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Structure of Cobalt(III) Complexes with (*R*,*R*)- and (*R*,*S*)-*N*,*N*,*N'*,*N'*-Tetrakis(2-aminoethyl)-2,4-pentanediamine and *N*,*N*,*N'*,*N'*-Tetrakis(2-aminoethyl)-1,3-propanediamine

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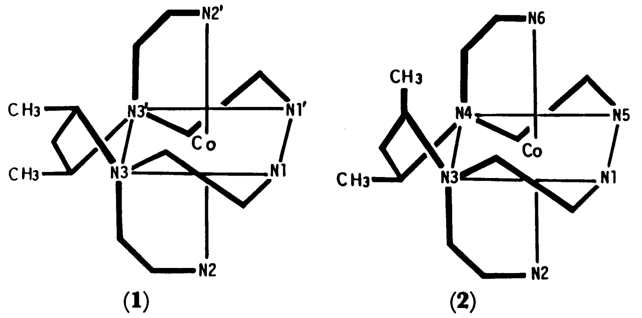
Crystal structures of the two isomeric Co(III) complexes with sexidentate ligands, $(NH_2CH_2CH_2)_2NC^*H(CH_3)CH_2C^*H(CH_3)N(CH_2CH_2NH_2)_2$ (hereafter abbreviated as *R*,*R*- and *R*,*S*-tptn) and of the Co(III) complex with a sexidentate ligand, $(NH_2CH_2CH_2)_2NCH_2CH_2CH_2N(CH_2CH_2NH_2)_2$ (abbreviated as ttn) were determined by an X-ray diffraction method. The crystal data and the final *R* factors are: (**1**) [Co(*R*,*R*-tptn)]$(ClO_4)_3 \cdot H_2O$, tetragonal, $P4_22_12$, a=12.800(1), c=15.312(1) Å, V=2509(1) Å^3, Z=4, R=0.053 for 1627 observed unique reflections, (**2**) [Co(*R*,*S*-tptn)]$Cl_3 \cdot 3H_2O$, monoclinic, $P2_1/a$, a=16.778(6), b=14.296(2), c=9.478(4) Å, β=110.99(3)°, V=2123(1) Å^3, Z=4, R=0.045 for 3583 reflections and (**3**) [Co(ttn)]$Br_3 \cdot H_2O$, trigonal, $P\bar{3}c1$, a=14.436(4), c=15.718(9) Å, V=2837(2) Å^3, Z=6, R=0.096 for 1183 reflections. The equatorial preference of the methyl groups in the central six-membered chelate ring formed by Co and 2,4-pentanediamine moiety of *R*,*R*- and *R*,*S*-tptn has been recognized. In (**1**) the six-membered chelate ring adopts a twist boat form as in (**3**) with the two C–CH_3 bonds in equatorial positions. In (**2**) the six-membered chelate ring takes a largely flattened chair form with the two C–CH_3 bonds again in equatorial positions. The effect of an elongation of the Co–N bond distance on the energy of the first absorption band was discussed.

New sexidentate ligands, *R*,*R*- and *R*,*S*-tptn and their Co(III) complexes were synthesized and characterized.[1] [Co(*R*,*R*-tptn)]$^{3+}$ gives the first absorption band at 20.8×10^3 cm^{-1}, whereas [Co(*R*,*S*-tptn)]$^{3+}$ shows the first absorption maximum at 20.0×10^3 cm^{-1}, indicating that the ligand field exerted by the *R*,*S*-tptn is weaker than that by the *R*,*R*-tptn. A simple molecular model indicates that both isomers act as a sexidentate ligand to give metal complexes analogous to those of 1,3-propanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (trdta) as shown in Fig. 1. The central six-membered chelate ring in $(-)_{546}$-$\Delta\Delta\Lambda$-[Co(trdta)]$^-$ takes a skew boat form.[2] The central six-membered chelate ring of [Co(*R*,*R*-tptn)]$^{3+}$ is expected to adopt a skew boat form with the two C–CH_3 bonds in equatorial positions. In this connection, the absolute configuration must be skew chelate pairs $\Delta\Delta\Lambda$. If the central six-membered chelate ring of [Co(*R*,*S*-tptn)]$^{3+}$ takes a skew boat form, one of the two C–CH_3 bonds will be equatorial and the other axial as shown in Fig. 1. Both of the methyl groups can be in equatorial positions if the central chelate ring takes a chair form with a distorted CoN_6 octahedron. In any case, the *R*,*S*-complex would be much deformed owing to the nonbonded interactions. Such a strained structure may be reflected in the absorption spectrum. In order to see how the distortion of the CoN_6 chromophore affects the absorption spectra, two complexes (**1**) and (**2**) were subjected to X-ray crystal structure analysis. In addition to this, the structure of (**3**), which has no C–CH_3 bonds in the central six-membered chelate ring, was determined in order to compare the conformation with (**1**) and (**2**).



(**1**) (**2**)

Fig. 1. Coordination of *R*,*R*- and *R*,*S*-tptn. The central six-membered chelate ring is assumed to take a skew boat form.

Experimental

Crystals of (**1**), (**2**), and (**3**) grown from aqueous solutions were kindly provided by Professor J. Fujita of Nagoya University. Experimental conditions and refinement informations are listed in Table 1. The preliminary determination of the lattice parameters and the space group of (**1**) and (**2**) was made with a Weissenberg camera. Intensities were measured using graphite monochromatized Mo *K*α radiation (λ=0.70926 Å) on an automated Rigaku four-circle diffractometer AFC-5. The θ–2θ scan technique was employed at a scan rate of 4° min^{-1} in θ.

The usual corrections were made for Lorentz and polarization factors. The structures of (**1**) and (**2**) were solved by the heavy atom method. Positions of Co and Cl atoms were determined from the Patterson function and the other non-hydrogen atoms were located by Fourier syntheses. All the hydrogen atoms except those of the water molecule in (**1**) were found on the difference synthesis. The Laue group and systematic absences showed that the space group of (**3**) is

TABLE 1. CRYSTAL DATA, EXPERIMENTAL CONDITIONS AND REFINEMENT DETAILS

	(1)	**(2)**	**(3)**
Chemical formula	$[Co(C_{13}H_{34}N_6)]\cdot(ClO_4)_3\cdot H_2O$	$[Co(C_{13}H_{34}N_6)]\cdot Cl_3\cdot 3H_2O$	$[Co(C_{11}H_{30}N_6)]\cdot Br_3\cdot H_2O$
Formula weight	649.8	493.8	563.1
Calculated density (Mg m^{-3})	1.72	1.55	1.98
μ(Mo $K\alpha$) (mm^{-1})	1.11	1.24	7.20
Color and Habit of crystals	orange-red bipyramids	red rhomboids	orange plates(100)
Size of specimen (mm^3)	$0.4\times0.4\times0.3$	$0.3\times0.3\times0.2$	$0.4\times0.4\times0.2$
Number of reflections and 2θ range(°) used for measuring lattice parameters	20 $40<2\theta<51$	20 $40<2\theta<55$	24 $30<2\theta<40$
$2\theta_{max}$(°)	65	55	55
Range of *h*, *k*, and *l*	$0\leqq h,\ k\leqq 16$ $k\leqq h$ $0\leqq l\leqq 19$	$-21\leqq h\leqq 20$ $0\leqq k\leqq 17$ $0\leqq l\leqq 11$	$0\leqq h\leqq 18$ $0\leqq k\leqq 18$ $0\leqq l\leqq 20$
Systematic absences	*h*00, *h* odd; 00*l*, *l* odd	*h*0*l*, *h* odd; 0*k*0, *k* odd	$h\bar{h}l$, *l* odd
Number of standard reflections and variation of their $\|F_o\|$ amplitudes, $\Sigma(\|F_o\|/\|F_o\|_{initial})/n$	3 0.99—1.00	3 0.97—1.00	5 0.09—1.00
Number of reflections measured	2576	5275	2283
Number of reflections observed above the threshold $[\|F_o\|>3\sigma(\|F_o\|)]$	1627	3583	1230
Absorption correction	no	no	$1.852\leqq$correction factor, $(A^*)^{1/2}\leqq 3.748$
R	0.053	0.045	0.096
wR	0.054	0.063	0.105
Weight $w^{-1}=\sigma^2(\|F_o\|)+(c\|F_o\|)^2$	$c=0.015$	$c=0.03$	$c=0.015$
$S=[\Sigma w(\|F_o\|-\|F_c\|)^2/(m-n)]^{1/2}$	2.0	1.6	3.4
Number of observed unique reflections, m	1627	3583	1183
Number of parameters, n	230	387	106
$(\Delta/\sigma)_{max}$ for non-H atoms	1.0	0.5	0.4

P3cl or P$\bar{3}$cl. Assuming the non-centrosymmetry, the structure was solved by direct methods.[3] The possible positions of the Br and Co atoms obtained from the E map were confirmed by the Patterson function. All the non-hydrogen atoms of the sexidentate ligand were found on the Fourier synthesis. A projection of the crystal structure at this stage of the refinement suggested that the Co lies on a twofold axis perpendicular to c. It is a special position **6f** of the space group P$\bar{3}$cl. Accordingly, the space group was determined to be P$\bar{3}$cl. The general position of P$\bar{3}$cl is twelvefold and there are six formula units in a unit cell. Hence, there are 18 Br atoms in the unit cell, sixteen of which were allocated on a set of general positions **12g** and a set of special positions **4d**. It was found that the remaining two Br atoms are disordered. The difference synthesis can be most conveniently accounted for if the Br atoms are distributed randomly on the sets of special positions **2b** and **4c**, and two sets of general positions **12g** (See Table 2). The population parameters of these Br atoms were estimated by the trial and error method in such a way that each isotropic thermal parameter took nearly equal value. Positions of the hydrogen atoms in (**3**) could not be deduced from the difference synthesis so that they were obtained by calculation and not refined.

Anisotropic thermal parameters were introduced for all the non-hydrogen atoms except for the disordered Br atoms of (**3**). The function, $\Sigma w\|\|F_o\|-\|F_c\|\|^2$ was minimized by block-diagonal least squares. Complex neutral-atom scattering factors were used.[4] The calculations were carried out on a FACOM M180 computer at Keio University with the Universal Crystallographic Computation Program System UNICS III.[5] The final atomic parameters are listed in Table 2.[6]

The absolute structure of (**1**) was determined with reference to the known absolute configuration of *R*,*R*-tptn prepared from (*R*,*R*)-2,4-diaminopentane.[7]

Results and Discussion

Perspective drawings of complexes (**1**), (**2**), and (**3**) and projections of the central six-membered chelate rings of these complexes along the twofold axis or along the pseudo twofold axis are presented in Fig. 2. The bond lengths and bond angles within the com-

TABLE 2. FRACTIONAL COORDINATES ($\times 10^4$, $\times 10^5$ FOR Co, $\times 10^3$ FOR DISORDED Br ATOMS IN **3**) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom		x	y	z	$B_{eq}/Å^2$
(1)	Co	20688(5)	20688	100000	1.9
	Cl(1)	5000	5000	7208(1)	3.0
	Cl(2)	6127(1)	1249(1)	8671(1)	3.4
	O(1)	6460(4)	504(4)	8031(3)	5.0
	O(2)	6874(5)	2075(4)	8696(4)	6.5
	O(3)	5125(4)	1657(4)	8440(3)	6.2
	O(4)	6102(4)	752(4)	9510(3)	5.5
	O(5)	5085(5)	4084(4)	7722(3)	6.2
	O(6)	4104(4)	4924(4)	6664(4)	6.0
	N(1)	716(4)	1905(4)	9408(3)	2.9
	N(2)	2758(4)	1332(4)	9031(3)	2.5
	N(3)	2257(3)	3369(3)	9272(2)	2.0
	C(1)	467(5)	2811(6)	8837(4)	3.7
	C(2)	1158(5)	3718(5)	9077(3)	3.1
	C(3)	2669(4)	1962(5)	8200(3)	2.8
	C(4)	2838(4)	3084(4)	8444(3)	2.6
	C(5)	2827(6)	5264(5)	9222(4)	4.5
	C(6)	2837(5)	4233(4)	9736(3)	2.9
	C(7)	3958(4)	3958	10000	3.2
	OW	3575(4)	3575	5000	4.9
(2)	Co	39470(3)	20737(3)	34063(5)	1.5
	Cl(1)	6361(1)	852(1)	5139(1)	2.9
	Cl(2)	525(1)	6071(1)	2112(1)	3.2
	Cl(3)	1113(1)	795(1)	2697(1)	3.3
	O(1)	621(2)	3913(2)	1360(3)	3.4
	O(2)	5552(3)	4541(3)	−1133(5)	6.9
	O(3)	7023(6)	5915(5)	1830(9)	13.7
	N(1)	4905(2)	2197(2)	5315(3)	2.1
	N(2)	3182(2)	1561(2)	4409(3)	2.1
	N(3)	3627(2)	3332(2)	4075(3)	1.8
	N(4)	3106(2)	2003(2)	1260(3)	1.7
	N(5)	4220(2)	771(2)	3105(4)	2.1
	N(6)	4760(2)	2504(2)	2464(3)	2.1
	C(1)	5154(2)	3207(3)	5623(4)	2.7
	C(2)	4451(2)	3850(3)	4627(4)	2.3
	C(3)	2798(3)	2296(3)	5073(4)	2.4
	C(4)	3389(2)	3117(3)	5432(4)	2.2
	C(5)	2985(3)	4950(3)	3214(5)	3.3
	C(6)	2870(2)	3899(3)	3012(4)	2.0
	C(7)	2574(2)	3631(3)	1349(4)	2.1
	C(8)	2323(2)	2609(3)	987(4)	2.1
	C(9)	1666(3)	2523(3)	−607(5)	3.4
	C(10)	2869(2)	990(3)	1033(4)	2.3
	C(11)	3668(3)	418(3)	1598(5)	2.7
	C(12)	3548(3)	2263(3)	192(4)	2.5
	C(13)	4309(3)	2878(3)	920(4)	2.6
(3)	Co	62191(22)	0	75000	2.1
	N(1)	5721(11)	840(11)	6912(9)	3.1
	N(2)	5626(12)	−1130(11)	6623(7)	2.7
	N(3)	7516(11)	714(11)	6738(8)	2.9
	C(1)	6518(17)	1541(14)	6255(12)	4.2
	C(2)	7582(15)	1748(14)	6492(11)	3.4
	C(3)	6197(14)	−720(15)	5713(11)	3.3
	C(4)	7336(14)	11(15)	5958(13)	3.8
	C(5)	8520(15)	941(15)	7126(12)	3.6
	C(6)	8595(17)	0	7500	7.0
	Br(1)	3296(2)	4121(2)	1169(1)	3.9
	Br(2)	3333	6667	2236(2)	3.0
	*Br(3)	0	0	0	3.6
	*Br(4)	0	0	59(3)	3.9
	*Br(5)	30(3)	29(3)	24(1)	3.9
	*Br(6)	2(9)	29(5)	24(2)	4.3

* Population parameters of Br atoms in disorder are as follows.

Atom	Wyckoff notation of the position	Population parameter	Number of atoms in a unit cell
Br(3)	2b	0.04	0.48
Br(4)	4c	0.025	0.30
Br(5)	12g	0.065	0.78
Br(6)	12g	0.0367	0.44
			Σ 2.00

plex ions are listed in Table 3. The absolute configuration of the complex (**1**) is $\Delta\Delta\Lambda$ as expected. The complex has a crystallographic twofold axis through the Co and C(7) atoms. The central six-membered chelate ring takes a skew boat form with the two methyl groups in equatorial positions. The C(6)–C(5) bond axis is inclined by 6.5(5)° with respect to the coordination plane formed by Co, N(3), and N(3′) atoms, from which the C(6) is shifted by 0.67(1) Å. There are two optical isomers $\Delta\Delta\Lambda$ and $\Delta\Lambda\Lambda$ in a unit cell of (**2**) and (**3**). Figure 2 depicts a $\Delta\Delta\Lambda$ isomer for the convenience of comparison with (**1**). The geometry of the complexes (**1**) and (**3**) is essentially identical. The difference of 0.039 Å in Co–N(1) bond lengths of (**1**) and (**3**) is not significant because of the large e.s.d. of the structural data of (**3**).

The central six-membered chelate ring of (**2**) is distorted unsymmetrically, exhibiting a largely flattened chair form with the two C–CH_3 bonds in equatorial positions. The Co, N(3), N(4), and C(6) are practically on one plane, from which the C(7) and C(8) atoms are shifted on opposite sides by 0.28(1) and 0.53(1) Å, respectively. The Co–N bond lengths in (**2**) are in the order Co-tertiary N>Co-apical primary N>Co-primary N atom which is in the trans position to the tertiary N atom. The Co–N(4) bond length of 2.021(3) Å agrees with the Co-tertiary N bond lengths of (**1**) and (**3**) [2.017(4) and 2.018(13) Å]. The Co-tertiary N bond lengths of (**2**) differ from each other, Co–N(3) being longer by 0.021(3) Å than Co–N(4). It

Table 3. Bond distances (l/Å) and angles (ϕ/°)

(1)			
Co-N (1)	1.966(5)	N (1) -Co-N (2)	89.8(2)
Co-N (2)	1.967(5)	N (1) -Co-N (3)	86.5(2)
Co-N (3)	2.017(4)	N (2) -Co-N (3)	85.7(2)
N (1) - C (1)	1.487(9)	Co-N (1) - C (1)	112.1(4)
N (2) - C (3)	1.511(7)	Co-N (2) - C (3)	110.2(3)
N (3) - C (2)	1.506(7)	Co-N (3) - C (2)	104.1(3)
N (3) - C (4)	1.514(6)	Co-N (3) - C (4)	108.8(3)
N (3) - C (6)	1.510(6)	Co-N (3) - C (6)	113.8(3)
C (1) - C (2)	1.505(10)	C (2) -N (3) - C (4)	111.4(4)
C (3) - C (4)	1.500(8)	C (2) -N (3) - C (6)	109.6(4)
C (5) - C (6)	1.537(8)	C (4) -N (3) - C (6)	109.2(4)
C (6) - C (7)	1.532(8)	N (1) - C (1) - C (2)	109.4(5)
		N (3) - C (2) - C (1)	111.6(5)
		N (2) - C (3) - C (4)	106.9(4)
		N (3) - C (4) - C (3)	111.6(4)
		N (3) - C (6) - C (5)	112.6(4)
		N (3) - C (6) - C (7)	114.6(4)
		C (5) - C (6) - C (7)	109.9(5)
		N (1) -Co-N (1′)	91.5(2)
		N (1) -Co-N (2′)	88.5(2)
		N (1) -Co-N (3′)	173.8(2)
		N (2) -Co-N (2′)	177.5(2)
		N (2) -Co-N (3′)	96.0(2)
		N (3) -Co-N (3′)	96.2(2)
		C (6) - C (7) - C (6′)	120.1(3)
(2)			
Co-N (1)	1.950(3)	N (1) -Co-N (2)	92.8(1)
Co-N (2)	1.990(4)	N (1) -Co-N (3)	81.6(1)
Co-N (3)	2.042(3)	N (1) -Co-N (4)	169.9(1)
Co-N (4)	2.021(3)	N (1) -Co-N (5)	93.6(1)
Co-N (5)	1.963(3)	N (1) -Co-N (6)	85.3(1)
Co-N (6)	1.977(4)	N (2) -Co-N (3)	83.7(1)
N (1) - C (1)	1.502(5)	N (2) -Co-N (4)	97.2(1)
N (2) - C (3)	1.485(6)	N (2) -Co-N (5)	86.8(1)
N (3) - C (2)	1.488(5)	N (2) -Co-N (6)	175.9(1)
N (3) - C (4)	1.509(5)	N (3) -Co-N (4)	101.0(1)
N (3) - C (6)	1.539(4)	N (3) -Co-N (5)	169.1(1)
N (4) - C (8)	1.517(5)	N (3) -Co-N (6)	99.6(1)
N (4) - C (10)	1.497(5)	N (4) -Co-N (5)	85.5(1)
N (4) - C (12)	1.500(6)	N (4) -Co-N (6)	84.7(1)
N (5) - C (11)	1.485(5)	N (5) -Co-N (6)	89.7(1)
N (6) - C (13)	1.485(4)	Co-N (1) - C (1)	110.3(2)
C (1) - C (2)	1.526(5)	Co-N (2) - C (3)	113.2(3)
C (3) - C (4)	1.495(6)	Co-N (3) - C (2)	103.5(2)
C (5) - C (6)	1.518(6)	Co-N (3) - C (4)	105.3(2)
C (6) - C (7)	1.522(5)	Co-N (3) - C (6)	120.5(2)
C (7) - C (8)	1.525(6)	C (2) -N (3) - C (4)	107.3(3)
C (8) - C (9)	1.523(5)	C (2) -N (3) - C (6)	114.4(3)
C (10) - C (11)	1.496(6)	C (4) -N (3) - C (6)	104.9(3)
C (12) - C (13)	1.499(6)	Co-N (4) - C (8)	113.1(2)
		Co-N (4) - C (10)	104.3(2)
		Co-N (4) - C (12)	109.3(3)
		C (8) -N (4) - C (10)	111.0(3)
		C (8) -N (4) - C (12)	110.5(3)
		C (10) -N (4) - C (12)	108.2(3)
		Co-N (5) - C (11)	111.4(2)
		Co-N (6) - C (13)	111.5(2)
		N (1) - C (1) - C (2)	111.0(3)
		N (3) - C (2) - C (1)	109.4(3)
		N (2) - C (3) - C (4)	107.4(4)
		N (3) - C (4) - C (3)	108.8(3)
		N (3) - C (6) - C (5)	113.6(3)
		N (3) - C (6) - C (7)	115.6(3)
		C (5) - C (6) - C (7)	111.1(3)
		C (6) - C (7) - C (8)	115.8(3)
		N (4) - C (8) - C (7)	110.9(3)
		N (4) - C (8) - C (9)	113.5(3)
		C (7) - C (8) - C (9)	110.1(3)
		N (4) - C (10) - C (11)	108.6(3)
		N (5) - C (11) - C (10)	109.2(4)
		N (4) - C (12) - C (13)	112.3(3)
		N (6) - C (13) - C (12)	107.0(3)
(3)			
Co-N (1)	1.927(18)	N (1) -Co-N (2)	92.3(7)
Co-N (2)	1.974(12)	N (1) -Co-N (3)	86.4(7)
Co-N (3)	2.018(13)	N (2) -Co-N (3)	85.2(5)
N (1) - C (1)	1.500(22)	Co-N (1) - C (1)	110.7(12)
N (2) - C (3)	1.609(20)	Co-N (2) - C (3)	112.7(9)
N (3) - C (2)	1.498(28)	Co-N (3) - C (2)	104.0(13)
N (3) - C (4)	1.529(25)	Co-N (3) - C (4)	109.3(10)
N (3) - C (5)	1.451(27)	Co-N (3) - C (5)	115.6(11)
C (1) - C (2)	1.459(33)	C (2) -N (3) - C (4)	111.1(14)
C (3) - C (4)	1.493(23)	C (2) -N (3) - C (5)	109.0(14)
C (5) - C (6)	1.533(27)	C (4) -N (3) - C (5)	107.8(16)
		N (1) - C (1) - C (2)	109.6(17)
		N (3) - C (2) - C (1)	109.0(15)
		N (2) - C (3) - C (4)	102.2(12)
		N (3) - C (4) - C (3)	115.9(16)
		N (3) - C (5) - C (6)	117.8(13)
		N (1) -Co-N (1′)	93.1(8)
		N (1) -Co-N (2′)	86.0(7)
		N (1) -Co-N (3′)	171.2(8)
		N (2) -Co-N (2′)	177.7(5)
		N (2) -Co-N (3′)	96.4(7)
		N (3) -Co-N (3′)	95.5(7)
		C (5) - C (6) - C (5′)	118.2(20)

suggests a distortion of the CoN_6 octahedron. N(3)–Co–N(4) angle of 101.0(1)° in (**2**) is larger by 4.8 (2)° than N(3)-Co-N(3′) angle in (**1**). Edge-on view of the five-membered chelate rings are shown in Fig. 3. They adopt an envelope conformation except B ring of (**2**). N(1)-Co-N(3) angle of the chelate ring B, 81.6(1)° and N(2)-Co-N(3) angle of the ring E, 83.7(1)° are smaller than the corresponding angles in the chelate rings C and D by 3.9(1) and 1.0(1)°, respectively.

In Fig. 3 the tertiary N atoms are hatched. The conformations of the apical chelate rings D and E of

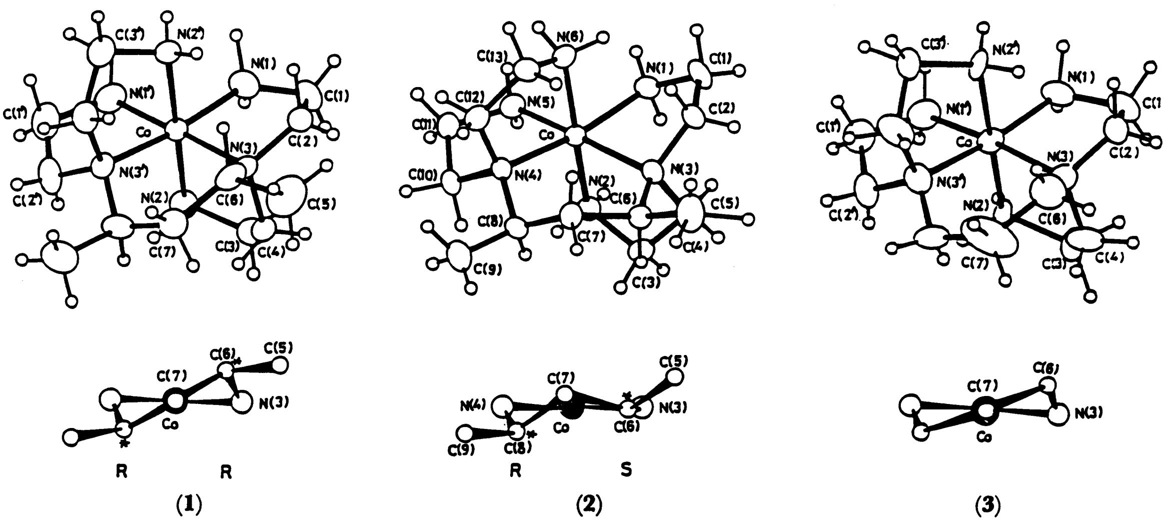


Fig. 2. Molecular structures of (**1**), (**2**), and (**3**). Projections of the central six-membered chelate rings along the midpoint of two tertiary N atoms to the Co are also shown.

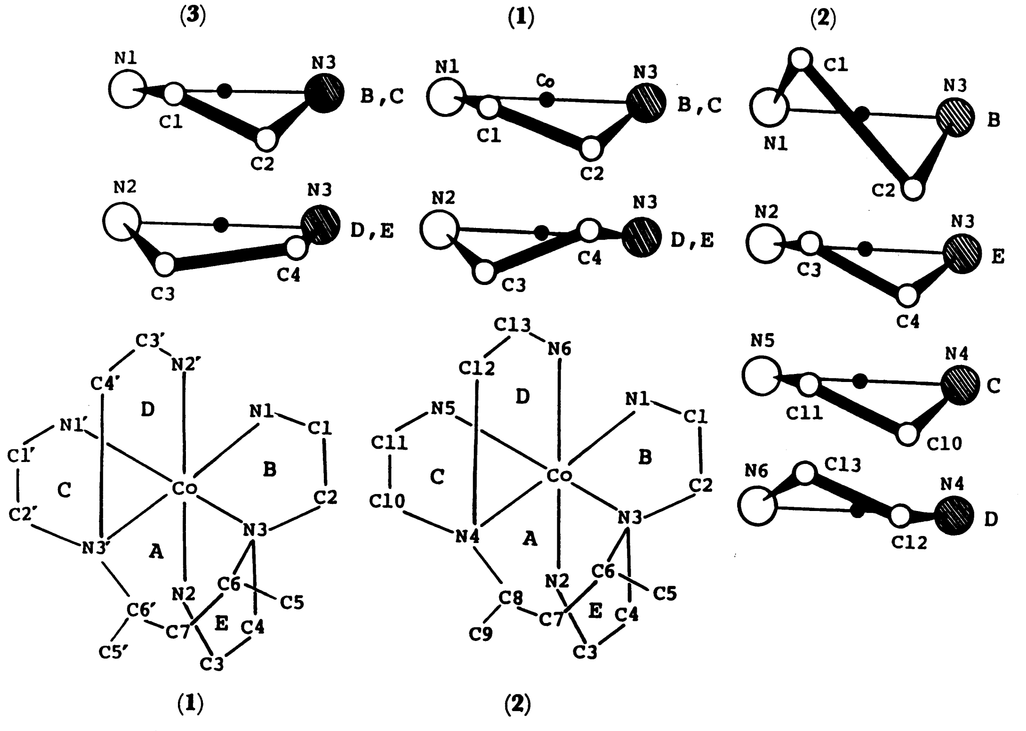


Fig. 3. Edge-on views of the five-membered chelate rings. The shaded circles stand for the tertiary N atoms, the black circles for the Co atoms.

(**1**) and (**2**) differ from each other. The simple molecular model indicates that the ring D in (1) avoids a short contact between H(C6) and one of the H atoms bonded to C(3′), and that the conformation of the ring E in (**2**) is the result of the flattened chair form of the central chelate ring, A. Table 4 lists the hydrogen bonds. The ring D in (**2**) takes a conformation which can form two hydrogen bonds, O(1)···H(N6)1–N(6) and Cl(3)···H(N6)2–N(6) in the crystal. Co–N(3)–C(6) angle of (**2**) is 120.5(2)°. It nearly equals to the mean Co–N–C angle of 122.2(2)° in $[Co(tn)_3]^{3+}$ (tn=1,3-propanediamine), which takes the C_3-chair$_3$ conformation.[8] The N–Co–N angle in the ring E of (**1**) and (**3**) agrees with that of 85.4(1)° in *lel*$_3$-$[Co(en)_3]^{3+}$ (en=1,2-ethanediamine),[9] and smaller by *ca.* 1° than that in the ring B.

The octahedral splitting parameter *10D*$_q$ can be easily shown to be proportional to r^{-5}, where r is the Co–N distance, if simple electrostatic model is assumed for the ligand field as a crude approximation.[10] In Fig. 4, the energy of the first absorption maxima of some Co(III) complexes with CoN_6 chromophore are plotted against the inverse fifth power of the average Co–N bond distances. A positive correlation is observed. It

TABLE 4. INTERMOLECULAR HYDROGEN BONDS (distances in Å)

A···H–B (symmetry code)		A···B	A···H	H···B
(1)				
O(6)···H(N1)1–N(1)	(i)	3.029(7)	2.01(6)	1.02(5)
Ow···H(N1)2–N(1)	(ii)	2.952(5)	1.92(6)	1.11(6)
(2)				
Cl(2)···H(N1)2–N(1)	(iii)	3.213(4)	2.27(5)	0.97(5)
Cl(2)···H(N2)1–N(2)	(iii)	3.308(3)	2.45(4)	0.94(4)
Cl(1)···H(N5)2–N(5)	(iv)	3.204(4)	2.39(5)	0.83(5)
O(1)···H(N6)1–N(6)	(v)	2.893(5)	2.03(5)	0.88(5)
Cl(3)···H(N6)2–N(6)	(v)	3.281(4)	2.45(5)	0.98(4)
Cl(2)···H(O1)2–O(1)	(vi)	3.161(3)	2.33(4)	0.85(4)
(3)				
Br(2)···H(N1)1–N(1)	(vii)	3.420(13)	2.48	1.02
Br(1)···H(N1)2–N(1)	(viii)	3.313(16)	2.30	1.03

Symmetry codes: (i) $1/2-x, 1/2+y, 3/2-z$, (ii) $1/2+x, 1/2-y, 3/2-z$, (iii) $1/2-x, 1/2+y, 1-z$, (iv) $1-x, -y, 1-z$, (v) $-1/2+x, 1/2-y, z$, (vi) $-x, 1-y, -z$, (vii) $1-x, 1-y, 1-z$, (viii) $x+y, -y, -1/2+z$.

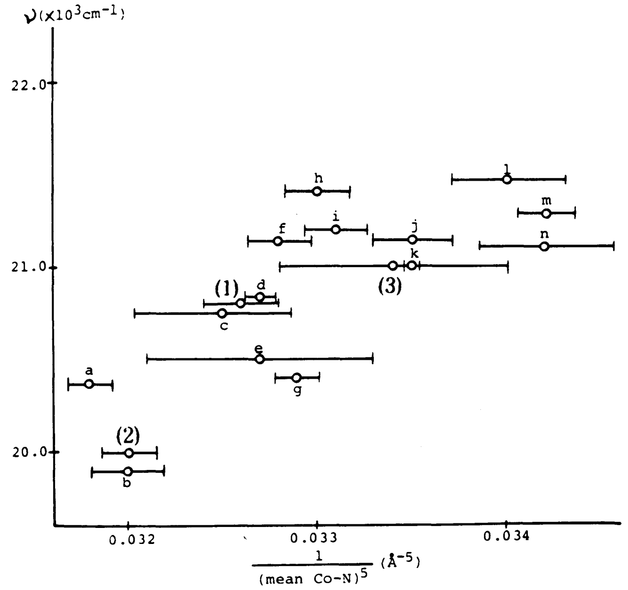


Fig. 4. Plot of the energy of the first absorption band against the inverse fifth power of the mean Co–N bond length of Co(III)N_6 complexes: a) $(+)_{589}$-*fac*-$[Co(R,S\text{-ptn})_3]^{3+}$,[11] b) $(+)_{589}$-$[Co(tmd)_3]^{3+}$,[12] c) $(-)_{546}$-$[Co(R,R\text{-ptn})_3]^{3+}$,[13] d) $(+)_{470}$-*cis*-$[Co(NH_3)_2(R,R\text{-ptn})_2]^{3+}$,[14] e) $(+)_{589}$-$[Co(ten)]^{3+}$,[15] f) $(+)_{589}$-(ob_3)-$[Co(chxn)_3]^{3+}$,[16] g) $(-)_{589}$-$[Co(tn)_3]^{3+}$,[8] h) $(+)_{589}$-(lel_3)-$[Co(en)_3]^{3+}$,[9] i) $(+)_{589}$-$[Co(linpen)]^{3+}$,[17] j) $(-)_{589}$-(lel_2ob)-$[Co(chxn)_3]^{3+}$,[18] k) $[Co(NH_3)_6]^{3+}$,[19] l) $(+)_{589}$-*mer*-$[Co(dien)_2]^{3+}$,[20] m) $(+)_{589}$-$[Co(en)_2(3,3'\text{-dmbpy})]^{3+}$,[21] n) $(-)_{589}$-$[Co(R,R\text{-chxn})_2(3,3'\text{-dmbpy})]^{3+}$,[22]. Error bars show ±(e.s.d.)/2.

was shown that the Co–N bond elongation in (**2**) which is caused by the nonbonded interactions is an important factor for the lower energy of the first absorption band than that of (**1**).

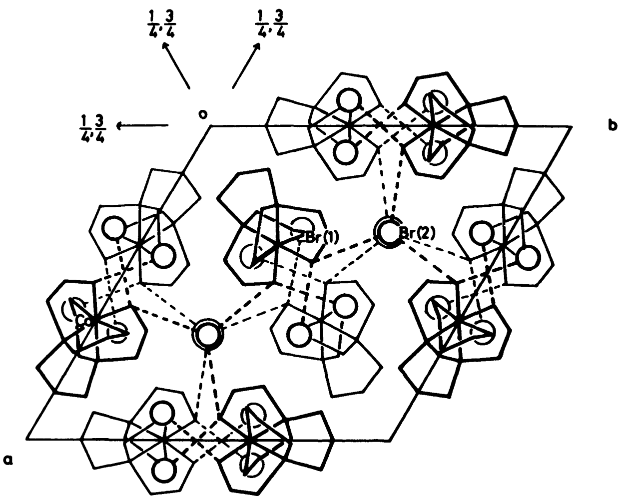


Fig. 5. A projection of the crystal structure of (**3**) along *c*. The broken lines indicate the hydrogen bonds.

A remark will be given on the disorder of the bromide ions in (**3**). The complex ions $[Co(ttn)]^{3+}$ and bromide ions Br(2) are held together by N–H···Br hydrogen bonds to form layers approximately perpendicular to *c* as shown in Fig. 5. These layers are stacked parallel to form a three-dimensional framework by attraction of Br(1) anions between the layers to the complex cations. There exists a hollow around the origin, in which the disordered bromide ions lie. The shortest interatomic distance involving Br(3) atom is 3.38 Å for Br(3)···H(C4)1 ($-y, 1-x, -1/2+z$), longer than 3.05 Å, the sum of the van der Waals radius of Br and H atoms.[23]

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