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The Crystal Structure and Absolute Configuration of $(-)_{589}$-Bis(2,4-pentanedionato)(1,3-propanediamine)chromium(III) Iodide Monohydrate

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The crystal structure of $(-)_{589}$-[Cr(acac)$_2$(tn)]I·H$_2$O has been determined from the X-ray diffraction data collected on a diffractometer. The crystal is orthorhombic, with the space group $P2_12_12_1$ and with $a=20.834(6)$, $b=12.015(3)$, $c=7.621(2)$ Å, and $Z=4$. Block-diagonal least-squares refinement for 1426 independent reflections with $F_o^2 > 3\sigma(F_o^2)$ converged to $R=4.91\%$. The complex cation has the Δ absolute configuration. The 1,3-propanediamine ligand assumes a chair conformation. One of the 2,4-pentanedionato chelate rings is almost planar, while in the other the 2,4-pentanedionato plane is bent away from the plane defined by Cr and 2 O donor atoms because of the intramolecular repulsion, the interplanar angle being 9.4°. The interrelation between the absolute configuration and the circular dichroism was discussed for the $[\mathrm{Cr(acac)}_n(\mathrm{tn})_{3-n}]^{(3-n)+}$-type complexes.

The optically pure $(-)_{589}$-[Cr(acac)$_3$] (acac=2,4-pentanedionate anion) was isolated by Mason *et al.*[1] using asymmetric synthesis. The circular dichroism spectrum(CD) of the complex had previously been related to those of Λ-$(+)_{589}$-[Cr((+)-atc)$_3$][2] ((+)-atc=(+)-3-acetylcamphorate anion) and Λ-*trans*-$(-)_{589}$-[Cr(*d*-hmc)$_3$][3] (*d*-hmc=*d*-hydroxymethylenecamphorate anion) the structures of which had already been determined by means of X-ray analysis and stereoselectivity respectively. The Δ configuration had thus been given to $(-)_{589}$-[Cr(acac)$_3$]. Recent X-ray work has confirmed that the assignment of the Δ configuration to $(-)_{589}$-[Cr(acac)$_3$] is correct.[4]

The $(-)_{589}$-[Cr(acac)$_2$(tn)]$^+$ (tn=1,3-propanediamine) complex was prepared and resolved by Nakano and Kawaguchi.[5] The CD curve of the complex is similar in shape to that of Λ-$(+)_{589}$-[Cr(acac)$_3$], although the former is shifted to a higher wave number. Therefore, the Λ configuration could be assigned to the $(-)_{589}$-[Cr(acac)$_2$(tn)]$^+$ complex. The $(-)_{589}$-[Cr(acac)$_2$(tn)]I·H$_2$O crystal was subjected to X-ray structure analysis in order to confirm the absolute configuration of the complex cation.

Experimental

X-Ray Data Collection. Preliminary photographic data obtained using a Weissenberg camera indicated that the Laue symmetry was mmm and that the space group was $P2_12_12_1$. The specimen employed for the data collection was an approximate sphere, the diameter of which was 0.3 mm. The crystal was mounted on a glass fibre along the c axis.

The cell dimensions were obtained by the least-squares refinement of the θ values of 26 automatically centered reflections by means of a Philips PW1100 four-circle diffractometer.

Crystal Data: $(-)_{589}$-[Cr(C$_5$H$_7$O$_2$)$_2$(C$_3$H$_{10}$N$_2$)]I·H$_2$O, *F.W.*=469.3, orthorhombic, $a=20.834(6)$ Å, $b=12.015(3)$ Å, $c=7.621(2)$ Å, $U=1907.7(9)$ Å^3, $Z=4$, $D_x=1.63$, $D_m=1.62$ g·cm^{-3}, space group $P2_12_12_1$, μ(Mo $K\alpha$)=22.8 cm^{-1}, λ(Mo $K\alpha$)=0.7107 Å.

The intensity data ($2\theta \leqq 55°$) were collected at room temperature by the use of graphite-monochromated Mo $K\alpha$ radiation. The ω-scan mode was employed, since the reflections were rather broad. The scan range was $(1.6+0.5 \tan\theta)°$, and the scan speed, 2°/min; the background was counted for 10 s at each side of the scan range. During the data collection, the intensities of three standard reflections were monitored every 180 min in order to check the orientation and stability of the crystal. No appreciable decay was observed. A total of 1426 reflections with $F_o^2 > 3\sigma(F_o^2)$ were observed and used in the subsequent structure determination and refinement. The observed intensities were corrected for Lorentz-polarization and absorption effects ($r=0.015$ cm), and the relative structure factors were derived.[6]

Structure Determination and Refinement. The crystal structure was solved by the heavy-atom method. The parameters of all the non-hydrogen atoms were refined by

Table 1. Positional and thermal parameters

Atom	$10^4 x$	$10^4 y$	$10^4 z$	$10B$/Å^2
I	3959.0 (5)	901.3 (7)	212.1 (14)	a
Cr	3930 (1)	6720 (1)	606 (2)	a
O (1)	3445 (4)	5447 (7)	1492 (12)	36 (2)
O (2)	3939 (4)	6080 (6)	−1754 (10)	34 (1)
O (3)	3158 (4)	7542 (6)	−64 (12)	34 (2)
O (4)	3919 (4)	7415 (6)	2950 (10)	31 (1)
N (1)	4784 (5)	5914 (8)	1181 (13)	30 (2)
N (2)	4461 (5)	8041 (8)	−293 (14)	31 (2)
C (1)	2947 (7)	3680 (13)	1713 (21)	46 (3)
C (2)	3262 (5)	4583 (9)	616 (16)	26 (2)
C (3)	3369 (7)	4448 (12)	−1130 (20)	42 (3)
C (4)	3678 (6)	5169 (11)	−2235 (19)	34 (2)
C (5)	3725 (8)	4997 (15)	−4198 (23)	53 (3)
C (6)	2223 (7)	8696 (12)	100 (23)	50 (3)
C (7)	2788 (6)	8109 (10)	956 (17)	30 (2)
C (8)	2882 (6)	8234 (11)	2790 (17)	32 (2)
C (9)	3450 (6)	7916 (10)	3625 (17)	28 (2)
C (10)	3521 (7)	8235 (12)	5592 (19)	42 (3)
C (11)	5314 (6)	5965 (11)	−89 (19)	41 (2)
C (12)	5519 (7)	7126 (11)	−578 (19)	40 (2)
C (13)	5023 (7)	7799 (12)	−1520 (19)	39 (3)
O(H$_2$O)	4813 (5)	3400 (9)	1269 (14)	47 (2)

a) Anisotropic thermal parameters(×10^5) in the form of: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	289(2)	564(4)	2387(17)	30(7)	−115(15)	−81(18)
Cr	161(4)	382(10)	1236(32)	1(14)	17(25)	−124(32)

TABLE 2. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES OF SOME BIJVOET PAIRS

h k l	$\lvert F_c(hkl)\rvert$	Obsd	$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$
1 1 1	42.5	<	69.3
3 1 1	22.3	>	18.0
3 2 1	227.0	>	212.0
8 2 1	24.5	>	14.0
1 5 1	105.3	>	96.5
5 1 2	22.3	>	19.8
1 3 2	10.0	<	14.3
2 3 2	174.8	>	166.5
3 3 2	27.0	>	23.0
4 3 2	52.8	>	39.0
3 4 2	23.0	<	32.6

the block-diagonal least-squares method, using the anisotropic temperature factors for the I and Cr atoms. Although the difference Fourier map computed at this stage showed the positions of all the hydrogen atoms except for those of the hydrogen atoms of the CH_3 groups and the water of crystallization, the hydrogen atoms were located in geometrically calculated positions (N–H, C–H=1.03 Å, B=4.0 Å^2) and their contributions to the structure factors were taken into account. However, their parameters were not refined. The final agreement indices R and $R'=[\sum w\Delta F^2/\sum wF_o^2]^{1/2}$, were 0.0491 and 0.0640 respectively. A weighting scheme of $w=(44.4/F_o)^2$ for $F_o>44.4$, $w=1$ for $17.8\leqq F_o\leqq 44.4$, and $w=0.6$ for $17.8>F_o$ was used to make $w\Delta F_o^2$ approximately constant over the whole range of F_o values. All the parameter shifts in the final cycle refinement were less than 0.2σ. The atomic scattering factors were taken from Ref. 7. The real and imaginary parts of the anomalous dispersion correction were applied for the I and Cr atoms.7) The final difference Fourier map was rather flat, the largest peak being 0.6 e/Å^3. The atomic coordinates and the temperature factors are listed in Table 1. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7934).

The absolute configuration of the complex cation was determined by the anomalous dispersion technique. Table 2 gives the calculated structure amplitudes of several Bijvoet pairs and the observed inequality relationships which were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation. The observed relationships indicate that the absolute configuration of the complex cation is $\mathit{\Lambda}$.

The computer programs used in the calculations included the local version of the UNICS.8) All the calculations were performed on a FACOM 230-60 computer at Osaka City University.

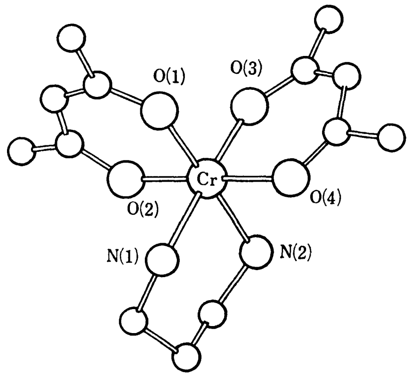

Fig. 1. A perspective view of $(-)_{589}$-$[Cr(acac)_2(tn)]^+$.

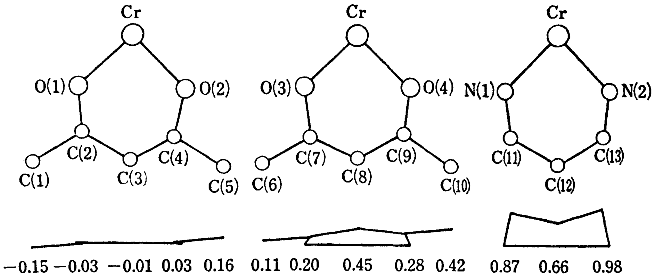

Fig. 2. Projections of the three chelate rings.

Results and Discussion

Figure 1 shows a view of the $(-)_{589}$-$[Cr(acac)_2(tn)]^+$ complex. The absolute configuration of the complex cation has been determined as $\mathit{\Lambda}$. The projections of the three chelate rings are given in Fig. 2, along with the deviations(Å) of the atoms from the planes formed by the Cr and two ligator atoms. One of the Cr-acac six-membered chelate rings is nearly planar, and the [Cr, O(1), O(2)] and [O(1), O(2), C(1), C(2), C(3), C(4), C(5)] planes make an angle of 2.6°, while the other somewhat deviates from a plane, the interplanar angle between the [Cr, O(3), O(4)] and [O(3), O(4), C(6), C(7), C(8), C(9), C(10)] planes being 9.4°. The Cr-tn chelate ring is of a chair form. The average length of the Cr–O bonds is 1.96(1) Å, which is in agreement with the 1.951(7), 1.97 (1), and 1.964(5) Å found in $[Cr(acac)_3]$,9) $\mathit{\Lambda}$-$(+)_{589}$-$[Cr((+)\text{-}atc)_3]^{3+}$,2) and $(-)_{589}$-$[Cr(acac)_3]$4) respectively. The chelate bite angle (90.6(4)°) in the Cr-acac ring is slightly smaller than 91.9(6)°9) and 91.9(1)°2) in these related complexes, but it agrees well with 90.8(2)° in $(-)_{589}$-$[Cr(acac)_3]$.4) Both the Cr–N distance (2.06(1) Å) and the N–Cr–N angle (88.2(4)°) are normal compared with the values previously reported.10,11) The bond distances and angles are given in Table 3.

Figure 3 gives the CD spectra of the four $[Cr(acac)_n(tn)_{3-n}]^{(3-n)+}$-type complexes in the octahedral $^4A_{2g}\rightarrow{}^4T_{2g}$ transition, whose absolute configurations are considered to be $\mathit{\Lambda}$. The X-ray diffraction study of $(-)_{589}$-$[Cr(acac)_3]$ indicates that this complex has the $\mathit{\Delta}$ absolute configuration. The $\mathit{\Lambda}$ configuration is, therefore, given to the enantiomeric form $(+)_{589}$-$[Cr(acac)_3]$ of the complex. The present X-ray study has revealed that the configuration of $(-)_{589}$-$[Cr(acac)_2(tn)]^+$ is $\mathit{\Lambda}$. In the case of $(+)_{589}$-$[Cr(acac)(tn)_2]^{2+}$, the structure of the corresponding Co(III) complex was determined by the X-ray method.12) The $(+)_{589}$-$[Co(acac)(tn)_2]^{2+}$ complex, which shows a positive CD peak in the first absorption band region, has the $\mathit{\Lambda}$ configuration. As the CD curve of $(+)_{589}$-$[Cr(acac)(tn)_2]^{2+}$ is similar to that of the cobalt analogue, the configuration of $(+)_{589}$-$[Cr(acac)(tn)_2]^{2+}$ is $\mathit{\Lambda}$. In the CD spectrum of $(-)_{589}$-$[Cr(tn)_3]^{3+}$, the positive CD peak was identified as the ^4E component from the ion-pairing effect.13) Therefore, the configuration may be $\mathit{\Lambda}$.

Table 3. Interatomic distances and bond angles

Bond length(l/Å)		Bond angle(φ/°)	
Cr-O (1)	1.95(1)	O (1) -Cr-O (2)	90.9(4)
Cr-O (2)	1.96(1)	O (3) -Cr-O (4)	90.7(4)
Cr-O (3)	1.96(1)	N (1) -Cr-N (2)	88.2(4)
Cr-O (4)	1.97(1)	Cr-O (1) - C (2)	127.1(8)
Cr-N (1)	2.07(1)	Cr-O (2) - C (4)	126.6(8)
Cr-N (2)	2.05(1)	Cr-O (3) - C (7)	127.0(8)
O (1) - C (2)	1.29(2)	Cr-O (4) - C (9)	125.6(8)
O (2) - C (4)	1.28(2)	Cr-N (1) - C (11)	119.1(8)
O (3) - C (7)	1.29(2)	Cr-N (2) - C (13)	118.1(8)
O (4) - C (9)	1.26(2)	O (1) - C (2) - C (3)	123.6(12)
N (1) - C (11)	1.47(2)	O (2) - C (4) - C (3)	124.5(13)
N (2) - C (13)	1.53(2)	O (3) - C (7) - C (8)	124.6(11)
C (1) - C (2)	1.52(2)	O (4) - C (9) - C (8)	127.1(12)
C (2) - C (3)	1.36(2)	N (1) - C (11) - C (12)	114.5(11)
C (3) - C (4)	1.37(2)	N (2) - C (13) - C (12)	109.9(11)
C (4) - C (5)	1.51(2)	C (2) - C (3) - C (4)	127.2(13)
C (6) - C (7)	1.52(2)	C (7) - C (8) - C (9)	122.4(11)
C (7) - C (8)	1.42(2)	C (11) - C (12) - C (13)	115.0(11)
C (8) - C (9)	1.40(2)	O (1) - C (2) - C (1)	114.7(11)
C (9) - C (10)	1.55(2)	O (2) - C (4) - C (5)	111.9(12)
C (11) - C (12)	1.51(2)	O (3) - C (7) - C (6)	116.8(11)
C (12) - C (13)	1.50(2)	O (4) - C (9) - C (10)	116.0(11)
		C (1) - C (2) - C (3)	121.6(12)
		C (5) - C (4) - C (3)	123.6(13)
		C (6) - C (7) - C (8)	118.7(11)
		C (10) - C (9) - C (8)	116.9(11)

Table 4. Possible hydrogen bonds(l/Å)

I···O(H_2O)	3.58(1)
N(1)···O(H_2O)	3.02(2)
O(4)···O(H_2O)($1-x$, $1/2+y$, $1/2-z$)	2.96(2)
N(2)···I(x, $1+y$, z)	3.61(1)

N(1)-H	1.02	H···O(H_2O)	2.07
N(2)-H	1.03	H···I(x, $1+y$, z)	2.97

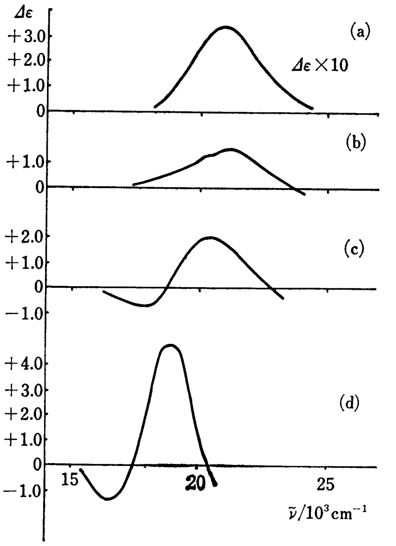

Fig. 3. CD spectra of $[\mathrm{Cr(acac)}_n\mathrm{(tn)}_{3-n}]^{(3-n)+}$-type complexes in the region of the octahedral $^4A_{2g}$-$^4T_{2g}$ absorption.
(a) $(-)_{589}$-$[\mathrm{Cr(tn)_3}]^{3+}$, (b) $(+)_{589}$-$[\mathrm{Cr(acac)(tn)_2}]^{2+}$, (c) $(-)_{589}$-$[\mathrm{Cr(acac)_2(tn)}]^{+}$, (d) $(+)_{589}$-$[\mathrm{Cr(acac)_3}]$.

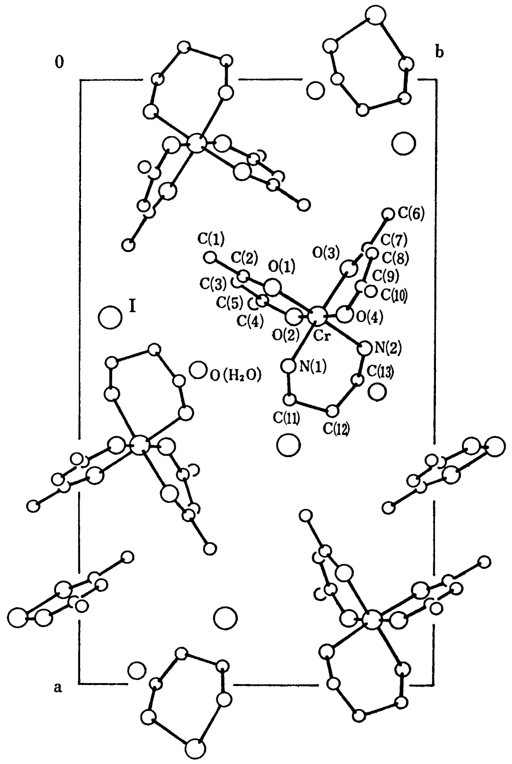

Fig. 4. A projection of the crystal structure along the c axis.

In the CD spectrum of $(+)_{589}$-$[\mathrm{Cr(acac)_3}]$, the negative CD peak at the lower wave number is assigned to the $^4A_1$ component, and the positive CD peak at the higher wave number, to the ^4E component.[14] The CD spectrum of $(-)_{589}$-$[\mathrm{Cr(acac)_2(tn)}]^+$ is similar in shape to that of $(+)_{589}$-$[\mathrm{Cr(acac)_3}]$, although the former is shifted to a higher wave number. Therefore, the positive CD peak of $(-)_{589}$-$[\mathrm{Cr(acac)_2(tn)}]^+$ is mainly due to the ^4E component of the $^4T_{2g}$ transition of $(+)_{589}$-$[\mathrm{Cr(acac)_3}]$. The $(+)_{589}$-$[\mathrm{Cr(acac)(tn)_2}]^{2+}$ complex gives two positive CD components in the region of the octahedral $^4T_{2g}$ absorption. The two components are due to the combined $^4A_1$, $^4B_2$, and $^4B_1$ components derived from the octahedral $^4T_{2g}$ transition of Cr(III)[15,16] and seem to have a sign reflecting that of the positive CD peak of $(-)_{589}$-$[\mathrm{Cr(acac)_2(tn)}]^+$. The combined $^4A_1$, $^4B_2$, and $^4B_1$ components of $(+)_{589}$-$[\mathrm{Cr(acac)(tn)_2}]^{2+}$ have the same sign as the CD of $(-)_{589}$-$[\mathrm{Cr(tn)_3}]^{3+}$, and the CD peaks of the two complexes are observed at approximately equal energies. Therefore, the positive CD peaks of $(+)_{589}$-$[\mathrm{Cr(acac)(tn)_2}]^{2+}$ and $(-)_{589}$-$[\mathrm{Cr(tn)_3}]^{3+}$ are likely to have the same origin. Consequently, the absolute configuration of $(-)_{589}$-$[\mathrm{Cr(tn)_3}]^{3+}$ is Λ, in accordance with the assignment from the ion-pairing effect.[13]

Figure 4 gives the crystal structure viewed down the c axis. Possible hydrogen bonds are summarized in Table 4. The Cr-acac six-membered chelate ring containing the O(3) and O(4) atoms is bent away from the [Cr, O(3), O(4)] plane to C(1)(1/2−x, 1−y, 1/2+z) by 9.4° (Fig. 2). As the interatomic distances between C(10) and C(1) (1/2−x, 1−y, 1/2+z) and that between C(10) and C(11) (1−x, 1/2+y, 1/2−z) are 3.92 and 4.11 Å respectively, the large deviation of the acac ring from the coordination plane (9.4°) may result from an intramolecular repulsion.

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