The Absolute Configuration of the (−)$_{589}$-Tris(acetylacetonato)germanium(IV) Ion

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Abstract

Crystals of the perchlorate salt of the title complex ion, (−)$_{589}$-[Ge(C$_5$H$_7$O$_2$)$_3$](ClO$_4$), are trigonal, space group $P3_1$, with $a = 11\cdot592$ (1), $c = 12\cdot983$ (3) Å and $Z = 3$. The structure has been refined to give an R value of 0·045 for the 2006 observed reflexions collected by X-ray diffractometry. The complex ion has a tris-chelated structure with approximate D_3 symmetry. The absolute configuration of the complex cation can be designated as Δ.

Introduction

Absolute configurations of bis- or tris-chelated dissymmetric metal complexes containing unsaturated organic ligands have been deduced from the pattern of the major circular dichroism (CD) bands associated with the absorptions due to the $\pi–\pi^*$ transitions of ligands. This approach is based on the exciton CD theory (Bosnich, 1969; Mason, 1971). The absolute configurations predicted from the exciton CD spectra have been confirmed in some cases by X-ray analyses (Mason, 1971). However, such X-ray studies have been carried out only on transition-metal complexes, except for our previous work on the (−)$_{589}$-tris(1,2-benzene-diolato)arsenate(V) ion, (−)$_{589}$-[As(cat)$_3$]$^-$, (Muto, Ito, Marumo & Saito, 1972). For confirmation of the validity of the exciton approach to the determination of the absolute configurations of metal complexes by an X-ray method, transition-metal complexes would not be adequate. This is because the CD spectra of transition-metal complexes in the accessible region are usually associated not only with the absorptions due to the ligand $\pi–\pi^*$ transitions but also with those due to the $d–d$ transitions of the metal ion and metal–ligand charge-transfer transitions. Although the three types of electronic excitation in a coordination compound are considered to be discrete to a good approximation, they often have small frequency separations and small mixing energies. On the other hand, in the exciton approximation, it is assumed that there is no electron

exchange between a ligand and a metal ion or between the individual ligands of the complexes. Our previous X-ray study on the non-transition-metal complex (−)$_{589}$-[As(cat)$_3$]$^-$ indicates that the absolute configuration is the same as deduced from the major CD bands. However, the CD spectrum of (−)$_{589}$-[As(cat)$_3$]$^-$ is not completely consistent with the pattern expected from a simple exciton model, indicating that the electronic structure is not so simple (Ito, Muto, Marumo & Saito, 1971). It was desired to verify directly the validity of the exciton approach by an X-ray analysis on a non-transition-metal complex which has the simplest electronic structure. We have selected for the present purpose (−)$_{589}$-tris(acetylacetonato)germanium(IV) perchlorate, (−)$_{589}$-[Ge(acac)$_3$](ClO$_4$), which was recently synthesized in an optically pure form (Nagasawa & Saito, 1974). This complex would be most suitable, since the electronic absorptions in the accessible region are due only to the single $\pi–\pi^*$ transition of the ligand acac and the complications that arise in transition-metal complexes are not present. The electronic and CD spectra of (−)$_{589}$-[Ge(acac)$_3$](ClO$_4$) show the expected exciton pattern, indicating that the absolute configuration is Δ (Nagasawa & Saito, 1974).

Experimental

Crystals were prepared as reported previously (Nagasawa & Saito, 1974). They are colorless hexagonal plates. A specimen with dimensions 0·3 × 0·3 × 0·2 mm was selected for the intensity measurements. Intensities of reflexions were measured on a Rigaku automated four-circle diffractometer AFC-5 with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å), the $\theta–2\theta$ scan technique being employed. Of 3276 observed reflexions within the range $2\theta \leq 60°$, 2006 independent reflexions with $|F_o| > 3\sigma(|F_o|)$ were selected and used in the structure analysis. To determine the absolute configuration, 818 intensities of $hk\bar{l}$ reflexions were also measured up to $2\theta = 40°$. The

intensity data were corrected for Lorentz–polarization effects. No absorption correction was applied. Unit-cell dimensions were determined on the diffractometer.

Crystal data are: $C_{15}H_{21}GeO_6^+ \cdot ClO_4^-$, $M_r = 469 \cdot 3$, trigonal, $P3_1$, $Z = 3$, $a = 11 \cdot 592$ (1), $c = 12 \cdot 983$ (3) Å, $D_x = 1 \cdot 55$, $D_m = 1 \cdot 56$ Mg m^{-3}, $\mu(Mo\,K\alpha) = 1 \cdot 793$ mm^{-1}.

Determination of the structure

The structure was solved by the conventional heavy-atom method. The positions of all the H atoms were identified in subsequent difference-Fourier maps. The structure was refined by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The scattering factors and the anomalous-scattering corrections for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974). For H, the values given by Stewart, Davidson & Simpson (1965) were used. The weighting scheme, $w = [\sigma^2_{count} + (0 \cdot 015|F_o|)^2]^{-1}$, was employed. At the final stage, refinements were carried out on two enantiomeric structures. The R and R_w values were reduced to 0·0446 and 0·0414, respectively, for the space group $P3_1$, whereas the values were 0·0505 and 0·0490 for $P3_2$, indicating $P3_1$ to be the true space group of the crystal. Application of the R-factor ratio test showed that the space group $P3_2$ can be rejected at the 0·005 level (Hamilton, 1965). This result for the absolute structure was also confirmed by a comparison of the observed relations between the hkl and $\overline{hkl}$ reflexions with the calculated intensity relations (Table 1). The atomic parameters are listed in Table 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35553 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Observed and calculated intensity relations between some Bijvoet pairs*

$h\,k\,l$	$F_o(hkl)[F_c(hkl)]$	$F_o(\overline{hkl})[F_c(\overline{hkl})]$	$\dfrac{F_o(\overline{hkl})}{F_o(hkl)}\left[\dfrac{F_c(\overline{hkl})}{F_c(hkl)}\right]$
0 4 1	10·4 (10·4)	17·8 (17·4)	1·71 (1·67)
2 0 1	35·4 (35·3)	39·4 (40·1)	1·11 (1·14)
1 3 2	9·3 (8·6)	17·7 (17·7)	1·90 (2·06)
1̄ 2 3	92·8 (92·3)	100·6 (100·8)	1·08 (1·09)
0 0 3	89·4 (89·7)	97·9 (98·9)	1·10 (1·10)
1 1 3	59·5 (59·5)	64·1 (65·0)	1·08 (1·09)
2 2 3	35·4 (38·3)	42·0 (45·7)	1·19 (1·19)
0 1 4	66·8 (67·5)	61·6 (62·9)	0·92 (0·93)
2 3 4	23·3 (24·1)	17·6 (18·5)	0·76 (0·77)
0 0 6	27·8 (27·5)	20·4 (19·8)	0·73 (0·72)

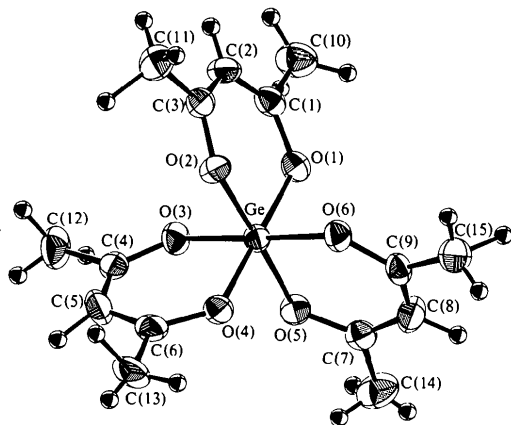Table 2. *Atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters*

	x	y	z	B_{eq}/B_{iso} (Å^2)
Ge	3521 (1)	3547 (1)	0 (0)	3·4
O(1)	5132 (4)	3806 (4)	543 (3)	4·2
O(2)	4375 (4)	4829 (4)	−1033 (3)	4·3
O(3)	3486 (4)	2192 (4)	−812 (3)	4·5
O(4)	1918 (4)	3306 (4)	−545 (3)	4·2
O(5)	2613 (4)	2240 (4)	991 (3)	4·3
O(6)	3601 (4)	4911 (4)	807 (3)	4·4
C(1)	6222 (6)	4273 (6)	22 (5)	4·3
C(2)	6445 (6)	4943 (6)	−888 (5)	4·9
C(3)	5559 (6)	5253 (6)	−1373 (5)	4·3
C(4)	2759 (6)	1657 (6)	−1604 (5)	4·5
C(5)	1763 (7)	1874 (7)	−1912 (6)	5·6
C(6)	1372 (6)	2687 (6)	−1385 (5)	4·8
C(7)	2364 (5)	2445 (6)	1924 (5)	4·4
C(8)	2708 (7)	3662 (7)	2313 (5)	5·7
C(9)	3251 (6)	4824 (6)	1759 (5)	4·5
C(10)	7264 (7)	4083 (8)	504 (7)	6·9
C(11)	5923 (8)	6095 (7)	−2308 (5)	5·8
C(12)	3087 (9)	748 (7)	−2192 (6)	6·6
C(13)	290 (6)	2902 (8)	−1770 (6)	6·6
C(14)	1649 (8)	1202 (9)	2574 (7)	7·2
C(15)	3471 (7)	6074 (7)	2232 (6)	6·6
Cl	3232 (2)	3576 (2)	5568 (2)	6·1
O(7)	3952 (7)	4550 (7)	4803 (5)	10·5
O(8)	2216 (8)	2431 (8)	5147 (8)	14·0
O(9)	4089 (7)	3247 (7)	6114 (6)	10·1
O(10)	2681 (7)	4114 (6)	6264 (5)	9·5
H(1)	719 (5)	525 (5)	−120 (4)	4·6 (1·3)
H(2)	112 (6)	141 (6)	−240 (5)	6·3 (1·6)
H(3)	252 (6)	364 (6)	302 (5)	7·7 (1·9)
H(4)	725 (6)	432 (6)	124 (5)	6·5 (1·6)
H(5)	795 (6)	452 (6)	3 (5)	7·1 (1·7)
H(6)	685 (7)	317 (6)	55 (5)	7·3 (1·7)
H(7)	593 (6)	683 (6)	−226 (5)	8·1 (1·9)
H(8)	670 (7)	611 (7)	−251 (5)	8·4 (1·9)
H(9)	507 (7)	557 (7)	−290 (6)	8·7 (2·0)
H(10)	357 (7)	126 (7)	−283 (6)	10·7 (2·3)
H(11)	324 (6)	28 (6)	−159 (5)	7·9 (1·8)
H(12)	246 (6)	5 (6)	−256 (5)	6·9 (1·8)
H(13)	12 (5)	350 (5)	−125 (4)	4·3 (1·2)
H(14)	71 (7)	354 (6)	−249 (6)	8·8 (1·9)
H(15)	−25 (5)	237 (5)	−193 (4)	4·3 (1·2)
H(16)	105 (6)	80 (6)	215 (5)	7·1 (1·7)
H(17)	135 (6)	142 (6)	296 (5)	6·0 (1·5)
H(18)	193 (7)	51 (6)	247 (6)	8·3 (2·0)
H(19)	403 (4)	681 (4)	192 (4)	3·1 (1·1)
H(20)	405 (7)	611 (7)	299 (6)	9·7 (2·1)
H(21)	287 (6)	589 (6)	261 (5)	7·4 (1·7)

Description of the structure and discussion

Fig. 1 shows a perspective view of the complex cation $(-)_{589}$-[Ge(acac)$_3$]$^+$ along the pseudo threefold axis. Bond lengths and bond angles are listed in Table 3. The Ge atom is surrounded octahedrally by six O atoms of the ligand acetylacetonato ions with an average Ge—O distance of 1·870 (2) Å, giving a tris-chelated structure with virtual D_3 symmetry. The complex cation has no crystallographic symmetry but chemically equivalent

Table 3. *Bond distances (Å) and angles (°) with their estimated standard deviations (in parentheses)*

Ge—O(1)	1·874 (5)	C(1)—C(2)	1·366 (10)
Ge—O(2)	1·876 (4)	C(2)—C(3)	1·396 (11)
Ge—O(3)	1·875 (5)	C(4)—C(5)	1·359 (12)
Ge—O(4)	1·874 (5)	C(5)—C(6)	1·410 (12)
Ge—O(5)	1·861 (4)	C(7)—C(8)	1·357 (11)
Ge—O(6)	1·860 (5)	C(8)—C(9)	1·370 (10)
O(1)—C(1)	1·289 (7)	C(1)—C(10)	1·471 (12)
O(2)—C(3)	1·284 (8)	C(3)—C(11)	1·481 (10)
O(3)—C(4)	1·276 (7)	C(4)—C(12)	1·497 (13)
O(4)—C(6)	1·286 (7)	C(6)—C(13)	1·482 (12)
O(5)—C(7)	1·295 (8)	C(7)—C(14)	1·510 (10)
O(6)—C(9)	1·290 (8)	C(9)—C(15)	1·475 (11)
		Cl—O(7)	1·420 (7)
		Cl—O(8)	1·373 (8)
		Cl—O(9)	1·419 (9)
		Cl—O(10)	1·418 (9)

O(1)—Ge—O(2)	93·1 (2)	O(1)—C(1)—C(10)	114·8 (6)
O(3)—Ge—O(4)	93·4 (2)	O(2)—C(3)—C(11)	115·5 (7)
O(5)—Ge—O(6)	94·1 (2)	O(3)—C(4)—C(12)	114·5 (7)
		O(4)—C(6)—C(13)	114·5 (7)
Ge—O(1)—C(1)	124·0 (4)	O(5)—C(7)—C(14)	114·5 (6)
Ge—O(2)—C(3)	126·1 (5)	O(6)—C(9)—C(15)	115·4 (6)
Ge—O(3)—C(4)	126·3 (5)		
Ge—O(4)—C(6)	125·3 (5)	C(2)—C(1)—C(10)	121·1 (6)
Ge—O(5)—C(7)	125·8 (4)	C(2)—C(3)—C(11)	122·4 (6)
Ge—O(6)—C(9)	126·4 (4)	C(5)—C(4)—C(12)	121·2 (6)
		C(5)—C(6)—C(13)	122·1 (6)
O(1)—C(1)—C(2)	124·1 (7)	C(8)—C(7)—C(14)	121·3 (6)
O(2)—C(3)—C(2)	122·0 (6)	C(8)—C(9)—C(15)	121·1 (6)
O(3)—C(4)—C(5)	124·3 (7)		
O(4)—C(6)—C(5)	123·5 (7)	O(7)—Cl—O(8)	111·6 (5)
O(5)—C(7)—C(8)	124·2 (6)	O(7)—Cl—O(9)	110·5 (5)
O(6)—C(9)—C(8)	123·5 (7)	O(7)—Cl—O(10)	108·2 (5)
		O(8)—Cl—O(9)	108·5 (5)
C(1)—C(2)—C(3)	125·6 (6)	O(8)—Cl—O(10)	108·8 (5)
C(4)—C(5)—C(6)	124·6 (6)	O(9)—Cl—O(10)	109·2 (5)
C(7)—C(8)—C(9)	125·3 (6)		

Table 4. *Deviations (Å) from the least-squares plane of each chelate ring with their estimated standard deviations in parentheses*

Plane A		Plane B		Plane C	
O(1)	0·045 (5)	O(3)	0·029 (5)	O(5)	−0·003 (5)
O(2)	−0·028 (5)	O(4)	−0·029 (5)	O(6)	−0·011 (5)
C(1)	−0·017 (7)	C(4)	0·006 (7)	C(7)	0·010 (7)
C(2)	−0·065 (7)	C(5)	0·005 (8)	C(8)	0·075 (9)
C(3)	−0·016 (7)	C(6)	−0·006 (7)	C(9)	0·011 (7)
C(10)	0·022 (9)	C(12)	−0·021 (9)	C(14)	−0·043 (10)
C(11)	0·060 (8)	C(13)	0·016 (9)	C(15)	−0·040 (9)
Ge	−0·377 (2)*	Ge	0·297 (2)*	Ge	0·105 (2)*

* Ge atom is not included in the least-squares calculations.
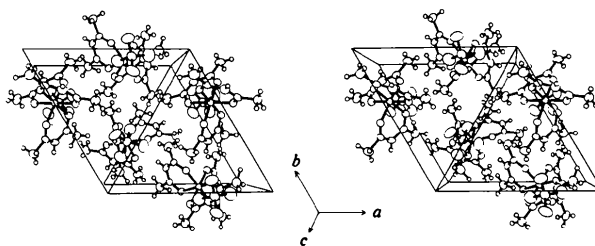
Fig. 2. Stereoscopic drawing of the crystal structure along the *c* axis.

within the acetylacetonato moieties given in Table 3 compare favorably with those in other structures.

Within experimental error, each acetylacetonato skeleton is planar. However, the Ge atom does not lie in the ligand planes as shown in Table 4. This results in the chelate ring being bent along a line through the two chelate O atoms by 17·4, 13·4, and 5·1° with respect to the planes A, B, and C in Table 4, respectively. The distortion of the structure such that the metal atom deviates from the chelate-ring plane has been noted in studies of several acetylacetonato complexes, $M^{II}(acac)_3$, $M^{III}(acac)_3$ or $M^{IV}(acac)_4$, and is ascribed to the packing forces in the crystals [$M = Ni^{II}$ (Watson & Lin, 1966); $M = V^{III}$ (Morosin & Montgomery, 1969); $M = Sc^{III}$ (Anderson, Neuman & Melson, 1973); $M = Ce^{IV}$ (Titze, 1969, 1974); $M = U^{IV}$ (Titze, 1970)].

A stereoscopic view of the crystal structure is shown in Fig. 2. No remarkable close contacts were observed in the crystal. The shortest intermolecular contacts were observed between methyl C and perchlorate O: O(9)···C(12), 3·35 (1) Å; O(10)···C(13), 3·50 (1) Å. These contacts, however, cannot explain why Ge is appreciably out of the ligand planes. Subtle packing forces are likely to be responsible for the somewhat larger deviation also present in this crystal, although these are not readily apparent from the packing data.

The absolute configuration of the complex ion, $(-)_{589}$-[Ge(acac)$_3$]$^+$, can be designated as Δ. This assignment accords with results obtained from the


Fig. 1. A perspective drawing of the complex cation, $(-)_{589}$-[Ge(acac)$_3$]$^+$.

bond distances and bond angles are, respectively, equal within experimental errors. Fackler & Avdeef (1974) compared the structural dimensions of various monomeric tris(acetylacetonato) complexes. The dimensions

exciton CD approach as discussed below. Although the studies on the electronic structure of $(-)_{589}$-$[Ge(acac)_3]^+$ have not been reported so far, that of $(-)_{589}$-$[Si(acac)_3]^+$ has been fully elucidated on the basis of the electronic and CD spectral data and the theoretical studies as well (Larsen, Mason & Searle, 1966; Hanazaki & Nagakura, 1969). The present study has been undertaken on $(-)_{589}$-$[Ge(acac)_3]^+$ instead of $(-)_{589}$-$[Si(acac)_3]^+$, because the crystals of the completely resolved optical isomer of $[Si(acac)_3]^+$ could not be obtained.* However, the low-lying excited states of $(-)_{589}$-$[Si(acac)_3]^+$ and $(-)_{589}$-$[Ge(acac)_3]^+$ are expected to be very similar in the light of their electronic configurations. In fact, the electronic and CD spectra of these complexes are essentially the same and both show the expected exciton splitting and the typical exciton DC pattern. Therefore, the discussion and results of the exciton approach reported for $(-)_{589}$-$[Si(acac)_3]^+$ can be directly applicable to $(-)_{589}$-$[Ge(acac)_3]^+$. On this basis, $(-)_{589}$-$[Ge(acac)_3]^+$ can be assigned the absolute configuration Δ.

The present study has proved the validity of the exciton approach to the determination of the absolute configurations of dissymmetric metal complexes.

The calculations were performed on the HITAC M-180 computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICS* III (Sakurai & Kobayashi, 1978).

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* The CD spectrum of $(-)_{589}$-$[Si(acac)_3]^+$ reported by Larsen, Mason & Searle (1966) was obtained from a partially resolved sample.

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