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Crystal and Molecular Structure of

(-)₅₈₉-*cis*-Dinitrobis((2*S*)-2-amino-4-azapentane)cobalt(III) Chloride,

(-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]Cl

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The crystal and molecular structure of (-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]Cl has been determined from three-dimensional X-ray counter data. The complex forms orthorhombic crystals with $a = 13.568$ (1) Å, $b = 15.498$ (3) Å, $c = 7.596$ (1) Å, and $Z = 4$, in space group $P2_12_12_1$. The structure has been refined by block-diagonal matrix least-squares methods with anisotropic temperature factors to an R value of 0.039 for 2246 independent reflections with $F_o > 3\sigma(F_o)$. Six nitrogen atoms of the diamine and nitro groups are bonded nearly octahedrally to the central cobalt atom. The complex cation has approximately symmetry 2 (C_2). The complex cation has the absolute configuration Λ , and the conformations of the chelate rings are both δ , the two N -methyl and the two C -methyl groups being in equatorial positions with respect to the chelate rings. The absolute configurations of the two asymmetric nitrogen atoms are both R . The N -methyl groups are *cis* to one another, and the C -methyl groups are *trans* to each other.

Introduction

In recent years, the H-H nonbonded atomic interaction between ligands containing N -methyl groups in octahedral metal complexes has been of much interest. Several dinitrobis(N -methyl substituted 1,2-diamine)cobalt(III) complexes have been prepared.¹⁻³ Nitro groups are *trans* to each other in their complexes.

A *cis*-dinitro isomer of cobalt(III) complex with (2*S*)-2-amino-4-azapentane (abbreviated as N²-Me-(*S*)-pn) was prepared and isolated as a chloride salt, (-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]Cl, in our laboratory.

In our previous X-ray structure analysis study of [Co(ox)(N,N' -Me₂en)₂]ClO₄ (ox = oxalato dianion and N,N' -Me₂en = N,N' -dimethylethylenediamine), each diamine ring has an axial and an equatorial N -methyl group.⁴ Thus, there are two possible orientations for the N -methyl groups.

Since the ¹H NMR spectrum of (-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]⁺ in D₂O showed only a C -methyl doublet, this complex cation has symmetry 2 (C_2). But it is difficult to determine the geometry of this complex from the absorption, circular dichroism (CD), and ¹H NMR spectrum. And the relationship between the absolute configuration of the optically active *cis*-dinitrobis(N -methyl group substituted 1,2-diamine)cobalt(II) complex cation and the CD spectrum has not been known. To elucidate the stereochemistry of this system, the molecular and crystal structure of (-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]Cl has been determined by X-ray structure analysis.

Experimental Section

A sample of (-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]Cl was supplied by Dr. T. Kitamura of this University.

The specimens are yellow prismatic crystals elongated along the b axis. Weissenberg photographs indicated orthorhombic symmetry with the systematic absence of ($h00$) for h odd, ($0k0$) for k odd, and ($00l$) for l odd. Since the compound is optically active, the space group of the crystal is defined as $P2_12_12_1$. The precise lattice constants were obtained by a least-squares refinement of the 2θ angles of the 12 reflections carefully measured on a Rigakudenki four-circle automatic diffractometer, using Mo $K\alpha$ radiation (λ 0.7107 Å). The values obtained are $a = 13.568$ (1) Å, $b = 15.498$ (3) Å, and $c = 7.596$ (1) Å. The calculated density of 1.51 g/cm³ for the four formula units in the unit cell agrees well with the density of 1.52 g/cm³ measured by the flotation method in a mixture of chloroform and carbon tetrachloride.

The crystals used in the data collection had dimensions 0.2 × 0.2 × 0.3 mm. The crystal was mounted with the b axis parallel to the ϕ axis of the diffractometer. The 2θ - ω scan technique was employed

with Mo $K\alpha$ radiation monochromated by a LiF crystal. The scan rate was 1°/min. Backgrounds were measured for 10 s at both limits of the scan. As a general check on the electronic and crystal stability, the intensities of four standard reflections were monitored every 50 reflections. These reflections showed only a 1-2% random variation in intensity, for which no correction was made. Data were collected in the range $0 \leq 2\theta \leq 60^\circ$. Reflections for which the intensities were less than 3 times their standard deviations were regarded as "unobserved" and were not included in subsequent calculations. Thus, 2246 independent reflections were selected and used for the structure analysis. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was made since μ (13.0 cm⁻¹) was low.

Structure Solution and Refinement

An unsharpened three-dimensional Patterson function revealed the position of the cobalt atom. The initial positions of all nonhydrogen atoms were obtained from a three-dimensional Fourier synthesis phased by the cobalt atom. Block-diagonal least-squares refinement, in which all atoms were assigned variable isotropic vibrational parameters, gave factors $R_1 = 0.101$ and $R_2 = 0.134$, where $R_1 = \sum ||F_o| - |F_c||/|F_o|$ and R_2 (the weighted R factor) = $(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. The atomic scattering factors were taken from ref 5. Further refinement using both positional and anisotropic temperature parameters for nonhydrogen atoms reduced the R_1 and R_2 values to 0.052 and 0.057. A difference electron density map calculated at this stage showed the positions of almost all of the hydrogen atoms. The positions of the remaining six hydrogen atoms were assigned from the conventional bond distances and angles. Further refinement was carried out including the contributions of the hydrogen atoms. Temperature factors for the hydrogen atoms were assumed to be isotropic. The refinement converged with $R_1 = 0.040$ and $R_2 = 0.038$. Unit weight was given for all $|F_o|$'s larger than 10.0 and 0.71 for remainders.

The absolute configuration of the complex cation was originally solved as Λ . Next, the effects of anomalous dispersion were introduced in F_c to determine the absolute configuration of the complex.⁶ The values of $\Delta f'$ and $\Delta f''$ for Co and Cl were taken from Cromer's tabulation.⁷ Two refinements were carried out. In the first refinement no change was made in the model. This refinement converged to an R_1 factor of 0.039 and a weighted R_2 factor of 0.037. In the second refinement the y coordinates of all atoms were reversed in sign in order to test the Δ configuration. This refinement converged to an R_1 factor of 0.048 and a weighted R_2 factor of 0.045. Thus, the absolute configuration was taken to be Λ . This result agrees with the absolute configuration deduced from the known absolute configuration of the two asymmetric carbon atoms. Final atomic parameters and their estimated standard deviations are listed in Table I.

The calculation of the lattice constants, the Fourier synthesis, the least-squares analysis, and drawings of the crystal or molecular structures were carried out on a HITAC 8700/8800 computer at the Computer Center of this University, by using the RSCL3, ANSFR-2, HBLS-4, and ORTEP⁸ programs of the UNICS system, respectively.

Table I. Final Atomic Parameters

(a) Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses) ^a							
atom	x	y	z	atom	x	y	z
Co	1244.8 (3)	2105.8 (2)	1706.8 (6)	H(3)	240 (3)	204 (3)	430 (6)
Cl	7851.1 (9)	1871.0 (9)	4000.7 (16)	H(4)	74 (3)	177 (2)	565 (6)
N(1)	277 (2)	1469 (2)	3122 (5)	H(5)	210 (3)	84 (3)	564 (7)
N(2)	2238 (2)	1614 (1)	3400 (5)	H(6)	171 (3)	33 (3)	363 (8)
C(1)	692 (2)	1238 (2)	4873 (6)	H(7)	305 (4)	76 (3)	178 (8)
C(2)	1743 (3)	935 (2)	4489 (6)	H(8)	355 (3)	91 (3)	375 (7)
C(3)	3191 (2)	1266 (3)	2722 (7)	H(9)	355 (3)	166 (3)	233 (7)
C(4)	91 (3)	553 (3)	5819 (7)	H(10)	16 (4)	-4 (3)	528 (8)
N(3)	2238 (2)	2768 (2)	398 (4)	H(11)	38 (3)	49 (3)	708 (7)
N(4)	1099 (2)	3186 (1)	3162 (5)	H(12)	-61 (4)	68 (3)	596 (9)
C(5)	2473 (3)	3600 (2)	1310 (6)	H(13)	206 (3)	291 (3)	-70 (7)
C(6)	1503 (3)	3907 (2)	2112 (6)	H(14)	272 (5)	245 (5)	25 (11)
C(7)	110 (3)	3435 (3)	3920 (9)	H(15)	152 (4)	315 (4)	412 (9)
C(8)	2893 (4)	4296 (3)	88 (9)	H(16)	286 (3)	350 (3)	236 (7)
N(5)	236 (2)	2491 (2)	64 (5)	H(17)	155 (3)	448 (3)	265 (7)
O(1)	437 (2)	2851 (4)	-1294 (6)	H(18)	104 (4)	406 (3)	100 (8)
O(2)	-595 (2)	2367 (4)	391 (8)	H(19)	-32 (4)	353 (3)	261 (9)
N(6)	1419 (2)	1108 (2)	203 (5)	H(20)	20 (4)	404 (3)	455 (7)
O(3)	2009 (2)	1131 (2)	-1023 (5)	H(21)	-10 (4)	303 (3)	490 (8)
O(4)	933 (3)	441 (2)	440 (5)	H(22)	245 (4)	437 (3)	-107 (8)
H(1)	21 (4)	90 (3)	232 (8)	H(23)	340 (4)	414 (3)	-43 (8)
H(2)	-27 (4)	177 (3)	310 (8)	H(24)	288 (3)	487. (3)	80 (7)

(b) Final Thermal Parameters (× 10⁴) and Their Estimated Standard Deviations (in Parentheses)^b

	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Co	16.5 (1)	18.6 (1)	81.3 (6)	0.3 (1)	-3.8 (3)	-0.6 (3)
Cl	43.3 (6)	51.6 (6)	129.6 (20)	8.1 (5)	16.9 (10)	-11.7 (10)
N(1)	22 (1)	29 (1)	107 (6)	0 (1)	-1 (2)	8 (2)
N(2)	21 (1)	23 (1)	105 (5)	1 (1)	-3 (2)	3 (2)
C(1)	29 (2)	32 (1)	103 (7)	-3 (1)	0 (3)	6 (3)
C(2)	29 (2)	30 (1)	122 (7)	-3 (1)	-5 (3)	14 (3)
C(3)	22 (1)	47 (2)	167 (9)	9 (1)	3 (3)	18 (4)
C(4)	41 (2)	52 (2)	160 (10)	-10 (2)	2 (4)	34 (4)
N(3)	26 (1)	25 (1)	96 (5)	-1 (1)	3 (2)	-2 (2)
N(4)	30 (1)	23 (1)	123 (6)	2 (1)	5 (3)	-4 (2)
C(5)	42 (2)	28 (1)	128 (9)	-9 (1)	3 (3)	-4 (3)
C(6)	52 (2)	19 (1)	160 (10)	-1 (1)	13 (4)	0 (3)
C(7)	43 (2)	42 (2)	321 (17)	10 (2)	53 (6)	-18 (5)
C(8)	84 (4)	39 (2)	213 (13)	-23 (2)	44 (6)	-2 (5)
N(5)	25 (1)	35 (1)	135 (6)	0 (1)	-17 (2)	13 (3)
O(1)	47 (2)	168 (4)	245 (11)	-6 (3)	-29 (4)	126 (7)
O(2)	25 (1)	195 (5)	427 (16)	-18 (2)	-47 (4)	198 (8)
N(6)	38 (2)	27 (1)	107 (6)	0 (1)	-15 (3)	-6 (2)
O(3)	63 (2)	43 (1)	169 (7)	-3 (1)	40 (3)	-27 (3)
O(4)	89 (3)	31 (1)	202 (8)	-20 (1)	36 (4)	-25 (3)

^a The values have been multiplied by 10⁴ for the nonhydrogen atoms and by 10³ for the hydrogen atoms. ^b Parameters have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Bond Distances (Å) and Their Estimated Standard Deviations (in Parentheses)

Co-N(1)	1.963 (5)	C(1)-C(4)	1.519 (12)
Co-N(2)	2.013 (5)	N(3)-C(5)	1.497 (9)
Co-N(3)	1.965 (5)	N(4)-C(6)	1.479 (10)
Co-N(4)	2.016 (6)	N(4)-C(7)	1.511 (12)
Co-N(5)	1.946 (6)	C(5)-C(6)	1.526 (11)
Co-N(6)	1.936 (6)	C(5)-C(8)	1.533 (13)
N(1)-C(1)	1.488 (9)	N(5)-O(1)	1.204 (11)
N(2)-C(2)	1.497 (9)	N(5)-O(2)	1.171 (12)
N(2)-C(3)	1.494 (10)	N(6)-O(3)	1.229 (9)
C(1)-C(2)	1.530 (10)	N(6)-O(4)	1.239 (9)

Results and Discussion

Description of the Molecular Structure. A perspective drawing of the complex cation showing ellipsoids of thermal motion is given in Figure 1. The complex cation has approximately symmetry 2 (C₂). The nitro groups are in *cis* positions. The absolute configuration of the complex cation is Λ , as determined from the anomalous dispersion of X-rays. This result agrees with the absolute configuration deduced from the known absolute configuration of the N²-Me-(*S*)-pn ligand. Each conformation of the two diamine chelate rings

Table III. Bond Angles (deg) and Their Estimated Standard Deviations (in Parentheses)

N(1)-Co-N(2)	84.7 (2)	N(1)-C(1)-C(2)	104.8 (5)
N(1)-Co-N(3)	177.1 (3)	N(1)-C(1)-C(4)	112.8 (5)
N(1)-Co-N(4)	92.9 (2)	C(2)-C(1)-C(4)	112.1 (6)
N(1)-Co-N(5)	92.0 (2)	N(2)-C(2)-C(1)	107.9 (5)
N(1)-Co-N(6)	90.2 (2)	Co-N(3)-C(5)	111.2 (3)
N(2)-Co-N(3)	93.5 (2)	Co-N(4)-C(6)	107.2 (3)
N(2)-Co-N(4)	91.7 (2)	Co-N(4)-C(7)	120.6 (4)
N(2)-Co-N(5)	175.5 (3)	C(6)-N(4)-C(7)	110.0 (6)
N(2)-Co-N(6)	89.6 (2)	N(3)-C(5)-C(6)	105.7 (5)
N(3)-Co-N(4)	84.8 (2)	N(3)-C(5)-C(8)	113.9 (5)
N(3)-Co-N(5)	89.9 (2)	C(6)-C(5)-C(8)	110.1 (6)
N(3)-Co-N(6)	92.0 (2)	N(4)-C(6)-C(5)	107.4 (5)
N(4)-Co-N(5)	91.6 (2)	Co-N(5)-O(1)	122.2 (4)
N(4)-Co-N(6)	176.7 (3)	Co-N(5)-O(2)	119.4 (5)
N(5)-Co-N(6)	87.3 (3)	O(1)-N(5)-O(2)	118.4 (8)
Co-N(1)-C(1)	111.0 (3)	Co-N(6)-O(3)	120.3 (3)
Co-N(2)-C(2)	108.6 (3)	Co-N(6)-O(4)	121.0 (3)
Co-N(2)-C(3)	119.8 (3)	O(3)-N(6)-O(4)	118.8 (6)
C(2)-N(2)-C(3)	109.0 (5)		

is presented in Figure 2. All *C*-methyl and *N*-methyl groups have equatorial orientations with respect to the chelate rings. Both five-membered chelate rings form the δ -*gauche* con-

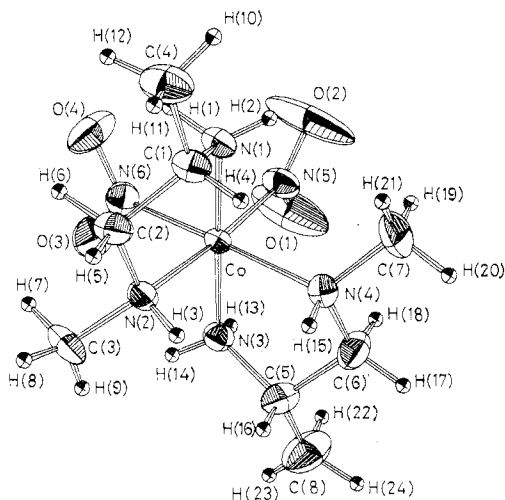


Figure 1. Perspective drawing of the complex cation $(-)_589\text{-cis-}[\text{Co}(\text{NO}_2)_2(\text{N}^2\text{-Me-(S)-pn})_2]^+$ and the numbering scheme for the atoms.

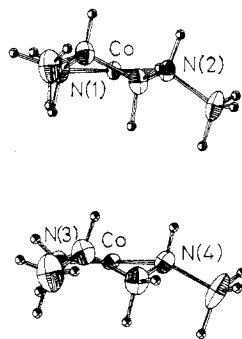


Figure 2. Perspective drawing of the chelate rings.

formation. Therefore this cation has the $\Lambda\text{-(lel,lel)}$ configuration. The absolute configurations around methyl-substituted nitrogen atoms are both *S*. By considering the non-bonded interaction between hydrogen atoms of *N*-methyl groups, we found it interesting that the *N*-methyl groups occupy cis positions to each other. Intramolecular bond distances and angles are given in Tables II and III. The Co–N bond lengths of Co–N(1) and Co–N(3) are 1.963 (5) and 1.965 (5) Å, respectively. These values are comparable with 1.96 (2) Å in $(+)_589\text{-cis-}[\text{Co}(\text{NO}_2)_2(-)_589\text{-1,2-propylenediamine}]_2\text{Cl}^9$ which has a structure similar to the cation except for absence of the *N*-methyl groups. However, the two nitrogen atoms N(2) and N(4), which occupy the site trans to the nitro groups, are coordinated at the distances of 2.013 (5) and 2.016 (6) Å, which are significantly longer than those of Co–N(1) and Co–N(3). The Co–N(nitro group) distances are 1.946 (6) and 1.936 (6) Å, which are slightly shorter than the Co–N(diamine) distances. This is regarded as the effect of the $d\pi\text{-}p\pi$ bonding from the Co(III) d_{xy} electrons to the nonhybridized *p* orbital of the nitrogen atoms of the nitro groups. The ring angles at the cobalt atom for the five-membered chelate rings, N(1)–Co–N(2) and N(3)–Co–N(4), are 84.7 (2) and 84.8 (2)°, respectively. These angles appear normal for Co(III) five-membered chelate rings and can be compared with the mean value of 85.0 (2)° for $(-)_589\text{-cis-}[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+^{10}$ and the mean value of 85.1 (2)° averaged over six determinations for the $[\text{Co}(\text{en})_3]^{3+}$ cation.^{11–16}

Description of the Unit Cell. The unit cell, Figure 3, consists of four complex cations and the chloride counterions. The bonding in the unit cell appears to be mostly electrostatic with hydrogen bondings. The relevant distances are given in Table IV. Each complex cation has hydrogen bonds to a chloride anion and oxygen atoms of the nitro groups. There are four

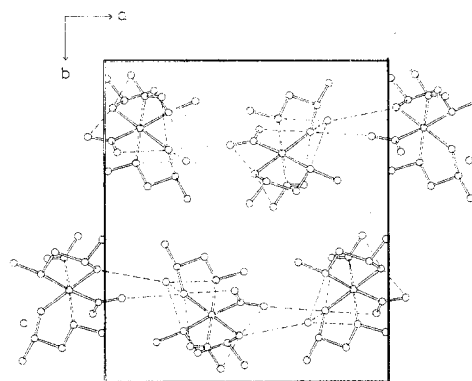


Figure 3. Unit cell contents viewed down the *c* axis. The hydrogen bonds are shown by broken lines. The chained line indicates that an atom at one end displaced by a unit translation along *c* is hydrogen bonded to the atom at the other end.

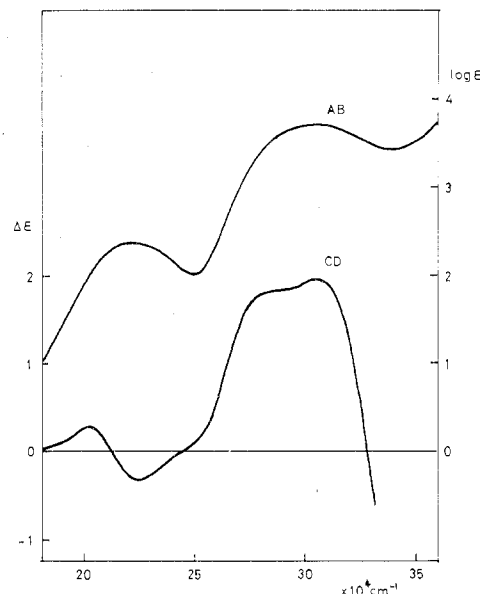


Figure 4. Absorption (AB) and CD spectra of $\Lambda\text{-}(-)_589\text{-cis-}[\text{Co}(\text{NO}_2)_2(\text{N}^2\text{-Me-(S)-pn})_2]\text{Cl}$ in H_2O .

Table IV. Intra- and Interionic Close Contacts (Å)

(a) Intraionic Distances			
O(1)–H(13)	2.26	O(3)–H(14)	2.47
O(2)–H(2)	2.30	O(4)–H(1)	1.87
(b) Interionic Distances ^a			
	symmetry of atom 2	dist	
H(2)–Cl	$x - 1, y, z$	2.64	
O(3)–H(5)	$x, y, z - 1$	2.58	
O(4)–H(11)	$x, y, z - 1$	2.66	
O(2)–H(14)	$x - 1/2, 1/2 - y, -z$	2.34	
H(3)–Cl	$x - 1/2, 1/2 - y, 1 - z$	2.20	
H(15)–Cl	$x - 1/2, 1/2 - y, 1 - z$	2.29	
H(20)–H(8)	$x - 1/2, 1/2 - y, 1 - z$	2.58	
H(21)–H(8)	$x - 1/2, 1/2 - y, 1 - z$	2.65	
O(4)–H(20)	$-x, y - 1/2, 1/2 - z$	2.66	
H(10)–H(18)	$-x, y - 1/2, 1/2 - z$	2.38	
O(4)–H(8)	$1/2 - x, -y, z - 1/2$	2.56	
H(7)–H(5)	$1/2 - x, -y, z - 1/2$	2.65	
H(22)–H(17)	$1/2 - x, 1 - y, z - 1/2$	2.42	
H(22)–H(24)	$1/2 - x, 1 - y, z - 1/2$	2.69	
H(23)–H(17)	$1/2 - x, 1 - y, z - 1/2$	2.58	

^a All distances up to 2.7 Å are listed.

N–H...Cl hydrogen bonds linking the chloride ion tetrahedrally, with two of the distances (N–H...Cl angles) being 2.20 (9) Å (170.7°) and 2.29 (12) Å (168.3°), implying strong interactions to hydrogen atoms H(3) and H(15), which belong

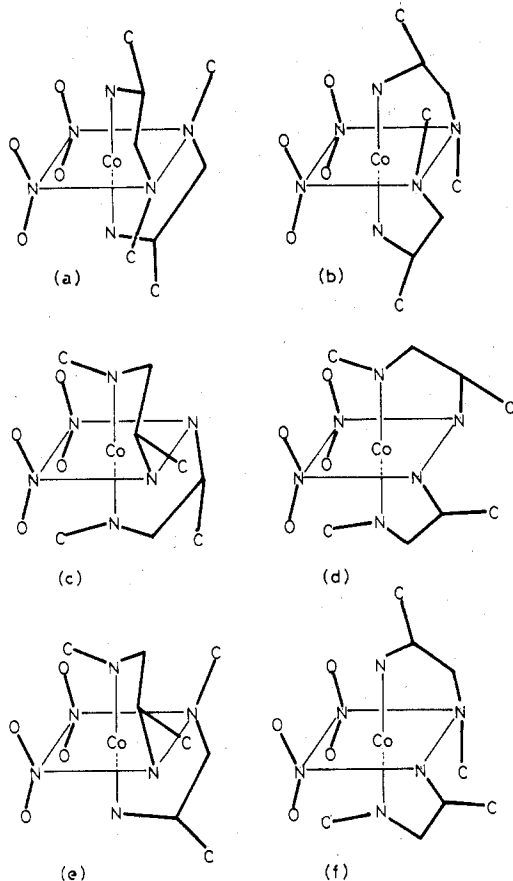


Figure 5. Six possible isomers of *cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]⁺: (a) Λ -*cis*-C²-*cis*, (b) Δ -*cis*-C²-*cis*, (c) Λ -*cis*-C²-*trans*, (d) Δ -*cis*-C²-*trans*, (e) Λ -*cis*-C¹-*cis*, (f) Δ -*cis*-C¹-*cis*.

to secondary amino groups of the same complex cation. The residual two interactions are weak and contacted to H(2) and H(13) ($x - 1/2, 1/2 - y, -z$), of lengths (angles) 2.64 (10) Å (147.8°) and 2.74 (10) Å (141.8°).

Four intramolecular hydrogen bonds are listed in Table IV. Oxygen atoms of nitro groups are linked to hydrogen atoms of primary amino groups. It seems that these interactions orient the two nitro groups nearly parallel to the planes containing N(1)-N(5)-N(3) or N(1)-N(6)-N(3), respectively. The short distance of 1.87 (6) Å between H(1) and O(4) suggests strong linkage between this nitro group and the amino group. This observation would explain its smaller thermal motions than those found for the other nitro group (Figure 1). Moreover, the second group could potentially form any of three hydrogen bonds, two of the intra- and one of the intermolecular type (Table IV), and the combined result is such as to allow more librational freedom. These intramolecular hydrogen bonds of the nitro groups to the apical N-H are usually observed in such *cis*-dinitro Co(III) complexes.^{9,10,17}

Circular Dichroism and Absolute Configuration. Some X-ray structure analysis and circular dichroism studies of *cis*-

[Co(NO₂)₂(diamine)₂]⁺ suggest the following empirical rule: When these type of complexes give a lower energy positive Cotton effect in the first absorption region, they should be assigned to the Λ configuration.^{9,17,18} In the CD spectrum of the Λ -*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]⁺, a lower energy positive Cotton effect has been observed in the first absorption region (Figure 4). Consequently, the simple empirical rule between the sign of the longer wavelength circular dichroism band and the absolute configuration around the metal atom was found to hold even in the case of the *N*-methyl-substituted diamine as well as in the case of the ordinary diamines.

Stereochemistry. The *cis*-dinitro complex of this diamine contains six isomers as illustrated in Figure 5. Two of them are trans isomers with respect to *N*-methyl groups and receive little stabilization via hydrogen bonding between nitro groups and apical amino groups because of methyl substitution in apical amino groups. Isomers (e) and (f) also have a similar disadvantage. In the Δ isomer (b) and (f), methyl substitution on the nitrogen atoms on opposite sides of the nitro groups causes steric repulsion with the methylene proton of the other chelate ring. These interactions are also observed in the similar complex [Co(ox)(*N,N'*-Me₂en)₂]⁺.⁴ Methyl-methyl repulsion is also apparent in *N*-methyl *cis* isomer (e) for its equatorial orientation. These considerations of nonbonded interactions and intramolecular hydrogen bonds may explain the relative stability of this complex cation.

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Registry No. (-)₅₈₉-*cis*-[Co(NO₂)₂(N²-Me-(*S*)-pn)₂]Cl, 69126-61-0.

Supplementary Material Available: A listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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