Atropisomerism in Metal Chelates. The Crystal Structure and Absolute Configuration of $(-)_{589}$-3-(2,4-Dinitro-1-naphthyl)-2,4-pentanedionato[tris(2-aminoethyl)amine]cobalt(III) Dibromide

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The crystal structure and the absolute configuration of $(-)_{589}$-3-(2,4-dinitro-1-naphthyl)-2,4-pentanedionato[tris(2-aminoethyl)amine]cobalt(III) dibromide were determined by X-ray diffraction. The complex crystallizes as the orthorhombic space group $P2_12_12_1$, with $a=13.738(2)$, $b=15.446(1)$, $c=12.243(1)$ Å, and $Z=4$. The structure was solved by the Patterson-Fourier method and refined to a final R_1 value of 0.038 for the 3347 observed reflections with $|F_o|>3\sigma(|F_o|)$. The acetylacetonate (acac) ring adopts a more deformed boat conformation than that in 3-(6-methyl-2,4-dinitrophenyl)-2,4-pentanedionato analogue. The three chelate rings of tris(2-aminoethyl)amine (tren) have envelope conformations and adopt λ, λ, and δ conformations. The absolute configuration of the title compound can be designated as R.

One of the present authors (Y. N.) has synthesized and resolved a series of optically active complexes whose optical activity arises from the restricted rotation of an aromatic ring system. The crystal structure of a member of the series has been determined by X-ray diffraction (Complex II in Fig. 1).[1] In this complex, the $[CoN_4O_2]$ chromophore possesses approximately the C_{2v} symmetry, while the two apical five membered chelate rings formed by tren have enantiomeric conformations. Although the 6-methyl-2,4-dinitrophenyl group is, as expected, almost perpendicular to the acac ring, the acac ring bends slightly toward the 2-nitro group.

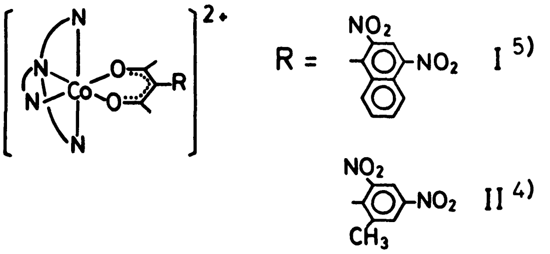

Fig. 1. Skeletal stucture of 3-aryl-2,4-pentanedionato-[tris(2-aminoethyl)amine]cobalt(III) cation.

Since the title complex has the same chromophore as Complex II, except for its π-electronic system of the aromatic ring, almost all the transitions in the CD spectrum of Complex II should also appear in that of Complex I. In fact, the CD spectrum of the title complex showed the same sign and reasonable rotational strength compared to that of $(-)_{589}$-complex II in the first absorption region. Accordingly, the following structural features, observed in Complex II, were also expected for Complex I: (1) The relative configuration of the 2-nitro group with respect to the tren chain, (2) the bent structure of the acac ring, and (3) the disposition of the aromatic system relative to the acac ring.

The authors' interest lies in clarifying the structural details, such as those described above and other structural factors which may contribute to the rotatory strength.

Experimental

The present complex[2] consists of orange-red plates. The crystal data and data collection detailes are summarized in Table 1. The intensities were corrected for Lorentz and polarization effects and for absorption. The structure was solved by the heavy-atom method. All the parameters for non-hydrogen atoms were refined by a block-diagonal least-squares method with anisotropic thermal parameters. The weights for the refinement were $w=1/[\sigma^2(|F_o|)+(0.015|F_o|)^2]$. The refinement converged to $R_1=0.038$ and $R_2=0.042$. The final positional parameters shift of C(2) was 1.5σ, those of the other non-hydrogen atoms were less than their σ. The final difference Fourier maps showed no peaks greater than 0.6 e/Å^3.

TABLE 1. THE CRYSTAL DATA[a)] AND DATA COLLECTION

$C_{21}H_2Br_2CoN_6O_6$	
Orthorhombic	$P2_12_12_1$
$a=13.738(2)$ Å, $b=15.446(1)$ Å, $c=12.243(1)$ Å, $V=2598.1(4)$ Å^3	
$D_x=1.74$, $D_m=1.73$ g cm^{-3}; $Z=4$, $\mu=40.0$ cm	
Crystal used	A sphere 0.35 mm in diameter
Diffractometer	Rigaku AFC-3 automated four-circle diffractometer
Radiation	Mo $K\alpha$ (monochromated with graphite), $\lambda=0.71069$ Å
Data-collection range	$3<2\theta<60°$
Scan mode	θ-2θ scan(2°/min in θ)
Total data collected	4375
Data with $\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$	3347

a) The lattice constants were obtained by a least-squares calculation based on 31 reflections with $12.1<\theta<21.3°$.

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TABLE 2. ATOMIC PARAMETERS, WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	$U_{eq}/\text{Å}^2$ a) or $U_{iso}/\text{Å}^2$
Co	0.35086(4)	0.20621(4)	0.90118(5)	0.0210(3)
Br(1)	0.56479(5)	0.17166(4)	1.22141(5)	0.0462(3)
Br(2)	0.12908(4)	0.12748(4)	1.17904(5)	0.0480(3)
C(1)	0.3975(4)	0.0287(3)	0.9186(5)	0.037(3)
C(2)	0.3418(4)	0.0344(3)	1.0239(4)	0.036(3)
C(3)	0.4915(4)	0.1395(3)	0.8160(5)	0.040(3)
C(4)	0.5492(4)	0.1696(3)	0.9145(5)	0.040(3)
C(5)	0.3195(4)	0.1091(3)	0.7665(4)	0.038(3)
C(6)	0.2193(4)	0.1103(4)	0.8170(5)	0.044(3)
C(7)	0.3711(4)	0.4142(3)	0.7377(4)	0.034(3)
C(8)	0.3546(3)	0.3681(3)	0.8446(4)	0.024(2)
C(9)	0.3417(3)	0.4132(3)	0.9420(4)	0.024(2)
C(10)	0.3118(3)	0.3701(3)	1.0385(4)	0.025(2)
C(11)	0.2770(4)	0.4225(3)	1.1328(4)	0.037(3)
C(12)	0.3492(3)	0.5097(3)	0.9479(4)	0.026(2)
C(13)	0.4316(4)	0.5524(3)	0.9811(4)	0.031(2)
C(14)	0.4389(5)	0.6433(3)	0.9846(4)	0.040(3)
C(15)	0.3597(5)	0.6917(3)	0.9592(4)	0.041(3)
C(16)	0.2710(4)	0.6553(3)	0.9265(4)	0.037(3)
C(17)	0.1870(5)	0.7035(4)	0.8956(5)	0.053(4)
C(18)	0.1036(5)	0.6634(4)	0.8662(5)	0.057(4)
C(19)	0.0968(4)	0.5729(4)	0.8665(5)	0.050(4)
C(20)	0.1773(4)	0.5234(3)	0.8930(4)	0.034(3)
C(21)	0.2661(4)	0.5628(3)	0.9212(4)	0.029(2)
N(1)	0.3928(3)	0.1136(2)	0.8557(3)	0.028(2)
N(2)	0.3514(3)	0.1230(2)	1.0690(3)	0.028(2)
N(3)	0.4882(3)	0.2339(3)	0.9737(3)	0.029(2)
N(4)	0.2179(3)	0.1755(3)	0.9055(3)	0.029(2)
N(5)	0.5186(3)	0.5069(3)	1.0204(4)	0.041(3)
N(6)	0.3720(5)	0.7856(3)	0.9747(4)	0.064(3)
O(1)	0.3524(2)	0.2855(2)	0.8335(2)	0.024(1)
O(2)	0.3077(2)	0.2887(2)	1.0521(3)	0.026(2)
O(3)	0.5102(3)	0.4378(3)	1.0676(4)	0.052(2)
O(4)	0.5971(3)	0.5430(3)	1.0067(5)	0.071(3)
O(5)	0.4502(5)	0.8170(3)	0.9525(5)	0.093(4)
O(6)	0.3050(5)	0.8262(3)	1.0138(6)	0.108(5)
H(C1A)	0.454(4)	0.015(3)	0.928(4)	0.044(16)
H(C1B)	0.376(4)	−0.018(4)	0.865(5)	0.060(19)
H(C2A)	0.365(4)	−0.005(3)	1.071(4)	0.038(15)
H(C2B)	0.277(4)	0.022(3)	1.011(4)	0.041(15)
H(N2A)	0.403(3)	0.123(3)	1.108(4)	0.019(12)
H(N2B)	0.306(4)	0.132(4)	1.099(5)	0.054(18)
H(C3A)	0.482(3)	0.190(3)	0.768(4)	0.022(12)
H(C3B)	0.521(4)	0.092(3)	0.777(4)	0.041(15)
H(C4A)	0.606(4)	0.194(3)	0.892(4)	0.041(15)
H(C4B)	0.562(5)	0.120(4)	0.951(5)	0.066(20)
H(N3A)	0.500(3)	0.284(3)	0.952(4)	0.029(13)
H(N3B)	0.502(4)	0.224(3)	1.058(4)	0.043(16)
H(C5A)	0.330(3)	0.155(2)	0.720(3)	0.008(10)
H(C5B)	0.333(3)	0.061(3)	0.739(4)	0.027(13)
H(C6A)	0.175(3)	0.124(3)	0.758(4)	0.027(13)
H(C6B)	0.202(4)	0.059(3)	0.842(4)	0.040(16)
H(N4A)	0.188(4)	0.224(3)	0.881(4)	0.035(15)
H(N4B)	0.186(4)	0.154(3)	0.963(4)	0.041(15)
H(C7A)	0.334(3)	0.393(3)	0.693(4)	0.026(13)
H(C7B)	0.355(4)	0.473(3)	0.744(5)	0.046(16)
H(C7C)	0.422(4)	0.402(4)	0.708(5)	0.053(17)
H(C11A)	0.218(4)	0.468(3)	1.112(4)	0.041(16)
H(C11B)	0.249(4)	0.390(4)	1.190(5)	0.055(18)
H(C11C)	0.326(3)	0.453(3)	1.154(4)	0.027(13)
H(C14)	0.493(4)	0.664(3)	1.011(4)	0.037(15)
H(C17)	0.197(4)	0.763(3)	0.891(4)	0.042(16)
H(C18)	0.051(5)	0.693(4)	0.835(6)	0.073(21)
H(C19)	0.035(4)	0.539(3)	0.837(4)	0.037(15)
H(C20)	0.168(4)	0.462(3)	0.883(4)	0.032(14)

a) $U_{eq}=(U_{11}+U_{22}+U_{33})/3$.

The positional parameters of all the atoms with their standard deviations, are listed in Table 2. The thermal parameters[3] and observed and calculated structure factors[3] are kept in the office of the Chemical Society of Japan. The atomic-scattering factors were taken from Ref. 4. The calculations were performed on a FACOM 230-48 computer of this Institute with a local version of UNICS.[5]

The absolute configuration was determined by anomalous-scattering techniques. Some Friedel pairs were examined on equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation. Observed and calculated intensities are compared, for which $|F_c(hkl)|$ and $|F_c(h\bar{k}l)|$ differd by more than 35%.[3] The concordance of the intensities indicated that the absolute configuration of this complex is *R*, according to the Cahn-Ingold-Prelog notation.[6] When the enantiomeric structure was refined under identical conditions, it converged to $R_1=0.056$ and $R_2=0.058$. An application of the residual-index-ratio-test[7] showed that this structure could be rejected at the 0.005 significance level in favor of the *R* configuration.

Description of Structure and Discussion

Figures 2 and 3 show the projection of the crystal structure along the c and b axes respectively. The complex cations are linked through N–H···Br hydrogen bonds to form zigzag chains along the a axis. The interatomic distances and bond angles of the hydrogen bonds[3] and the short intermolecular distances[3] are listed in the supplementary materials.

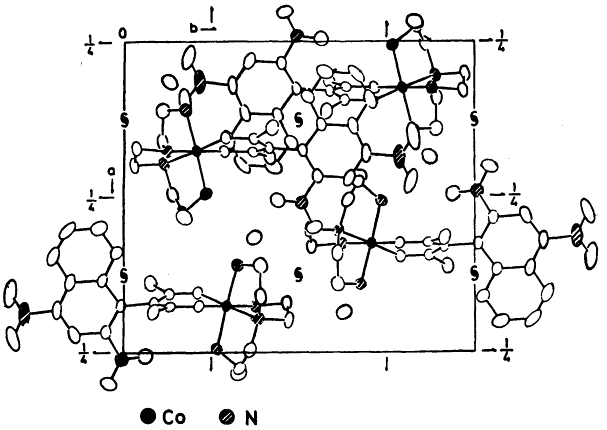

Fig. 2. A projection of the unit cell along the c axis.

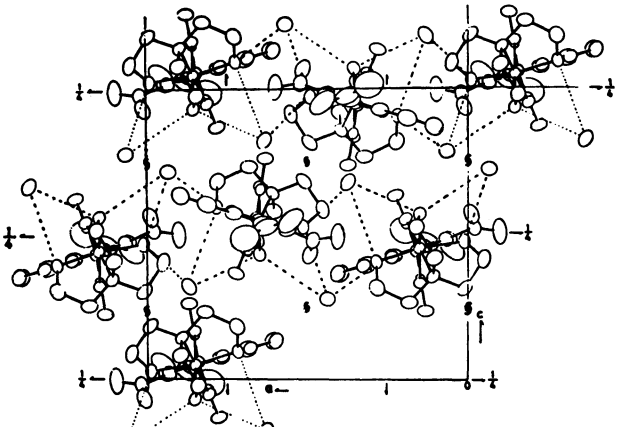

Fig. 3. A projection of the unit cell along the b axis. Broken lines indicate hydrogen bonds.

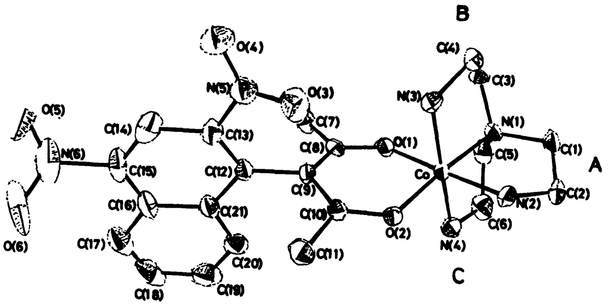

Fig. 4. A perspective drawing of the complex cation and the numbering scheme of the atoms. The three chelate rings are denoted by A, B, and C.

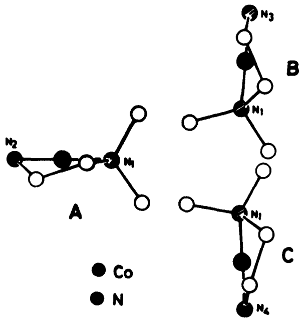

Fig. 5. Conformation of the tren chain.

A perspective drawing of the complex ion is shown in Fig. 4. In contrast to the case of Complex II, neither disorder in the chelate-A ring nor a large libration of the aromatic ring was observed. The chelate rings of tren (labeled A, B, and C, as are shown in Fig. 5) adopt the envelop conformation. The B and C rings are almost enantiomeric, and their conformations are λ and δ respectively, whereas A ring takes a λ conformation. The conformation of the rings favors the formation of hydrogen bonds between the primary amino groups and bromide ions (see Fig. 3).[3] Bond distances and angles in the cation are listed in Table 3.[3] The Co–N(1) and Co–N(2) bonds in the chelate ring A are significantly shorter than the other two, Co–N(3) and Co–N(4) (see Table 3). The Co–N(3) and Co–N(4) bonds are not colinear, the N(3)–Co–N(4) angle being 171.4(2)°. Such a deformation is attributable to the strain due to fused chelate-ring formation. Similar distortions are observed in Complex II and other related chelate complexes.[8,9]

Figure 6 shows a projection of the complex cation along the line through the two oxygen atoms of the acac ring. The ring assumes a boat conformation similar to that in Complex II.[1] This seems to be due to electrostatic interaction between the amino and 2-nitro groups as will be described below. The deformation of the acac ring in this complex is larger than that in Complex II. The mean plane of O(1), O(2), C(8), and C(10) makes dihedral angles of 15.3° with respect to the coordination plane of the acac ring and 7.9° with respect to the plane of C(8), C(9), and C(10). The bonds around the atoms

TABLE 3. BOND LENGTHS AND ANGLES; WITH THEIR STANDARD DEVIATIONS

	Bond lengths(l/Å)		
Co–N(1)	1.936(4)	Co–N(2)	1.933(4)
Co–N(3)	1.954(4)	Co–N(4)	1.968(4)
Co–O(1)	1.891(3)	Co–O(2)	1.871(3)
C(7)–C(8)	1.507(6)	C(8)–C(9)	1.393(6)
C(9)–C(10)	1.415(6)	C(8)–O(1)	1.284(5)
C(10)–O(2)	1.270(5)	C(10)–C(11)	1.489(7)
C(9)–C(12)	1.497(6)	C(13)–N(5)	1.468(7)
N(5)–O(3)	1.218(6)	N(5)–O(4)	1.225(6)
	Bond Angles(ϕ/°)		
N(1)–Co–N(2)	87.6(2)	N(1)–Co–N(3)	87.7(2)
N(1)–Co–N(4)	85.8(2)	N(3)–Co–N(4)	171.4(2)
N(3)–Co–O(1)	87.4(2)	N(4)–Co–O(1)	87.1(2)
O(1)–Co–O(2)	93.8(1)	Co–O(1)–C(8)	124.3(3)
Co–O(2)–C(10)	125.0(3)	O(1)–C(8)–C(7)	112.4(4)
O(2)–C(10)–C(11)	115.0(4)	O(1)–C(8)–C(9)	125.8(4)
O(2)–C(10)–C(9)	126.0(4)	C(8)–C(9)–C(10)	121.1(4)
C(8)–C(9)–C(12)	122.0(4)	C(10)–C(9)–C(12)	116.6(4)
C(12)–C(13)–N(5)	122.6(5)	O(3)–N(5)–O(4)	123.2(5)

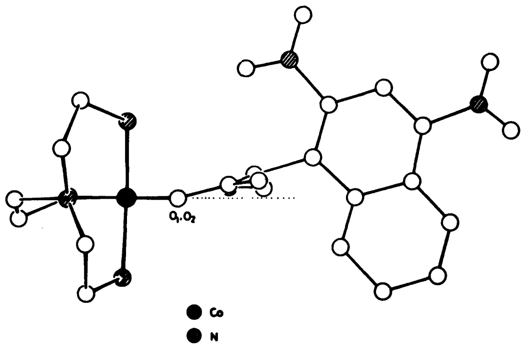

Fig. 6. A projection of the complex cation along the line of two oxygen atoms, O(1) and O(2).

of C(8) and C(10) have the sp^2 character. Thus, the two sets of groups, O(1), C(7), C(8), and C(9), and O(2), C(9), C(10), and C(11), are almost planar. The maximum shifts of the atoms from the least-squares planes of the two groups are 0.01 and 0.02 Å respectively. The former plane makes dihedral angles of 4.2° with respect to the plane of O(1), O(2), C(8), and C(10), and the latter, 8.0°. Consequently, the C(7) and C(11) atoms shift from the plane of O(1), O(2), C(8), and C(10) to the opposite side of the C(9) atom.

The two coordination bonds of the acac ring differ significantly from each other. Such a difference was also observed in Complex II. The bond distance, Co–O(2), is shorter than Co–O(1) by 0.020 Å. Mitsui observed a similar shortening in an analogous glycine chelate.[8] The pivot bond, C(9)–C(12), tilts by 5.1(4)° from the plane of C(8), C(9), and C(10). The aromatic system tilts slightly around the pivot bond, so that the 2-nitro group approaches the O(2) atom. The direction of the tilt is opposite to that found in Complex II. The angle between the O(1)–Co–O(2) plane and the mean plane of the aromatic system is 85.4°. In this complex, the distances between the amino nitrogen atom, N(3), and the oxygen atom of the 2-nitro, is 3.367(6) Å, while that between O(3) and H(N3A) is 2.77(5) Å. The bond angle of N(3)–H(N3A)–O(3) is 130(4°). These values suggest that the formation of a strong hydrogen bond between N(3) and O(3) is not favored. Electrostatic interaction between the amino and 2-nitro groups may force the acac ring to adopt a boat conformation.

In an aqueous solution, all the polar groups and the bromide ions will be solvated; interactions between the 2-nitro group and the amino group will diminish, and the hydrogen bonds between the bromide ions and the amino groups will be broken. These changes will lead to random conformations of the tren instead of rigid dissymmetric conformations. Therefore, the disposition and configuration of the aromatic system relative to the tren chain seems to contribute most to the rotational strength in the present complex.

In the resolution chromatography of the complexes, I and II, *R* isomers are eluted faster than *S* isomers. The *R* isomers associate with the $(+)_{589}$-tartratoantimonate(III) ion more strongly than the *S* isomers, and they can be dissociated more easily from the sulfonate groups of SP-Sephadex resin.[10] Furthermore, the pair of elution bands in Complex I are more separated than those in Complex II; the pair of the elution bands are completely separated in Complex I, but the tail of the *R*-isomer band overlaps the S isomer in Complex II. These facts suggest that the π-electronic system may play a role in discriminating the enantiomers. The associative complex of the *S* isomer with tartratoantimonate(III) ion are probably less stable than that of the *R* isomer because of the steric hindrance of the benzo moiety in the associative complex. A crystallographic study of the tartratoantimonate salt of the title complex would shed light on the problem.

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3) Supplementary materials (Document No. 8221) have been deposited at the office of the Chemical Society of Japan: a) Thermal parameters of non-hydrogen atoms; b) Table of $|F_o|$ and $|F_c|$; c) Observations of some Bijvoet pairs; d) Interatomic distances and angles of the hydrogen bonds; e) Table of close interatomic distances outside the complex ion; f) Non-essential data of bond length and angles.

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