mediate. A similar observation was made also for the competition studies with $[Co(NH_3)_5]^{3+}$.[14]

Surprisingly the PO_4^{3-} and SO_4^{2-} ions do not appear to be much more efficient than Y^- in scavenging the intermediate. Also the failure to observe measurable amounts of phosphate complex from the base hydrolysis of the bromo and nitrato complexes when it does appear from the chloro and iodo reactions is a puzzling feature of the results. However, other species appeared on the column which were not recovered. Also the sulfato complex absorbed maximally at 535 mμ instead of the expected 515 mμ and it is conceivable that $[Co(NH_3)_4SO_4]^+$ was the isolated product. In general the reactions with the multivalent ions appeared to be more complicated than those with the monovalent ions and they were not investigated further.

Acknowledgment. The authors wish to thank the Microanalytical Unit of the John Curtin School of Medical Research, Australian National University, for the N and H analyses.

The Stereochemistry of Complex Inorganic Compounds. XXXIII.[1] Reactions of Optically Active α-Dichlorotriethylenetetraminecobalt(III) Cation with Optically Active Propylenediamine

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Contribution from the William A. Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois. *Received April 25, 1966*

Abstract: The reaction of optically active $\alpha[CoCl_2(trien)]^+$ with racemic or optically active propylenediamine in aqueous solution leads to the formation of β-$[Co(pn)(trien)]^{3+}$ with an inversion of configuration about the cobalt atom. Several of the possible optical isomers have been prepared and their ORD curves measured. There seems to be only a minor stereospecific effect in the reaction which produces the complex, $[Co(pn)(trien)]^{3+}$. Complexes in which the chelate rings are in the same positions show almost the same rotatory dispersion curves, irrespective of the sign of rotation of the propylenediamine. It is believed that the inversion of configuration which is produced by the reaction of α-$[CoCl_2(trien)]^+$ with propylenediamine in aqueous solution, like that with other bases, proceeds by a base hydrolysis through the formation of β-$[Co(OH)_2(trien)]^+$ as an inverted intermediate.

In a previous paper,[1a] it was reported that under certain conditions optically active α-$[CoCl_2(trien)]^+$ reacts with ethylenediamine with almost complete inversion to the β configuration. The analogous reaction with 1,2-propanediamine (propylenediamine) would be expected to follow the same course, but the dissymmetry of the propylenediamine molecule may introduce stereospecific effects which will determine the ease of formation and the stabilities of the several possible isomers of the product. The reaction is of particular interest because the formation of a complex of this type, containing one optically active ligand, provides a simple example of the influence of stereospecific factors in optical inversions in the reactions of complexes.

Figure 1 shows the structures of the possible isomers of $[Co(pn)(trien)]^{3+}$. Several studies on the preparation of optically active complexes containing optically active ligands have been reported.[2-4] Studies by Dwyer and his co-workers on stereospecific effects in mixed ethylenediamine–propylenediamine complexes have shown that the stereoselectivity is relatively small energetically, but still sufficient to influence greatly the relative yields of the isomers formed.[5-7] Conformational analyses of complexes of ethylenediamine and propylenediamine,[8] based on X-ray measurements of bond lengths and bond angles,[9] has given a rational explanation for the differences in stability between the various isomers of complexes containing propylenediamine.

In the reaction of α- or β-$[CoCl_2(trien)]^+$ with propylenediamine, one might expect the formation of strain-free rings, with the cobalt–propylenediamine ring in a staggered, or *gauche*, form as it is in $[Co(pn)(en)_2]^{3+}$.[8] However, the presence of an additional chelate ring (between the two secondary nitrogen atoms and the cobalt atom) introduces stereochemical effects of unknown magnitude. Supposedly, the most stable structure will be that in which there is the least repulsion between the four chelate rings, taken as a whole. If stereospecific influences pay little or no part in the reaction, the optical activity of the product should be essentially the same, whether *d*- or *l*-propylenediamine is used. On the other hand, if the incoming propylenediamine molecule subjects the complex to strong stereospecific influences, certain isomers of the complex

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(1) (a) Paper XXXI: E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 88, 1125 (1966); (b) paper XXXII: T. Habu and J. C. Bailar, Jr., *ibid.*, 88, 1128 (1966).

(2) I. Lifschitz, *Z. Physik. Chem.*, **114**, 493 (1925).

(3) F. M. Jaeger and H. B. Blumendal, *Z. Anorg. Allgem. Chem.*, **175**, 161 (1928).

(4) J. C. Bailar, Jr., and J. P. McReynolds, *J. Am. Chem. Soc.*, **61**, 3199 (1939).

(5) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 1043 (1959).

(6) F. P. Dwyer, F. L. Garvan, and A. Schulman, *ibid.*, **81**, 290 (1959).

(7) F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5269 (1959).

(8) E. J. Corey and J. C. Bailar, Jr., *ibid.*, **81**, 2620 (1959).

(9) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 30, 158 (1957).

Table I. Reaction of Optically Active α-[CoCl$_2$(trien)]$^+$ with Racemic Propylenediamine in Aqueous Solution at 25°[a]

Form of starting complexes	Products	α^{25}D[b,c]	$[\alpha]^{25}$D[c]
D*-α-[CoCl$_2$(trien)]Cl	L*-β-[Co(r′-pn)(trien)]Cl$_3$	-0.0136 ± 0.0010	-65 ± 5
L*-α-[CoCl$_2$(trien)]Cl	D*-β-[Co(r′-pn)(trien)]Cl$_3$	$+0.0144$	$+72$
rac-α-[CoCl$_2$(trien)]Cl	rac-β-[Co(r′-pn)(trien)]Cl$_3$	0	0

[a] It is understood that a single molecule of propylenediamine cannot be racemic. The symbol r′ is used here to indicate that the pn ligand may be either *d* or *l*. Stereoselectivity may influence the ratio of *d*- and *l*-pn molecules which enter the optically active complex ion. [b] 0.2% aqueous solution. [c] Throughout the paper α^{25}D is expressed in deg/cm and $[\alpha]^{25}$D in deg × 100 dm × g of solute.

Table II. The Ultraviolet Spectra of the Products in Aqueous Solution

Complexes[a]	Adsorption maximum ν_1, 10^3 cm^{-1} (log ϵ)	 ν_2, 10^3 cm^{-1} (log ϵ)	 ν_3, 10^3 cm^{-1} (log ϵ)
L*-β-[Co(r′-pn)(trien)]Cl$_3$	21.23 (2.09)	29.50 (2.08)	45.05 (3.97)
D*-β-[Co(r′-pn)(trien)]Cl$_3$	21.23 (2.10)	29.50 (2.08)	45.05 (3.97)
rac-β-[Co(rac-pn)(trien)]Cl$_3$	21.23 (2.09)	29.50 (2.08)	45.05 (3.98)

[a] For an explanation of the symbol r′, see footnote *a*, Table I.

will be formed preferentially, and this will be reflected in the optical activity of the product.

We wish to report here the optical inversion observed in the reaction between the optically active complex and the optically active ligand.

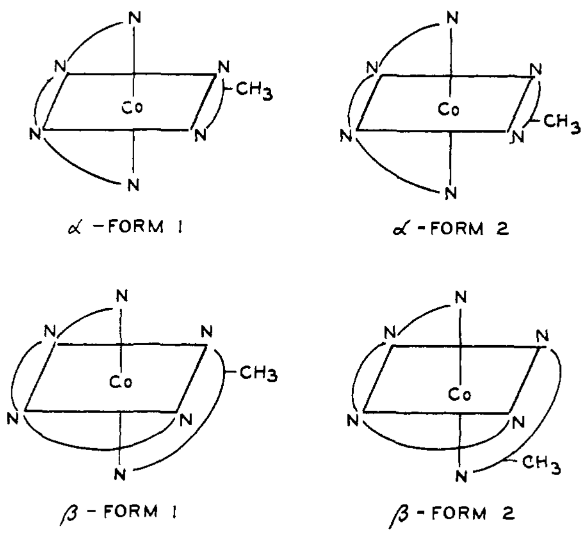

Figure 1. Structures of four possible isomers of [Co(pn)(trien)]$^{3+}$. (There are four enantiomorphs not shown.)

Results and Discussion

The reaction of D*- or L*-α-[CoCl$_2$(trien)]$^+$ with excess racemic propylenediamine in aqueous solution at room temperature gives the β form of [Co(pn)(trien)]$^{3+}$ with inversion of configuration of the complex as shown by the rotatory dispersion curves (Figure 2). It was also shown that the two products are enantiomers and give identical ultraviolet spectra (see Tables I and II).

The products show the same ultraviolet spectra, but the data do not indicate the extent of stereoselectivity, for pairs of complexes such as β-[Co(*l*-pn)(trien)]$^{3+}$ and β-[Co(*d*-pn)(trien)]$^{3+}$ might have about the same optical activity at any given wavelength, for in cases of this sort the activity of the complex as a whole often overshadows that of an optically active ligand.

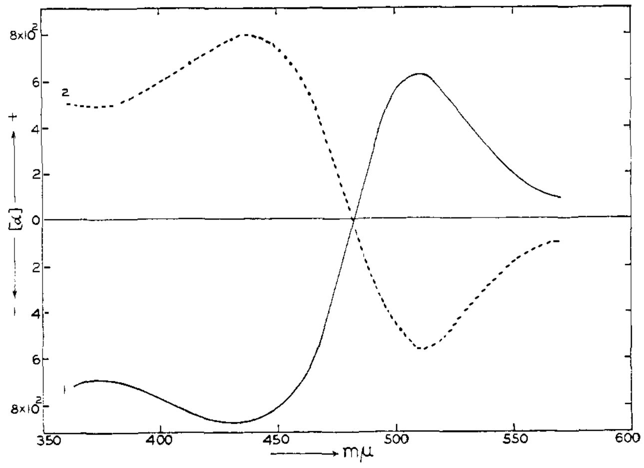

Figure 2. Optical rotatory dispersion curves of (1) (+)-D-β-[Co(r′-pn)(trien)]Cl$_3$, (2) (−)-D-β-[Co(r′-pn)(trien)]Cl$_3$.

The reactions between the optically active complexes and optically active ligands at room temperature gave similar results, each producing predominantly one optically active isomer. The results are summarized in Table III and Figure 3. It has been shown by Dwyer and co-workers that in cases of this sort the propylenediamine does not suffer any racemization upon coordination.[6,7] All of the isomers shown in Table III were obtained in good yield and all are stable in aqueous solution at room temperature. Figure 3 shows that D*-β-[Co(*d*-pn)(trien)]$^{3+}$ and L*-β-[Co(*l*-pn)(trien)]$^{3+}$ are enantiomers. In the ORD curves, the maxima of optical activity between the two differ by about 10 mμ.

The reaction of rac-[CoCl$_2$(trien)]$^+$ with optically active propylenediamine under similar conditions gives rac-[Co(*d*- or *l*-pn)(trien)]$^{3+}$ with essentially the optical activity of the coordinated ligand. A slight stereospecificity due to the optically active ligand may be present. The results are summarized in Table IV.

The optical rotatory dispersion curves show that these materials have equal but opposite rotatory power (Figure 4). The maxima of optical activity are shifted about 30 mμ toward the shorter wavelengths relative to those of D*- or L*-[Co(r′-pn)trien]$^{3+}$. This is

Table III. Reaction between Optically Active Complex and Optically Active Ligand in Aqueous Solution at 25°

Form of starting complexes	Reagents	Products	α^{25}D[a]	$[\alpha]^{25}$D
D*-α-[CoCl$_2$(trien)]Cl	*d*-pn	L*-β-[Co(*d*-pn)(trien)]Cl$_3$	−0.022 ± 0.0010	−110 ± 5
D*-α-[ClCl$_2$(trien)]Cl	*l*-pn	L*-β-[Co(*l*-pn)(trien)]Cl$_3$	−0.024	−120
L*-α-[CoCl$_2$(trien)]Cl	*d*-pn	D*-β-[Co(*d*-pn)(trien)]Cl$_3$	+0.022	+110
L*-α-[CoCl$_2$(trien)]Cl	*l*-pn	D*-β-[Co(*l*-pn)(trien)]Cl$_3$	+0.023	+115

[a] 0.2% aqueous solution.

Table IV. Reaction of *rac*-α-[CoCl$_4$(trien)]$^+$ with Optically Active Propylenediamine in Aqueous Solution at 25°[a]

Form of starting complexes	Reagent	Products	α^{25}D[b]	$[\alpha]^{25}$D
rac-α-[CoCl$_2$(trien)]Cl	*d*-pn	*R'*-β-[Co(*d*-pn)(trien)]Cl$_3$	−0.0096 ± 0.0010	+48 ± 5
rac-α-[CoCl$_2$(trien)]Cl	*l*-pn	*R'*-β-[Co(*l*-pn)(trien)]Cl$_3$	+0.0100 ± 0.0010	+50

[a] The symbol *R'* denotes a complex which contains one molecule of *d*- or *l*-pn but is otherwise racemic. [b] 0.2% aqueous solution.

probably due to the vicinal contributions ([Co(*l*- or *d*-pn)trien]$^{3+}$) and configurational contributions (D- or L-[Co(*r'*-pn)(trien)]$^{3+}$). The absolute configuration of [Co(*d*-pn)$_3$]$^{3+}$ is the same as that of (+)-D-[Co(en)$_3$]$^{3+}$,[8-10] and (+)-D-[CoCl$_2$(en)$_2$]$^+$, (+)-D-α-[CoCl$_2$(trien)]$^+$, and (+)-D-β-[CoCl$_2$(trien)]$^+$ have the same configuration.[11] Therefore, (+)-D-β-[Co(pn)(trien)]$^{3+}$ should have the same configuration about the central atom as (+)-D-[Co(en)$_3$]$^{3+}$. On the other hand, according to the results of equilibrium studies on the [Co(en)$_2$(*l*-pn)]$^{3+}$ system, the (+)-D complex was almost twice as abundant as the corresponding (−)-D one with a different configuration of chelate ethylenediamine rings but the same configuration of the propylenediamine ring.[7] The reaction of propylenediamine with optically active α-[CoCl$_2$(trien)]$^+$ was accompanied by a smaller degree of optically active change. It is possible to show that the stereoselectivity of both propylenediamine and the complex ion in the above substitution reaction are relatively small and are insufficient to influence greatly the relative optical activities of the products obtained.

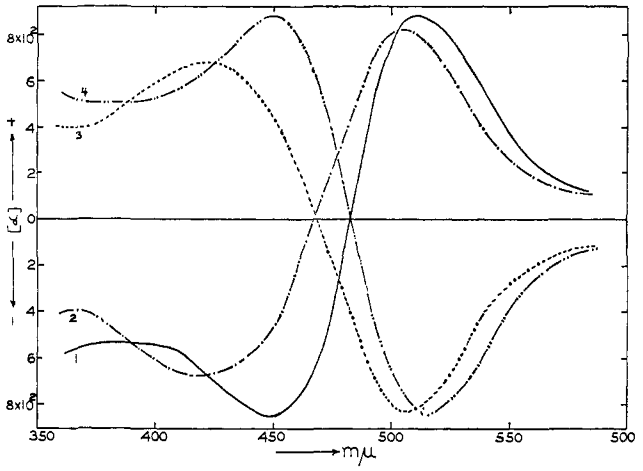

Figure 3. Optical rotatory dispersion of (1) (+)-D-β-[Co(*d*-pn)(trien)]Cl$_3$, (2) (+)-D-β-[Co(*l*-pn)(trien)]Cl$_3$, (3) (−)-D-β-[Co(*d*-pn)(trien)]Cl$_3$, (4) (−)-D-β-[Co(*l*-pn)(trien)]Cl$_3$.

The N–M–N angle in [Co(en)$_3$]$^{3+}$ has been found to be 86.2°, so it is only slightly distorted from a right angle.[7] The fusion of the chelate ring in [CoX$_2$(trien)]$^{n+}$ probably produces a somewhat greater distortion of this angle; this would be evidenced particularly in the distortion of the two "end" rings (Figure 5). Because of these distortions the entrance of propylenediamine

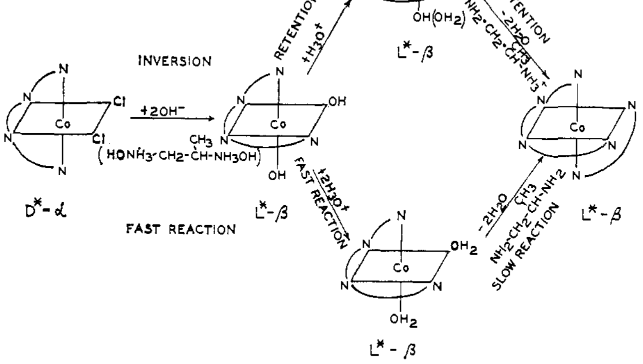

Figure 4. A possible mechanism for the reaction of D-α-[CoCl$_2$(trien)]$^+$ with propylenediamine.

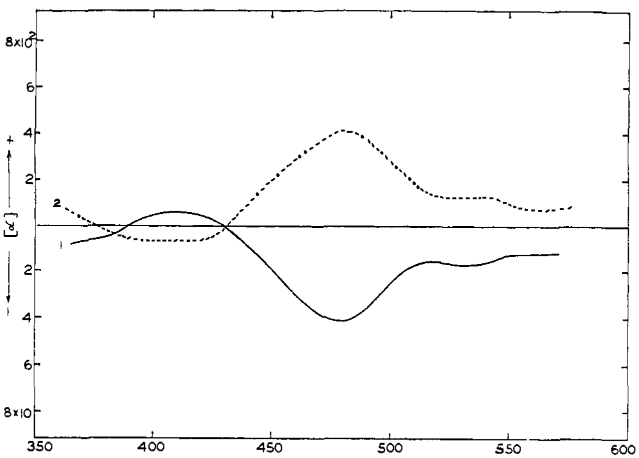

Figure 5. Optical rotatory dispersion curves of (1) *R'*-β-[Co(*d*-pn)(trien)]Cl$_3$ and (2) *R'*-β-[Co(*l*-pn)(trien)]Cl$_3$.

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(10) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

(11) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

Table V. The Ultraviolet Spectra of D*- or L*-β-[Co(d- or l-pn)(trien)]Cl_3

Complexes	Absorption maxima		
	ν_1, 10^3 cm^{-1} (log ε)	ν_2, 10^3 cm^{-1} (log ε)	ν_3, 10^3 cm^{-1} (log ε)
L*-β-[Co(d-pn)(trien)]Cl_3	21.23 (2.09)	29.50 (2.08)	45.05 (3.99)
L*-β-[Co(l-pn)(trien)]Cl_3	21.23 (2.09)	29.50 (2.07)	45.05 (3.97)
D*-β-[Co(d-pn)(trien)]Cl_3	21.28 (2.11)	29.50 (2.07)	45.05 (3.98)
D*-β-[Co(l-pn)(trien)]Cl_3	21.28 (2.10)	29.50 (2.08)	45.05 (3.96)

into the diaquo or aquo hydroxo trien complex may be less influenced by stereospecific effects than the corresponding reaction with $[CoX_2(en)_2]^{n+}$.[7]

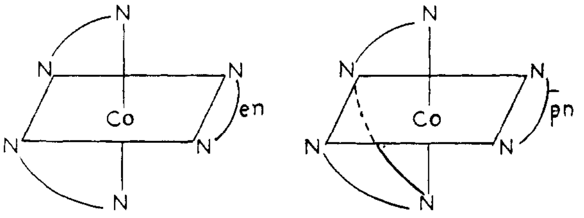

Figure 6. Absolute configurations about the central atom of (+)-D-$[Co(en)_3]^{3+}$ and (+)-D-β-$[Co(pn)(trien)]^{3+}$.

Experimental Section

The preparations of rac-α-[$CoCl_2$(trien)]Cl and D*-α-[$CoCl_2$(trien)]Cl were carried out according to standard procedures.[12]

Anal. Calcd for [$CoCl_2C_6H_{18}N_4$]Cl: C, 23.12; N, 17.85; H, 5.76; Cl, 33.73. Found for rac-α-[$CoCl_2C_6H_{18}N_4$]Cl: C, 23.01; N, 17.84; H, 5.70; Cl, 33.50. Found for D*-α-[$CoCl_2C_6H_{18}N_4$]Cl: C, 23.10; N, 18.04; H, 5.81; Cl, 33.70. $[\alpha]^{25}\text{D}$ +2770°, $[M]^{25}\text{D}$ +8630° (0.1% aqueous solution).[13]

L*-α-Dichlorotriethylenetetraminecobalt(III) Chloride L-α-[$CoCl_2$(trien)]Cl, and L*-α-Oxalatotriethylenetetraminecobalt(III) Nitrate, L*-α-[Co(ox)(trien)]NO_3. According to the standard procedure for preparing D*-α-[Co(ox)(trien)]NO_3,[12] rac-α-[Co(ox)(trien)]Cl (20 g, 0.054 mole) and ammonium d-α-bromocamphor-π-sulfonate (20 g, 0.05 mole) were used as starting materials. After the D*-α-[Co(ox)(trien)][$C_{10}H_{14}O_4SBr$] was removed by filtration, the filtrate was concentrated to dryness on a steam bath. The dried product, L*-α-[Co(ox)(trien)][$C_{10}H_{14}O_4SBr$], was ground in an ice-cold mortar for 5 min with 30 ml of a cold (1:1:1) mixture of concentrated HNO_3, ethanol, and ether. The product was washed with ethanol and ether: yield 10 g, $[\alpha]^{25}\text{D}$ −380° in 0.1% aqueous solution. After several recrystallizations from hot water, the pure crystals were washed and dried: yield 3.5 g, 34%. The sample used for analysis was dried at 100° for 2 hr: $[\alpha]^{25}\text{D}$ −798°, $[M]^{25}\text{D}$ −2866° (0.1% aqueous solution).

Anal. Calcd for [$Co(C_6H_{18}N_4)C_2O_4$]NO_3: C, 26.76; N, 19.50; H, 5.05. Found: C, 26.72; N, 19.45; H, 5.36.

L*-α-Dichlorotriethylenetetraminecobalt(III) Chloride, L*-α-[$CoCl_2$(trien)]Cl. The preparation was carried out according to the standard procedure for D*-α-[$CoCl_2$(trien)]Cl[12] using L*-α-[Co(ox)(trien)]NO_3 in place of D*-α-[Co(ox)(trien)]NO_3: yield 4.0 g, 90%; $[\alpha]^{25}\text{D}$ −2778°; $[M]^{25}\text{D}$ −8645° (0.1% aqueous solution).

Anal. Found for [$CoCl_2(C_6H_{18}N_4)$]Cl: C, 23.01; N, 17.44; H, 6.06; Cl, 33.13.

Resolution of Propylenediamine. The resolution was carried out by the standard method.[6] Anhydrous benzene solutions of the resolved material gave $\alpha^{25}\text{D}$ +0.0186°, $[\alpha]^{25}\text{D}$ +35.2° (concentration, 0.47%) and $\alpha^{25}\text{D}$ −0.0132°, $[\alpha]^{25}\text{D}$ −29.1° (concentration, 0.41%) for d- and l-propylenediamine, respectively. Both optically active samples were diluted to 25% with water before use in the experiments.

Reaction of Optically Active or rac-α-[$CoCl_2$(trien)]Cl with rac-Propylenediamine[14] in Aqueous Solution (the reaction described in Table I). Finely powdered racemic or optically active α-[$CoCl_2$(trien)]Cl (1.6 g, 0.005 mole) was added to 5 ml of 25% racemic propylenediamine solution (0.017 mole) at 25°. The mixture was ground for 10 min until the violet powder was dissolved, and an orange solution was formed. This was concentrated to dryness by aeration. The residue was ground with 30 ml of ice-cold absolute ethanol. The yellow-brown product was filtered and washed with absolute ethanol and ether and dissolved in 3 ml of water containing 0.5 ml of concentrated hydrochloric acid. After filtration, 40 ml of absolute ethanol was added and the process was repeated. The final products were dried at 80° *in vacuo* for 2 hr. They are strongly hygroscopic powders. The yields were as follows.

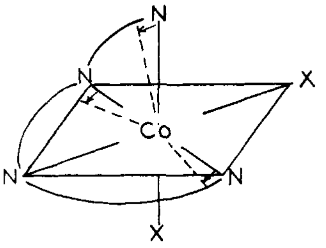

Figure 7. A possible structural distortion of β-$[CoX_2(trien)]^{n+}$

Starting complexes	Products	Yield g	Yield %
D*-α-[$CoCl_2$(trien)]Cl	L*-β-[Co(r′-pn)(trien)]Cl_3	1.4	73
L*-α-[$CoCl_2$(trien)]Cl	D*-β-[Co(r′-pn)(trien)]Cl_3	1.5	77
rac-α-[$CoCl_2$(trien)]Cl	rac-β-[Co(r′-pn)(trien)]Cl_3	1.4	73

Before analysis, the samples were purified by another precipitation and were dried at 100° for 2 hr.

Anal. Calcd for β-[$CoC_9N_6H_{28}$]Cl_3: C, 28.03; N, 21.89; H, 8.32. Found for D*-β-[Co(r′-pn)(trien)]Cl_3: C, 27.81; N, 20.96; H, 8.40. Found for L*-β-[Co(r′-pn)(trien)]Cl_3: C, 27.65; N, 20.88; H, 8.11. Found for rac-[Co(rac-pn)(trien)]Cl_3: C, 27.91; N, 20.91; H, 8.40.

Reaction of Optically Active α-[$CoCl_2$(trien)]Cl with Optically Active Propylenediamine in Aqueous Solution (the reaction described in Table III). This experiment was carried out in a similar way. The yields and products are as follows.

Starting complexes	Reagent	Products	Yield g	Yield %
D*-α-[$CoCl_2$(trien)]Cl_3	d-pn	L*-β-[Co(d-pn)(trien)]Cl_3	1.3	67
D*-α-[$CoCl_2$(trien)]Cl_3	l-pn	L*-β-[Co(l-pn)(trien)]Cl_3	1.4	73
L*-α-[$CoCl_2$(trien)]Cl_3	d-pn	D*-β-[Co(d-pn)(trien)]Cl_3	1.5	77
L*-α-[$CoCl_2$(trien)]Cl_3	l-pn	D*-β-[Co(l-pn)(trien)]Cl_3	1.4	73

Table VI. The Infrared Spectra (Nujol Mull in cm^{-1}) of D*- or L*-β-[Co(d- or l-pn)(trien)]Cl_3

3420 (m)	1160 (sh)	571 (m)
3150 (sh)	1130 (m)	510 (m)
1675 (s)	1090 (m)	486 (m)
1560 (s)	1063 (s)	456 (m)
1490 (sh)	1025 (sh)	437 (m)
1405 (sh)	848 (w)	405 (w)
1360 (sh)	830 (w)	375 (m)
1318 (w)	728 (m)	343 (m)
1270 (m)	611 (m)	

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[12] E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 87, 4458 (1965).

[13] For meanings of these notations see E. Kyuno and J. C. Bailar, Jr., *ibid.*, 88, 1121 (1966).

[14] Commercial propylenediamine (98–99%) was distilled and collected at 119–120°. For the preparations of complexes the distilled material was diluted with water to form a 25% solution.

Table VII. The Ultraviolet Spectra of *R'*-[Co(*d*- or *l*-pn)(trien)]Cl_3

Complexes	Absorption maxima ν_1, 10^3 cm^{-} (log ϵ)	ν_2, 10^3 cm^{-1} (log ϵ)	ν_3, 10^3 cm^{-1} (log ϵ)
R'-β-[Co(*d*-pn)(trien)]Cl_3	21.23 (2.09)	29.50 (2.08)	42.05 (3.97)
R'-β-[Co(*l*-pn)(trien)]Cl_3	21.23 (2.09)	29.50 (2.08)	42.05 (3.97)

The samples were purified by reprecipitation, as above, and were dried at 100° for 2 hr before analysis.

Reaction of Optically Active α-[$CoCl_2$(trien)]Cl with Optically Active Propylenediamine in Aqueous Solution (the reaction described in Table IV). Elemental analysis gave the following results. Found for L*-β-[Co(*d*-pn)(trien)]Cl_3: C, 27.75; N, 20.41; H, 7.91. Found for L*-β-[Cl(*l*-pn)(trien)]Cl_3: C, 27.90; N, 20.75; H, 7.50. Found for D*-β-[Co(*d*-pn)(trien)]Cl_3: C, 27.91; N, 20.85; H, 7.56. Found for D*-β-[Co(*l*-pn)(trien)]Cl_3: C, 27.74; N, 20.55; H, 7.39.

The ultraviolet spectra in aqueous solution and the infrared spectra are collected in Tables V and VI.

The experiment using *rac*-[$CoCl_2$(trien)]Cl and optically active propylenediamine was carried out and the products were treated in a similar way. The yield, in each case, was 1.4 g (73%).

Anal. Found for *R'*-[Co(*d*-pn)(trien)]Cl_3: C, 27.93; N, 20.21; H, 7.65. Found for *R'*-[Co(*l*-pn)(trien)]Cl_3: C, 27.62; N, 20.06; H, 7.77.

The ultraviolet spectra in aqueous solution are shown in Table VII. The infrared spectra of both were identical.

Optical rotatory dispersion curves were measured on 5.0×10^{-3} *M* solutions.

Spectrophotometric measurements were done on 1.0×10^{-2} *M* aqueous solutions.

The apparatus was described in an earlier paper.

Acknowledgment. The support received for this investigation from National Science Foundation Research Grant GP-191 is gratefully acknowledged, as are useful discussions with Dr. L. J. Boucher.

The Mass Spectrum and Preparation of Pure Manganese Pentacarbonyl Hydride[1]

Walter F. Edgell and William M. Risen, Jr.[2]

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. *Received June 29, 1966*

Abstract: The mass spectrum of $HMn(CO)_5$, prepared by the standard literature procedure, shows it to contain impurities. Modifications in the preparative scheme have resulted in a method for the preparation of pure $HMn(CO)_5$. The mass spectrum of the pure $HMn(CO)_5$ is reported. The fragment $Mn{-}H^+$ has been observed in the mass spectrum, providing direct evidence for the manganese–hydrogen bond. In addition, the loss of CO and H from $HMn(CO)_5$ are found to be competitive fragmentation processes.

Recently there have appeared several mass spectroscopic studies of organometallic compounds.[3–7] These studies have revealed a number of interesting aspects of the nature of such compounds. Winters and Kiser have investigated in detail the mass spectra of the monometallic transition metal carbonyls $Ni(CO)_4$ and $Fe(CO)_5$,[3] and the hexacarbonyls of chromium, molybdenum, and tungsten.[4] On the basis of their experimental data, they have proposed that the fragmentation of these transition metal carbonyl ions, produced in the spectrometer, occurs by successive removal of neutral CO groups. This proposed successive removal of CO groups has been substantiated for both the $M(CO)_n{}^+$ and $M(CO)_n{}^{2+}$ ions in a detailed metastable transition study of $Fe(CO)_5$.[8] Winters and Kiser[6] and King[7] have studied the mass spectra of polymetallic transition metal carbonyl compounds. Winters and Kiser reported that the spectrum of $Mn_2(CO)_{10}$ contained a peak for the $Mn_2{}^+$ ion, in accordance with the structure containing a manganese–manganese bond. King's[7] spectra of the polynuclear carbonyls $Co_4(CO)_{12}$ and $Ru_3(CO)_{12}$ exhibit mass peaks assigned to the bare metal cluster ions $Co_4{}^+$ and $Ru_3{}^+$, respectively. These ion clusters are in keeping with the established structures of the parent molecules. Thus, the mass spectra of organometallics clearly contain valuable information about the nature of these compounds.

In connection with studies of the infrared spectrum of $HMn(CO)_5$, we were led to examine the mass spectrum of the substance as prepared by the usual method.[9,10] It was found to be impure, but a modification of the method led to a pure product. We report here the mass spectrum of the resulting pure $HMn(CO)_5$.

Experimental Section

Reagents. The $Mn_2(CO)_{10}$ used was supplied by Alfa Inorganics, Inc., and was freshly sublimed, before use, to yield a bright yellow crystalline solid. Reagent grade tetrahydrofuran (Fisher Certified

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(2) Monsanto Predoctoral Fellow, 1965–1966.

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