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Synthesis, Characterization and Structure of *Cis* and *Trans* Cobalt(III) Bis Chelates of 2-Methyl-1,3-propanediamine, a Prochiral Sinambic Ligand

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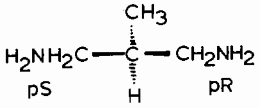
Cis *and* trans *isomers of* $[Co(metn)_2Cl_2]^+$ *(metn = 2-methyl-1,3-propanediamine) have been prepared and characterized. Owing to the presence of rotationally nonequivalent donor atoms in the prochiral ligand, three diastereomers are possible for the* cis *isomer (*C_2*(*anti*),* C_2*(*syn*), and* C_1*) and two diastereomers are possible for the* trans *complex (*C_{2h} *and* C_{2v}*). A crystal structure of the purple compound* $[Co(metn)_2Cl_2]Cl\cdot\frac{1}{4}CH_3OH$ *shows the presence of both the* cis C_2*(*anti*) and* trans C_{2h} *isomers. An uncompleted structure determination on greeen* $[Co(metn)_2Cl_2](H_3O)Cl_2\cdot H_2O$ *reveals only the* trans C_{2h} *isomer. X-Ray crystallography also shows a flattening of the 6-membered metn chelate ring compared with that of 1,3-propanediamine. Though* ^{13}C *NMR spectra of* trans-$[Co(metn)_2Cl_2]^+$ *show no evidence for more than one isomer in solution, this may be due to undetectably small chemical shift differences between the two diastereomers possible. IR spectra indicate a solid state* cis *to* trans *rearrangement of* $[Co(metn)_2Cl_2]^+$ *in the presence of KBr.*

Introduction

Atoms in a molecule which are not related by rotational symmetry are distinguishable [1]. If such atoms are the donor atoms of a bidentate ligand, the distinguishability can give rise to isomerism when the ligand is complexed. Well-known examples of this are found in complexes of *AB* ('unsymmetrical') bidentates. However, we have pointed out that lack of ligand symmetry is not necessary in order to have distinguishable donor atoms [2]. Despite the presence of nontrivial symmetry, the enantiotopic donor atoms of both meso and prochiral bidentate ligands are distinguishable and, when complexed, such ligands give isomers equal in number to those obtained with coordinated unsymmetrical bidentates. We have termed any bidentate ligand having rotationally nonequivalent donor atoms 'sinambic' (L. *sine ambito*: 'without rotation') [2].

2-Methyl-1,3-propanediamine (metn, *1*) is one example of a prochiral sinambic ligand. The two distinguishable donor atoms of this ligand can be



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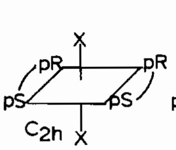
assigned prochiral labels '*pro-R*' and '*pro-S*' [3]. (In this paper, we use the shortened symbols '*pR*' and '*pS*'.) Octahedral bis chelates of such a ligand can exist as two *trans* diastereomers (*2* having C_{2h} symmetry and *3* having C_{2v} symmetry) and as



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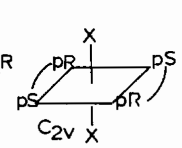

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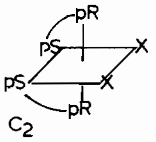
three *cis* diastereomers (*4* and *5* having C_2 symmetry and *6* with C_1 symmetry) [2]. The two C_2-symmetry



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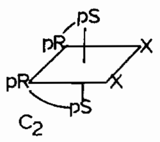

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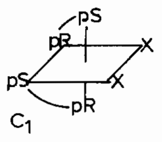

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isomers, shown here with Λ absolute configurations, can be distinguished by the designations '*trans-pR, pR'* (*4*) and '*trans-pS,pS*' (*5*) to denote the fact that, respectively, *pro-R* and *pro-S* groups are opposite each other in the coordination spheres.

We have reported the synthesis and separation of the two diastereomers of an octahedral tris chelate of metn [4]. In this paper we report the syntheses and characterization of some Co(III) bis chelates of metn, the structure of $[Co(metn)_2Cl_2]\cdot \frac{1}{4}CH_3OH$, a solid containing both *cis* and *trans* complexes, and evidence for a solid state interconversion of *cis* and *trans* compounds. This paper contains the first report of a structure determination for a *cis* geometry octahedral bis chelate containing prochiral sinambic ligands and the first satisfactory refinement of any X-ray structure for a compound containing the metn ligand.

Experimental

Preparation of Dichlorobis(2-methyl-1,3-propanediamine)cobalt(III) Chloride

To a solution of cobalt(II) chloride 6-hydrate (1.0 g, 4.2 mmol) dissolved in a minimum of methanol was added dropwise with vigorous stirring a filtered methanolic solution of the ligand prepared by mixing sodium hydroxide (0.67 g, 17 mmol) and 2-methyl-1,3-propanediamine dihydrochloride [4] (1.35 g, 8.4 mmol). The mixture, which turned from blue to dark green shortly after addition of the ligand, was stirred for 30 min and oxygen gas was then allowed to bubble through it for 5 h. During this time, fine purple needle-like crystals, which were shown by X-ray diffraction (*vide infra*) to contain a mixture of *cis-* and *trans-*$[Co(metn)_2Cl_2]Cl$, precipitated and were filtered off, washed with methanol and air-dried. Lattice methanol, found with partial occupancy in the structure determination, was apparently lost before or during the elemental analaysis. *Anal.* Calcd. for $Co(C_4H_{12}N_2)_2Cl_3$.: C, 28.13; H, 7.08; N, 16.40. Found: C, 28.17; H, 7.32; N, 16.73.

Evaporation to dryness of the methanolic filtrate obtained upon removal of the purple crystals gave a gray-green powder which was dissolved in a minimum of distilled water. Addition of a 10-fold volume of 12 *M* hydrochloric acid, heating on a steam bath for 30 min, and room-temperature evaporation gave a dark green crystalline precipitate which, when isolated, rapidly effloresced to a light-green powder. *Anal.* Calcd. for $Co(C_4H_{12}N_2)_2Cl_3$: C, 28.13; H, 7.08; N, 16.40. Found: C, 28.01; H, 7.16; N, 15.92.

IR spectra of the purple and green crystals (and also of green crystals of $[Co(metn)_2Cl_2](H_3O)Cl_2\cdot H_2O$ prepared for a crystal structure determination as described later in this paper) in a KBr matrix were indistinguishable; however, IR spectra in nujol mulls easily differentiated the purple and green compounds. A color change from purple to green occurred when the purple material was mixed with KBr. On the other hand, no color change occurred when this purple material was ground or compressed in a pellet press by itself.

Preparation of Diamminebis(2-methyl-1,3-propanediamine)cobalt(III) Chloride

Addition of a large excess of anhydrous liquid ammonia to the light green product from the preceding synthesis gave a red solid which slowly dissolved over a period of 10 min to give a red solution. A reddish orange material was obtained by evaporating the solution to dryness, washing the residue in a filter under suction with a minimum of water, and air-drying. *Anal.* Calcd. for $[Co(C_4H_{12}N_2)_2(NH_3)_2]Cl_3\cdot 2H_2O$: C, 23.34; H, 8.05; N, 20.41. Found: C, 23.66; H, 8.35; N, 20.11. An attempted chromatographic separation of the *cis* and *trans* isomers of $[Co(metn)_2(NH_3)_2]^{3+}$ shown to be present by ^{13}C NMR (*vide infra*) was unsuccessful.

^{13}C NMR Spectroscopy

Natural abundance ^{13}C NMR spectra of *trans-*$[Co(metn)_2Cl_2]Cl$ in both deuterated dimethylsulfoxide and methanol and of $[Co(metn)_2(NH_3)_2]Cl_3$ in D_2O were collected at ~35 °C on a Varian FT-80A NMR spectrometer using an observe frequency of 20.0 MHz and an external standard. All chemical shifts reported are relative to TMS. Spectra were collected with a 0.4-s acquisition time, 0.1-s pulse delay, a 4-μs pulse width (equivalent to a 40° pulse), a 4000-Hz sweep width, and noise modulated proton decoupling.

Crystal Structure Determination for $[Co(metn)_2Cl_2]Cl\cdot \frac{1}{4}CH_3OH$ (Purple Compound)

All X-ray data for this and the following structure were collected on a Syntex P3/F diffractometer system.

A purple needle-like crystal obtained from the reaction mixture in the initial synthesis of $[Co(metn)_2Cl_2]^+$ was mounted on a glass fiber and lattice parameters were determined from a least-squares fit to 25 automatically centered reflections. The systematic absences observed during the subsequent data collection were consistent with the space group $P2_1/n$. Crystallographic and data collection parameters are summarized in Table I.

The three crystallographically unique cobalt atoms were located using Patterson techniques. Repeated Fourier syntheses and structure factor calculations revealed the locations of the six unique chloride atoms and the nonhydrogen chelate ring atoms. Following anisotropic refinement of these atoms, hydrogen atom positions were calculated and these

TABLE I. Crystal and Data Collection Parameters for [Co(metn)$_2$Cl$_2$]Cl·¼CH$_3$OH (Purple Compound).

Formula weight	349.6
F_{000}	1424
a, Å	12.15(2)
b, Å	24.528(9)
c, Å	12.93(3)
β, deg	115.38(8)
V, Å^3	3481.5
Z	8
ρ(calcd), g/cm^3	1.47
Reflections measd	$+h, -k, \pm l$
Space group	$P2_1/n$
Crystal dimen, mm	0.1 × 0.1 × 0.3
Radiation	Mo Kα (λ = 0.71069 Å)
Absorption coefficient, cm^{-1}	14.6
Scan range, deg	1.3 below $2\theta(K\alpha_1)$ to 1.3 above $2\theta(K\alpha_2)$
Background time	0.5 × scan time
2θ limits, deg	3.0–55.0
Standards	$(\bar{1}, 1, 0)$ and $(1, 1, \bar{2})$ every 48 reflections
Collected reflections	5132
Unique reflections	4594
Unique data used	2695 with $I > 3.96\sigma(I)$
Variables refined	272
$R(F) = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.075
$R_w(F_1) = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.105
w^{-1}	$\sigma^2(F_o) + (gF_o)^2$, g = 0.08

atoms were added with a fixed isotropic thermal parameter (B_{iso} = 5) and with fixed positions.

Following further refinement, a Fourier difference map showed the presence of peaks which were best interpreted as due to partial occupancy by solvent. From the results of refinements using several different models, the best model was determined to be a half-weighted methanol molecule with an oxygen atom evenly disordered over two positions. Following several cycles of full matrix least-squares refinement, the hydrogen atom positions were recalculated, and refinement was continued until convergence. A final Fourier difference map revealed no significant features. Neutral atom scattering factors were used for all atoms but chlorine and cobalt which were taken as Cl^- and Co^{3+}. Anomalous dispersion corrections were applied to cobalt and chlorine. The XTL series of programs [5] were used for all calculations. Scattering factors and anomalous dispersion corrections were taken from standard sources [6]. Atomic coordinates and thermal parameters are given in Table II. A table of observed and calculated structure factor amplitudes is available from the Editor on request.

Crystal Structure Determination for [Co(metn)$_2$Cl$_2$](H$_3$O)Cl$_2$·H$_2$O (Green Compound)

A green pleochroic crystal was obtained by dissolving the purple *cis* plus *trans* compound in concentrated hydrochloric acid and then allowing evaporation to occur. Since the crystals rapidly effloresced, the crystal studied was coated with epoxy immediately upon removal from solution. Lattice parameters were determined from 25 auto-

TABLE II. Atomic Positions and Thermal Parameters for [Co(metn)$_2$Cl$_2$]Cl·¼CH$_3$OH (Purple Compound).[a]

Atom	x/a	y/b	z/c	B_{11} or B_{iso}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
				Molecule 1 (*Trans*)					
Co(1)	½	0	0	3.2(1)	2.3(1)	2.8(1)	−0.1(1)	0.4(9)	0.2(9)
Cl(1)	0.4307(3)	−0.0470(2)	−0.1672(3)	4.6(2)	3.4(2)	3.5(2)	−0.6(1)	0.8(1)	−0.7(1)
N(1)	0.3688(9)	−0.0345(4)	0.0312(9)	3.5(5)	2.0(5)	4.1(5)	−0.4(4)	1.2(4)	0.5(4)
N(2)	0.3860(9)	0.0604(4)	−0.0847(8)	3.3(5)	2.2(5)	3.6(5)	−0.4(4)	1.1(4)	0.3(4)
C(1)	0.2826(13)	−0.0012(6)	0.0603(11)	4.1(7)	4.1(7)	3.9(6)	−0.9(6)	1.3(6)	−0.5(6)
C(2)	0.2140(13)	0.0405(7)	−0.0306(12)	3.8(7)	4.1(8)	4.9(7)	0.4(6)	0.6(6)	0.2(6)
C(3)	0.3010(14)	0.0833(6)	−0.0424(12)	4.7(8)	3.1(7)	4.8(7)	1.1(6)	1.0(6)	1.3(6)
C(4)	0.1157(19)	0.0685(8)	−0.0044(19)	8.1(12)	4.6(10)	11.6(15)	1.5(9)	6.4(12)	2.3(9)
				Molecule 2 (*Trans*)					
Co(2)	0	0	½	5.7(2)	2.67(1)	2.5(1)	−0.9(1)	−0.5(1)	0.5(9)
Cl(2)	0.0982(4)	0.0553(2)	0.6525(3)	7.4(2)	4.0(2)	3.1(2)	−1.3(2)	−0.2(2)	0.0(1)
N(3)	0.1449(12)	−0.0488(5)	0.5583(10)	6.3(8)	3.6(7)	3.6(5)	−0.5(6)	−0.7(5)	1.2(5)
N(4)	0.0663(12)	0.0427(5)	0.4105(10)	6.4(8)	2.8(6)	3.3(5)	−0.4(5)	0.0(5)	0.5(4)
C(5)	0.2111(18)	−0.0649(8)	0.4891(15)	7.5(11)	6.2(11)	4.9(8)	1.1(9)	1.9(8)	0.7(8)

(continued overleaf)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c	B_{11} or B_{iso}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(6)	0.2531(21)	−0.0163(8)	0.4417(17)	9.8(14)	5.8(12)	7.2(11)	−0.9(10)	3.3(11)	0.6(9)
C(7)	0.1420(17)	0.0175(8)	0.3582(14)	7.0(11)	5.8(11)	4.3(8)	−1.6(8)	−0.4(8)	1.1(7)
C(8)	0.3351(28)	−0.0318(14)	0.3821(24)	14.4(23)	14.6(24)	11.4(18)	3.5(20)	6.8(18)	4.0(18)
				Molecule 3 (*Cis*)					
Co(3)	0.33562(15)	0.30111(7)	0.68922(13)	2.7(1)	2.2(1)	2.1(1)	0.0(1)	−0.1(1)	−0.1(1)
Cl(3)	0.3787(3)	0.3906(1)	0.6631(3)	4.0(2)	2.6(2)	4.0(2)	−0.4(1)	0.3(1)	0.3(1)
Cl(4)	0.3599(3)	0.3182(2)	0.8704(3)	4.9(2)	3.9(2)	2.6(1)	−0.1(1)	0.6(1)	−0.7(1)
N(5)	0.3128(10)	0.2858(4)	0.5303(8)	3.5(5)	2.2(5)	2.2(4)	0.6(4)	−0.2(4)	−0.1(4)
N(6)	0.5117(11)	0.2834(4)	0.7562(9)	5.0(6)	1.9(5)	2.6(4)	0.4(4)	−0.1(4)	0.3(4)
N(7)	0.3001(10)	0.2238(4)	0.7077(8)	3.3(5)	2.4(5)	3.1(5)	0.5(4)	0.5(4)	0.2(4)
N(8)	0.1618(10)	0.3243(4)	0.6323(9)	3.6(6)	2.7(5)	3.2(5)	−0.2(4)	0.8(4)	0.3(4)
C(9)	0.4118(14)	0.2904(7)	0.4960(12)	3.8(7)	7.1(10)	4.0(7)	0.2(7)	2.0(6)	0.1(7)
C(10)	0.5250(14)	0.2582(8)	0.5735(14)	3.9(8)	8.5(12)	4.6(8)	1.5(8)	1.5(6)	−0.9(8)
C(11)	0.5865(12)	0.2863(7)	0.6900(11)	2.7(6)	6.8(10)	2.8(6)	0.5(6)	−0.5(5)	0.4(6)
C(12)	0.6164(17)	0.2539(10)	0.5206(17)	4.7(9)	13.8(19)	6.5(10)	3.0(11)	2.2(8)	1.8(11)
C(13)	0.1986(14)	0.2069(7)	0.7318(13)	4.1(7)	4.4(9)	5.7(8)	0.4(6)	2.3(7)	0.9(6)
C(14)	0.0780(14)	0.2326(7)	0.6547(15)	3.8(8)	5.3(10)	6.6(9)	−1.9(7)	1.3(7)	−0.9(7)
C(15)	0.0750(15)	0.2944(6)	0.6619(14)	5.9(9)	3.3(8)	6.5(9)	1.9(7)	2.2(8)	0.1(7)
C(16)	−0.0261(13)	0.2071(8)	0.6785(14)	2.9(8)	7.5(11)	6.8(10)	−2.1(7)	1.0(7)	0.3(8)
Cl(5)	0.0502(3)	0.3448(1)	0.3551(3)	4.0(2)	3.0(2)	3.6(2)	0.1(1)	−0.6(1)	−0.9(1)
Cl(6)	0.2392(3)	0.1567(2)	0.4713(3)	4.7(2)	3.8(2)	3.8(2)	−0.5(2)	0.6(1)	−0.7(1)
O(1)[b]	0.387(4)	0.157(2)	0.310(3)	4.4(9)					
O(2)[b]	0.348(4)	0.121(2)	0.290(4)	5.5(10)					
C(17)[b]	0.453(3)	0.124(2)	0.349(3)	6.1(8)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}kha^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] O(1), O(2), and C(17) are atoms of the disordered methanol molecule and have respective population parameters of 0.25, 0.25, and 0.50.

TABLE III. Crystal Parameters for $[Co(metn)_2Cl_2\text{-}(H_3O)Cl_2 \cdot H_2O$ (Green Compound).

Formula weight	393.7
a, Å	9.065(3)
b, Å	9.182(3)
c, Å	11.685(4)
α, deg	96.98(3)
β, deg	104.67(3)
γ, deg	91.63(3)
V, Å^3	934.4
Z	2
Space group	P$\bar{1}$

matically centered reflections using a least squares procedure. Crystallographic information is given in Table III.

Two crystallographically unique cobalt ions, which sit on inversion centers, were located using Patterson techniques and all chlorine atoms and nonhydrogen chelate ring atoms were located in subsequent Fourier syntheses. At that time, one more chloride ion per complex was found than had been initially expected. Fourier difference calculations then revealed two water molecules one of which must be protonated to account for the charge from the extra chloride ion. The hydrogen positions were calculated and their positions fixed and the structure was refined to an R value of 0.083. Since this structure was found to contain a *trans* complex having the same isomeric form as found in the preceding structure determination, and since it was found necessary to collect additional data in order to satisfactorily refine the structure, a decision was made to discontinue this structure determination. No positional or thermal parameters are reported for this structure.

Results and Discussion

Structure of [Co(metn)$_2$Cl$_2$]·¼CH$_3$OH (Purple Compound)

Since it is commonly observed that *cis* and *trans*-dichlorobis(diamine)cobalt(III) compounds are purple and green respectively, we were surprised to find that the purple crystals isolated contained both *cis* and *trans* isomers with four of each in the unit

TABLE IV. Interatomic Distances (Å) for [Co(metn)$_2$Cl$_2$]Cl·¼CH$_3$OH (Purple Compound).

		Molecule 1	
Co(1)–Cl(1)	2.268(3)	C(1)–C(2)	1.51(2)
Co(1)–N(1)	1.99(1)	C(2)–C(3)	1.54(2)
Co(1)–N(2)	2.00(1)	C(2)–C(4)	1.54(3)
N(1)–C(1)	1.50(2)	C(3)–N(2)	1.47(2)
		Molecule 2	
Co(2)–Cl(2)	2.266(4)	C(5)–C(6)	1.52(3)
Co(2)–N(3)	1.99(1)	C(6)–C(7)	1.56(3)
Co(2)–N(4)	1.97(1)	C(6)–C(8)	1.55(4)
N(3)–C(5)	1.49(3)	C(7)–N(4)	1.49(2)
		Molecule 3	
Co(3)–Cl(3)	2.316(4)	C(10)–C(11)	1.53(2)
Co(3)–Cl(4)	2.270(4)	C(10)–C(12)	1.54(3)
Co(3)–N(5)	1.99(1)	C(11)–N(6)	1.49(2)
Co(3)–N(6)	1.98(1)	N(7)–C(13)	1.46(2)
Co(3)–N(7)	1.98(1)	C(13)–C(14)	1.51(2)
Co(3)–N(8)	2.00(1)	C(14)–C(15)	1.52(2)
N(5)–C(9)	1.45(2)	C(14)–C(16)	1.56(3)
C(9)–C(10)	1.53(2)	C(15)–N(8)	1.46(2)

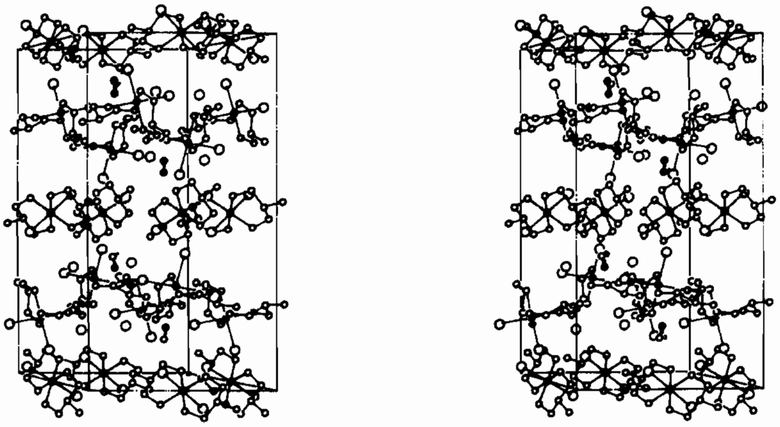


Fig. 1. Stereoscopic view of the contents of the unit cell for [Co(metn)$_2$Cl$_2$]Cl·¼CH$_3$OH (purple compound). The *a* axis is out of the page. A dot marks the unit cell origin. Hydrogen atoms are not shown.

cell. The two types of isomers are arranged in alternating layers perpendicular to the *b* axis with the layers separated by chloride ions and disordered methanol molecules having partial occupancy (Fig. 1). There are two crystallographically unique *trans* complexes (denoted as molecule 1 and molecule 2) sitting on inversion centers and a *cis* complex (molecule 3) residing at a general position. Owing, at least in part, to relatively large thermal motion in the four highly flexible crystallographically unique 6-membered chelate rings, the *R* factor is not as low as we might have wished; however, Fourier difference calculations show no disorder problem other than that experienced by the solvent molecule. Interatomic distances and angles are listed in Tables IV and V. The atom designations are given in Fig. 2.

The two crystallographically unique *trans* complexes, shown in stereo drawings in Figs. 3 and 4, both appear in the idealized C_{2h} diastereomeric form (*2*). This is the isomeric form also found in X-ray studies on the *trans* complexes [Cu(tnOH)$_2$X$_2$] (X = NO_3^-, Cl^-, SCN^-, $^-OOCC_6H_4COO^-$, and $SeCN^-$), where tnOH is the prochiral sinambic ligand 1,3-diamino-2-propanol [7–11]. Like the *trans*-[Co(metn)$_2$Cl$_2$]$^+$ structures reported here, in the solid state the copper(II) complexes show crystal-

TABLE V. Selected Bond Angles (°) for $[Co(metn)_2Cl_2]Cl \cdot \frac{1}{4}CH_3OH$ (Purple Compound).

		Molecule 1	
Cl(1)–Co(1)–N(1)	88.5(3)	Co(1)–N(1)–C(1)	121.8(9)
Cl(1)–Co(1)–N(2)	88.2(3)	Co(1)–N(2)–C(3)	120.7(9)
N(1)–Co(1)–N(2)	89.9(4)		
		Molecule 2	
Cl(2)–Co(2)–N(3)	88.9(4)	Co(2)–N(3)–C(5)	123.4(11)
Cl(2)–Co(2)–N(4)	89.8(4)	Co(2)–N(4)–C(7)	122.3(11)
N(3)–Co(2)–N(4)	91.4(5)		
		Molecule 3	
Cl(3)–Co(3)–Cl(4)	92.2(1)	N(5)–Co(3)–N(7)	90.2(4)
Cl(3)–Co(3)–N(5)	88.2(3)	N(5)–Co(3)–N(8)	90.9(4)
Cl(3)–Co(3)–N(6)	90.1(4)	N(6)–Co(3)–N(7)	89.3(5)
Cl(3)–Co(3)–N(8)	86.9(3)	N(7)–Co(3)–N(8)	93.8(4)
Cl(4)–Co(3)–N(6)	87.2(4)	Co(3)–N(5)–C(9)	122.3(9)
Cl(4)–Co(3)–N(7)	89.5(3)	Co(3)–N(6)–C11)	123.2(9)
Cl(4)–Co(3)–N(8)	88.7(3)	Co(3)–N(7)–C(13)	123.1(9)
N(5)–Co(3)–N(6)	93.2(5)	Co(3)–N(8)–C(15)	121.8(10)

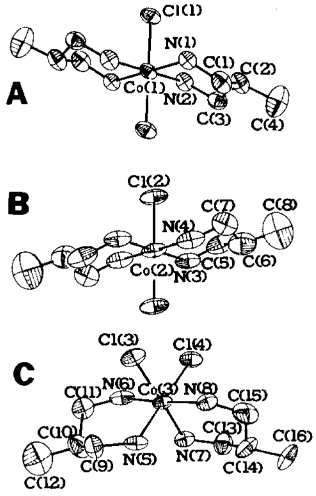


Fig. 2. The three crystallographically unique molecules found in crystals of $[Co(metn)_2Cl_2]Cl \cdot \frac{1}{4}CH_3OH$ (purple compound) with atom designations.

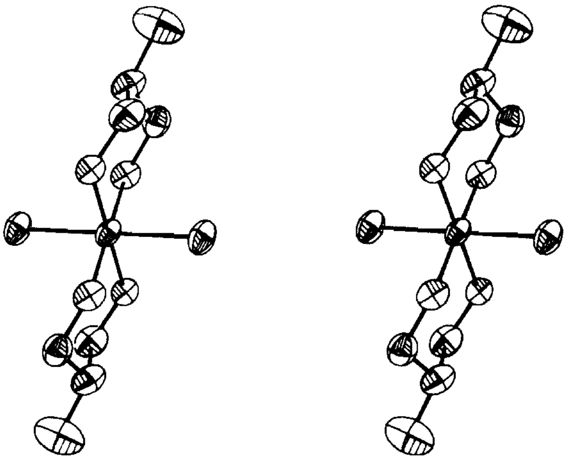
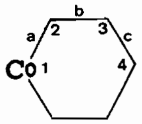


Fig. 3. Stereoscopic drawing of the *trans*-$[Co(metn)_2Cl_2]^+$ complex, molecule 1. The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown.

lographic symmetry C_i. It may be that both C_{2h} and C_{2v} diastereomers are present in solutions of the metn and tnOH complexes but that, owing to its centrosymmetric geometry, there is preferential deposition of the C_{2h} form. In fact, ^1H NMR spectra of $[Pt(tnOH)_2]^{2+}$ in solution indicates the presence of two isomers in approximately equal amounts [12]. On the other hand, molecular models do indicate a greater steric interaction between amine hydrogen atoms in a C_{2v} isomer than in a C_{2h} when the chelate rings have chair conformations.

The *cis* diastereomer, shown in the Δ form in Fig. 5, is found as the idealized C_2-symmetry pair of enantiomers, Λ(*trans-pR,pR*) (*4*), Δ(*trans-pS,pS*). The chair conformer chelate rings with equatorial methyl groups are folded away from each other to give an anti [13] overall conformation. If the unobserved *cis* diastereomers also had chair conformer chelate rings with equatorial methyl groups, the C_2 diastereomer Λ(*trans-pS,pS*) (*5*), Δ(*trans-pR,pR*) would be syn with the rings folded towards each other while the C_1 isomer would have chelate rings folded in the

TABLE VI. Chelate Ring Endocyclic and Dihedral Angles (°) for Complexes of 2-Methyl-1,3-propanediamine (metn) and 1,3-Propanediamine (tn) with Cobalt(III).[a]



Compound	Endocyclic Bond Angles				Dihedral Angles			Ref.
	1	2	3	4	a	b	c	
cis-$[Co(metn)_2Cl_2]^+$	93.5(3)	122.6(5)	114.0(12)	112.1(25)	26(1)	47(2)	65(5)	b
trans-$[Co(metn)_2Cl_2]^+$	90.6(7)	122.3(5)	113.7(9)	111.0(4)	36(3)	56(2)	63(1)	b
cis-$[Co(tn)_2(NO_2)_2]^+$	92.2(6)	121.7(2)	111.9(6)	113.2(2)	35(4)	54(3)	67(1)	16
trans-$[Co(tn)_2(NO_3)_2]^+$	87.7	119.0(11)	109.9(11)	113.3	51(2)	67(4)	64(2)	17
trans-$[Co(tn)_2(NO_2)_2]^+$	90.2	121.0(2)	111.8(4)	113.5	41.0(3)	57.5(4)	64.6(1)	18

[a] Average for the structure cited with average deviations in parentheses (except where there is only one value). [b] This work.

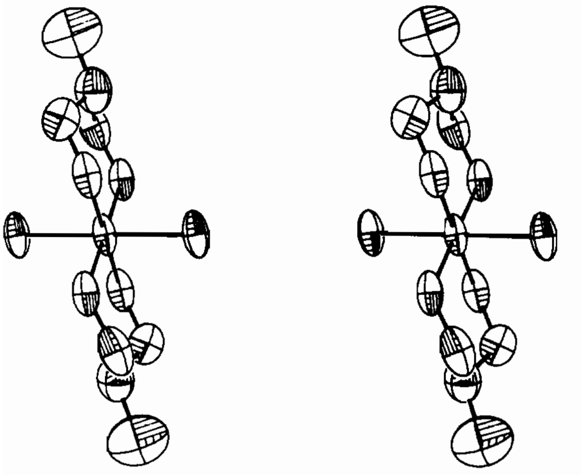


Fig. 4. Stereoscopic drawing of the *trans*-$[Co(metn)_2Cl_2]^+$ complex, molecule 2.

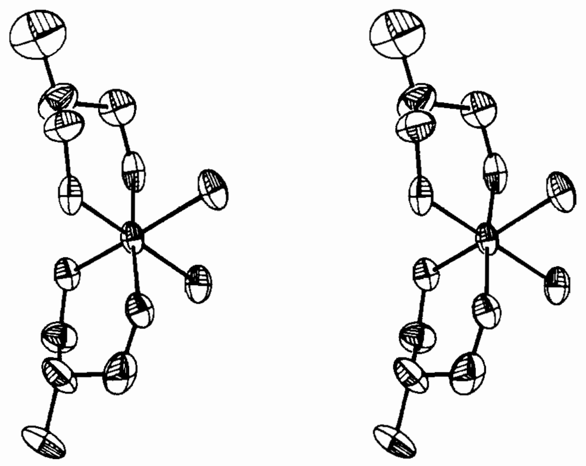


Fig. 5. Stereoscopic drawing of the *cis*-$[Co(metn)_2Cl_2]^+$ complex, molecule 3.

same direction. For *cis*-$[Co(tn)_2X_2]$ complexes (tn = 1,3-propanediamine), the relative enthalpies of these three conformers is believed to be *syn* $\gg$ C_1 > *anti*, though a symmetry-dependent entropy contribution of R ln2 to the stability of C_1 conformers may make C_1 and *anti* conformers nearly equal in stability [14, 15].

The structural data allow a comparison of chelate ring conformations of both *cis* and *trans* complexes of metn with conformations of 1,2-propanediamine (tn) in structurally similar compounds. Table VII, where only tn structures with chelate rings having chair conformations have been cited, contains the appropriate data. We note, first, general decreases in dihedral angles, and to a much smaller extent, increases in endocyclic bond angles upon going from a *trans* to a *cis* geometry for both metn and tn complexes. Such changes are indicative of a more puckered ring in the *trans* complexes. An increased puckering is also observed for the tn chelate ring compared to the metn ring (comparing *trans* with *trans* and *cis* with *cis*). Thus highly flattened rings are found in *cis*-$[Co(metn)_2Cl_2]^+$. There are only minor differences in other metn parameters compared to those of tn.

Structure of $[Co(metn)_2Cl_2](H_3O)Cl_2 \cdot H_2O$ *(Green Compound)*

The green crystal is found to contain two crystallographically unique *trans* complexes, each lying on an inversion center. Hydronium and chloride ions and water molecules are also present. Both crystallographically unique complexes, with idealized C_{2h} symmetry, have the same isomeric form as found for the *trans* complexes in the purple crystal.

^{13}C NMR Spectra

^{13}C NMR spectra of *trans*-$[Co(metn)_2Cl_2]^+$ show no evidence of more than one isomer in solution. Only three major peaks (assignable to methylene, methine, and methyl carbon atoms in the order given) are found in both methanol (δ = 45.94, 32.05, 16.39 ppm) and dimethylsulfoxide (δ = 46.08, 32.47, 18.22 ppm). The simple 3-peak spectra may be due to an undetectably small chemical shift difference between the two *trans* isomers possible. The large solvent dependence observed for the chemical shift of the terminal methyl carbon atom may indicate solvent coordination. Dimethylsulfoxide is known to compete with chloride ion for coordination with cobalt(III) [19] and, moreover, very small additional ^{13}C resonance peaks are observed near the major peaks in the spectrum of the dimethylsulfoxide solution (though these resonances, which are found at δ = 46.52, 45.73, 45.64, 32.89, 31.50, 31.10, 18.97, 18.80, and 18.68 ppm, are not close to those observed in methanol).

A ^{13}C NMR spectrum of $[Co(metn)_2(NH_3)_2]Cl_3 \cdot 2H_2O$ in D_2O shows more peaks than can be explained assuming the presence of only *trans* isomers. Resonances are observed at δ = 46.08, 45.82, 45.74, 45.50, and 45.38 ppm (assigned to methylene carbon atoms), at δ = 31.78 and 31.55 ppm (methine), and at δ = 17.50 and 17.40 ppm (methyl). Apparently at least partial *trans* to *cis* isomerism occurs upon amination of *trans*-$[Co(metn)_2Cl_2]^+$ as is found for *trans*-$[Co(en)_2Cl_2]^+$ [20].

Solid State Isomerization

The color change from purple to green when $[Co(metn)_2Cl_2]Cl \cdot \frac{1}{4}CH_3OH$ is mixed with KBr for IR pellet production (but not when ground or pressed by itself) and the identical IR spectra observed for this compound and *trans*-$[Co(metn)_2Cl_2]Cl$ in a KBr matrix (but not in nujol) indicate a *cis* to *trans* isomerization for $[Co(metn)_2Cl_2]^+$ in the presence of KBr. Similar isomerizations have been observed for bis chelates of ethylenediamine with cobalt(III) in the presence of ammonium salts (see, *e.g.*, [21]). That the IR spectra of $[Co(metn)_2Cl_2]Cl \cdot \frac{1}{4}CH_3OH$ after mixing with KBr is identical with that of *trans*-$[Co(metn)_2Cl_2](H_3O)Cl_2 \cdot H_2O$ is not necessarily proof that the rearranged complex has the C_{2h} isomeric form (as found in the crystal structure of the *trans* compound). The results of a structure determination on an individual crystal may not be indicative of the isomeric composition of the bulk material. Moreover, the presence of C_{2h} isomer already in the purple $[Co(metn)_2Cl_2]Cl \cdot \frac{1}{4}CH_3OH$ could obscure the presence of some C_{2v} isomer in the rearranged material.

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