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X-Ray Structure and Conformational Analyses of Cobalt(III) Complexes Containing 1,3-Propanediamine and 1,4-Butanediamine

Saeko Kurachi and Shigeru Ohba*
Department of Chemistry, Faculty of Science and Technology, Keio University,
3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223
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Crystal structures of octahedral cobalt(III) complexes containing diamines, $NH_2(CH_2)_nNH_2$ with $n=3$ or 4 (abbreviations are tn and tmd, respectively), were determined by X-ray analysis. In crystals of [Co(tn)(tmd)$_2$] Cl$_3$, (**1**), the tn chelate ring takes skew-boat form, and the conformation of the complex is *lel lel*$_2$. In crystals of [Co(tn)$_2$(tmd)]Br$_3\cdot$2.7H$_2$O, (**2**), both two independent complex cations take syn-chair$_2$ *lel* configuration. Molecular mechanics calculation indicated that the six-membered tn chelate ring may take skew-boat form in a crowded system to reduce the steric repulsions between the chelate rings, although the tn chelate ring originally prefers the chair form.

Six-membered chelate rings formed by tn and a metal atom are the chair form in crystals of [Co(en)$_2$(tn)]Br$_3$ (en=ethylenediamine),[1)] [Cr(en)$_2$(tn)]Br$_3\cdot$H$_2$O,[2)] [Cr(en)(tn)$_2$]I$_3\cdot$H$_2$O,[2)] (−)$_{589}$-[Co(tn)$_3$]Cl$_3\cdot$H$_2$O,[3)] and (−)$_{589}$-[Co(tn)$_3$]Br$_3\cdot$H$_2$O.[4)] However, the skew-boat form is also observed in [Cr(tn)$_3$] [Ni(CN)$_5$]$\cdot$2H$_2$O[5)] and (+)$_{589}$-[Co(en)(tn)(tmd)] [Co(CN)$_6$]$\cdot$H$_2$O.[6)] A molecular mechanics calculation for [Co(en)(tn)(tmd)]$^{3+}$ revealed that intra-strain energy of the six-membered chelate ring is smaller in the chair form than in the skew-boat form, but that the skew-boat form reduces the non-bonded H···H repulsions between the chelate rings.[7)] In order to examine further the deformation of the six-membered chelate ring in crowded systems, conformations of [Co(tn)(tmd)$_2$]$^{3+}$ and [Co(tn)$_2$(tmd)]$^{3+}$ have been investigated.

Nomenclature

Nomenclature of the isomers follows previous papers to describe the relative orientations of the chelate rings.[7)] The skew form of en, tn and tmd rings can be noted *lel* or *ob* when the line which connects two carbon atoms bonded to N is

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

	1	**2**
Chemical formula	[Co(tn)(tmd)$_2$] Cl$_3$	[Co(tn)$_2$(tmd)] Br$_3\cdot$2.7H$_2$O
Formula weight	409.7	577.6
Crystal system	Hexagonal	Monoclinic
Space group and Z	$P6_3/mmc$, 2	$P2_1/c$, 8
Lattice constants a/Å	11.495(2)	15.568(6)
b/Å		24.939(7)
c/Å	8.259(1)	13.458(7)
β/°		115.53
V/Å^3	945.2(3)	4714(3)
D_m and D_x/Mg m^{-3}	1.46(2), 1.44	1.70(2), 1.63
μ (Mo $K\alpha$)/mm^{-1}	1.336	5.781
Color and shape of crystals	Red prisms	Orange-red plate-like
Size of specimen/mm^3	0.10×0.15×0.50	Sphere of 0.50 mm in diameter
Number and range of 2θ for cell parameters	20($20<2\theta<30°$)	25($20<2\theta<30°$)
$2\theta_{max}$/°	55	55
Range of h, k, and l	$0\leqq h\leqq 14$	$-20\leqq h\leqq 20$
	$-14\leqq k\leqq 14$	$0\leqq k\leqq 32$
	$-10\leqq l\leqq 10$	$0\leqq l\leqq 15$
Systematic absences	hhl, l odd;	$h0l$, l odd;
	$00l$, l odd	$0k0$, k odd
Possible space group	$P\bar{6}2c$, $P6_3mc$, $P6_3/mmc$	$P2_1/c$
Variation in standard reflections, $\Sigma(\lvert F_o\rvert/\lvert F_o\rvert_{initial})/5$	0.99—1.00	0.84—1.01
Number of reflections measured	4479	9298
Number of reflections observed [$\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$]	3118	3266
Transmission factor	0.690—0.860	0.137—0.160
Number of unique reflections, R_{int}	365 (0.028)	3081 (0.021)
R	0.043	0.087
wR	0.065	0.100
S	3.35	3.03
$(\Delta/\sigma)_{max}$ for nonhydrogen atoms	0.07	0.36
$\Delta\rho$/e Å^{-3}	−0.27, 0.49	−0.81, 0.95

approximately parallel (*lel*) or oblique (*ob*) to the pseudo-threefold axis of the complex. Orientation of a chair-tn chelate ring relative to the other two chelate rings, L_1 and L_2, is written as chair (p, L_1) and chair (d, L_2), when the carbon atoms of the tn ring lie on near the one side of the chelate ring L_1, indicating that the chair is effectively proximal (p) to the ring L_1 and distal (d) to the ring L_2.

Referee commented that two geometries of the tmd chelate ring, "twist-chair" and "chair," were reported.[18] The "twist-chair" is described in this paper as a symmetric skew form, and the "chair form" corresponds to the asymmetric skew form (see Fig. 6). These two structures of tmd are not distinguished in this paper, as the same sense that an envelop form of the en chelate ring is one of the probable geometries for the skew form of en.

Experimental

X-Ray Crystal Structure Analysis. The complexes were synthesized by Kojima et al.[8] Red prismatic crystals of **1** and orange-red plate-like crystals of **2** were grown from aqueous solutions. Experimental conditions are listed in Table 1. X-Ray diffraction intensities were measured up to $2\theta=55°$ using graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) on a Rigaku four-circle diffractometer AFC-5 by the θ–2θ scan technique at a scan rate of 6° min^{-1} in θ. Absorption was corrected by a numerical integration method. Structures were solved by the heavy-atom method. Hydrogen atoms were not introduced in the refinement. The function, $\Sigma w||F_o|-|F_c||^2$, was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by the block-diagonal least squares. Complex atomic scattering factors were taken from International Tables for X-Ray Crystallography.[9] Calculations were carried out on a FACOM M780/10 computer at Keio University with the computation program system UNICS-III.[10] Atomic coordinates are listed in Table 2, and selected bond lengths and bond angles in Table 3.[12] Details of the structure determination are as follows:

(**1**) Laue group $6/mmm$ and systematic absences (hhl, l odd) indicated that the space group is $P\bar{6}2c$ (No. 190), $P6_3mc$ (No. 186), or $P6_3/mmc$ (No. 194). The crystal density indicates that $Z=2$, and the Co atom is required to lie on a special position. However, it seemed that special positions in these space groups were unsuitable for the Co atom because the complex cation does not have mirror symmetry nor an inversion center. Reflection data showed pseudo-systematic absences (hkl, l odd or $h-k\neq 3n$), which indicate that two positions of Co in an unit cell are $(2/3, 1/3, z)$ and $(1/3, 2/3, z+1/2)$. Assuming that the systematic absences (hhl, l odd) were pseudo, the structure could be solved in space group $P6_322$ (No. 182) with the Co atom located at a 32 (D_3) symmetry site. This structure model assumes spontaneous resolution of the Δ- and Λ-Co complexes and also assumes the orientational disorder of the complex around the intramolecular pseudo-threefold axis. At this stage of the refinement, $R=0.074$ for 367 observed unique reflections. Difference synthesis suggested another possible position of the N atom around the Co. The space group $P6_322$ is one of the subgroups of $P6_3/mmc$.[13] The structure model of $P6_322$ could be transferred into that of $P6_3/mmc$, asumming the

Table 2. Atomic Coordinates ($\times 10^4$, $\times 10^5$ for Cl), Equivalent Isotropic Temperature Factors ($\times 10$)[11] and Population Parameters

Atom	x	y	z	B_{eq}/Å^2	PP
(**1**)					
Co	3333	6667	2500	20	
Cl	−45161(4)	−90321[b]	25000	32	
N	1955(6)	5235(5)	3924(5)	26	1/2
C(1)	2035(32)	3975(5)	4276(7)	34[a]	1/2
C(2)	1104(10)	2761(10)	3356(12)	33[a]	1/3
C(3)	1598(2)	3197[b]	2500	38[a]	1/3
(**2**)					
Co(1)	2039(2)	3485(1)	9833(3)	21	
Co(2)	6227(2)	1556(1)	664(3)	20	
Br(1)	4999(2)	2191(1)	7160(2)	32	
Br(2)	4176(2)	223(1)	7772(3)	38	
Br(3)	3199(2)	2823(1)	3379(2)	35	
Br(4)	−872(2)	4216(1)	7699(4)	67	
Br(5)	2376(4)	5199(2)	7953(4)	58	2/3
Br(6)	9499(4)	3135(2)	462(5)	66	2/3
Br(7)	8769(4)	1955(2)	111(5)	63	2/3
N(1)	1580(13)	4241(7)	9306(16)	25	
N(2)	1707(12)	3531(7)	11088(16)	24	
N(3)	3311(13)	3770(7)	10825(17)	27	
N(4)	2315(12)	3385(7)	8519(14)	18	
N(5)	752(12)	3202(7)	8901(15)	22	
N(6)	2504(12)	2719(7)	10333(16)	29	
N(7)	4973(12)	1283(8)	−365(15)	23	
N(8)	5927(13)	1616(8)	1958(17)	31	
N(9)	6708(13)	809(7)	1178(15)	24	
N(10)	6572(14)	1554(8)	−619(16)	28	
N(11)	7515(13)	1823(8)	1664(17)	31	
N(12)	5739(12)	2303(7)	145(17)	27	
O(1)	7623(11)	1126(6)	4001(13)	31	
O(2)	670(14)	1226(7)	1520(17)	60	
O(3)	−734(18)	4070(8)	1813(26)	116	
O(4)1	6292(20)	676(11)	4568(25)	42[a]	0.6
O(4)2	7352(29)	312(17)	6478(36)	38[a]	0.4
O(5)1	1538(45)	611(27)	678(58)	111[a]	0.4
O(5)2	837(39)	314(22)	405(50)	132[a]	0.5
O(6)	5564(30)	−219(18)	6776(39)	86[a]	0.5
C(1)	1621(18)	4681(11)	10128(23)	42[a]	
C(2)	1081(16)	4522(10)	10809(21)	30[a]	
C(3)	1694(17)	4070(10)	11645(22)	37[a]	
C(4)	3921(17)	4053(11)	10329(22)	37[a]	
C(5)	4031(19)	3673(11)	9475(24)	46[a]	
C(6)	3118(18)	3702(10)	8389(22)	38[a]	
C(7)	551(18)	2727(10)	8191(23)	40[a]	
C(8)	440(18)	2206(11)	8672(24)	45[a]	
C(9)	1328(17)	1930(10)	9525(22)	33[a]	
C(10)	1905(17)	2290(10)	10576(21)	31[a]	
C(11)	4349(16)	981(10)	15(21)	32[a]	
C(12)	4235(16)	1290(9)	1008(20)	25[a]	
C(13)	5151(16)	1278(9)	2063(20)	26[a]	
C(14)	6696(16)	393(9)	410(20)	27[a]	
C(15)	7182(18)	596(10)	−305(22)	36[a]	
C(16)	6601(17)	1034(10)	−1169(21)	32[a]	
C(17)	7680(16)	2327(9)	2422(20)	26[a]	
C(18)	7775(17)	2848(10)	1889(21)	33[a]	
C(19)	6843(18)	3094(11)	989(23)	40[a]	
C(20)	6329(17)	2734(10)	18(21)	32[a]	

a) Refined isotropically. b) $y=2x$.

Table 3. Selected Bond Lengths (l/Å) and Bond Angles (ϕ/°)

(1)		
	Co–N	1.999(4)
	N–C(1)	1.52(2)
	C(1)–C(2)	1.48(1)
	C(1)–C(3)	1.66(6)
	C(2)–C(2^i)	1.55(2)
	N–Co–N^i	89.0(2)
	Co–N–C(1)	120(1)
	N–C(1)–C(2)	116(2)
	N–C(1)–C(3)	101(1)
	C(1)–C(2)–C(2^i)	111(1)
	C(1)–C(3)–C(1^i)	124.4(3)
(2)		
	Co(1)–N(1)	2.033(17)
	Co(1)–N(2)	1.971(24)
	Co(1)–N(3)	1.982(17)
	Co(1)–N(4)	2.007(22)
	Co(1)–N(5)	1.980(16)
	Co(1)–N(6)	2.051(17)
	Co(2)–N(7)	1.965(16)
	Co(2)–N(8)	1.994(26)
	Co(2)–N(9)	2.016(17)
	Co(2)–N(10)	2.017(25)
	Co(2)–N(11)	1.987(17)
	Co(2)–N(12)	2.019(17)
	N(1)–Co(1)–N(2)	93.6(9)
	N(3)–Co(1)–N(4)	96.1(8)
	N(5)–Co(1)–N(6)	89.6(7)
	N(7)–Co(2)–N(8)	96.1(9)
	N(9)–Co(2)–N(10)	95.4(9)
	N(11)–Co(2)–N(12)	92.6(7)

Symmetry code: (i) $-x+y, y, -z+1/2$.

co-existence of the Δ- and Λ-complexes at the same site.

The site symmetry of the Co became from 32 (D_3) to $\bar{6}m2$ (D_{3h}) as a result of the complicated disorder. The number of parameters reduced from 23 to 22. Two weak *hhl* reflections with *l* odd were excluded from the refinement. Final R=0.043 for 365 reflections.

(2) Radiation damage of the crystal was corrected based on the standard reflections. Space group was uniquely determined to $P2_1/c$ from the systematic absences. Since Z=8, two independent complex cations exist in the crystal. The positions of the Br^- ions and water molecules are disordered. Carbon and disordered water oxygen atoms were refined isotropically to avoid non-positive definite matrices for the thermal parameters. The relatively large R value (0.087) may be attributed to the positional disorder of the Br^- ions.

Molecular Mechanics Calculation. Strain-energy minimizations for $[Co(tn)(tmd)_2]^{3+}$ and $[Co(tn)_2(tmd)]^{3+}$ were carried out by the program CFF with a force field parameter set NIKIPAR6, which is listed in Table 4.[14] The conformational strain-energy was calculated as the sum over all individual interactions of bond stretching deformation (E_b), valence-angle deformation (E_θ), torsional strain (E_ϕ), and non-bonded interaction (E_{nb}) energies:

$$E_b = \Sigma_{bonds}\ {}^1\!/\!{}_2 K_b\,(b-b_0)^2,$$
$$E_\theta = \Sigma_{angles}\ {}^1\!/\!{}_2 K_\theta\,(\theta-\theta_0)^2,$$
$$E_\phi = \Sigma_{bonds}\ {}^1\!/\!{}_2 K_\phi\,(1+\cos n\phi),$$
$$E_{nb} = \Sigma_{non\text{-}bonds}\ A\,\exp(-Br) - C/r^6,$$

Table 4. Potential Parameter Set

(1) Bond	K_b kcal mol^{-1} Å^{-2}	b_0 Å	
M–N	251.65	2.000	
N–C	862.80	1.470	
C–C	719.00	1.540	
C–H	719.00	1.093	
N–H	805.28	1.011	
(2) Angle	K_θ kcal mol^{-1} rad^{-2}	θ_0 rad	
N–M–N	97.784	1.571	
M–N–H	28.760	1.911	
M–N–C	57.520	1.911	
N–C–C	143.800	1.911	
N–C–H	93.470	1.911	
H–N–H	76.214	1.911	
C–N–H	93.470	1.911	
H–C–H	74.776	1.911	
H–C–C	93.470	1.911	
C–C–C	143.800	1.911	
(3) Torsion	K_ϕ kcal mol^{-1}	n	
N–C–C–N	3.0	3	
C–C–C–N	3.0	3	
C–C–N–M	3.0	3	
N–M–N–C	0.0001	12	
(4) Non-bonding	A kcal mol^{-1}×10^{-4}	B Å^{-1}	C kcal mol^{-1} Å^6
H···H	0.66	4.08	49.2
H···C	3.14	4.20	121.1
H···N	2.81	4.32	99.2
C···N	21.21	4.44	244.0
C···C	23.70	4.32	297.8
M···H	3.14	4.20	121.1
M···C	23.70	4.32	297.8
N···N	18.64	4.55	200.0

$$E_T = E_b + E_\theta + E_\phi + E_{nb}.$$

The tmd chelate ring takes skew form with *lel* or *ob* orientation as the en ligand. The initial coordinates were prepared utilizing the coordinates for ten conformers of $[Co(en)_2(tn)]^{3+}$ and twenty conformers of $[Co(en)(tn)_2]^{3+}$, whose strain-energies have been already minimized.[15] The coordinates of the tmd moiety were taken from the crystal structure of $(+)_{589}$-$[Co(tmd)_3]Br_3$.[16]

Partitioning of the total strain-energy into the intra- and inter-chelate ring interactions was proposed in the previous paper.[7] The intra-chelate ring strain energies of the skew-boat tn and that of the chair tn rings for all the conformers were calculated to yield the average values, which are compared in Fig. 5 with those of the related complexes. For the calculation of free enthalpies, G in Tables 5 and 6, vibrational and external degrees of freedom were considered.[17]

Results and Discussion

Molecular and Crystal Structure. Partial projection of the crystal structure of **1** is illustrated in Fig. 1. The

Table 5. Strain-Energies and Free Enthalpies (kJ mol^{-1}) for Conformers of $[Co(tn)(tmd)_2]^{3+}$

No.	Conformer	Statistical weight	E_b	E_θ	E_ϕ	E_{nb}	E_T	ΔE_T	G	ΔG
1.	*lel lel*$_2$[a)]	1	8.23	39.17	64.44	3.89	115.735	0.000	1375.769	0.000
2.	chair *lel*$_2$	1	9.30	48.79	55.07	7.89	121.052	5.317	1380.643	4.874
3.	chair *ob*$_2$	1	10.19	61.84	47.21	5.11	124.356	8.621	1383.898	8.129
4.	chair (p, *ob*) *lelob*	1	10.16	62.05	48.44	5.67	126.322	10.587	1384.635	8.866
5.	*lel lelob*	2	8.87	53.81	59.11	7.04	128.835	13.100	1388.606	12.837
6.	*ob lel*$_2$	1	10.02	62.35	50.21	7.14	129.716	13.981	1390.195	14.426
7.	chair (p, *lel*) *lelob*	1	10.67	52.38	54.89	15.06	132.999	17.264	1393.141	17.372
8.	*ob ob*$_2$	1	12.25	43.30	62.98	16.10	134.631	18.896	1394.951	19.182
9.	*lel ob*$_2$	1	10.02	57.46	60.55	9.62	137.649	21.914	1397.226	21.457
10.	*ob lelob*	2	12.62	46.88	64.50	20.59	144.596	28.825	1403.478	27.709

a) This conformer exists in crystals of $[Co(tn)(tmd)_2]\ Cl_3$.

Table 6. Strain-Energies and Free Enthalpies (kJ mol^{-1}) for Conformers of $[Co(tn)_2(tmd)]^{3+}$

No.	Conformer	Statistical weight	E_b	E_θ	E_ϕ	E_{nb}	E_T	ΔE_T	G	ΔG
1.	*lel*$_2$ *lel*	1	7.22	29.10	48.63	0.81	85.758	0.000	1270.904	0.000
2.	C_1-chair$_2$ *ob*	1	8.03	54.11	28.75	−2.64	88.245	2.487	1273.039	2.135
3.	C_1-chair$_2$ *lel*	1	8.12	56.04	27.41	−2.76	88.810	3.052	1272.457	1.554
4.	chair (p, tmd) *lel lel*	1	8.13	38.84	38.95	3.81	89.745	3.987	1274.206	3.302
5.	chair (p, tn) *lel lel*	1	8.22	39.10	39.06	4.87	91.258	5.500	1276.060	5.156
6.	syn-chair$_2$ *lel*[a)]	1	10.05	46.67	30.48	6.79	93.993	8.253	1277.894	6.990
7.	anti-chair$_2$ *lel*	1	8.76	49.81	29.22	6.29	94.088	8.330	1279.103	8.199
8.	chair (p, tmd) *lel ob*	1	7.55	44.45	41.46	1.71	95.174	9.416	1279.200	8.296
9.	anti-chair$_2$ *ob*	1	10.41	47.64	31.12	6.80	95.968	10.210	1279.271	8.367
10.	chair (p, tmd) *ob ob*	1	8.08	45.08	40.96	2.40	96.527	10.769	1280.975	10.071
11.	chair (p, tn) *ob ob*	1	9.21	49.13	34.62	4.00	96.955	11.197	1282.601	11.697
12.	chair (p, tn) *ob lel*	1	9.03	51.29	33.96	3.58	97.853	12.095	1282.231	11.327
13.	chair (p, tn) *lel ob*	1	9.28	53.12	30.12	5.56	98.085	12.327	1283.607	12.703
14.	*lelob lel*	2	7.78	44.51	43.95	4.33	100.578	14.820	1285.973	15.069
15.	*lel*$_2$ *ob*	1	8.41	34.07	50.02	9.64	102.130	16.372	1284.956	14.052
16.	syn-chair$_2$ *ob*	1	11.31	48.22	30.72	12.29	102.539	16.781	1284.351	13.447
17.	chair (p, tmd) *ob lel*	1	9.89	44.51	38.44	11.29	104.130	18.372	1288.694	17.790
18.	*ob*$_2$ *ob*	1	10.88	34.56	47.57	12.55	105.560	19.802	1290.745	19.841
19.	*lelob ob*	2	8.91	48.26	45.14	7.17	109.485	23.727	1294.139	23.235
20.	*ob*$_2$ *lel*	1	11.82	38.89	48.41	17.73	116.857	31.099	1299.306	28.402

a) This conformer exists in crystals of $[Co(tn)_2(tmd)]\ Br_3 \cdot 2.7H_2O$.

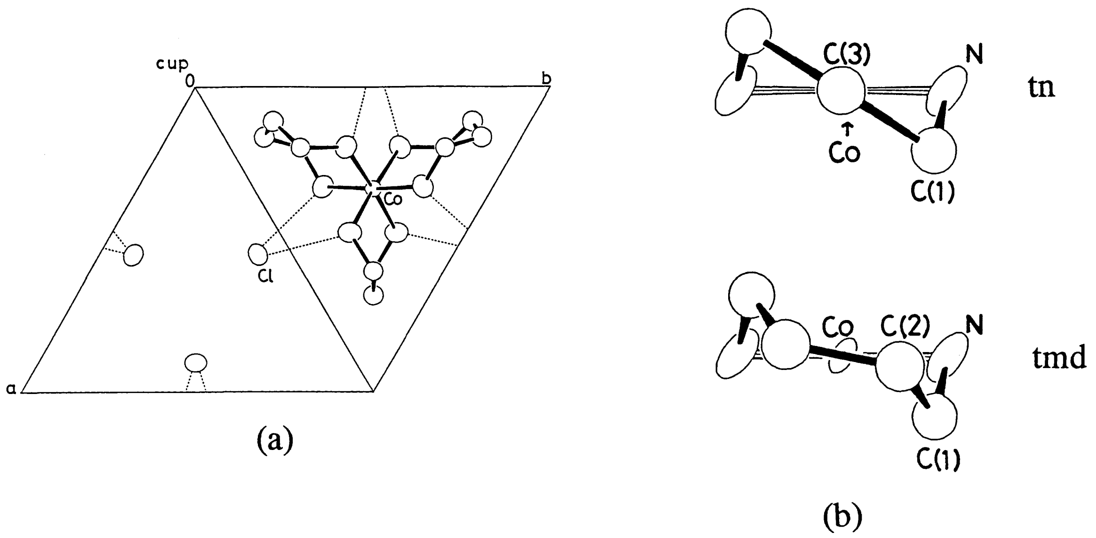
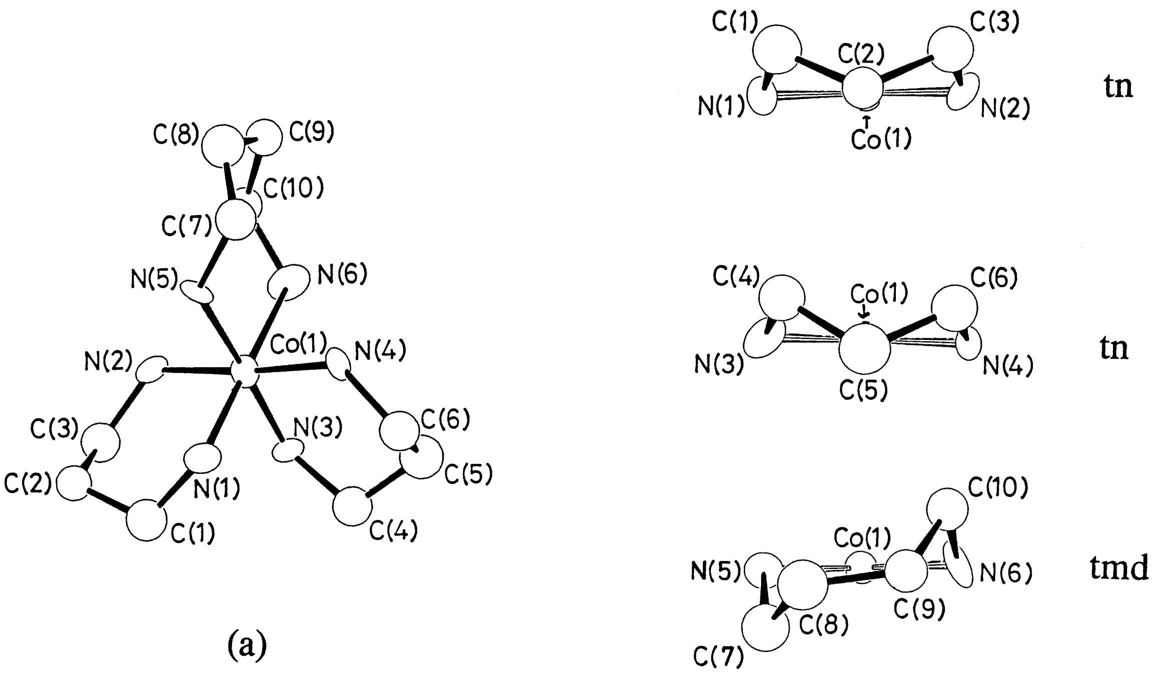


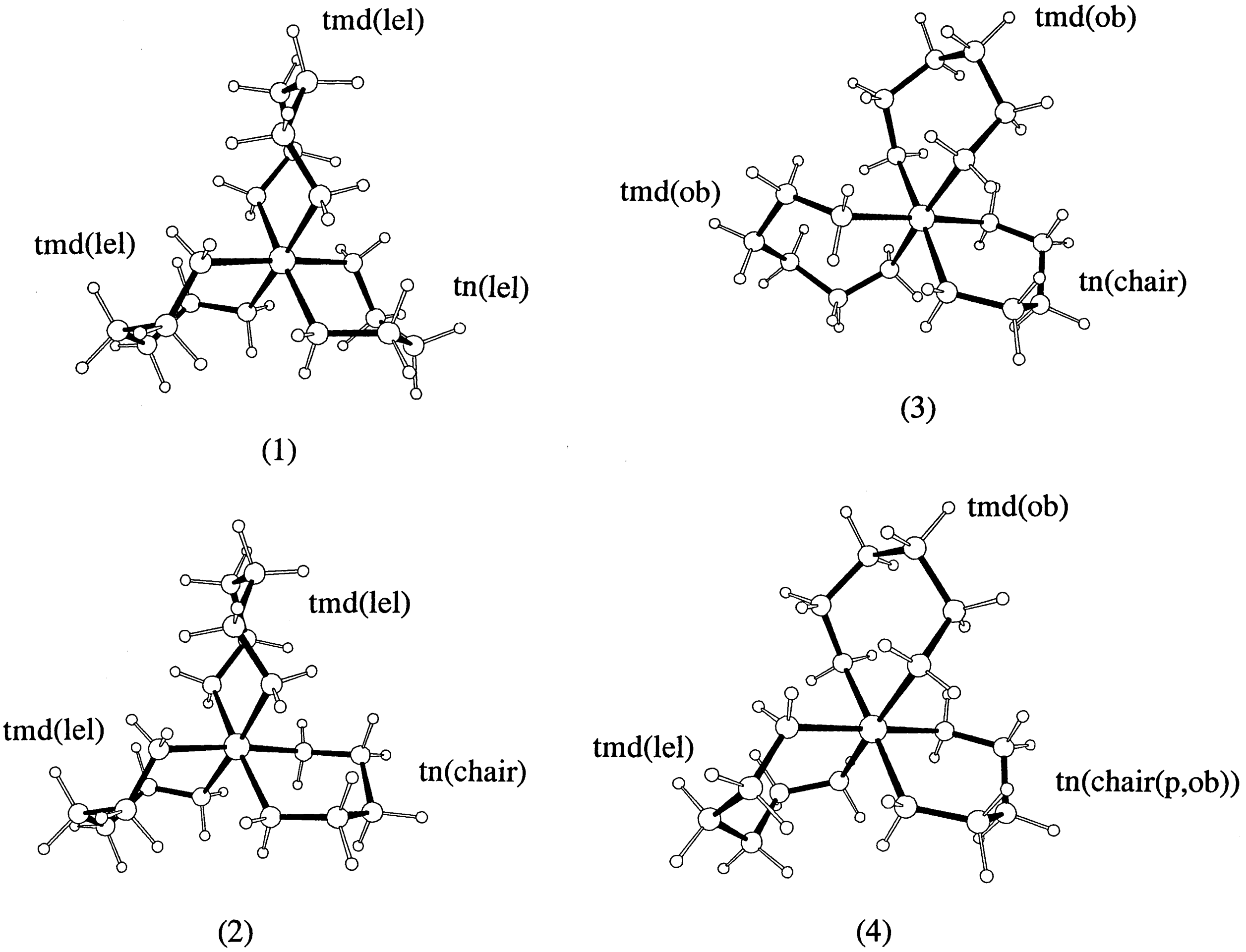
Fig. 1. (a) Partial projection of the crystal structure of **1** along *c* ($0<z<1/2$) and (b) edge-on view of the chelate rings. Only Λ-complex in one of the three possible orientations is illustrated for clarity. Broken lines indicate hydrogen bonds.



(a)

(b)

Fig. 2. Molecular structure of one of the independent complex cations in **2** and edge-on view of the chelate rings.



(1)

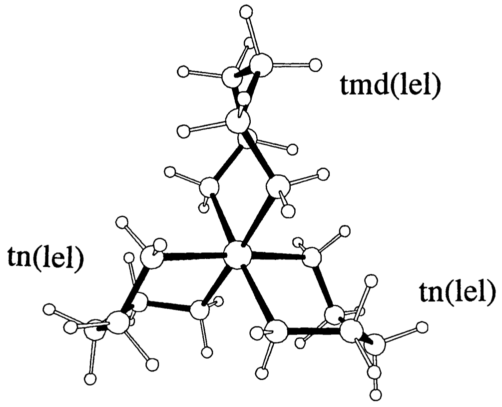
(3)

(2)

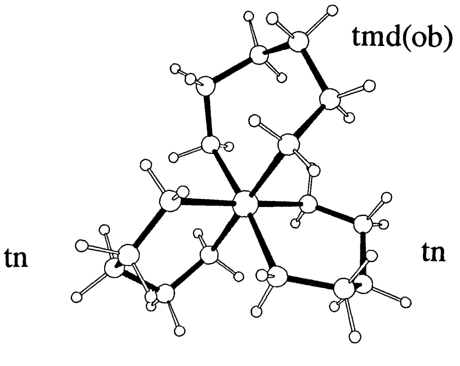
(4)

Fig. 3. Conformers of the $[Co(tn)(tmd)_2]^{3+}$ complex with ΔG less than 10 kJ mol^{-1}.

Co atom of $[\mathrm{Co(tn)(tmd)_2}]^{3+}$ lies on a crystallographic D_{3h} site, and the Δ- and Λ-complex cations co-exist at the same site with 50% probabilities. Furthermore, six- and seven-membered chelate rings interchange their positions due to the orientational disorder around the intramolecular pseudo-threefold axis, which becomes crystallographic threefold axis. In the structure analysis, positions of the N and a carbon atom bonded to N could be treated common for the tn and tmd ligands. Among twelve equivalent positions of N around the Co atom, six are for Δ-complex and the other six are for Λ-complex. There are two independent hydrogen bonds between the N and Cl atoms with N···Cl=3.23(1) and 3.25(1) Å. Edge-on view of the chelate rings is also shown in Fig. 1.

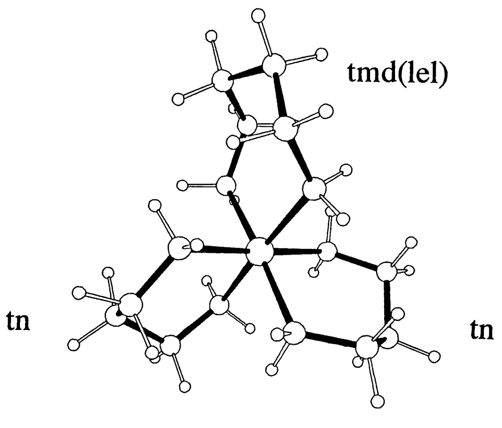


(1)



C$_1$-chair$_2$

(2)



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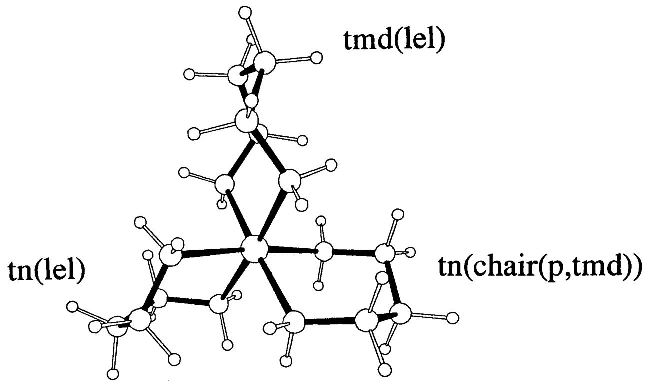
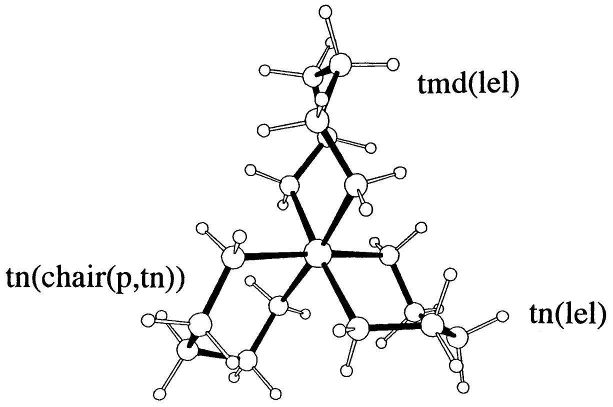
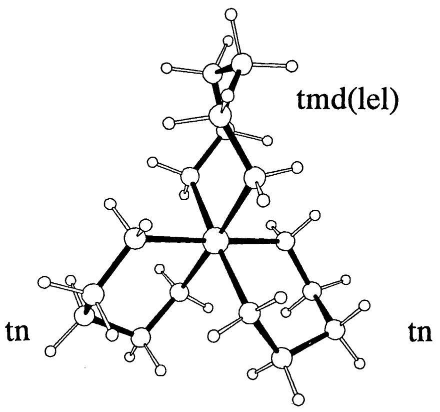


(4)

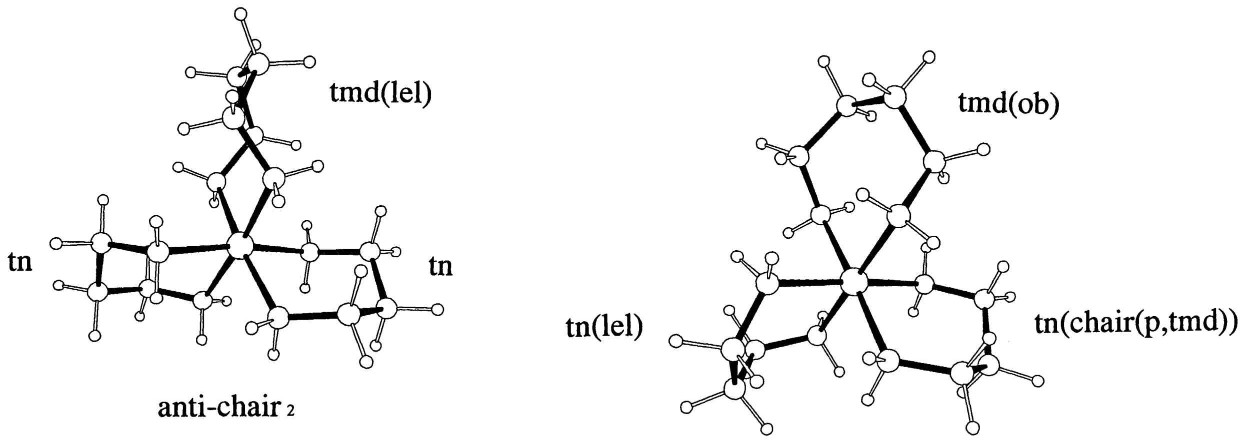


(5)



syn-chair$_2$

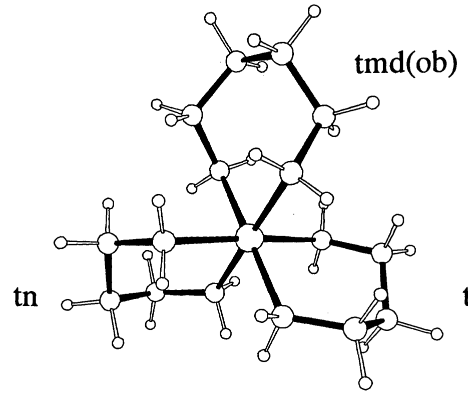
(6)



anti-chair 2

(7)

(8)



anti-chair 2

(9)

Fig. 4. Conformers of the $[Co(tn)_2(tmd)]^{3+}$ complex with ΔG less than 10 kJ mol^{-1}.

The seven-membered tmd ring is a skew conformation (*lel*) as observed in $(+)_{589}$-$[Co(tmd)_3]Br_3$.[16] The six-membered tn ring is in the skew-boat form (*lel*). As a total, the conformation of the complex cation in **1** is *lel lel*$_2$. The orientational disorder of the complex results from almost the same size and shape of the skew-boat tn and the skew tmd chelate rings. Similar disorder was observed in the crystals of $(+)_{589}$-$[Co(en)(tn)(tmd)][Co(CN)_6]\cdot H_2O$.[6] The *lel*$_3$-$[Co(en)(tn)(tmd)]^{3+}$ complex cation takes two possible orientations around the intramolecular pseudo-twofold axis with interchanging the tn and tmd positions. The orientational disorder seems to be unavoidable when the complex has pseudo rotational symmetry.

In crystals of **2**, both two independent complex cations take syn-chair$_2$ *lel* configuration as shown in Fig. 2. The tmd chelate ring is in the skew form, and two chair tn rings are proximal to each other. There is an extensive hydrogen-bonding network involving the cation, Br anions, and water molecules. The shortest N···Br distance is 3.28(2) Å.

Conformational Analysis. Strain-energies and free enthalpies for the ten conformers of $[Co(tn)(tmd)_2]^{3+}$ are listed in Table 5. The structures for the four conformers of the lowest strain-energy are shown in Fig. 3. The molecular mechanics calculation showed that the *lel lel*$_2$ conformer is most favorable, and it actually is observed in the crystal **1**.

On the other hand, the syn-chair$_2$ *lel* conformer of $[Co(tn)_2(tmd)]^{3+}$ is the sixth lowest among the twenty configurations (see Table 6 and Fig. 4). The difference of the strain-energy to the most stable one (ΔE_T) is 8.25 kJ mol^{-1}. Another example of the discrepancy between the crystal structure and molecular mechanics calculation was reported that the syn-chair$_2$ *lel* conformer exists in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ in spite of the calculated value of $\Delta E_T=11.79$ kJ mol^{-1}.[15] The *lel* syn-chair$_2$ conformer of $[Co(en)(tn)_2]^{3+}$ is the second lowest in strain-energy with $\Delta E_T=1.35$ kJ mol^{-1}.[15] It seems that the parameter set NIKIPAR6 overestimates the steric repulsion between the chelate rings in crowded systems. An improvement of accuracy in the calculation may be achieved by optimization of the potential parameters and/or utilizing more flexible potential functions. The syn-chair$_2$ *ob* conformer of $[Co(tn)_2(tmd)]^{3+}$ is 16th lowest in the strain-energy, although the *ob* syn-chair$_2$ conformer of $[Co(en)(tn)_2]^{3+}$ has the 3rd lowest strain-energy among twenty conformers. It indicates that the combination of tn(chair) and tmd(*ob*) in the chair(d, *ob*-tmd) orientation is unfavorable.

The crowdedness of the complex $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ ($x+y+z=3$) may be roughly measured by the sum of the members of the chelate rings, $N(=5x+6y+7z)$. The skew-boat form of the tn chelate ring is observed in the crowded complexes with N greater than 18 as listed in Table 7. The molecular mechanics calculation showed that an unreal molecule, Co(tn), has smaller stain-energy in the chair form than in the skew-boat form with energy difference 12.1 kJ mol^{-1}.[7] However, the skew-boat form may be preferable in reducing the non-bonded interactions between the chelate rings. Average values of the intra-chelate ring strain-energy of tn, E_{tn}, for the skew-boat and that for the chair form among all of the conformers are plotted in Fig. 5 against the crowdedness of the complex. Increase of E_{tn} with N is the result from the deformation of the tn ring to relax the inter-chelate ring repulsions.

The energy difference of E_{tn} between the skew-boat and chair forms decreases with the increase of N. Therefore, the skew-boat form of the six-membered tn chelate ring appears in crowded complexes.

Table 7. Conformation of $[M(en)_x(tn)_y(tmd)_z]^{3+}$ ($x+y+z=3$; $y \geqq 1$) in Crystals

Crystal	Conformation	N[b]
$[Co(en)_2(tn)]\ Br_3$[1]	*lel*$_2$ chair	16
$[Cr(en)_2(tn)]\ Br_3 \cdot H_2O$[2]	*lelob* chair (p, *ob*)	16
$[Cr(en)(tn)_2]\ I_3 \cdot H_2O$[2]	*lel* chair$_2$ (C_1)	17
$(-)_{589}$-$[Co(tn)_3]\ Cl_3 \cdot H_2O$[3]	C_3-chair$_3$	18
$(-)_{589}$-$[Co(tn)_3]\ Br_3 \cdot H_2O$[4]	C_3-chair$_3$	18
$[Cr(tn)_3]\ [Ni(CN)_5] \cdot 2H_2O$[5]	syn-chair$_2$ *lel**	18
$[Co(en)(tn)(tmd)]\ [Co(CN)_6] \cdot H_2O$[6]	*lel lel* lel*	18
$[Co(tn)_2(tmd)]\ Br_3 \cdot 2.7H_2O$[a]	syn-chair$_2$ *lel*	19
$[Co(tn)(tmd)_2]\ Cl_3$[a]	*lel** *lel*$_2$	20

* Skew-boat form of the tn chelate ring. a) This work. b) $N=5x+6y+7z$.

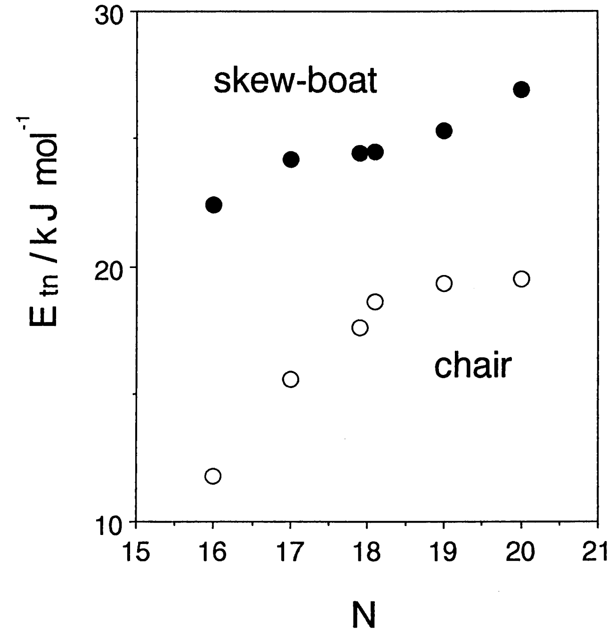


Fig. 5. Plot of the average value of intra-chelate ring strain-energy for chair and skew-boat tn ring among all of the conformers of the $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ complex against the crowdedness, $N(=5x+6y+7z)$. Two points at $N=18$ are for $[Co(en)(tn)(tmd)]^{3+}$ and $[Co(tn)_3]^{3+}$.

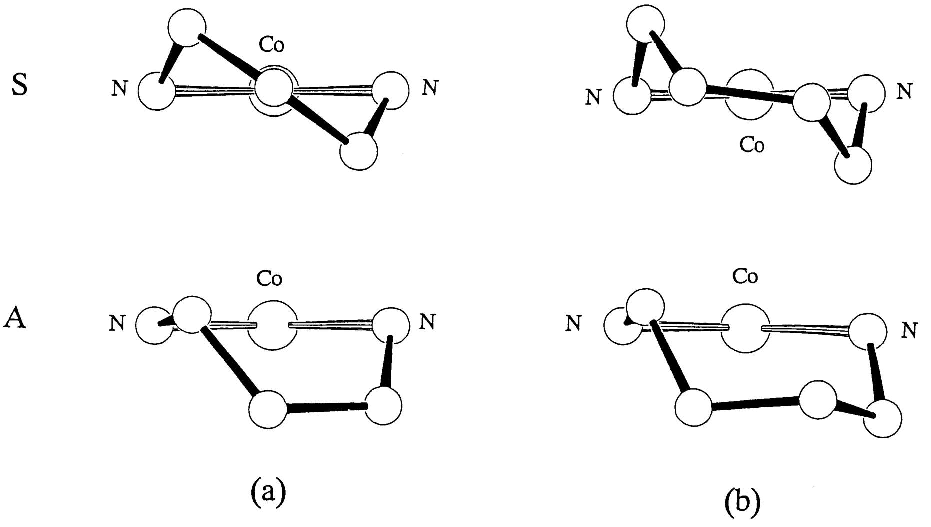


Fig. 6. Side view of the symmetric (S) and asymmetric (A) skew forms of (a) tn and (b) tmd chelate rings. The figures of S are the tn(*lel*) and tmd(*lel*) moieties in Fig. 4(1). The figures of A are the tn(*lel*) in Fig. 4(8), and the tmd(*lel*) in Fig. 4(3).

Intra-chelate ring strain-energies of the skew tn and tmd rings seem to be the smallest with their symmetric forms.[7] The asymmetric forms illustrated in Fig. 6 indicate the steric repulsion between the chelate rings. An asymmetric skew form of tmd observed in crystals of *trans*-$[Co(NO_2)_2(tmd)_2]NO_3\cdot H_2O$ is attributed to the short O···C contacts involving the nitro oxygen atoms.[18]

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