

postulated that these different straight lines were obtained because of the differences in double bonded character of the chelating groups. Such a difference in intercepts is not found for the corresponding phenanthroline-bipyridine complexes. The difference in double bonded character does not appear to be a factor in this case.

**Oxidation-Reduction Potentials.**—The linear dependence of  $\log k_{\text{diss}}$  upon  $\log K_a$  suggests that other relationships between various properties of the series of compounds studied might add to the understanding of related systems. Since the series studied included only the 5-substituted phenanthrolines, the question naturally arises as to the possibility of extending the observed generalizations to other related compounds. The extent to which this type of approach can be extended will ultimately determine their usefulness. Data for the oxidation-reduction potentials are given in Table I.<sup>7</sup> The logarithms of the oxidation-reduction potentials may be plotted against  $\log k_{\text{diss}}$  for the complexes and a straight line results. It has been observed that in many of the iron(II)-phenanthroline complexes a change in hydrogen ion concentration from 0.1 *F* to 1.0 *F* causes approximately a 0.03–0.04 volt change in formal potential. If one substitutes the expressions for the appropriate dissociation constants into the Nernst

equation, it is possible to calculate the stabilities of the ferric complexes. The calculated values for 1,10-phenanthroline agree approximately with those obtained by Lee, Kolthoff and Leussing<sup>2b</sup> from potentiometric measurements only if a 1:1 combination of  $\text{Fe}(\text{Phen})_3^{+++}$  and  $\text{H}^+$  is assumed. However, the assumption of a protonated ferric complex does not appear to be logical when this is not postulated for the ferrous complex. It does not seem reasonable, either, that the ferric ion with its higher charge would need an extra proton to ensure stability while the ferrous complex is apparently unaffected by hydrogen ion.

It is noted that if the data for the bipyridine complex are included on the graph of the oxidation-reduction potential against  $\log k_{\text{diss}}$  the resulting point does not fall on the line obtained for the 5-substituted phenanthrolines.

Work by Mellon and Hale on the 3-carbethoxy-4-hydroxyphenanthroline complex with iron(II) points to another apparent exception.<sup>8</sup> Although the oxidation-reduction potential would indicate that this latter complex would be more stable than any of the complexes studied here, it was reported to be relatively unstable. In these cases other factors which were unimportant in the 5-substituted compounds, may influence the stability of the complexes.

(7) G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," The G. Frederick Smith Chemical Company, Columbus, Ohio, 1944.

(8) M. N. Hale and M. G. Mellon, *THIS JOURNAL*, **72**, 3217 (1950).  
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## The Stereoisomerism of Complex Inorganic Compounds. XIV. Studies upon the Stereochemistry of Saturated Tervalent Nitrogen Compounds<sup>1</sup>

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The reactions of N,N-diethylglycine and N-methyl-N-ethylglycine with cobalt(III) and platinum(II) have been studied. A satisfactory synthesis for potassium dinitro-(N-methyl-N-ethylglycine)-platinate(II) has been developed. That an asymmetric nitrogen atom exists in this compound was demonstrated through its resolution by fractionation with *l*-quinine and treatment with optically active quartz powder.

The problem of resolving into optically active antipodes compounds containing properly substituted nitrogen atoms has attracted interest for many years. Early investigators worked chiefly with organic compounds, and many resolutions of quaternary ammonium salts and tertiary amine oxides have been reported.<sup>2</sup>

In 1924, Meisenheimer and his co-workers<sup>3</sup> claimed to have shown the existence of the required four optical isomers of sarcosine-bis-ethylenediaminecobalt(III) chloride,  $[\text{Co en}_2\text{sarc}]\text{Cl}_2$ ,<sup>4</sup> by frac-

tional crystallization of the bromocamphorsulfonate salt. The interpretation of this work is complicated by the fact that the activity due to the cobalt ion is very large relative to that of the nitrogen atom and by the fact that when the resolving agent was removed, no nitrogen activity was detectable, but only that due to the cobalt ion; both of these factors cast doubt on the validity of the work. In addition, Basolo<sup>5</sup> was unsuccessful in an attempt to repeat Meisenheimer's procedure.

Later, Mann<sup>6</sup> prepared tetrachloro-(diethylenetriamine monohydrochloride)-platinum(IV) monohydrate  $[\text{Pt}(\text{dien} \cdot \text{HCl})\text{Cl}_4] \cdot \text{H}_2\text{O}$ , but was not able to resolve it.

In these previous attempts to resolve inorganic rotatory, and *l* = levorotatory. *D*- and *L*- represent the observed rotatory behavior of the complex ions. All rotations were measured at the *D* line of sodium.

(5) F. Basolo, Thesis, Doctor of Philosophy, University of Illinois, 1943.

(6) F. G. Mann, *J. Chem. Soc.*, 486 (1934).

(1) The work reported in this article was taken from the doctorate thesis of J. R. Kuebler, Jr., 1951.

(2) R. L. Shriner, Roger Adams and C. S. Marvel, "Organic Chemistry," Ed. 2, Vol. 1, H. Gilman, ed., John Wiley and Sons, Inc., New York, N. Y., pp. 413–418.

(3) J. Meisenheimer, L. Angermann, H. Holsten and E. Kiderlen, *Ann.*, **438**, 269 (1924).

(4) Abbreviations used herein include dien = diethylenetriamine, en = ethylenediamine, amac = N,N-diethylglycinate ion, AMAC = N-methyl-N-ethylglycinate ion, glyc = glycinate ion, quin = quinine ion, sarc = sarcosinate ion, stry = strychnine ion, *d* = dextro-

complex compounds containing an asymmetric nitrogen atom, one of the four groups attached to the nitrogen was a hydrogen atom. It is now believed that in such cases the hydrogen atom is labile enough to ionize to a slight extent, thus causing continuous racemization of the optical forms. It seemed reasonable that this process occurred in the above complexes, especially since Block and Bailar<sup>7</sup> were able to treat the  $[\text{Au(en)}_2]^+{}^3$  ion with one equivalent of base to form the  $[\text{Au(en)(en-H)}]^+{}^2$  ion. ("en-H" represents a molecule of ethylenediamine from which one hydrogen atom has been completely lost.) Consequently, N-methyl-N-ethylglycine was selected as a coordinating agent.

It was realized that, although such complexes might be optically stable, the tertiary nitrogen atom would have a decreased tendency to form a coordinate bond with a metal ion. However, the possibility of chelation through the carboxyl group should largely overcome this disadvantage. In addition, it seemed desirable to synthesize a compound in which the type and configuration of the other ligands offered no possibility of optical isomerism, so that the activity, if found, would necessarily be due to the nitrogen atom alone.

While studying the synthesis of complex compounds, N,N-diethylglycine was used as a "practice" coordinating agent since starting materials for its preparation were more readily available than those for the methyl-ethyl compound. Clearly, this compound differs from N-methyl-N-ethylglycine only in its inability to form an asymmetric nitrogen atom upon coordination to a metal ion, and subsequent results have shown that the two amino acids react otherwise in the same manner.

First, the reaction of N,N-diethylglycine with several cobalt compounds was investigated. Attempted replacement of the chloride, ammonia, or sulfite, respectively, in *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ,  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$  and  $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$  by the amino acid was unsuccessful. Furthermore, the amino acids, glycine, sarcosine and N,N-diethylglycine, were made to react with cobaltic hydroxide by the method of Ley and Winkler,<sup>8</sup> to determine the effect of substitution of the nitrogen atom on complex stability. Glycine forms the very stable *tris* complex,  $[\text{Co}(\text{glyc})_3]\cdot 2\text{H}_2\text{O}$ . Evidence of an analogous, but less stable, sarcosine complex was obtained, although the compound was never isolated in pure form. N,N-Diethylglycine, however, showed no reaction. It was concluded that the tertiary nitrogen, even though aided by the possibility of chelation, was not capable of forming a stable cobalt-nitrogen bond.

Next, the use of platinum(II) as a central ion was investigated. Even though the tendency for platinum-oxygen coordination is not very pronounced, a number of compounds are known which contain stable platinum-oxygen bonds,<sup>9</sup> and it appeared probable that N-methyl-N-ethylglycine would coordinate.

N,N-Diethylglycine allowed to react with potas-

sium tetrachloroplatinate(II) to form bis-(N,N-diethylglycine)-platinum(II),  $[\text{Pt}(\text{amac})_2]$ . No attempt was made to prepare the analogous potentially active compound,  $[\text{Pt}(\text{AMAC})_2]$ , since it would be a non-electrolyte and not amenable to the conventional method of resolution by salt formation with an optically active compound. In addition, it would contain two identical asymmetric nitrogen atoms, and thus could conceivably occur in an inactive, *meso* form.

From the above results, it was concluded that a resolvable platinum(II) compound could be prepared from a platinum(II) complex containing two halogen atoms and two other negative or neutral groups that are so strongly coordinated to the platinum(II) ion that there is no possibility of their being displaced by the amino acid. Potassium diiodo-dinitro-platinate(II) dihydrate,  $\text{K}_2[\text{Pt}(\text{NO}_2)_2\text{I}_2]\cdot 2\text{H}_2\text{O}$ , was prepared by a modification of the method of Nilson<sup>10</sup> and its *cis* configuration was demonstrated by its ready conversion to  $[\text{Pt}(\text{NO}_2)_2\text{en}]$ .

A solution of  $\text{K}_2[\text{Pt}(\text{NO}_2)_2\text{I}_2]\cdot 2\text{H}_2\text{O}$  was shaken with excess silver oxide, the silver oxide and silver iodide were filtered off and the amino acid complex was obtained by treating the strongly basic filtrate with the amino acid nitrate. Both  $\text{K}[\text{Pt}(\text{NO}_2)_2\text{amac}]$  and  $\text{K}[\text{Pt}(\text{NO}_2)_2\text{AMAC}]$  were readily prepared in this manner; however, they were so hygroscopic that it was necessary to convert them to the strychnine salts in order to obtain reliable elemental analyses. The nitrate of the amino acid was used rather than the hydrochloride, because the nitrate ion, being a poor coordinating agent, could not compete with the tertiary nitrogen atom for a place in the coordination sphere of platinum(II).

The resolution of potassium dinitro-(N-methyl-N-ethylglycine)-platinate(II) was achieved in two ways, by fractionation of an optically active alkaloid salt, and by adsorption on optically active quartz powder. Cinchonine, brucine and strychnine salts were found to be too insoluble to be of use. The *l*-quinine salt was too insoluble to give an observable rotation, but it was found possible to convert it to the potassium salt,  $\text{K}[\text{Pt}(\text{NO}_2)_2\text{AMAC}]$ , several fractions of which exhibited small rotations which fell to zero in the course of five to six hours. The fact that all the fractions examined showed only *levo* rotation does not appear implausible, due to the manner in which they were obtained. The quinine salt of the *levo* isomer was apparently the less soluble of the two and concentrated in the crystals as the solution was evaporated. The more soluble dextro isomer concentrated in the solution, but as the evaporation was slow and the fractions were removed only every 12 hours, the dextro isomer had ample time to racemize.

Early investigators<sup>11</sup> observed that when solutions of racemic mixtures of certain complexes were stirred or shaken with *d*- or *l*-quartz, the solutions showed optical activity. This was attributed to a preferential adsorption of one isomer by the optically active quartz. However, the mechanism in-

(7) B. P. Block and John C. Bailar, Jr., *THIS JOURNAL*, **73**, 4722 (1951).

(8) H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909).

(9) H. F. S. King, *J. Chem. Soc.*, 1338 (1938); R. C. Menzies, *ibid.*, 565 (1928); H. Ley and K. Ficken, *Ber.*, **45**, 377 (1912).

(10) L. F. Nilson, *J. prakt. Chem.*, [ii] **21**, 172 (1880).

(11) R. Tsuchida, M. Kobayashi and A. Nakamura, *J. Chem. Soc., Japan*, **56**, 1339 (1935); *Bull. Chem. Soc. Japan*, **11**, 38 (1936).

volved in this case may not be merely a preferential surface adsorption, for it was noted that prolonged stirring of the active solutions with the quartz caused an increase in the racemization rate. Such a process could be caused by either a catalytic action by the quartz on the racemization rate, or by a difference in the rates of adsorption of the two isomers. This technique was successfully applied to 1.0% solutions of  $K[Pt(NO_2)_2AMAC]$ . Solutions which had been shaken with *l*-quartz gave a positive rotation, while those that had been shaken with *d*-quartz gave a negative rotation. In each case, the optically active component racemized in five to six hours.

### Experimental

#### Preparation of N-Methyl-N-ethylglycine Hydrochloride.

A modification of the method of Jones and Major<sup>12</sup> was used. The methylethylamine hydrochloride (Eastman Kodak Company) was purified by recrystallization from absolute alcohol and absolute ether. To 10.9 g. (0.114 mole) of methylethylamine hydrochloride 25 ml. of 50% potassium hydroxide solution was added slowly from a dropping funnel. The flask was heated on a steam-cone and the methylethylamine distilled into a flask packed in ice. The product was dried for 12 hours over potassium hydroxide pellets.

To a solution of the methylethylamine in 50 ml. of absolute ether was added, dropwise, a solution of 12.6 ml. (0.114 mole) of ethyl bromoacetate in 50 ml. of absolute ether. A white precipitate of methylethylamine hydrobromide started to form at once and was filtered after one-half hour. Anhydrous hydrogen chloride gas was bubbled into the filtrate until precipitation of the amino acid ester hydrochloride was complete. The precipitate was filtered, washed with absolute ether, and dissolved in water. The aqueous solution was extracted three times with ether to remove the last traces of unreacted ethyl bromoacetate, and the extracts discarded. The solution was made alkaline with 5% sodium hydroxide solution and extracted eight to twelve times with 15-ml. portions of ether. The ether solution was dried over anhydrous calcium sulfate. After distillation of the ether and unreacted methylethylamine, the oily residue of amino acid ester was hydrolyzed with 50 ml. of 1.0 *N* hydrochloric acid solution. The amino acid ester hydrochloride was recovered by evaporating the solution to a sirup on the steam-cone. The product was dried in a vacuum desiccator over phosphorus pentoxide, and purified by recrystallization from absolute alcohol and absolute ether. It is very hygroscopic and melts at 110–112°. The yield was 2.1 g., or 24%. *Anal.* Calcd. for  $C_5H_{12}O_2NCl$ : C, 39.10; H, 7.86; N, 9.13. Found: C, 39.16; H, 8.02; N, 8.98.

**N,N-Diethylglycine hydrochloride** was prepared and purified in a similar fashion. The hygroscopic, white crystals melt at 125–128°. The yield was 5.0 g., or 30%. *Anal.* Calcd. for  $C_6H_{14}O_2NCl$ : C, 43.00; H, 8.43; N, 8.36. Found: C, 43.18; H, 8.39; N, 8.46.

**Preparation of Bis-(N,N-diethylglycine)-platinum(II),  $[Pt(amac)_2]$ .**—The freshly prepared silver oxide from 2.4 g. (0.014 mole) of silver nitrate was vigorously shaken for ten minutes with 5 ml. of water and 1.21 g. (0.007 mole) of N,N-diethylglycine hydrochloride; a few glass beads were added to break up the precipitate. The precipitated silver chloride and excess silver oxide were filtered and washed several times with water.

To the filtrate was added a solution of 3.0 g. (0.007 mole) of  $K_2[PtCl_4]$  in 20 ml. of water. The volume of the solution was 40 ml. and its pH 4.0; this was adjusted to pH 8.5 with a few drops of 5% sodium hydroxide solution. The solution was heated 12 hours at 70°, after which the pH was 4.0. The pH was adjusted to 9.0 as before and the solution heated at 70° for ten hours. Three more times, the solution was heated to 70° for two-hour intervals and the pH adjusted to 9.0. The final pH of the pale yellow solution was 7.0. The small deposit of platinum which had formed was filtered and the filtrate concentrated to crystallization at room temperature by passing a gentle stream of air over the surface. The white, crystalline plates were filtered on sintered

glass, washed with alcohol and ether, and recrystallized from water. *Anal.* Calcd. for  $[Pt(amac)_2]$ : C, 31.65; H, 5.32; N, 6.16. Found: C, 31.40; H, 5.28; N, 6.17.

**Preparation of Potassium Tetranitroplatinate(II) Dihydrate,  $K_2[Pt(NO_2)_4] \cdot 2H_2O$ .**—Potassium tetrachloroplatinate(II)<sup>13</sup> was converted to the tetranitro compound by the method of Vezex.<sup>14</sup> Two and two-tenths grams (0.005 mole) of potassium tetrachloroplatinate(II) was dissolved in 10 ml. of water and heated on a steam-cone. To this was added a solution of 3.2 g. (0.034 mole) of potassium nitrite in 5 ml. of hot water. The deep red color of potassium tetrachloroplatinate(II) immediately changed to pale yellow, and upon cooling the solution in an ice-bath, white needles of  $K_2[Pt(NO_2)_4] \cdot 2H_2O$  separated. A second crop was obtained by evaporation of the filtrate on a steam cone to one-half its volume, then cooling again. The crystals were washed with a small portion of ice water, then alcohol and ether and dried in the air. The total yield was 2.0 g., or 76%.

**Preparation of Potassium Diiododinitroplatinate(II) Dihydrate,  $K_2[Pt(NO_2)_2I_2] \cdot 2H_2O$ .**—Six and five-tenths grams (0.014 mole) of  $K_2[Pt(NO_2)_4] \cdot 2H_2O$  was dissolved in 110 ml. of water and 110 ml. of alcohol was added. To this was added a solution of 3.65 g. (0.014 mole) of iodine in 230 ml. of 50% alcohol. When the solution was heated on a steam-cone for one-half hour, acetaldehyde was evolved and the initial deep red color changed to a yellow-brown. The solution was concentrated to a volume of about 80 ml. by heating on a steam-cone while air was passed over the surface of the solution. The small amount of black residue which formed was removed, and the bright yellow solution was evaporated to dryness in a vacuum desiccator over phosphorus pentoxide. The yellow residue was recrystallized from boiling, absolute alcohol. Yellow leaflets separated from the solution upon cooling in an ice-bath, and were filtered and washed with cold alcohol. A second crop was recovered from the filtrate by adding twice its volume of absolute ether. The over-all yield was 7.6 g., or 88%. *Anal.* Calcd. for  $K_2[Pt(NO_2)_2I_2] \cdot 2H_2O$ : I, 38.65. Found: I, 38.85.

**Preparation of Dinitroethylenediamineplatinum(II) Dihydrate,  $[Pt(NO_2)_2en] \cdot 2H_2O$ , and Dinitroethylenediamineplatinum(II),  $[Pt(NO_2)_2en]$ .**—One and three-tenths grams (0.002 mole) of  $K_2[Pt(NO_2)_4] \cdot 2H_2O$  was shaken one-half hour with 100% excess silver oxide and 5 ml. of water. The resulting solution was deep yellow and had a pH of 12.0. To this was added 0.38 ml. (0.003 mole) of 16.72 *N* ethylenediamine solution, and the pH adjusted to 9.0 with dilute nitric acid solution. The volume at this point was 100 ml. The solution was evaporated to about 50 ml. at room temperature and, after cooling in an ice-bath, yellow, crystalline plates of  $[Pt(NO_2)_2en] \cdot 2H_2O$  were filtered, washed with cold water, then alcohol and ether. The yield was 0.31 g., or 40% of theory. *Anal.* Calcd. for  $[Pt(NO_2)_2en] \cdot 2H_2O$ : Pt, 51.00. Found: Pt, 51.25.

The yellow crystals were placed in an Abderhalden drying pistol at 100° for 12 hours, after which time the product was a very pale pink in color. *Anal.* Calcd. for  $[Pt(NO_2)_2en]$ : Pt, 56.30; C, 6.93; H, 2.32; N, 16.15. Found: Pt, 56.35; C, 7.22; H, 2.36; N, 15.96.

**Preparation of Potassium Dinitro-(N-methyl-N-ethylglycine)-platinate(II)  $K[Pt(NO_2)_2AMAC]$ .**—Ninety-three hundredths gram (0.006 mole) of the amino acid hydrochloride was converted to the nitrate by shaking it for ten minutes with 5 ml. of water and 100% excess silver oxide, followed (after removal of the silver salts) by the addition of 60.60 ml. (0.006 mole) of 0.0984 *N* nitric acid. The pH of the resulting solution was 2.0. Three and ninety-seven hundredths grams (0.006 mole) of  $K_2[Pt(NO_2)_4] \cdot 2H_2O$  was shaken one-half hour with 5 ml. of water and 100% excess silver oxide. The pH of the dark yellow filtrate was 12.0. This solution and that of the amino acid nitrate were mixed. The total volume was about 100 ml. and the pH was 7.0. A small amount of a brownish-yellow solid separated. This became dark brown after heating on the steam-cone for three hours. The material was filtered and discarded, and the pale yellow filtrate evaporated to dryness in a vacuum over phosphorus pentoxide. The white residue was extracted with several 20-ml. portions of boiling methyl alcohol, and from the filtrate white  $K[Pt(NO_2)_2AMAC]$  was

(12) L. W. Jones and R. T. Major, *THIS JOURNAL*, **52**, 1082 (1930).

(13) R. N. Keller, *Inorganic Syntheses*, **2**, 247 (1946).

(14) M. Vezex, *Ann. chim. phys.*, **29**, 160 (1893).

precipitated with absolute ether. The yield was 1.7 g., or 64%. The salt is very hygroscopic and must be stored in a desiccator.

This compound could not be entirely freed from potassium nitrate, so the strychnine salt was prepared in a pure form in order to confirm the composition of the platinum complex. The impure  $K[Pt(NO_2)_2AMAC]$  was dissolved in 200 ml. of water and added to 100 ml. of a solution containing 0.080 g. (0.002 mole) of strychnine nitrate. A white, flocculent precipitate formed slowly, and was filtered after cooling one hour in an ice-bath. It was recrystallized from hot water. *Anal.* Calcd. for  $(stry)[Pt(NO_2)_2AMAC]$ : Pt, 26.45; C, 42.35; H, 4.50; N, 9.49. Found: Pt, 26.35; C, 42.87; H, 4.31; N, 9.51.

**Resolution of  $K[Pt(NO_2)_2AMAC]$ .**—The instrument used was a Schmidt and Haensch Polarimeter No. 9143, calibrated to 0.001 degree and giving reproducible results to  $\pm 0.003$  degree. The readings given represent an average of ten settings.

**(a) Resolving Agent: Quinine Bisulfate.**—The resolving agent was prepared by dissolving 1.835 g. of quinine in 9.45 ml. of 0.599 *M* sulfuric acid and diluting to 100 ml. Twenty milliliters (0.0023 mole) of this solution was added to a solution of 1.000 g. (0.0023 mole) of  $K[Pt(NO_2)_2AMAC]$  in 100 ml. of water. The resulting solution was diluted to about 200 ml., and the fractions were obtained by evaporation in a vacuum desiccator over phosphorus pentoxide. Table I shows the volume of solution at which the fractions were removed and the weight of each.

TABLE I

Fraction	Volume when fractions removed (ml.)	Weight of fraction (g.)
1	125	0.151
2	40	.140
3	15	.442

It was not possible to remove the adsorbed potassium bisulfate from the  $(quin)[Pt(NO_2)_2AMAC] \cdot 2H_2O$ , but from the analytical data, the values of the elemental analyses could be calculated. Table II gives analytical values for the carbon, hydrogen and nitrogen compositions of the various fractions of the quinine salt, corrected for potassium bisulfate in the sample and potassium sulfate in the ash.

TABLE II

Fraction	Analyses, %		
	Carbon	Hydrogen	Nitrogen
1	39.40	4.92	9.02
2	39.00	5.10	9.04
3	39.20	4.85	9.05
Calcd. for $(quin)[Pt(NO_2)_2AMAC] \cdot 2H_2O$	39.30	5.10	9.18

Portions of each of the fractions were ground for one hour in a mortar at 0° with 2 molar equivalents of potassium hy-

droxide solution. The precipitated quinine was filtered and the filtrate was diluted to 10 ml. and examined for optical activity in a 1.0-dm. polarimeter tube. All three fractions showed levo activity and racemized upon standing. The results are summarized in Table III.

TABLE III

Fraction	Salt used, g.	Initial rotation	Time to reach zero rotation (hr.)
1	0.096	$-0.012^\circ$	6.25
2	.100	$-0.020^\circ$	6.00
3	.200	$-0.021^\circ$	5.00

TABLE IV

Type of quartz	Run No.	Initial rotation (2-dm. tube)	Time to racemize, hr.
Dextro	1	$-0.024^\circ$	7.0
Dextro	2	$-0.023$	6.5
Dextro	3	$-0.016$	6.5
Levo	1	$+0.034$	5.0
Levo	2	$+0.028$	4.5
Levo	3	$+0.010$	5.0
Levo	4	$+0.014$	5.5

In each case, both the filtrate and the residual quinine contained platinum. From this it was concluded that the  $(quin)[Pt(NO_2)_2AMAC] \cdot 2H_2O$  and quinine alkaloid were somewhat similar in solubility, so that even one hour of trituration was not enough to convert all the quinine ion to the free alkaloid. However, as no precipitate formed in the filtrates, the decreasing rotation was taken as evidence of the presence of  $L-K[Pt(NO_2)_2AMAC]$  in the solution.

**(b) Resolving Agent: Optically Active Quartz.**—The quartz powder employed was made by grinding crystals of optically active quartz in an iron mortar. The iron was removed by treatment with concentrated nitric acid followed by repeated washing with water. The particle size of the powder was between 140 and 200 mesh.

Twenty-five milliliters of a 1.0% solution of  $K[Pt(NO_2)_2AMAC]$  was stirred mechanically with 1.0 g. of dextro-quartz for 15 minutes. The solid was filtered, 1.0 g. of fresh dextro-quartz was added and the suspension stirred for 25 minutes. The quartz was removed by filtration and the solution was found to exhibit a negative rotation which fell to zero in the course of approximately six hours. The experiment was repeated on both the same solution and a fresh one with similar results. When a 1.0% solution of  $K[Pt(NO_2)_2AMAC]$  was stirred in a similar manner with 1.0 g. of levo-quartz for ten minutes, the solution showed a positive rotation which fell to zero in about five hours. Repetition of the experiment with other  $K[Pt(NO_2)_2AMAC]$  solutions gave similar results. Table IV summarizes the experiments.

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