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X-Ray Crystal Structures of *cis*- and *trans*-Dinitrobis(1,4-butanediamine)cobalt(III) Nitrates. Conformation of Seven-Membered Chelate Rings

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The structures of *cis*- and *trans*-dinitrobis(1,4-butanediamine)cobalt(III) nitrates were determined by the single-crystal X-ray diffraction method. *cis*-$[Co(NO_2)_2(tmd)_2]NO_3$ (tmd=$H_2N(CH_2)_4NH_2$) is monoclinic with the space group $P2_1/a$; the cell constants are a=23.878(4), b=8.403(1), c=16.675(3) Å, β=103.24(1)°; Z=8, and the final R value was 0.051. *trans*-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot H_2O$ is triclinic with the space group $P\bar{1}$; the cell constants are a=9.753(3), b=13.909(4), c=6.327(1) Å, α=102.07(2), β=91.05(2), γ=87.83(3)°; Z=2, and the final R value was 0.058. Both complexes have a slightly distorted octahedral geometry around the cobalt center. The conformations of the seven-membered chelate rings have twist-chair and chair forms for the cis and trans complexes, respectively.

Chelate rings containing more than six atoms have been scarce until recently, whereas numerous examples of five- and six-membered chelate rings have been known.[1] The stability of a chelate ring depends on its size. Thus, reactions between $[CoCl_2(en)_2]Cl$[2] and α,ω-alkanediamines in dimethyl sulfoxide gave no monomeric $[Co(en)_2(H_2N(CH_2)_nNH_2)]^{3+}$ for n=5—8, whereas the corresponding complexes were obtained for n=2—4 and 9—14.[1,3] Similar results were also obtained for the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with α,ω-alkanediamines.[4] 1,4-Butanediamine (tetramethylenediamine) has the longest chain in the smaller chelate ring family.[2] Therefore the conformations of tmd chelate rings are of great interest. Only the structure of $(+)_{589}$-$[Co(tmd)_3]^{3+}$ was reported.[5,6] The conformation is 'lel$_3$' and the seven-membered rings take twist-chair forms. Preliminary reports on the crystal structures of *trans*-$[CoCl_2(tmd)_2]Cl \cdot H_2O$[7] and Δ-$[Co(en)(tn)(tmd)][Co(CN)_6] \cdot H_2O$[8] do exist but the full report is still lacking.

We have succeeded in the preparation of both *cis*- and *trans*-$[Co(NO_2)_2(tmd)_2]^+$ complexes using dimethyl sulfoxide as a solvent. The geometrical configurations were determined on the basis of their electronic and Raman spectra.[9] To elucidate the conformation of the seven-membered chelate rings we have determined the crystal structures of *cis*- and *trans*-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot nH_2O$ (n is 0 for the cis and 1 for the trans complex).

Experimental

The compounds were prepared by the method reported in a previous paper,[9] and recrystallized from water. The reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation (the scan speed was 4° min^{-1}). The crystal data and the conditions of data collection are shown in Table 1.

The structures were solved by the heavy-atom method. For the trans complex, the reflections with odd $h+k$ indexes were very weak. Two models were therefore taken into consideration for this pseudo C lattice. In the first model the two crystallographically independent molecules were situated at the centers of symmetry: (0, 0, 0) and (1/2, 1/2, 0). In the second model the complex was situated in the general position, the two molecules being separated by about (0.5, 0.5, 0) and related through the center of symmetry. The second model gave a satisfactory result.

The positions of the central metal atoms and some coordinated atoms were deduced from the three-dimentional Patterson maps. The positional and thermal parameters were refined by the block-diagonal least-squares method. The positions of the hydrogen atoms, except for the amine and

Table 1. Crystal Data for *cis*- and *trans*-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot nH_2O$

	cis-$[Co(NO_2)_2(tmd)_2]NO_3$	*trans*-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot H_2O$
Formula	$C_8H_{24}CoN_7O_7$	$C_8H_{26}CoN_7O_8$
F. W.	389.25	407.27
C. S.	Monoclinic	Triclinic
S. G.	$P2_1/a$	$P\bar{1}$
$a(l/Å)$	23.878(4)	9.753(3)
$b(l/Å)$	8.403(1)	13.909(4)
$c(l/Å)$	16.675(3)	6.327(1)
$\alpha(\phi/°)$		102.07(2)
$\beta(\phi/°)$	103.24(1)	91.05(2)
$\gamma(\phi/°)$		87.83(3)
$U(v/Å^3)$	3256.9(8)	838.6(4)
$D_m(d/g\,cm^{-3})$	1.57	1.62
$D_c(d/g\,cm^{-3})$	1.59	1.61
Z	8	2
μ(Mo $K\alpha$)(n/cm^{-1})	1.15	1.12
Crystal size(l/mm)	0.35×0.35×0.45	0.16×0.08×0.26
Scan Mode	ω	ω-2θ
Scan width$(\omega/°)$	1.3+0.5 tanθ	1.2+0.5 tanθ
$2\theta_{max}(\phi/°)$	65	65
Refls. measured	$\pm h, k, l$	$\pm h, \pm k, l$
No. of refls. measured	12595	6108
No. of unique data used for calc. ($\|F_o\|>3\sigma(F_o)$)	7153	3884
R[a]	0.051	0.058
R_w[b]	0.063	0.053

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$ b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w=[\sigma^2(|F_o|)+aF_o^2]^{-1}$, where a=0.015.

the water hydrogens in the trans complex, were deduced from difference Fourier synthesis, and refined with isotropic thermal parameters. The positions of the amine hydrogens in the trans complex were calculated and fixed; they were included in the calculation of structure factors.

All the calculations were carried out on a Nippon Electric Co. ACOS-1000 computer at the computer center of Tohoku University, using the Universal Crystallographic Computation Program System UNICS III.[10] The atomic-scattering factors were taken from Ref. 11 for non-hydrogen atoms and from Ref. 12 for hydrogen atom.

Table 2. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for *cis*-$[Co(NO_2)_2(tmd)_2]NO_3$

Atom	x	y	z	B_{eq}/Å^{2} a)
Co(1)	1568.6(1)	1573.7(4)	609.7(2)	2.3
Co(2)	1635.0(1)	4647.1(4)	5676.0(2)	2.3
N(11)	1695(1)	2827(3)	1615(2)	3.6
N(12)	2230(1)	2737(3)	415(2)	3.5
N(13)	2090(1)	−84(3)	1183(1)	3.0
N(14)	894(1)	558(3)	899(1)	2.9
N(15)	1045(1)	3223(3)	28(2)	3.3
N(16)	1507(1)	320(3)	−419(1)	2.8
N(21)	1835(1)	3405(3)	6684(2)	3.3
N(22)	2388(1)	4052(4)	5498(2)	3.8
N(23)	1988(1)	6530(3)	6280(2)	3.1
N(24)	876(1)	5134(3)	5907(1)	2.5
N(25)	1287(1)	2720(3)	5094(2)	3.6
N(26)	1488(1)	5951(3)	4657(1)	2.9
O(11)	1428(1)	4056(4)	1622(2)	6.5
O(12)	2044(1)	2410(4)	2239(1)	6.0
O(13)	2720(1)	2246(4)	679(2)	6.2
O(14)	2166(1)	4013(4)	46(2)	6.0
O(21)	1840(1)	1956(3)	6657(2)	6.3
O(22)	1978(1)	4052(3)	7359(1)	4.8
O(23)	2823(1)	4755(4)	5834(2)	6.6
O(24)	2433(1)	2900(4)	5065(2)	6.9
C(11)	1927(1)	−1787(4)	1232(2)	3.4
C(12)	1676(1)	−2149(4)	1962(2)	4.1
C(13)	1042(2)	−1784(5)	1858(2)	4.5
C(14)	878(1)	−54(4)	1731(2)	3.5
C(15)	534(1)	2894(4)	−660(2)	3.4
C(16)	667(2)	2943(5)	−1492(2)	4.3
C(17)	951(2)	1488(5)	−1754(2)	4.4
C(18)	1535(1)	1065(4)	−1224(2)	3.6
C(21)	1718(1)	8130(4)	6268(2)	4.0
C(22)	1381(2)	8335(4)	6918(2)	4.6
C(23)	792(2)	7551(4)	6753(2)	4.5
C(24)	781(1)	5776(4)	6703(2)	3.4
C(25)	774(1)	2694(4)	4389(2)	4.0
C(26)	906(2)	2916(5)	3558(2)	4.9
C(27)	1016(2)	4606(5)	3331(2)	5.0
C(28)	1550(1)	5374(5)	3834(2)	4.4
N(3)	4610(1)	2333(3)	800(2)	4.6
O(31)	4642(1)	3690(3)	552(2)	5.1
O(32)	4131(1)	1775(4)	719(4)	12.9
O(33)	5057(1)	1585(3)	1088(2)	6.5
N(4)	4893(1)	3068(3)	5900(2)	4.5
O(41)	4791(1)	1770(3)	5546(2)	4.7
O(42)	5400(1)	3467(4)	6112(2)	7.6
O(43)	4498(2)	3806(5)	6034(4)	13.2

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

Results and Discussion

Final atomic parameters for the cis and trans complexes are listed in Tables 2 and 3, respectively. Relevant interatomic distances and angles are summarized in Tables 4 and 5.[13] The structures of complex cations with atom numbering scheme are depicted in Figs. 1 and 2. The configurations of the complexes agree with those proposed previously.[9]

The crystal of *cis*-$[Co(NO_2)_2(tmd)_2]NO_3$ consists of two crystallographically independent complex cations and nitrate ions. The structures of both cations were essentially the same as shown in Fig. 1 and Table 4. The coordination geometry around the cobalt atom is a slightly deformed octahedron and resembles the structure of $[Co(tmd)_3]^{3+}$ [5,6] except for the nitro groups. The Co-N(NO_2) bond lengths range from 1.943(3) to 1.953(3) Å, and are a little longer than the values for *cis*-$[Co(NO_2)_2(en)_2]^+$ complexes (1.887—1.936 Å)[14-16] and *cis*-$[Co(NO_2)_2(tn)_2]^+$ (1.924 and 1.936 Å).[17] The Co-N(amine) bond lengths span the range between 1.959(3) and 1.990(3) Å and are normal, although the Co-N(amine) bond lengths trans to NO_2 ligands are longer than those cis to NO_2 ligands by 0.014—0.023 Å. These differences are attributable to trans-influence of NO_2 as observed for the *cis*-

Table 3. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for *trans*-$[Co(NO_2)_2(tmd)_2]NO_3\cdot H_2O$

Atom	x	y	z	B_{eq}/Å^{2} a)
Co	2454.5(6)	2456.0(5)	4890.7(9)	1.4
N(1)	1987(3)	3184(2)	2668(5)	2.1
N(2)	2911(4)	1753(2)	7152(5)	2.2
N(3)	4166(4)	3173(3)	5543(5)	2.3
N(4)	1414(4)	3398(2)	7145(5)	2.1
N(5)	758(3)	1720(2)	4230(5)	2.0
N(6)	3502(3)	1530(2)	2604(5)	2.0
O(1)	796(3)	3333(3)	2166(6)	3.6
O(2)	2919(3)	3476(3)	1675(5)	3.5
O(3)	4108(3)	1599(3)	7680(5)	3.4
O(4)	1970(3)	1472(3)	8157(5)	3.3
C(1)	1125(5)	4459(4)	7087(8)	3.3
C(2)	2230(7)	5117(4)	8148(9)	4.4
C(3)	3648(7)	4951(4)	7137(9)	4.5
C(4)	4418(5)	4008(4)	7346(7)	3.2
C(5)	3925(4)	507(3)	2757(7)	2.6
C(6)	2860(5)	−237(3)	1849(7)	2.9
C(7)	1465(5)	−71(3)	2940(8)	3.1
C(8)	604(4)	802(3)	2559(7)	2.4
N(7)	6999(4)	2260(3)	2583(7)	3.1
O(5)	6790(4)	1957(4)	4285(7)	5.6
O(6)	6043(3)	2483(3)	1502(6)	4.0
O(7)	8201(3)	2331(3)	1996(7)	4.8
O(8)	8640(4)	2708(3)	7717(7)	5.2

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

Table 4. Selected Interatomic Distances and Angles for *cis*-$[Co(NO_2)_2(tmd)_2]NO_3$

Bond length	*l*/Å	Bond length	*l*/Å
Co(1)-N(11)	1.944(3)	Co(2)-N(21)	1.943(3)
Co(1)-N(12)	1.946(3)	Co(2)-N(22)	1.953(3)
Co(1)-N(13)	1.964(2)	Co(2)-N(23)	1.959(2)
Co(1)-N(14)	1.979(3)	Co(2)-N(24)	1.980(2)
Co(1)-N(15)	1.967(2)	Co(2)-N(25)	1.971(3)
Co(1)-N(16)	1.990(2)	Co(2)-N(26)	1.985(3)
N(13)-C(11)	1.490(4)	N(23)-C(21)	1.489(4)
N(14)-C(14)	1.487(4)	N(24)-C(24)	1.497(4)
N(15)-C(15)	1.496(4)	N(25)-C(25)	1.490(4)
N(16)-C(18)	1.496(4)	N(26)-C(28)	1.494(5)
C(11)-C(12)	1.505(5)	C(21)-C(22)	1.501(6)
C(12)-C(13)	1.515(5)	C(22)-C(23)	1.520(5)
C(13)-C(14)	1.509(5)	C(23)-C(24)	1.494(5)
C(15)-C(16)	1.494(5)	C(25)-C(26)	1.501(5)
C(16)-C(17)	1.510(6)	C(26)-C(27)	1.508(6)
C(17)-C(18)	1.513(5)	C(27)-C(28)	1.503(5)
O(11)···H(N15A)	2.00(3)	O(11)···N(15)	2.697(4)
O(12)···H(N13B)	2.08(4)	O(12)···N(13)	2.757(4)
O(13)···H(N13A)	2.11(4)	O(13)···N(13)	2.718(4)
O(14)···H(N15B)	1.94(5)	O(14)···N(15)	2.752(4)
O(21)···H(N25A)	2.25(3)	O(21)···N(25)	2.715(4)
O(22)···H(N23B)	2.08(3)	O(22)···N(23)	2.755(4)
O(23)···H(N23A)	2.13(3)	O(23)···N(23)	2.726(4)
O(24)···H(N25B)	2.16(3)	O(24)···N(25)	2.753(4)
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
N(11)-Co(1)-N(12)	84.3(1)	N(21)-Co(2)-N(22)	86.6(1)
N(11)-Co(1)-N(13)	90.5(1)	N(21)-Co(2)-N(23)	89.8(1)
N(11)-Co(1)-N(14)	89.9(1)	N(21)-Co(2)-N(24)	89.9(1)
N(11)-Co(1)-N(15)	90.0(1)	N(21)-Co(2)-N(25)	88.7(1)
N(12)-Co(1)-N(13)	89.4(1)	N(22)-Co(2)-N(23)	89.0(1)
N(12)-Co(1)-N(15)	90.7(1)	N(22)-Co(2)-N(25)	90.8(1)
N(12)-Co(1)-N(16)	91.4(1)	N(22)-Co(2)-N(26)	90.0(1)
N(13)-Co(1)-N(14)	92.1(1)	N(23)-Co(2)-N(24)	92.2(1)
N(13)-Co(1)-N(16)	87.5(1)	N(23)-Co(2)-N(26)	88.0(1)
N(14)-Co(1)-N(15)	87.9(1)	N(24)-Co(2)-N(25)	88.0(1)
N(14)-Co(1)-N(16)	94.5(1)	N(24)-Co(2)-N(26)	93.6(1)
N(15)-Co(1)-N(16)	92.0(1)	N(25)-Co(2)-N(26)	93.4(1)
Co(1)-N(13)-C(11)	124.3(2)	Co(2)-N(23)-C(21)	126.1(2)
Co(1)-N(14)-C(14)	124.9(2)	Co(2)-N(24)-C(24)	125.3(2)
Co(1)-N(15)-C(15)	124.2(2)	Co(2)-N(25)-C(25)	125.3(2)
Co(1)-N(16)-C(18)	122.8(2)	Co(2)-N(26)-C(28)	124.9(2)
N(13)-C(11)-C(12)	113.3(3)	N(23)-C(21)-C(22)	113.3(3)
N(14)-C(14)-C(13)	113.8(3)	N(24)-C(24)-C(23)	113.9(3)
N(15)-C(15)-C(16)	113.4(3)	N(25)-C(25)-C(26)	114.7(3)
N(16)-C(18)-C(17)	113.4(3)	N(26)-C(28)-C(27)	113.7(3)
C(11)-C(12)-C(13)	116.1(3)	C(21)-C(22)-C(23)	116.5(3)
C(12)-C(13)-C(14)	115.6(3)	C(22)-C(23)-C(24)	116.6(3)
C(15)-C(16)-C(17)	116.9(3)	C(25)-C(26)-C(27)	115.7(3)
C(16)-C(17)-C(18)	115.9(3)	C(26)-C(27)-C(28)	116.0(3)

Table 5. Interatomic Distances and Angles for *trans*-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot H_2O$

Bond length	*l*/Å	Bond length	*l*/Å
Co-N(1)	1.936(4)	Co-N(2)	1.931(4)
Co-N(3)	1.970(4)	Co-N(4)	1.988(3)
Co-N(5)	1.971(3)	Co-N(6)	1.992(3)
N(3)-C(4)	1.473(5)	N(4)-C(1)	1.500(6)
N(5)-C(8)	1.489(5)	N(6)-C(5)	1.490(6)
C(1)-C(2)	1.497(8)	C(2)-C(3)	1.524(9)
C(3)-C(4)	1.515(8)	C(5)-C(6)	1.514(6)
C(6)-C(7)	1.525(7)	C(7)-C(8)	1.508(7)
O(1)···H(N5A)	2.208(4)	O(1)···N(5)	2.824(6)
O(2)···H(N3A)	2.109(3)	O(2)···N(3)	2.816(5)
O(3)···H(N3B)	2.268(4)	O(3)···N(3)	2.806(6)
O(4)···H(N5B)	2.129(3)	O(4)···N(5)	2.812(5)
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
N(1)-Co-N(2)	178.9(2)	N(1)-Co-N(3)	90.5(2)
N(1)-Co-N(4)	93.1(1)	N(1)-Co-N(5)	90.0(1)
N(1)-Co-N(6)	86.0(1)	N(2)-Co-N(3)	89.2(2)
N(2)-Co-N(4)	85.8(1)	N(2)-Co-N(5)	90.4(2)
N(2)-Co-N(6)	95.1(1)	N(3)-Co-N(4)	92.9(1)
N(3)-Co-N(5)	179.2(1)	N(3)-Co-N(6)	86.6(2)
N(4)-Co-N(5)	87.8(1)	N(4)-Co-N(6)	179.0(2)
N(5)-Co-N(6)	92.7(1)		
Co-N(3)-C(4)	127.1(3)	Co-N(4)-C(1)	124.2(3)
Co-N(5)-C(8)	125.7(3)	Co-N(6)-C(5)	123.6(3)
N(3)-C(4)-C(3)	113.9(4)	N(4)-C(1)-C(2)	113.0(4)
N(5)-C(8)-C(7)	115.0(4)	N(6)-C(5)-C(6)	113.1(4)
C(1)-C(2)-C(3)	117.1(4)	C(2)-C(3)-C(4)	116.2(5)
C(5)-C(6)-C(7)	115.6(4)	C(6)-C(7)-C(8)	116.6(4)

$[Co(NO_2)_2(en)_2]^{2+}$ complexes.[14,15]

As shown in Fig. 2, the complex cation in the crystal of *trans*-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot H_2O$ is pseudo-centrosymmetric and the coordination geometry is also a slightly distorted octahedron. Co-N(NO_2) bond lengths, 1.931(4) and 1.936(4) Å, are normal and a little shorter than in the cis-isomer. Both NO_2 ligands are almost in a plane containing the cobalt atom: The deviations from the least-squares plane are Co −0.016, N(1) 0.015, N(2) −0.013, O(1) −0.002, O(2) −0.002, O(3) 0.009, and O(4) 0.009 Å. Such coplanarity is a common feature of trans-dinitro cobalt complexes.[15,18–21] Co-N(amine) bond lengths range between 1.970(4) and 1.992(3) Å.

Figures 3 and 4 show the packing diagrams for the two complexes. Some hydrogen bonding was observed between the amine nitrogens, nitrate ions, and water

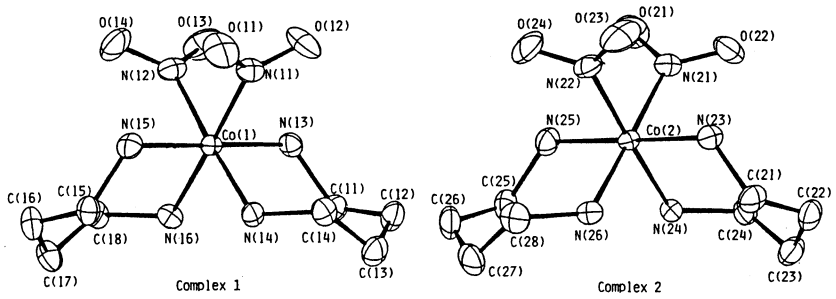

Fig. 1. ORTEP drawing of *cis*-$[Co(NO_2)_2(tmd)_2]^+$ ions.

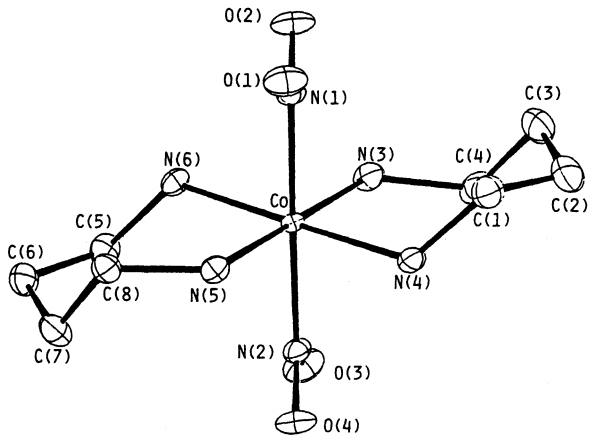

Fig. 2. ORTEP drawing of *trans*-$[Co(NO_2)_2(tmd)_2]^+$ ion.

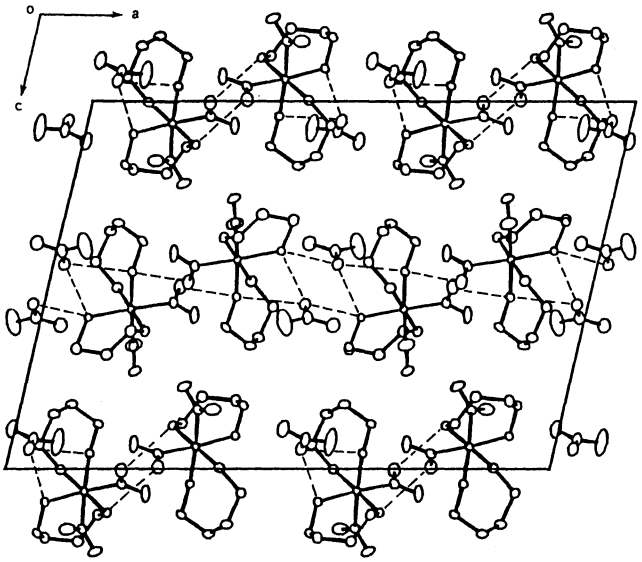

Fig. 3. Projection of the unit cell of *cis*-$[Co(NO_2)_2(tmd)_2]NO_3$ along b axis. Complex 1's and 2's are lying almost in the (0 0 1) and (0 0 2) plane, respectively. Interionic hydrogen bonds are indicated with broken lines.

molecules. Interatomic distances for hydrogen bonded atoms are listed as the supplementary data.[13]

Conformations of Chelate Rings. Bond lengths and angles in the chelate rings are almost the same for the cis and trans complexes, as shown in Tables 4 and 5. All the chelate rings in the cis complexes have a similar conformation. The two chelate rings in the trans complex are also similar to each other, but different from those in the cis complex. Figure 5 shows the projections of the chelate rings along the bisectors of the N-Co-N angle and the atom deviations from the N-Co-N plane.

The conformations of the chelate rings in the cis complex are quite similar to those in $[Co(tmd)_3]^{3+}$ [5,6]: The carbon atoms next to the nitrogens are displaced by 0.73—0.88 Å on the opposite sides of the plane formed by the cobalt and two nitrogen atoms, and the remaining carbon atoms are nearly in this plane. The deviations from the plane are 0.03 to 0.25 Å. This conformation corresponds to the twist-chair form of the cycloheptane ring.[22] The torsion angles shown in Table 6 indicate that only the central C-C bonds take gauche conformation. In contrast to the cis complex, the chelate rings of the trans complex take the chair form. One of the carbon atoms next to the nitrogen lies almost on the N-Co-N plane, and the other three carbon atoms deviate from the plane by more than 0.97 Å.

A conformation analysis of cycloheptane revealed that the chair form is less stable than the twist-chair form for seven-membered alkane ring, although the energy difference is quite small (2.16 kcal mol^{-1}).[22] Repulsion between hydrogen atoms across the ring is serious, especially in the chair-form.

However, such transannular interaction is not important in the chelate rings, because the corresponding H···H interatomic distances in the trans complex are only slightly shorter than the sum of the van der Waals radii: H(C4A)···H(N4A) 2.32(4) and H(C8A)···H(N6A) 2.18(5) Å. The difference in the conformations of the chelate rings in cis and trans complexes

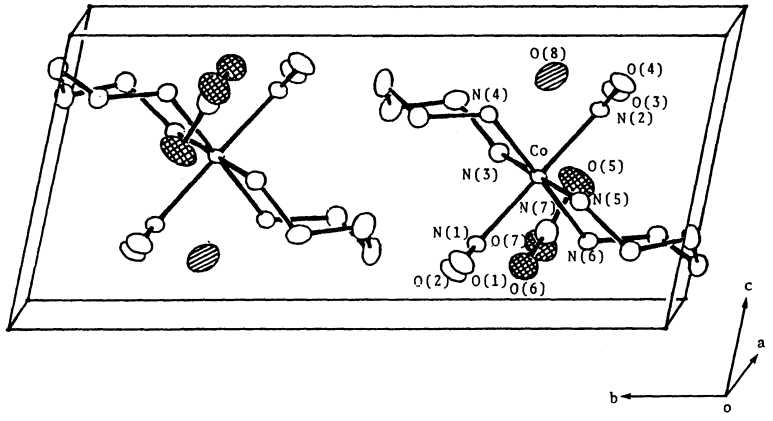

Fig. 4. Perspective of the unit cell of *trans*-$[Co(NO_2)_2(tmd)_2]$-$NO_3 \cdot H_2O$. The water oxygens are hatched and the nitrate oxygens are cross-hatched.

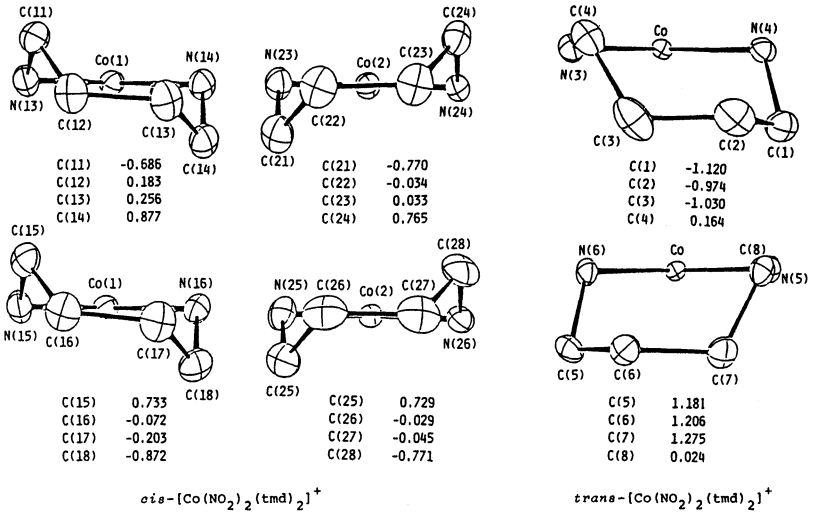

Fig. 5. Projections of tmd chelate rings along the bisector of the N-Co-N angle and the atom deviations (l/Å) from the N-Co-N plane.

Table 6. Torsion Angles in the Chelate Rings

Torsion angle[a]	ϕ/°	Torsion angle	ϕ/°
cis-$[Co(NO_2)_2(tmd)_2]NO_3$			
N(14)-Co(1)-N(13)-C(11)	33.8(2)	N(16)-Co(1)-N(15)-C(15)	36.5(2)
N(13)-Co(1)-N(14)-C(14)	45.9(2)	N(15)-Co(1)-N(16)-C(18)	44.2(2)
Co(1)-N(13)-C(11)-C(12)	−89.1(3)	Co(1)-N(15)-C(15)-C(16)	−90.6(3)
Co(1)-N(14)-C(14)-C(13)	−91.5(3)	Co(1)-N(16)-C(18)-C(17)	−93.0(3)
N(13)-C(11)-C(12)-C(13)	82.5(4)	N(15)-C(15)-C(16)-C(17)	79.4(4)
N(14)-C(14)-C(13)-C(12)	73.4(4)	N(16)-C(18)-C(17)-C(16)	75.3(4)
C(11)-C(12)-C(13)-C(14)	−63.6(4)	C(15)-C(16)-C(17)-C(18)	−61.5(4)
N(24)-Co(2)-N(23)-C(21)	−40.1(3)	N(26)-Co(2)-N(25)-C(25)	−36.6(3)
N(23)-Co(2)-N(24)-C(24)	−39.0(2)	N(25)-Co(2)-N(26)-C(28)	−39.3(3)
Co(2)-N(23)-C(21)-C(22)	89.5(3)	Co(2)-N(25)-C(25)-C(26)	86.6(3)
Co(2)-N(24)-C(24)-C(23)	88.3(3)	Co(2)-N(26)-C(28)-C(27)	87.8(3)
N(23)-C(21)-C(22)-C(23)	−76.9(4)	N(25)-C(25)-C(26)-C(27)	−79.0(4)
N(24)-C(24)-C(23)-C(22)	−76.9(4)	N(26)-C(28)-C(27)-C(26)	−78.7(4)
C(21)-C(22)-C(23)-C(24)	64.1(4)	C(25)-C(26)-C(27)-C(28)	66.6(5)
trans-$[Co(NO_2)_2(tmd)_2]NO_3 \cdot H_2O$			
N(4)-Co-N(3)-C(4)	7.9(3)	N(6)-Co-N(5)-C(8)	1.1(3)
N(3)-Co-N(4)-C(1)	65.2(3)	N(5)-Co-N(6)-C(5)	−71.6(3)
Co-N(3)-C(4)-C(3)	−70.5(5)	Co-N(5)-C(8)-C(7)	63.6(4)
Co-N(4)-C(1)-C(2)	−88.9(4)	Co-N(6)-C(5)-C(6)	89.8(4)
N(3)-C(4)-C(3)-C(2)	90.9(5)	N(5)-C(8)-C(7)-C(6)	−93.8(4)
N(4)-C(1)-C(2)-C(3)	63.7(6)	N(6)-C(5)-C(6)-C(7)	−60.7(5)
C(1)-C(2)-C(3)-C(4)	−69.8(7)	C(5)-C(6)-C(7)-C(8)	−70.9(5)

a) Looking from atom 2 to atom 3, the clockwise rotation of bond 3-4 with reference to bond 2-1 is given.

may be due to the interaction of the NO_2 ligands and the chelate rings. The oxygen atoms of the NO_2 ligands form intramolecular hydrogen bonds to amine groups of the chelate rings as shown in Tables 4 and 5. Such hydrogen bonds have been observed for *trans*-$[Co(NO_2)_2(en)_2]NO_3$,[15] *cis*-$[Co(NO_2)_2(en)_2]Cl$,[16] and *cis*-$[Co(NO_2)_2(tn)_2]Cl \cdot H_2O$.[17] Furthermore, the oxygen atoms of the nitro groups interact with the methylene groups adjacent to the tmd-nitrogens. Figure 6 shows the projection of the trans complex along the Co-N(NO_2) axis. The two nitro groups lie in a plane containing the cobalt atom, and the angle between Co-N(3) and the plane is 30.0°. Broken lines show the hypothetical structure with the twist-chair form for the chelate rings. To minimize the repulsion between the oxygen atoms of the nitro groups and the carbon atoms adjacent to the tmd-nitrogens in the hypothetical structure, the NO_2 ligands should lie in the plane bisecting the angle N(3)-Co-N(6). Even for this conformation, four O···C interatomic distances

Table 7. Comparison of Bond Angles between 5-, 6-, and 7-Membered Chelate Rings

Complex	ϕ/°			
	N-Co-N	Co-N-C	N-C-C	C-C-C
$[Co(en)_3]^{3+}$ a)	85.4	108.4	105.8	
$[Co(tn)_3]^{3+}$ b)	91.0	122.0	112.3	113.6
$[Co(tmd)_3]^{3+}$ c)	89.8	122.3	113.5	115.2
cis-$[Co(NO_2)_2(tmd)_2]^+$ d)	92.4(6)	124.7(9)	113.7(4)	116.2(4)
trans-$[Co(NO_2)_2(tmd)_2]^+$ d)	92.8(1)	125.2(14)	113.8(8)	116.4(5)

a) M. Iwata, K. Nakatzu, and Y. Saito, *Acta Crystallogr.,Sect. B*, **25**, 2562 (1969). b) R. Nagao, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 2438 (1973). c) Ref. 5. d) This work.

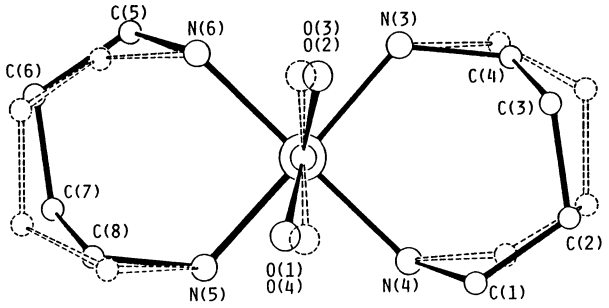

Fig. 6. Projection of the *trans*-$[Co(NO_2)_2(tmd)_2]^+$ ion along the Co–N(NO_2) axis. Broken lines show the hypothetical molecular structure with the chelate rings in the twist-chair form.

(O(1)···C(1), O(1)···C(8), O(3)···C(4), and O(3)···C(5)) are about 3.19 Å, i.e. shorter than the sum of the van der Waals radii, 3.40 Å. The adopted chair form and the inclination of the nitro groups help with alleviating this repulsion: Only two O···C distances in the real complex are shorter than the sum of the van der Waals radii, O(1)···C(1) 3.196(6) and O(3)···C(5) 3.172(5) Å.

There exists only one such O···C interatomic distance in the cis complex (O(22)···C(24) 3.167(4) Å).

Table 7 compares the bond angles for the five-, six-, and seven-membered chelate rings. The larger deviations from the tetrahedral angle for nitrogen and carbon atoms in tmd complexes clearly show the instability of seven-membered chelate rings.

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