Stereospecific Influences in Metal Complexes Containing Optically Active Ligands.[1] Part V. Absolute Stereospecificity in Metal Complexes of Optically Active Polyaminocarboxylic Acids

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Metal complexes of the optically active 1,2-propylenediamine- and *trans* 1,2-cyclohexanediaminetetraacetic acids, in which the ligand is sexadentate and quinquedentate in function, have been prepared. One form only, *e.g.*, D*l* in the cobalt(III) sexadentate complexes, could be isolated. The other isomer, (D*d*), appeared to be very small in amount or excluded, *i.e.*, $K > 99$ and $-\Delta F^0 > 3$ kcal./g. mole. The quinquedentate rhodium complex of *l*-propylenediaminetetraacetic acid, obtained in a single isomeric form, mutarotated to a low value in the light, but the rotation was regained in the dark. None of the complexes, even those containing Cu(II) and Cr(III) could be isomerized by heating in aqueous solution or in the presence of charcoal. From Courtauld atomic models one optical isomer of the complex, whether the ligand is sexadentate or quinquedentate in function, appeared to be sterically hindered. Atom crowding due to the methyl group of the asymmetric carbon does not appear sufficient to exclude completely the strained isomer, but its concentration in the equilibrium mixture would be small. On the other hand, it was evident from models that one of the isomers of the metal complexes of *l*-cyclohexanediaminetetraacetic acid involved considerable distortion of the cyclohexane ring, and would appear to be excluded.

The "inert" metal complexes of optically active 1,2-propylenediamine and *trans*-1,2-cyclohexanediamine tetraacetic acids provide simple stable systems for the study of stereospecific influences, since only two optical isomers, *e.g.*, D*d*, D*l*, may arise from one optical form of the polyaminocarboxylic acid. The optical isomers of the former acid have been obtained by direct synthesis from active 1,2-propylenediamine or by decomposition of the resolved cobalt(III) complex.[2] Commercial 1,2-cyclohexanediaminetetraacetic acid (H₄CDTA) is considered to exist in the 1e;2e, *trans* form,[3,4] and the *cis*-isomer (1e;2a) seems to have defied all attempts at preparation.[5] Resolution of the acid with *d*-phenylethylamine, *l*-quinine,[6] and in the present work, with *d*-cinchonine was fruitless. The optical isomers ($[\alpha]_D = \pm 53°$) were obtained ultimately by the decomposition of the cobalt(III) complex which had been resolved through the *cis*-dinitrobis-(ethylenediamine)-cobalt(III) salt.

Though previous work with *cis*-dinitro-ethylenediamine-propylenediamine cobalt(III) and bis-(ethylenediamine)-*d*-(cyclopentanediamine)-cobalt(III) ions[7,8] suggested that little stereospecificity would be expected, especially in the [Co(PDTA)]⁻ ion, complete stereospecificity, ($K > 99$, $-\Delta F^0 > 3$ kcal./g. mole), was found. No trace of a second isomer was detected when active barium *l*-pro-

pylenediaminetetraacetatocobaltate(III), prepared from the pure levo acid, was fractionally crystallised from aqueous alcohol. The diastereoisomer with *cis*-[Coen₂(NO₂)₂]⁺ ion was then prepared and recrystallized several times, but the rotation of the recovered barium salt was unchanged. The high solubility of salts of the optically active [Co(CDTA)]⁻ ion prevented similar studies. However, unlike the active [Co(EDTA)]⁻ ion, which racemized slowly[9] (half-life = 168 min., 100°), no rotational change occurred when solutions of salts of the [Co(PDTA)]⁻ and [Co(CDTA)]⁻ ions were kept at 98° for several hours. Similarly, although the [Co(EDTA)]⁻ ion racemized completely in aqueous solution in the presence of activated charcoal, no rotational change occurred in 2 hr. with the [Co(PDTA)]⁻ and [Co(CDTA)]⁻ ions.

Quinquedentate Complexes.—No evidence was found other than for a single geometrical or optical isomer in the quinquedentate cobalt(III) complexes of optically active propylenediaminetetraacetic acid with chloro or nitro groups occupying the unique coördination position. Each optical configuration of the organic moiety permits the formation of four geometrical isomers depending on the position of the nitro (or chloro) group with respect to the methyl group and the two nitrogen atoms. The resolution of DL-K[Co(*dl*-H·PDTA)-Cl] yielded only two isomers, D*d* and L*l*, identical with the isomers prepared from the optically active complexing agent. Both isomers were transformed with complete retention of configuration to the pure sexadentate complexes discussed above. Similarly, the blue chloro complex could be prepared in almost 100% yield from the sexadentate

(1) For previous papers in this series see *J. Am. Chem. Soc.*, **81**, 290, 1043, 5269, 5272 (1959).

(2) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959).

(3) D. G. Barton and R. C. Cookson, *Quart. Revs. (London)*, **10**, 44 (1956).

(4) P. Anderson, O. Hassel and K. Lunde, *Acta Chem. Scand.*, **6**, 966 (1952).

(5) G. Schwarzenbach, private communication.

(6) B. A. Ferrone, Thesis, Univ. Illinois, 1957.

(7) A. Werner and A. P. Smirnoff, *Helv. Chim. Acta*, **1**, 5 (1918).

(8) F. M. Jaeger and H. B. Blumendal, *Z. anorg. Chem.*, **175**, 161 (1928).

(9) F. P. Dwyer, D. P. Mellor and E. C. Gyarfas, *J. Phys. Chem.*, **59**, 296 (1955).

complex with complete retention. The changes in sign in these reactions, e.g., Dl sexadentate → Ll quinquedentate, are due to rotatory dispersion phenomena.[10] The quinquedentate chloro cobalt(III) complex of cyclohexanediaminetetraacetic acid could be obtained in solution in hydrochloric acid, but the solid could not be isolated, and the sexadentate complex reformed rapidly on dilution. Similarly, attempts to prepare the nitro complex were fruitless.

The quinquedentate aquo chromium(III) complex of l-propylenediaminetetraacetic acid could be synthesized directly from the optically active complexing agent and then isolated completely from the solution as the salt of the *trans*-dinitrobis-(ethylenediamine)-cobalt(III) cation. Despite extensive fractional crystallization, all fractions gave the same specific rotation, ($[\alpha]_{5461} = -800°$), as the levo isomer prepared by the resolution of the racemic complex with either optically active $[Coen_2(NO_2)_2]^+$ or $[Coen_2(C_2O_4)]^+$ ions. The levo isomer could not be racemized by boiling the aqueous solution. This is in marked contrast to the $[CrH_2O(EDTA)]$ anion which could not be resolved under a variety of conditions and with a range of resolving cations.[11] Levo-aquo-(l-propylenediaminetriacetato acetic acid)-rhodium(III) 1-hydrate, L-$[RhH_2O(l$-H·PDTA$)]·H_2O$, could be prepared from rhodium(III) hydroxide and l-H$_4$PDTA in an autoclave at 145°. The pale yellow substance was then crystallized fractionally from the reaction mixture. The major portion of the material, (~90%), had a strong levo rotation ($[\alpha]_D = -125$ to $-70°$), and the remainder a much smaller rotation ($[\alpha]_D = -30°$). The pure levo isomer, $[\alpha]_D = -159°$ could be obtained by repeated crystallization of the most active fractions in diffuse light. No isomer with a positive rotation could be detected even after transformation to the barium salt, Ba$[RhH_2O(l$-PDTA$)]_2$ and resolution through the d-$[Coen_2(NO_2)_2]^+$ cation. The possibility of partial stereospecificity was complicated by the mutarotation of the most active material in the presence of light and the observation that slight decarboxylation had occurred during the preparative reaction, which may have yielded small amounts of other complexes. The infrared spectrum of $[RhH_2O(H·PDTA)]·H_2O$ showed one peak at 1732 cm.$^{-1}$, due to the free carboxylic acid group, and a broader peak at 1620 cm.$^{-1}$ due to the coördinated carboxylate groups. A molecule of water must occupy the sixth coördination position, giving rise to the possibility of four isomers.[11] Small amounts of these isomers may also account for the lower rotations of the more soluble fractions. Unlike the optical forms of the $[RhH_2O(EDTA)]^-$ ion, which racemized, no rotational change occurred when solutions of L-Ba$[RhH_2O(l$-PDTA$)]_2$ were heated in the dark at 96° for 6 hr. However, solutions of $[RhH_2O(H·PDTA)]·H_2O$ and its barium salt slowly lost their activity at 20° in the diffuse laboratory light. As with the rhodium ethylenediaminetetraacetic acid complex,[11] the absorption band with a maximum at 348 mμ appeared to be responsible for the rotational change. When exposed to the light from a 125 watt mercury lamp, the rotation of the barium salt decreased from $[\alpha]_{5461} = -168°$ to $-55°$ within 2 hr. and then remained constant. Likewise, the rotation of L-$[RhH_2O(l$-H·PDTA$)]$ changed from $[\alpha]_{5461} = -158°$ to $-50°$ in a similar exposure time. When the fully mutarotated solutions were kept in the dark, they regained their initial rotations in about three days and then remained constant. The cycle of rotational changes in the light and in the dark seemed to be capable of many repetitions.

The possible mechanism of the photoracemization of the $[RhH_2O(EDTA)]^-$ ion has been discussed previously.[11] The mutarotation of the $[RhH_2O(PDTA)]^-$ ion may arise in a similar manner from photo-induced breaking of a carboxylate-rhodium bond, followed by aquation. The diaquo isomer(s) would not be inactive, even if the asymmetry about the metal were lost, because of the optical activity of the complexing acid. The absorption spectra of the exposed and unexposed solutions were almost identical, with absorption maxima at 295 and 348 mμ. This requires the not unreasonable postulate that the monaquo and diaquo species have almost the same absorption curves. Dilute potassium permanganate was not reduced by the solutions that had been exposed to light, nor did the rotation change. The rotational changes are therefore not due to photoreduction, followed by slow oxidation in the dark.

Kirschner[12] concluded from infrared studies and the asymmetric equilibrium in the presence of the *levo* quinine cation that ethylenediaminetetraacetic acid was sexadentate in its Cu(II) complex and, further, that the enantiomorphous forms were too labile to permit isolation. X-Ray powder photographs have shown the isomorphism of the salts Ba$[NiH_2O(EDTA)]·4H_2O$ and Ba$[CuH_2O(EDTA)]$ ·4H$_2$O and of the acidic complexes H·$[NiH_2O-(EDTA)]$ and H$[CuH_2O(EDTA)]$. The recent complete crystal analysis[13] of the $[NiH_2O(EDTA)]^-$ anion has demonstrated that the complexing agent is quinquedentate in function, with a molecule of water in the plane of the nitrogen atoms occupying the sixth coördination position about the nickel atom. It can be concluded that the stereochemistry of the copper atom in the $[CuH_2O(EDTA)]^-$ anion must be the same. Though attempts to resolve the $[CuH_2O(EDTA)]^-$ anion were fruitless, resolution of D,L-$[CuH_2O(d,L$-PDTA$)]^-$ anion was easily carried out through the d or l-$[Coen_2-(NO_2)_2]^+$ cation. Elimination of the copper from the isomeric anions D-$[CuH_2O(l$-PDTA$)]^-$ and L-$[CuH_2O(d$-PDTA$)]^-$ yielded the pure optical forms of the acid H$_4$PDTA·H$_2$O in good yield.

Nature of Stereospecific Influence.—Courtauld models of the sexadentate cobalt complex showed that one isomer was sterically hindered. This could be demonstrated most convincingly by constructing the model of one optical isomer of the $[Co(EDTA)]^-$ anion and then replacing, in turn, one or other of the hydrogen atoms of a methylene group linking the two nitrogen atoms. In this

(10) For convention adopted in expressing configuration, see F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1956).

(11) F. P. Dwyer and F. L. Garvan, *ibid.*, **82**, 4823 (1960).

(12) S. Kirschner, *ibid.*, **78**, 2372 (1956).

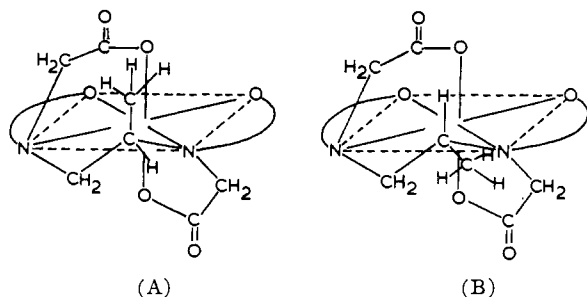(13) H. H. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

(A)   (B)

Fig. 1.—The strained (A), Ll form of the [Co(l-PDTA)]$^-$ ion showing atom crowding due to the CH$_3$ group of the asymmetric carbon atom, and (B), the strain-free Dl form. In (B) the CH$_3$ group lies in front of the lower chelate ring, and below the plane containing the apparently close nitrogen atom, which is not subject to interference.

way, one obtained, in turn, the optical isomers of propylenediaminetetraacetic acid attached in one configuration of the metal complex. With one isomer, designated on the experimental evidence as Dl, the complex was as strainless as in the original [Co(EDTA)]$^-$ anion. In the other isomer, (Ll), the methyl group crowded the carbonyl group of the acetic acid residue attached to the nitrogen atom remote from the asymmetric carbon atom. This is shown in outline in Fig. 1. The extent of the atom-crowding did not seem sufficient to exclude completely the Ll isomer, but a free-energy difference of only 3 kcal./g. mole between the strained and unstrained isomers would mean that less than 1% of the strained isomer would be present in the equilibrium mixture. It will be evident that similar atom-crowding would occur in the metal complexes of isobutylenediamine- and *meso*-2,3-butanediaminetetraacetic acids irrespective of the optical configuration of their metal complexes and should be reflected in markedly reduced stabilities.

Models of the isomers of the sexadentate cobalt-(III) complexes with cyclohexanediaminetetraacetic acid showed that two, designated Dl, Ld, were strain free but the other pair (Dd, Ll), could be formed only by considerable distortion of the cyclohexane ring and probably would be completely excluded.

The optical stability of the quinquedentate [CrH$_2$O(l-PDTA)]$^-$ and [CuH$_2$O(l-PDTA)]$^-$ ions which contrasts so strongly with the optical lability of the EDTA complexes, as well as the behavior of the [RhH$_2$O(l-PDTA)]$^-$ ion in the light-dark cycle, are consistent with the strong stereospecificity imposed by the ligand. It will be evident that the usual intermediate in the racemization process, *i.e.*, a form lacking enantiomorphism about the metal atom, whether arising from thermal or photo-activation, must necessarily revert to the original optical form. It can be seen from Fig. 1 that crowding due to the methyl group of the asymmetric carbon atom occurs in the quinquedentate (or even quadridentate), complexes provided that the carboxylate groups are attached in the polar (1,6), positions. Courtauld models show that the carboxylate groups of EDTA, attached to a metal in the plane of the nitrogen atoms, are strained. This is confirmed by the crystal structure of the [NiH$_2$O(EDTA)]$^-$ anion[13] in which a

molecule of water is attached in one of the positions in the plane.

Experimental

Unless otherwise stated all rotations were measured at 20° in a 1 dm. tube.

L-Aquo (*l*-propylenediaminetriacetato-acetic acid)-rhodium(III) 1-Hydrate.—Rhodium(III) hydroxide, from rhodium nitrate solution containing 1.11 g. of rhodium, was suspended in water (70 ml.) containing *l*-propylenediaminetetraacetic acid 1-hydrate, the mixture placed in a Pyrex tube, which was sealed. and heated at 145° in an autoclave. The preparation was done in triplicate. After 6 hr., the tubes were cooled and opened carefully, because of a small internal pressure, probably the result of slight decarboxylation of the acid. A small amount of rhodium hydroxide and metal were filtered off and the yellow filtrate evaporated to 70 ml. on the steam-bath in a current of air. Ethanol (120 ml.) was added at 50°C., whereupon fraction 1 crystallized. Six more fractions were obtained by gradual evaporation and addition of alcohol and acetone. All fractions were levorotatory, ranging from [α]$_{5461}$ = −158° for fraction (1) to −103° for fraction 4, for a total wt. of material of 11.4 g. The three last fractions (1.1 g.) had an average rotation of −40° (yield 12.6 g., 95%). Fractional crystallization of the first fraction failed to increase the rotation. The infrared spectrum of the complex in Nujol showed in the carbonyl region two bands at 1732 cm.$^{-1}$ (free carboxylic acid), and 1620 cm.$^{-1}$ (coördinated carboxyl groups).

Anal. Calcd. for [RhH$_2$O(C$_{11}$H$_{15}$N$_2$O$_8$)]·H$_2$O: C, 29.88; H, 4.33; N, 6.34. Found: C, 29.88; H, 4.48; N, 6.18.

L-Barium Aquo (*l*-Propylenediaminetriacetatoacetate)-rhodium(III) 7-Hydrate.—The more soluble fractions of the acid complex above (6.4 g.) were dissolved in water containing barium hydroxide 8-hydrate (2.36 g.) and mixed with a solution of *d*-[Coen$_2$(NO$_2$)$_2$]$_2$SO$_4$, (from *d*-[Coen$_2$(NO$_2$)$_2$] Br,[14] (5.22 g.) and silver sulfate (2.33 g.), in 200 ml. water). After stirring at 60° for 0.5 hr., the mixed barium sulfate-silver bromide precipitate was filtered off, the filtrate evaporated at 55° to 30 ml., and then cooled in ice. The yellow diastereoisomer was collected, washed with alcohol, acetone and air-dried. A 0.25% solution gave [α]$_D$ = −82°, [α]$_{5461}$ = −94°. The rotation was unchanged by recrystallization from warm water.

Anal. Calcd for [Co(C$_2$H$_8$N$_2$)$_2$(NO$_2$)$_2$][RhH$_2$O(C$_{11}$H$_{14}$N$_2$O$_8$)]·H$_2$O: C, 25.30; H, 4.81; N, 15.73. Found: C, 25.11; H, 4.65; N, 15.61.

The diastereoisomer (1.0 g.) was shaken with water (7 ml.) containing barium perchlorate (5 g.) and then cooled to 4° and the perchlorate of the resolving agent removed. The active barium salt precipitated from the filtrate with ethanol, was recrystallized twice from water (5 ml.), by adding ethanol. A 0.25% solution gave [α]$_{5461}$ = −168° and [α]$_D$ −140°. The barium salt recovered from the filtrate, after the separation of the diastereoisomer above, had a small levo rotation, [α]$_D$ = −22°, but could not be characterized analytically.

Anal. Calcd. for Ba[RhH$_2$O(C$_{11}$N$_{14}$N$_2$O$_8$)]$_2$·7H$_2$O: C, 23.81; H, 4.18; N, 5.05. Found: C, 23.59; H, 4.02; N, 5.28.

D,L-Aquo (*d,l*-Propylenediaminetriacetato-acetic acid)-chromium(III) 1-Hydrate.—Racemic H$_4$(PDTA) (31 g., 0.1 mole) dissolved in lithium hydroxide 1-hydrate (8 g., 0.2 mole) in water (50 ml.), at 60° was treated with chromium (III) nitrate 9-hydrate (40 g., 0.1 mole) and the mixture boiled for 0.5 hr. Concentrated nitric acid (10 ml.) was then added to the cooled, dark violet solution, which slowly deposited deep purple granules. After two days the product was collected, washed with alcohol and recrystallized by dissolution in 10% sodium acetate solution (40 ml.), followed by acidification to *p*H 1 with sulfuric acid (yield 25 g. 70%).

Anal. Calcd. for [CrH$_2$O(C$_{11}$H$_{15}$N$_2$O$_8$)]·H$_2$O: C, 33.76; H, 4.89; N, 7.16. Found: C, 33.38; H, 4.76; N, 7.14.

The infrared spectrum in Nujol showed, in the carbonyl region, peaks at 1725 and 1662 cm.$^{-1}$ ascribed, respectively, to free carboxylic acid and coördinated carboxylate groups.

(14) F. P. Dwyer and F. L. Garvan. "Inorganic Syntheses," E. Rochow, Ed., Vol. VI, in publication.

trans - Dinitrobis - (ethylenediamine) - cobalt(III) -D - aquo-
(propylenediaminetriacetatoacetate) - chromate(III) 2 - Hy-
drate.—The racemic chromium complex above (3.9 g.) was
shaken with barium hydroxide solution (30 ml.) containing Ba-
$(OH)_2 \cdot 8H_2O$, (1.6 g.) until completely dissolved and then
addeo to a solution of d-[Coen$_2$(NO$_2$)$_2$]$_2$SO$_4$, prepared from d-
[Coen$_2$(NO$_2$)$_2$]Br[14] (3.6 g.) and silver sulfate (1.6 g.), dissolved
in water (200 ml.), at 60°. The mixture was evaporated at
55° in a stream of air to a volume of 80 ml. and the mixed
barium sulfate-silver bromide precipitate removed. The
filtrate was further evaporated to 30 ml., and on the addition
of acetone, the maroon colored diastereoisomer l-[Coen$_2$-
(NO$_2$)$_2$] D-[CrH$_2$O(d-PDTA)]·H$_2$O separated. It had a
small positive rotation in the mercury green line and was re-
crystallized from water by adding acetone. A 0.01% solu-
tion gave $[\alpha]_{5461} = +800°$, and further recrystallization did
not improve this value.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$(NO$_2$)$_2$]CrH$_2$O(C$_{11}$H$_{14}$N$_2$-
O$_8$)·H$_2$O: C, 27.24; H, 5.18; N, 16.95. Found: C,
27.02; H, 5.11; N, 16.86.

The resolving agent was removed as the iodide by adding
potassium iodide to an aqueous solution of the diastereoiso-
mer and the potassium salt of the chromium complex caused
to crystallize by the addition of alcohol. The potassium
salt then was dissolved in an aqueous solution of *trans*
[Coen$_2$(NO$_2$)$_2$(OOCCH$_3$)] (from the *trans*[15] chloride and silver
acetate) and alcohol added, when the required salt crystal-
lized. A 0.01% solution gave $[\alpha]_{5461} = +900°$. The res-
olution was performed in the same manner as above using
l-[Coen$_2$(C$_2$O$_4$)]$_2$SO$_4$[16] as the resolving agent with an identical
result. Finally, [CrH$_2$O(H·PDTA)] was prepared as above,
using d-H$_4$PDTA instead of the racemic form. At the end
of the heating period, the reaction mixture was brought to
pH 6, and the whole of the chromium complex precipitated
with *trans*-[Coen$_2$(NO$_2$)$_2$(OOCCH$_3$)]. This material gave
$[\alpha]_{5461} = +900°$, and the rotation was unchanged despite
repeated crystallization.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$(NO$_2$)$_2$][CrH$_2$O(C$_{11}$H$_{14}$-
N$_2$O$_8$)]·2H$_2$O: C, 26.46; H, 5.34; N, 16.50. Found: C,
26.9; H, 5.26; N, 16.3. By the use of d-[Coen$_2$(NO$_2$)$_2$]Br,
the levo isomer was isolated in an analogous manner, $[\alpha]_{5461}$
$= -900°$

Anal. Found: C, 26.58; H, 5.30; N, 16.51.

Hydrogen Aquo (propylenediaminetriacetato-acetic acid)-
cuprate(II) 1-Hydrate.—Finely powdered dl-H$_4$PDTA·H$_2$O,
(30.6 g.) gradually was added to a boiling solution of copper
(II) acetate, 1-hydrate (20 g.), in water (200 ml.). When
dissolution was complete the blue solution was evaporated
on the steam-bath to 80 ml. and cooled. The deep blue
crystals were washed with ethanol, (yield, 38 g., 94%).

Anal. Calcd. for H[CuH$_2$O(C$_{11}$H$_{15}$N$_2$O$_8$)]·H$_2$O: C, 32.71;
H, 4.99; N, 6.94. Found: C, 32.25; H, 5.21; N, 6.94.

D-Barium Aquo (*l*-propylenediaminetriacetatoacetate)-
cuprate(II) 2-Hydrate and *l*-Propylenediaminetetra-acetic
Acid.—The acid H[CuH$_2$O(H·PDTA)]·H$_2$O above (12 g.) in
water (150 ml.) was neutralized with Ba(OH)$_2$·8H$_2$O (4.8
g.) in water (150 ml.) and the resulting barium salt added to
a solution (500 ml.) containing d-[Coen$_2$(NO$_2$)$_2$]Br (10.5 g.)
and silver sulfate (4.8 g.). The mixture was evaporated at
50–60° to 400 ml., the mixed barium sulfate-silver bromide
precipitate removed and the evaporation continued to 90
ml., whereupon the diastereoisomer d-[Coen$_2$(NO$_2$)$_2$] D-
[CuH$_2$O(l-H·PDTA)]·H$_2$O separated. The yellow-green
solid was washed with 50% aqueous alcohol and alcohol. A
0.4% solution in 10% sodium acetate gave $[\alpha]_{5461} = +130°$.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$(NO$_2$)$_2$][CuH$_2$O(C$_{11}$H$_{15}$-
N$_2$O$_8$)]·H$_2$O: C, 27.48; H, 5.07. Found: C, 27.22; H,
5.16.

The diastereoisomer (9.2 g.) was ground up in a mortar
with Ba(OH)$_2$·8H$_2$O (2.1 g.) BaI$_2$·2H$_2$O (7.0 g.) and water
(20 ml.) to precipitate the insoluble iodide of the resolving
agent, which was then filtered off. The blue solid, precip-
itated from the filtrate with ethanol, was recrystallized
twice from a little water by adding alcohol. A 0.4% solu-
tion gave $[\alpha]_{5461} = +73°$. The same substance was pre-
pared directly from l-H$_4$PDTA·H$_2$O, (3.24 g.) and a boiling
aqueous solution of CuSO$_4$·5H$_2$O (2.5 g.) by adding Ba-

$(OH)_2 \cdot 8H_2O$ (6.2 g.) in hot water (100 ml.). After 10 min-
utes boiling, removal of the barium sulfate precipitate, con-
centration to 30 ml., and adding ethanol (100 ml.), the
crystalline material that separated gave $[\alpha]_D = +74°$.

Anal. Calcd. for Ba[CuH$_2$O(C$_{11}$H$_{14}$N$_2$O$_8$)]·2H$_2$O: C,
23.70; H, 3.62; N, 5.03. Found: C, 23.92; H, 4.16;
N, 5.13.

For the recovery of the l-H$_4$PDTA, the barium salt (5.56
g.) in hot water (100 ml.) was treated with exactly one equiv-
alent of sulfuric acid (10.0 ml., 1.0 N), heated to boiling
and saturated with hydrogen sulfide. The mixed barium
sulfate-copper sulfide precipitate was removed, the filtrate
evaporated to 30 ml. and cooled. Traces of inactive acid
were removed and the solution concentrated to 10 ml. and
allowed to crystallize at 4°. The white crystals were the
pure 1-acid, $[\alpha]_D = -47°$ (yield 2 g.). The d-isomer was
recovered from the filtrate from the separation of the di-
astereoisomer above, by concentration at 50–60° in a stream
of air to 20 ml. A mixture of Ba(OH)$_2$·8H$_2$O (2.1 g.) and
BaI$_2$·2H$_2$O (7 g.) was added, the insoluble [Coen$_2$(NO$_2$)$_2$]I
removed and the barium salt of the copper complex precip-
itated with alcohol as before. The pure dextro acid was
recovered in the same manner as the levo acid ($[\alpha]_D = +47°$,
yield 2.0 g.).

Isomorphism of Quinquedentate Copper and Nickel Com-
plexes.—The complexes H[CuH$_2$O(H·EDTA)] and H[Ni-
H$_2$O(H·EDTA)] were prepared as described previously,[12,13]
and the barium salts Ba[MH$_2$O(EDTA)]·4H$_2$O obtained
therefrom by neutralization with barium hydroxide and pre-
cipitation with methanol. The X-ray powder photographs,
obtained with Cu Kα radiation and a camera of 114.6 mm.
diameter, showed the complete isomorphism of the pairs of
complexes.

Cobalt Complexes Containing Quinquedentate Propyl-
enediaminetetraacetic Acid

(1) The D,L-Potassium-(d,1-propylenediaminetriacetato-
acetic acid)-chlorocobaltate(III) 2-Hydrate.—Racemic K-
[Co(d,l-PDTA)]·2H$_2$O[17] (10 g.) was stirred with con-
centrated hydrochloric acid (5 ml.) on the steam-bath until
almost dry. The resulting blue-green mass was cooled,
broken up, stirred with ice-water (15 ml.) and finally ethanol
(200 ml.). The crude salt (9.7 g.) was dissolved in cold 25%
potassium acetate solution (30 ml.) and concentrated hydro-
chloric acid (10 ml.) added to the deep blue solution. Potas-
sium chloride was washed out of the blue solid with cold
50% aqueous ethanol.

Anal. Calcd. for K[Co(C$_{11}$H$_{15}$N$_2$O$_8$)Cl]·2H$_2$O: C, 27.95;
H, 4.05; N, 5.93; Cl, 7.50. Found: C, 28.00; H, 4.05;
N, 5.92; Cl, 7.52.

(2) D-K[Co(d-H·PDTA)Cl]·2H$_2$O.—The racemic salt
above (2.3 g.) was dissolved in a solution of d-[Coen$_2$(NO$_2$)$_2$]
Cl (0.8 g.) in water (25 ml.) at 60°. The green diastereoiso-
mer d-[Coen$_2$(NO$_2$)$_2$] D-[Co(d-H·PDTA)Cl], that separated
on cooling, gave $[\alpha]_{5461} = +500°$. The resolving agent was
removed as the insoluble iodide in the usual way by grinding
with potassium iodide (5 g.), potassium acetate (2 g.) in
water (10 ml.). The active potassium salt separated on the
addition of ethanol (30 ml.) and concentrated hydrochloric
acid (1.3 ml.) to the filtrate. It was recrystallized from a
little water by adding ethanol. A 0.01% solution gave
$[\alpha]_{5461} = +800°$. A 0.01% solution of the active isomer,
($[\alpha]_{5461} = +0.08°$ in a 1 dm. tube.) treated with a small
crystal of mercury(II) nitrate changed color from blue to the
violet of the [Co(PDTA)]-anion and the rotation to $-0.10°$.
The expected rotation for full retention of configuration was
$-0.09_4°$. Conversely, pure L-K[Co(l-H·PDTA)Cl] was
obtained from D-K[Co(l-PDTA)] by treatment with hydro-
chloric acid as above and then recrystallization of the blue
solid from water by the addition of alcohol.

Anal. Calcd. for K[Co(C$_{11}$H$_{15}$N$_2$O$_8$)Cl]·2H$_2$O: C, 27.95;
H, 4.05; N, 5.93. Found: C, 28.20; H, 4.18; N, 6.0.

The levo isomer was isolated from the filtrate remaining
from the separation of the diastereoisomer d-[Coen$_2$(NO$_2$)$_2$]
D-[Co(d-H·PDTA)Cl] above, by precipitation with ethanol
(100 ml.). The pale blue salt (1.2 g.), after recrystalliza-
tion from water by adding ethanol, gave $[\alpha]_{5461} = -800°$.

Anal. Found: C, 27.73; H, 4.02; N, 5.98.

(15) H. F. Holtzclaw, D. P. Sheetz and B. D. McCarthy, "Inorganic
Syntheses" (IV), 176 (1953).

(16) A. Werner and J. Bosshart, *Ber.*, **47**, 2171 (1914).

(17) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955
(1959).

(3)   D,L-Sodium-(*d,l*-propylenediaminetriacetato-acetic acid)-nitrocobaltate(III) 1-Hydrate.—The complex anion was prepared in the same manner as the EDTA analog[18] from racemic propylenediaminetetraacetic acid, and, because of the high solubility of the sodium salt, isolated in the first place as the salt of the *trans*-dinitrobis-(ethylenediamine)-cobalt(III) cation, by stirring a slight excess of finely powdered [Coen$_2$(NO$_2$)$_2$]Cl into the reaction mixture. The fawn-colored product was recrystallized from hot water.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$(NO$_2$)$_2$][Co(C$_{11}$H$_{15}$N$_2$O$_8$)-NO$_2$]: C. 26.53; H, 4.60· N, 18.7. Found: C, 26.80; H, 4.93; N, 18.56.

The pure substance (13.8 g.) was ground up in a mortar with sodium iodide (12 g.), sodium acetate 3-hydrate (5 g.) and water (30 ml.) and kept at 5° for 0.5 hr. After removal of the [Coen$_2$(NO$_2$)$_2$]I, concentrated hydrochloric acid (3 ml.) was added to the brownish-purple filtrate, followed by a liter of ethanol. The fine mauve crystals, that separated after cooling in ice, were recrystallized from 0.2 *N* hydrochloric acid (30 ml.) by the addition of ethanol (300 ml.) and air dried.

Anal. Calcd. for Na[Co(C$_{11}$H$_{15}$N$_2$O$_8$)NO$_2$]·H$_2$O: C, 29.41; H, 3.82; N, 9.36. Found: C, 29.31; H, 3.97; N, 9.47.

(4)   L-Na[Co(*d*-H·PDTA)NO$_2$]·2H$_2$O.—The sodium salt above (2.2 g.) was dissolved in a solution of *d*-[Coen$_2$(NO$_2$)$_2$·Cl (0.8 g.) in water (20 ml.) at 65°. The chocolate diastereoisomer, *d*-[Coen$_2$(NO$_2$)$_2$ L-[Co(*d*-H·PDTA)NO$_2$)]·2H$_2$O, that separated almost immediately, was washed with icewater. A 0.01% solution gave [α]$_{5461}$ = −450°. The resolving agent was eliminated by grinding the diastereoisomer, (1.7 g.) in water (10 ml.) with sodium acetate 3-hydrate (2 g.) and sodium iodide (5 g.) at 5°. After filtration, hydrochloric acid (10 *N* 2.5 ml.) and alcohol (70 ml.) was added to the filtrate, when the *levo* sodium salt separated and was recrystallized from warm water by adding ethanol. A 0.01% solution gave [α]$_{5461}$ = −850°.

Anal. Calcd. for Na[Co(C$_{11}$H$_{15}$N$_2$O$_8$)NO$_2$]·2H$_2$O: C, 28.28; H, 4.10; N, 9.0. Found: C, 28.30; H, 4.12; N, 9.15.

The dextro isomer was obtained from the filtrate from the diastereoisomer above by adding ethanol (70 ml.), acetone (70 ml.), hydrochloric acid (3 *N*, 2 ml.) and ether (110 ml.) in that order at 5°. The mauve solid after recrystallization from water (9 ml.) by adding ethanol (30 ml.) gave [α]$_{5461}$ = +850°.

Anal. Found: C, 28.26; H, 4.12; N, 8.95.

Elimination of the nitro group to yield the sexadentate complex anion [Co(PDTA)] ⁻ was carried out as described previously[18] with urea and hydrochloric acid. After the reaction, the rotation [α]$_{5461}$ of a solution of D-Na[Co(*l*-H·PDTA)NO$_2$]·2H$_2$O, (0.0257 g.) in water (250 ml.) was + 0.10°. From the stoichiometry of the reaction and the value [α]$_{5461}$ = +1000° for D-K[Co(*l*-PDTA)]·3H$_2$O the expected value for complete retention of configuration was + 0.10°.

Resolution of *trans*-1,2-Cyclohexanediaminetetra-acetic Acid, and the Sexadentate Cobalt(III) Complex. D,L-Potassium (*d,l*-cyclohexanediamine-tetraacetato)-cobaltate (III) 3-Hydrate.—Racemic H$_4$CDTA (18.2 g., 0.05 mole) in water (400 ml.) containing potassium acetate (30 g.) was added to a solution of cobalt(II) acetate 4-hydrate (12.5 g., 0.05 mole) in water (100 ml.) followed by activated charcoal (5 g.) and hydrogen peroxide, (30%, 25 ml.). Air was drawn through the mixture for 24 hr., the charcoal removed, the filtrate evaporated to 80 ml. on the steam-bath in a current of air and then cooled to 5°. The red violet crystals were washed with alcohol and acetone and air-dried (yield, 19.8 g.; 80%).

Anal. Calcd. for K[Co(C$_{14}$H$_{18}$N$_2$O$_8$)]·3H$_2$O: C, 34.00; H, 4.89; N, 5.67. Found: C, 33.67; H, 4.99; N, 5.67.

The racemic barium salt was prepared in a similar manner using Ba(OH)$_2$·8H$_2$O (94.8 g.), racemic H$_4$CDTA (73 g.) in

water (1 liter) at 90°, and adding CoSO$_4$·7H$_2$O, (56.2 g.) in water (200 ml.). The mixture was allowed to cool to room temperature and oxidized in the presence of charcoal, as before. After filtration, the volume was reduced to 150 ml. and crystallization took place on cooling to 5° (yield, 84.5 g.; 77%).

Anal. Calcd. for Ba[Co(C$_{14}$H$_{18}$N$_2$O$_8$)]$_2$·9H$_2$O: C, 30.51; H, 4.57; N, 5.09. Found: C, 30.25; H, 4.70; N, 5.23.

D-Barium(cyclohexanediaminetetraacetato)-cobaltate(III) 9-Hydrate.—*Levo-cis-*dinitrobis-(ethylenediamine)-cobalt-(III) bromide (21.1 g.) was transformed to the sulfate by shaking with silver sulfate (9.4 g.) in water (800 ml.) at 60° and the mixture added, with shaking, to a solution to the racemic barium salt (33.1 g.) in water (200 ml.) at 60°. The mixture then was evaporated at 55° in a stream of air to 200 ml., filtered and the filtrate cooled to 5°. Crystallization was induced by the addition of a small amount of alcohol, and after 3 hr. the fine maroon crystals were collected (yield, 13.9 g., [α]$_{5461}$ = +700°). Recrystallization of the diastereoisomer, *l*-[Coen$_2$(NO$_2$)$_2$] D-[Co(*l*-CDTA)]·5H$_2$O did not improve the rotation. The resolving agent was removed by shaking with 40% barium iodide solution (40 ml.) and after filtration the barium salt of the complex precipitated by adding ethanol. A 0.01% solution gave [α]$_{5461}$ = +900°. No rotational charge occurred on heating the aqueous solution at 98° for 10 hr., nor on stirring for a day at 25° with activated charcoal.

Anal. Found: C, 30.28; H, 4.87; N, 5.09.

The levo isomer ([α]$_{5461}$ = − 900°) was prepared in the same manner using *d*-[Coen$_2$(NO$_2$)$_2$]Br to resolve the racemic complex or the partly resolved substance. This was recovered from the filtrate above by adding barium iodide, filtering and then precipitating with alcohol ([α]$_{5461}$ = −600°).

Anal. Found: C, 30.37; H, 4.98; N, 4.98. The potassium salts, prepared from the optically active barium salts by double decomposition with potassium sulfate, filtration and precipitation with alcohol gave [α]$_{5461}$ = ±1100°.

Anal. Calcd. for K[Co(C$_{14}$H$_8$N$_2$O$_8$)]·H$_2$O: C, 36.67; H, 4.40; N, 6.11. Found, L form: C, 36.46; H, 4.53; N, 6.10.

A blue solution resulted when L-K[Co(*d*-CDTA)]·H$_2$O (0.1 g.) was heated at 80° with concentrated hydrochloric acid for 5 min., but attempts to remove the excess acid led to regeneration of the original material. The blue substance in solution, however, gave [α]$_{5461}$ = +600° and was probably the chloro complex D-K[Co(*d*-H·CDTA)Cl].

d-trans-1,2-Cyclohexanediaminetetraacetic Acid.—The levo barium salt above (8.06 g.) in water (150 ml.) at 90° was treated with potassium sulfate (1.30 g.). Potassium cyanide (7.0 g.) was added to the filtered solution, which then was boiled until the color became greenish yellow. Complete oxidation to hexacyanocobaltate(III) ion was effected by adding hydrogen peroxide (5 ml., 3%), then acetic acid was added to *p*H 5 and the hydrogen cyanide boiled off. Copper(II) acetate 1-hydrate (9.0 g.) was added at 80°, the insoluble copper hexacyanocobaltate removed after cooling at 5° for 1 hr. The deep blue filtrate evaporated to 300 ml. then was shaken with two portions (100 ml.) of the hydrogen form of the cation exchange resin Zeo Karb 225 (20 NC), to remove all potassium and uncomplexed copper ions. After evaporation to 10 ml., blue plates of [Cu(*d*-H$_2$·CDTA)]·H$_2$O (3 g.) were deposited. The copper was removed by passing hydrogen sulfide in hot solution and the colorless solution of the acid *d*-H$_4$CDTA evaporated to 8 ml. A mixture of absolute ethanol (80 ml.) and acetone (20 ml.) was added, and after a day at 5° a faint pink solid (1.6 g.) had deposited. A second fraction (0.5 g.) was obtained by adding more acetone (70 ml.). The substance was recrystallized by dissolving in hot 95% acetic acid in the presence of a little charcoal, filtering, cooling and adding ether until slightly turbid. The product was collected, washed with cold glacial acetic acid, ethanol and then acetone. It was dried at 116°, 3 mm. pressure, to remove a variable amount of acetic acid of crystallization. The anhydrous acid (m.p. 237°) was soluble in water, and a 0.5% solution gave [α]$_D$ = +53° (2 dm. tube).

(18) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

Anal. Calcd. for $C_{14}H_{22}N_2O_8$: C, 48.54; H, 6.40; N, 8.09. Found: C, 48.57; H, 6.39; N, 8.03.

The levo acid prepared in the same manner from D-Ba-[Co(*l*-CDTA)]·9H₂O gave [α]D ▬ −53°.

Anal. Found: C, 48.41; H, 6.30; N, 8.06.

[Contribution from the University of Michigan, Ann Arbor, Michigan, and the Polytechnic Institute of Brooklyn, Brooklyn, New York]

An Investigation of the Complexes of Platinum(II) with Pyridine-2-aldoxime. *cis–trans* Isomerism[1]

By Chui Fan Liu and C. H. Liu

Chloride, bromide and tetrachloroplatinate(II) salts of the monohydrogen bis-pyridine-2-aldoxime platinum(II) ion have been prepared. The inner complex bis-pyridine-2-aldoxime platinum(II) dihydrate has also been obtained and has been shown to exist in both the *cis* or the *trans* configurations. The *cis* is converted to the *trans* by heating at 140° or by heating in 1 N hydrochloric acid followed by neutralization of the solution. The *trans* is converted into the *cis* by heating in 0.1 N hydrochloric acid, to form the intermediate monohydrogen bis-pyridine-2-aldoxime platinum(II) ion, and then neutralizing this ion with sodium hydroxide.

Introduction

Complexes of platinum(II) with both mono- and dioximes are known. The structure of the dimethyl glyoxime complex[2] of platinum(II) is probably similar to that of the inner complex nickel and palladium compounds. The two protons on the oxime groups are symmetrically located, and the complex affords a good example of intramolecular hydrogen bonding. Recently, Krouse and Busch[3] reported the preparation of an inner complex between platinum(II) and pyridine-2-aldoxime. The present study is concerned with this same subject but particularly with the *cis–trans* isomerism of the inner complex.

Since pyridine-2-aldoxime(A) is an unsymmetrical chelating ligand, the two-to-one complex with platinum(II) can assume either the *cis*(B) or the

A
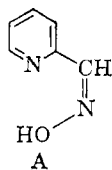
trans (C) form. These can lose their protons to give the corresponding inner complexes. Upon

B   C
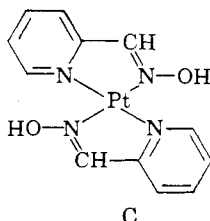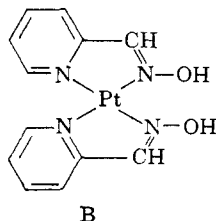
losing one proton the *cis* configuration should be capable of intramolecular hydrogen bond formation. In fact, it might be expected that the formation

of this extra chelate ring may render the *cis*-configuration more easily obtainable than the *trans*.

Experimental

Starting Materials.—Potassium chloroplatinate(II) was obtained by a modified method of Cooley and Busch.[4] Potassium hexachloroplatinate(IV) was reduced with hydrazine dihydrochloride. The resulting solution was evaporated until crystallization takes place, then cooled. The crystals obtained were washed with a small amount of water. Pyridine-2-aldoxime was obtained from the Aldrich Chemical Co. All the other chemicals used were of commercial reagent grade.

Infrared Spectra.—All spectra were obtained on a Perkin–Elmer Model 21 double beam instrument. Nujol Mulls were employed in all cases.

Analysis.—Platinum analyses were carried out by ignition. The microanalyses of carbon, hydrogen and nitrogen were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Preparation of Compounds. Monohydrogen-bis-(pyridine-2-aldoxime) Platinum(II) Chloride and Monohydrogen Bis-(pyridine-2-aldoxime) Platinum(II) Tetrachloroplatinate(II).—A solution of two grams of potassium tetrachloroplatinate(II) in approximately 100 ml. of water and a solution of 1.2 g. of pyridine-2-aldoxime in 50 ml. of 95% ethanol were mixed, and the mixture was heated on the steam-bath for 5 hr. During this time, orange crystals formed. After cooling, the crystals were filtered, washed thoroughly with distilled water, alcohol and ether and air dried. The product was found to be the tetrachloroplatinate-(II) salt.

Anal. Calcd. for $[Pt(C_6H_5N_2O)_2H]_2[^-PtCl_4]$: C, 23.74; H, 1.81; N, 9.23; Pt, 48.2. Found: C, 23.73; H, 1.90; N, 9.15; Pt, 47.6.

The mother liquor from the above preparation was evaporated on the steam-bath until crystallization began. On cooling, fine dark needles formed. These were washed successively with a small amount of cold water, 95% alcohol and ether and were dried in vacuum at room temperature. This compound proved to be the monochloride.

Anal. Calcd. for $[Pt(C_6H_5N_2O)H]Cl$: C, 30.44; H, 2.31; N, 11.8; Pt, 41.2. Found: C, 29.3; H, 2.65; N, 11.1; Pt, 41.0.

Monohydrogen Bis-(pyridine-2-aldoxime) Platinum(II) Bromide.—Two tenths of a gram of monohydrogen bis-(pyridine-2-aldoxime) chloride was dissolved in about 30 ml. of water. Excess sodium bromide was added and crystals immediately formed. These were filtered, washed with distilled water and recrystallized from water.

(1) Part of this work was done at the University of Connecticut, Storrs, Conn.

(2) J. Pech, M. Polster and A. Rezabek, *Chem. Listy*, **43**, 180–182 (1949).

(3) R. A. Krouse, and D.H. Busch, *J. Am. Chem. Soc.*, **82**, 4830 (1960).

(4) W. E. Cooley and D. H. Busch, "Inorganic Synthesis," Vol. V. McGraw-Hill Book Co., New York, N. Y., p. 208.