pepinsky, private communication, Pennsylvania State University, University Park, Pennsylvania.

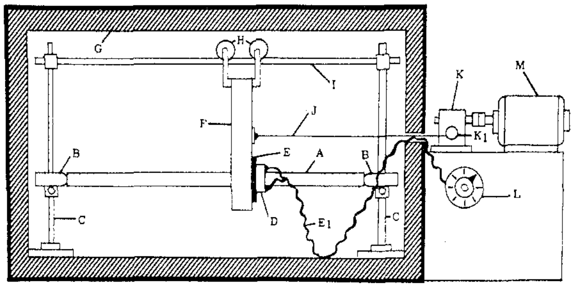

Fig. 1.—Zone melting apparatus.

A. Pyrex tube holding the solution
B. Glass stoppers with standard joints
C. Supports for the tube
D. Resistance heater; wattage: 35
E. Asbestos plate, insulating heater from cooling unit
E_1. Wire connected to Variac
F. Cooling unit, container holding Dry Ice and alcohol
G. Deep freeze chamber
H. Wooden pulleys
I. Supporting rail
J. Wire pulling the heater and cooling unit simultaneously
K. Gear train reduction
K_1. Output of gear train, 1/60 r.p.m., with changeable spool
L. Variac
M. Standard brand split-phase motor, $^1/_4$ h.p., 1725 r.p.m., 115 v., 60 c.p.s.

proximately equal concentrations in a solvent. It is expected that during the zone melting process the more soluble component would advance more rapidly with the moving molten zone toward the end of the charge than the less soluble component, for systems in which the more soluble component dissolves more rapidly than the less soluble one in the molten (liquid) form of the solvent. The less soluble component, in the main, therefore would tend to remain behind in relatively greater concentration nearer the beginning of the charge. This will be true to an even greater extent if the liquid form of the solution is saturated (at the temperature of the molten zone) with respect to the less soluble component only, since the molten zone will be becoming richer in the more soluble component as it traverses the system, but will exhibit no change in concentration of the less soluble component because the system already is saturated with respect to this component at the temperature of the molten zone.[4] However, if the difference in solubilities of the two components (hereinafter called Δ) is very small, the system may become saturated with respect to both components during the zone melting process, and thereafter no separation is achieved.

Therefore, in order to effect a separation, it is advantageous for a system to be at or just below saturation at the temperature of the molten zone with respect to the less soluble component only. According to normal freezing law relationships there will not be any separation of the two components if they are both below saturation, since they will be relatively equally enriched in the liquid zone, and, therefore, throughout the charge, unless the rates of dissolution or the distribution coefficients of the two components are different.[3] Since this rate of dissolution difference often exists for substances of widely differing solubilities and since it is expected that the rate of dissolution of the more soluble component usually will be greater than that of the less soluble one, then the relative quantity of the more soluble component traveling with the zone will be greater than for the less soluble one and a separation may be effected. This actually was observed in several cases.

For the inorganic salt systems, both components had cations in the same oxidation state and identical anions, in order to simulate as closely as possible the conditions which would hold for diastereoisomeric salt mixtures. The solutions also were equimolar with respect to both components. It was felt that if a resolution or partial resolution of such systems could be achieved, this technique also should be applicable to the resolution of diastereoisomers. Partial resolution actually was achieved in both cases, and both solubility differences and rate of dissolution differences apparently play an important role in the separations.

In addition, an inner complex, for which the method of diastereoisomeric resolution usually is ruled out, was partially resolved successfully. This resolution is based upon the different activities (and presumably solubilities and, therefore, rates of dissolution in the molten zone) of the *dextro* and *levo* isomers of such a complex in an asymmetric environment (*i.e.*, an asymmetric solvent or an inactive solvent to which a chemically inert, asymmetric substance has been added).[5,6]

Experimental and Results

Apparatus and Procedure.—The entire zone melting apparatus shown in Fig. 1 was immersed in a deep freeze

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(4) No concentration change in the less soluble component was observed as the concentration of the more soluble component changed, under the experimental conditions used in this work.

(5) F. P. Dwyer, E. C. Gyarfas, and M. F. O'Dwyer, *Nature* **167**, 1036 (1951).

(6) F. P. Dwyer and E. C. Gyarfas, *ibid.*, **168**, 29 (1951).

TABLE I

THE PARTIAL RESOLUTION OF TWO-COMPONENT INORGANIC SALT SYSTEMS IN AQUEOUS SOLUTION

Couple (more soluble salt listed first)	Δ (g./100 g. H_2O at 0°)	% decrease[b] at beginning of charge in			% increase[b] at end of charge in			Enrichment[c] of less soluble component at beginning of charge	Enrichment[c] of more soluble component at end of charge
		Cu	Ba	Ca	Cu	Ba	Ca		
$CuCl_2 \cdot 2H_2O$									
$BaCl_2 \cdot 2H_2O$	71.1	61.00	49.0	...	89.5	30.5	...	12.0	59.0
$Ca(C_2H_3O_2)_2 \cdot H_2O$									
$Cu(C_2H_3O_2)_2 \cdot H_2O$	36.31	4.00	...	4.70	17.0	...	17.4	0.70	0.41
$Cu(NO_3)_2 \cdot 3H_2O$	132.85								
$Ba(NO_3)_2$	(238.75)[a]	47.6	26.2	...	78.3	4.00	...	21.35	74.3

[a] At 25.4° there is a transition from $Cu(NO_3)_2 \cdot 3H_2O$ to $Cu(NO_3)_2 \cdot 6H_2O$, which is the solid phase below this temperature; the solubility and Δ value correspond to this solid phase. [b] Compared to the concentration of the original solution. [c] Enrichment = [percentage change of more soluble component] − [percentage change of less soluble component].

chamber. The apparatus consists essentially of a container for the solution to be zone melted, which is a Pyrex tube, 60 cm. long, fitted with standard joint glass stoppers and a 35-watt heating unit, operated at 55 volts a.c., which has a width of 0.55 cm. If L = tube length in cm. and l = heater width in cm., then $L/l = 109$, *i.e.*, the tube is 109 theoretical zone lengths long. In practice the zone length fluctuates between 1.5 and 2 cm., which corresponds to an L/l value of between 30 and 40.

The rate of travel of the heater used in these experiments was 6 cm./hr., which provided adequately rapid refreezing of the zone behind the heater. In order to achieve as short a molten zone as practicable, a cooling unit containing Dry Ice and ethanol was constructed so as to trail the heater and was separated from it by an insulating disk of asbestos on which the heater was mounted. The cooling unit caused rapid refreezing of the molten zone behind the heater, which reduced the amount of back diffusion to a minimum and helped provide more efficient separations than otherwise would have occurred. Without the cooling unit the zone grew quite long (6–8 cm.) in spite of the relatively low temperature in the deep freeze chamber (approximately −50°). The cooling unit held a 12-hr. supply of coolant and the apparatus in the deep freeze chamber could be operated overnight without being attended. The unit traveled on wooden pulleys and metal bars so that the Pyrex tube would not have to support its weight. The motor and gear train which pulled the heater and cooling unit was located outside the deep freeze chamber.

The Pyrex tube was almost filled with the solution to be zone melted. After the contents of the tube had frozen, the tube was placed in a horizontal position, the heater was turned on, and the first zone was allowed to melt, after which the cooling unit was filled and the motor was turned on. An arbitrary number of passes was chosen (six) and, with each sample, these passes were carried out under as similar conditions as possible, using the minimum amount of heat necessary to melt a zone at the given rate of travel. After the sixth pass, samples from the beginning and end of the tube were removed (by melting them) for study. The results are shown in Table I.

In parts (a) and (b) below, resistance heaters insulated with asbestos were used without the after-cooling unit. This usually resulted in zone lengths of 5–6 cm. The cooling unit was used in all other experiments. The rate of travel of the heater was 6.2 cm./hr., and it was driven by a clock motor. Only the minimum temperature necessary to melt the zone at the given rate of travel was applied. Measurements of optical rotation were made on a high precision Rudolph polarimeter, Model 80, at 5461 Å., except for parts (a) and (b), where the measurements were made at the sodium D line.

Salt Systems.—(1) **Copper(II) Chloride Dihydrate–Barium Chloride Dihydrate.**—Both salts (0.4 mole of each) were dissolved in the least amount of water at room temperature and the solution was diluted 1:1 with water, analyzed for the metal ions, and zone melted.

(2) **Calcium Acetate Monohydrate–Copper(II) Acetate Monohydrate.**—Both salts (0.07 mole of each) were dissolved and treated as in (1).

(3) **Copper(II) Nitrate Trihydrate–Barium Nitrate.**—Both salts (0.06 mole of each) were dissolved and treated as in (1).

Analytical Methods.—Copper was determined electrolytically, barium was determined gravimetrically as the sulfate, and calcium was determined gravimetrically as the oxalate. All chemicals were of analytical grade.

Chemicals.—All chemicals were of analytical grade except the propylenediamine, which was technical grade. It was dried over potassium hydroxide and distilled. The fraction boiling between 117 and 119° was used.

(a) **The Partial Resolution of D,L-[Co(en)$_3$]Cl$_3$.**—This complex was synthesized according to the method of Work.[7] Diastereoisomers were prepared by a modification of the method of Werner,[8] according to the reaction[9]

$$4\text{-D,L-}[Co(en)_3]Cl_3 + 6d\text{-}Ag_2C_4H_4O_6 = \text{D-}[Co(en)_3]_2(d\text{-}C_4H_4O_6)_3 + \text{L-}[Co(en)_3]_2(d\text{-}C_4H_4O_6)_3 + 12AgCl$$

The complex (9.7 g., 2.43×10^{-2} mole of the trihydrate) was treated with silver tartrate (13.25 g., 3.65×10^{-2} mole) in 200 ml. of water. The precipitated silver chloride was washed until the washings were colorless and the wash water was added to the filtrate. The diastereoiso-

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[7] J. B. Work, "Inorganic Syntheses," Vol. 2, W. C. Fernelius, ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 221ff.

[8] A. Werner, *Ber.*, **45**, 121 (1912).

[9] en = ethylenediamine, $C_4H_4O_6^{-2}$ = tartrate anion.

mers were not crystallized, about 11.2 g. of diastereoisomers being contained in 378 ml. of solution at this point. The solution was frozen and subjected to zone melting as described below.

The process was carried out in a Pyrex tube 60 cm. long and 21 mm. in outer diameter which was placed in a horizontal position. Prior to zone melting, the solution containing the diastereoisomeric mixture (50 ml.) was frozen in the tube (held vertically) and an equal volume of water was allowed to freeze on top of it. A resistance heater (2.5 cm. wide, 42.4 watts) was driven by a clock motor *via* a pulley system (Fig. 1). The $[Co(en)_3]^{+3}$ cation was recovered as the chloride salt according to a method similar to that of Werner[8] and its specific rotation was determined. A typical series of results in which the more soluble (end) fraction was removed after three passes and the less soluble (beginning) fraction after ten passes is given in Table II.

TABLE II

THE PARTIAL RESOLUTION OF DIASTEREOISOMERS OF D,L-$[Co(en)_3]_2(d\text{-}C_4H_4O_6)_3$

	Concn. (g./ml.)	$\alpha_{obsd.}$	$[\alpha]^{25}_{D}$
End fraction	6.8×10^{-4}	0.013	+17.6
Beginning fraction	3.04×10^{-3}	.026	+ 8.58
Original diastereoisomeric soln.	4.12×10^{-3}	.048	+11.65

(b) **The Partial Resolution of Racemic Propylenediamine.**—The solution containing the diastereoisomers of propylenediamine dihydrogen acid tartrate was prepared by known methods[10-13] and the solution was made just dilute enough so that the diastereoisomers would not crystallize. *d*-Tartaric acid (7.1 g., 4.72×10^{-2} mole) was dissolved in 95 ml. of water at 95°. To this solution racemic propylenediamine (2.1 g., 2.83×10^{-2} mole) was added slowly and with stirring. On cooling, the distereoisomers began to precipitate, but the minimum volume of water was added to keep them in solution. The specific rotation of the solution was determined at 25°.

The zone melting runs were carried out with a 21-mm. Pyrex tube (50 cm. long) held in a vertical position using the same heater described in part (a). The solution of diastereoisomers (60 ml.) was allowed to freeze in the tube. An equal volume of distilled water then was allowed to freeze on top of it. The pass was begun from the bottom of the tube and after the first pass a 3-cm. fraction was removed from the end (top) of the tube. It was too dilute to show optical rotation and a second fraction from the top also was removed.

After four passes another top fraction was removed, and after nine passes a bottom fraction was removed. Because the fractions were quite dilute, the resolving anion was not removed by metathesis, but by an anion-exchange resin (Dowex 1-8) in the chloride form. That complete removal of the resolving anion was achieved was confirmed by treating a sample of the solution containing both diastereoisomers with the resin and observing that the resulting solution showed no activity. (Removal of the resolving anion is complete in dilute solutions having a pH of about 5. If the solutions are more concentrated and have a pH of about 2, not all of the resolving anion is removed by the resin. In this case the propylenediamine must be distilled over potassium hydroxide and its rotation determined as the free base.) The individual fractions (after treatment with the ion-exchange resin and determination of optical rotation) were concentrated under vacuum at room temperature to a final volume of about 4 ml. This solution (containing partially resolved propylenediamine dihydrochloride) was treated with an excess of potassium hydroxide and distilled under reduced pressure in a micro distillation apparatus. The free propylenediamine was collected, diluted to about 8 ml., and observed for optical rotation. The results are shown in Table III.

The primary reactions involved are[14]

$$2d,l\text{-pn} + 4d\text{-H}_2\text{tart} = d\text{-pnH}_2(d\text{-Htart})_2 + l\text{-pnH}_2(d\text{-Htart})_2$$

$$\text{pnH}_2(\text{Htart})_2 + 4\text{RCl} = 2\text{R}_2\text{tart} + 2\text{HCl} + \text{pn}\cdot 2\text{HCl}$$

$$\text{pn}\cdot 2\text{HCl} + 2\text{KOH} = 2\text{KCl} + 2\text{H}_2\text{O} + \text{pn}$$

(c) **The Partial Resolution of Racemic Tris-(acetylacetonato)-cobalt(III).**—The complex was synthesized according to the method of Bryant and Fernelius.[15] Dibenzoyl-*d*-tartaric acid[16] (1 g.) was dissolved in about 60 ml. of water which contained sufficient sodium hydroxide to dissolve the acid.[17] To this solution was added 60 ml. of dioxane and 0.74 g. of the racemic complex. The solution was frozen and subjected to eight zone melting passes. Samples then were withdrawn from the beginning and end of the charge. The samples were extracted with benzene and the complex entered the benzene layer whereas the sodium dibenzoyl-*d*-tartrate remained in the aqueous layer. Prior experiments showed that this procedure results in complete separation of the complex and the sodium (−)-dibenzoyl-*d*-tartrate. Polarimetric observations of the complex were made with benzene solutions against a blank of the racemic complex in benzene. The results are given in Table IV.

Conclusions

From Table I it can be seen that as the difference in solubility of the two components increases, the % resolution of the compounds also increases. These successful separations indicated that the zone melting technique should be applicable to the resolution of two-component diastereoisomeric systems in aqueous solution.

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(10) G. Bauman, *Ber.*, **28**, 1176 (1895).

(11) M. Delepine and R. Cheritat, *Bull. soc. chim. France*, **11**, 3209 (1944).

(12) J. C. Bailar, Jr., C. A. Steigman, J. H. Balthis, and E. H. Huffman, *J. Am. Chem. Soc.*, **61**, 2402 (1939).

(13) L. S. Tschugaeff and W. Sokoloff, *Ber.*, **40**, 3461 (1907).

(14) pn = propylenediamine, tart = tartrate anion (dinegative).

(15) B. E. Bryant and W. C. Fernelius, "Inorganic Syntheses," Vol. 5, T. Moeller, ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1957, p. 188.

(16) F. Zetzsche and M. Hubacher, *Helv. Chim. Acta*, **9**, 291 (1926).

(17) C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, **55**, 2605 (1933).

TABLE III

THE PARTIAL RESOLUTION OF RACEMIC PROPYLENEDIAMINE

Diastereoisomeric solution				Free propylenediamine		
Fraction	$\alpha_{obsd.}$ (°)	$[\alpha]_D$ (°)	Concn. (g./ml.)	$\alpha_{obsd.}$ (°)	$[\alpha]_D$ (°)	Concn. (g./ml.)
Top fraction (1 pass)	+0.014	...	Too dilute for determination	...	...	...
Second fraction from top (1 pass)	+0.068	+24.4	2.78×10^{-3}	+0.015	+13.6	1.1×10^{-3}
Top fraction (4 passes)	+0.241	+27	8.9×10^{-3}	No obsd. rot.	...	...
Bottom fraction (9 passes)	+0.352	+23.5	1.49×10^{-2}	−0.029	− 2.3	1.26×10^{-2}
Original diastereoisomeric soln.	+0.215	+23.88	9×10^{-3}	...	...	...

TABLE IV

THE PARTIAL RESOLUTION OF RACEMIC TRIS-(ACETYLACETONATO)-COBALT(III)

	$\alpha_{obsd.}$ (°)	Concn. (g./ml.)	$[\alpha]_{5461}$ (°)	$[\alpha]_M$ (°)[a]
Experiment 1				
Beginning fraction	−0.033	3×10^{-4}	−109	−39,200
End fraction	+0.069	5×10^{-4}	+137	+49,200
Experiment 2				
Beginning fraction	−0.038	3×10^{-4}	−128	−46,000
End fraction	+0.030	2×10^{-4}	+150	+53,000

[a] Where $[\alpha]_M = [\alpha] \times$ molecular weight.

It is of interest to note that the degree of resolution of the components is more pronounced at the end of the charge than at the beginning. This is not unexpected, however, since, at the beginning of the charge the solution is unsaturated and the resolution in this region probably is due primarily to differences in the rate of dissolution of the solids at the solid–liquid interface. As the zone advances and the solution becomes more concentrated, it approaches saturation, especially with respect to the less soluble component, and the separation at the end of the charge probably is due both to differences in the rates of dissolution as well as saturation with respect to the less soluble component at the temperature of the molten zone. That is, as saturation of the less soluble component is achieved (toward the end of the charge) the concentration of the less soluble component does not increase but remains constant, while the concentration of the more soluble component increases in the molten zone as it moves further toward the end of the charge.

That this explanation is plausible is supported by the fact that as Δ increases, the difference between the % resolution at the beginning and end of a charge increases as well, because for pairs of large Δ, the solution can readily become saturated with respect to the less soluble component only.

It was believed that these results justified further attempts to apply this method to the resolution of diastereoisomers. However, the fact that for pairs with a relatively large Δ value of 36.31 g./100 g. of water at 0° a resolution of only 0.5% was achieved, indicates that the resolution obtained for diastereoisomers (if any) might be quite small. It should be mentioned at this point that resolutions could be carried out by normal freezing or fractional crystallization, provided that the difference in solubility between the two components is sufficiently large. However, the usefulness of this method becomes obvious if its possible applicability to systems which do not readily give crystals but have a tendency to form sirups or oils is considered.

Regarding the diastereoisomeric and racemic mixtures of optically active compounds, the results obtained indicate that at least partial resolution was obtained in each case. For optically active isomers of $[Co(en)_3]Cl_3$ the observed readings on the recovered bromides were low because of the small quantities of material obtained, but observed rotations of the diastereoisomeric solutions clearly indicate a partial resolution. Any possibility of specific rotation change as a result of concentration changes is ruled out because the beginning and end fractions were made identical in concentration.

The observed rotation of the *d*-propylenediamine is very low because of high dilution and should be considered with some reservation, but the negative fraction, which was more concentrated, gave a reliable reading.

The results obtained for the tris-(acetylacetonato)-cobalt(III) complex agree approximately with the values obtained by Moeller and Gulyas,[18] who achieved a partial resolution of this

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(18) T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 245 (1958).

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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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Separation of Inorganic Stereoisomers by Adsorption Chromatography. I. Non-electrolytic Geometric Isomers of Platinum(II)[1]

BY GEORGE B. KAUFFMAN, ROBERT P. PINNELL, AND LLOYD T. TAKAHASHI

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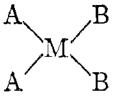
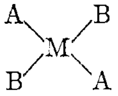
By the use of chromatographic columns of silica gel, Porocel (activated bauxite), activated alumina, and Linde Molecular Sieves, *cis–trans* isomer pairs of the mononuclear complexes dichlorobis-(tri-*n*-butylphosphine)-platinum(II), dichlorobis-(diethyl sulfide)-platinum(II), and dichlorodipyridineplatinum(II) and the binuclear complex *sym*-di-μ-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-μ-ethylthiodichlorobis-(*tri-n*-propylphosphine)-diplatinum(II), and *sym*-di-μ-*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.