BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2424—2428 (1973)

The Crystal Structure of $(-)_{589}$-Acetylacetonatobis(trimethylenediamine)cobalt(III) Arsenic(V) (+)-Tartrate Monohydrate

Keiji MATSUMOTO, Hiroshi KAWAGUCHI,* Hisao KUROYA, and Shinichi KAWAGUCHI
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

(Received January 8, 1973)

The crystal structure of $(-)_{589}$-[Co acac tn_2][As-(+)-tart$]_2\cdot H_2O$ has been determined by the X-ray diffraction method. The crystals are monoclinic, with lattice constants of $a=12.02(1)$ Å, $b=13.73(2)$ Å, $c=9.02(1)$ Å, and $\beta=107.4(3)°$, and with the space group of $P2_1$, containing two formula units in a cell. The structure was determined by the application of Patterson and Fourier techniques and was refined by the least-squares method to an R factor of 10.4%. The absolute configuration of $(-)_{589}$-[Co acac $tn_2]^{2+}$ can be denoted as Δ. The two Co-tn chelate rings assume the chair form, and the Co-acac chelate ring is almost planar. The geometry of [As-(+)-tart$]_2^{2-}$ is identical with that of [Sb-(+)-tart$]_2^{2-}$.

Several investigations have been made regarding the assignment of the CD spectrum of $\Delta(+)_{589}$-[Co $tn_3]^{3+}$ in the region of the octahedral T_{1g} absorption. Those who studied the solution spectra of the complex have identified the negative CD peak in the lower frequency as the E_a component.[1–3] On the other hand, Judkins and Royer indicate that the E_a component has a positive CD peak in the shorter wavelength region,[4] and they support the distortion theories.[5–7]

According to Mason *et al.*,[8] the single CD peak of $(-)_{589}$-[Co acac $tn_2]^{2+}$ in the visible region has the same negative sign as the E_a component of the parent trigonal complex, $\Delta(+)_{589}$-[Co $tn_3]^{3+}$. If the absolute configuration of $(-)_{589}$-[Co acac $tn_2]^{2+}$ is determined, it will be possible to assign the E_a component of $\Delta(+)_{589}$-[Co $tn_3]^{3+}$ on the basis of Mason's rule.[8] Therefore, we carried out the crystal-structure determination of $(-)_{589}$-[Co acac tn_2][As-(+)-tart$]_2\cdot H_2O$ by the X-ray method. A preliminary report of this work has been published.[9]

Experimental

The brownish-yellow, plate-like crystals of $(-)_{589}$-[Co-acac tn_2]][As-(+)-tart$]_2\cdot H_2O$ were prepared by Hiroshi Kawaguchi and Shinichi Kawaguchi. Using Ni$K\alpha$ radiation, the unit-cell dimensions were obtained from a least-squares treatment of 29 θ-values on $0kl$ and $h0l$ Weissenberg photographs calibrated with aluminum powder ($a=4.0494$ Å). The systematic absences of $0k0$ for k odd suggest that the space group is $P2_1$ or $P2_1/m$. However, since the compound is optically-active, $P2_1$ was chosen. The crystal data are as follows:

monoclinic
$a=12.02(0.01)$Å
$b=13.73(0.02)$Å
$c=\ 9.02(0.01)$Å
$\beta=107.4(0.3)°$
space group $P2_1$
$Z=2(D_m=1.79,\ D_c=1.79\ \text{g.cm}^{-3})$
$\mu(\text{Ni}K\alpha)=54.4\ \text{cm}^{-1}$

Multiple-film, equi-inclination Weissenberg photographs were taken for the 0—7 and 0—6 layers about the b and a axes with Ni$K\alpha$ radiation ($\lambda=1.6591$ Å). For both sets of films, prismatic specimens (∼0.1×0.2×0.5 mm) were used. The intensities were estimated by visual comparison with the calibrated intensity scales. After correction for the ususl

---

* Present adress: Faculty of Literature and Science, Kochi University, Asakura, Kochi.

[1] J. R. Gollogly and C. J. Hawkins, *Chem. Commun.*, **1968**, 689.

[2] P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).

[3] F. Woldbye, ORD of transition metal complexes, European Research Office, U. S. Army, Frankfurt a. M. (1959); *Record of Chemical Progress*, **24**, 197 (1963).

[4] R. R. Judkins and C. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).

[5] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

[6] A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).

[7] M. Shinada, *J. Phys. Soc. Japan*, **19**, 1607 (1964).

[8] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

[9] H. Kawaguchi, K. Matsumoto, H. Kuroya, and S. Kawaguchi, *Chem. Lett.*, **1972**, 125.

Lp factor and the spot shape,[10] the structure amplitudes were placed on a common arbitrary scale by internal correlation. A total of 2241 independent reflections were collected, but 454 of these were too weak to be observed. Therefore, they were assumed to be zero. No correction for absorption was applied.

Determination of the Crystal Structure

The initial coordinates of the cobalt and two arsenic atoms were deduced from a three-dimensional Patterson function. A three-dimensional Fourier synthesis phased on these heavy atoms revealed the positions of nine light atoms of the complex cation and five oxygen atoms of tartrate anions. Three cycles of refinement were carried out for the positional and thermal parameters by the least-squares method, and the resulting parameters were used to compute a Fourier function, which gave the probable positions of the three chelate rings around the cobalt atom, but not those of all the atoms of tartrate ions. The subsequent Fourier synthesis phased on these atoms showed the coordinates of all the remaining non-hydrogen atoms. The three cycles of block-diagonal least-squares refinement yielded an R factor of 12.5%, isotropic temperature factors being used for all the atoms. Three more cycles of refinement, in which anisotropic temperature factors were applied for the three heavy atoms, reduced the R factor to 10.4% for 1787 observed reflections. The following weighting scheme was employed:

$$w=0.3 \quad \text{for } F_0<12.2$$

$$w=1.0 \quad \text{for } 12.2\leq F_0\leq 93.5$$

$$w=93.5/F_0 \quad \text{for } F_0>93.5$$

Throughout the refinement, atomic scattering factors taken from the International Tables for X-ray Crystallography[11] were used. A difference Fourier synthesis obtained at this stage did not show any peaks attributable to hydrogen atoms. The final atomic coordinates and thermal parameters are given in Table 1. The observed and calculated structure factors are preserved by the Chemical Society of Japan.[12]

The absolute structure of the crystal was assigned on the basis of the known configuration of the (+)-tartrate ion,[13] and was found to correspond to the inversed set of the atomic coordinates given in Table 1; the Δ configuration has been assigned to the complex cation on the basis of the present X-ray study.

Discussion

The crystal consists of the $(-)_{589}$-[Co acac $tn_2]^{2+}$ cations, the [As-(+)-tart$]_2{}^{2-}$ anions, and water molecules, which are held together by N–H···O and O–H···O hydrogen bonds. Projections of the absolute structures viewed along b and c axes are presented in Figs. 1 and 2 respectively. Possible hydrogen bonds are summarized in Table 2. All the hydrogen atoms of N(3) and N(4) and one of the hydrogen atoms linked to N(1) and N(2) participate in the N–H···O hydrogen bonds. The interatomic distance between O(H_2O) and O(10) is 3.10 Å, and that between O(H_2O) and O(4), 2.86 Å. The O(4)–O(H_2O)–O(10) angle is

TABLE 1. FINAL ATOMIC COORDINATES[a)] AND TEMPERATURE FACTORS WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	B
As(1)	0.1609(2)	0.0000	0.0395(3)	b)
As(2)	0.1270(2)	−0.0408(3)	0.5402(3)	b)
Co	0.3142(3)	0.4810(4)	0.7276(4)	b)
N(1)	0.192(1)	0.467(2)	0.525(2)	3.7(4)
N(2)	0.446(2)	0.434(2)	0.652(2)	3.9(4)
C(1)	0.223(2)	0.473(3)	0.374(3)	4.9(6)
C(2)	0.328(3)	0.406(3)	0.382(3)	5.1(7)
C(3)	0.443(2)	0.447(3)	0.485(3)	5.1(6)
N(3)	0.191(2)	0.509(2)	0.829(2)	4.2(4)
N(4)	0.346(2)	0.619(2)	0.690(2)	3.9(5)
C(4)	0.208(3)	0.597(3)	0.931(3)	5.3(7)
C(5)	0.216(3)	0.691(3)	0.843(4)	6.9(9)
C(6)	0.340(3)	0.690(3)	0.815(3)	5.3(7)
O(1)	0.285(1)	0.348(1)	0.755(2)	3.7(4)
O(2)	0.429(1)	0.496(1)	0.921(2)	3.4(3)
C(7)	0.293(3)	0.192(3)	0.883(4)	5.7(8)
C(8)	0.331(2)	0.296(2)	0.880(3)	3.7(5)
C(9)	0.413(2)	0.334(3)	1.009(3)	4.5(6)
C(10)	0.456(2)	0.424(2)	1.023(3)	3.3(5)
C(11)	0.553(2)	0.461(3)	1.170(3)	5.1(6)
O(3)	0.331(2)	0.035(1)	0.178(2)	4.7(4)
O(4)	0.414(2)	0.153(2)	0.345(2)	5.5(5)
O(5)	0.118(2)	0.083(1)	0.172(2)	4.2(6)
O(6)	0.233(2)	0.032(2)	0.487(2)	5.2(4)
O(7)	0.023(2)	0.081(2)	0.481(2)	5.5(5)
O(8)	0.044(2)	0.239(2)	0.425(3)	6.4(5)
C(12)	0.329(2)	0.109(2)	0.263(3)	3.5(5)
C(13)	0.207(2)	0.142(2)	0.271(3)	4.1(6)
C(14)	0.207(3)	0.134(2)	0.434(3)	4.4(6)
C(15)	0.079(3)	0.155(3)	0.445(3)	5.4(7)
O(9)	0.767(2)	0.348(2)	0.471(2)	5.3(5)
O(10)	0.769(2)	0.212(2)	0.614(3)	6.9(6)
O(11)	0.963(2)	0.417(2)	0.649(2)	4.3(4)
O(12)	0.810(2)	0.391(2)	0.851(2)	4.5(4)
O(13)	1.118(2)	0.339(2)	0.994(2)	5.5(5)
O(14)	1.007(2)	0.462(2)	1.023(2)	4.5(4)
C(16)	0.811(3)	0.289(3)	0.587(3)	5.3(7)
C(17)	0.930(3)	0.321(3)	0.698(3)	4.7(6)
C(18)	0.908(2)	0.331(2)	0.835(3)	3.6(5)
C(19)	1.019(2)	0.375(2)	0.967(4)	4.3(6)
H_2O	0.521(2)	0.225(2)	0.652(3)	8.2(7)

a) This atomic coordinate set corresponds to the mirror image of the absolute crystal structure.

b) Anisotropic thermal parameters ($\times 10^4$) are given below. Temperature factors are of the form: $\exp[(-h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As(1)	64(2)	70(2)	110(3)	−3(4)	40(4)	3(5)
As(2)	68(2)	79(2)	114(4)	−4(4)	29(4)	9(6)
Co	50(3)	70(4)	86(5)	−7(7)	20(6)	8(8)

---

[10] D. C. Philips, *Acta Crystallogr.*, **7**, 746 (1954).

[11] "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), pp. 201.

[12] The complete data of the F_0-F_c table are kept as Document No. 7314 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number.

[13] J. M. Bijvoet, A. J. van Bommel, and A. F. Peerdeman, *Nature*, **168**, 271 (1951).

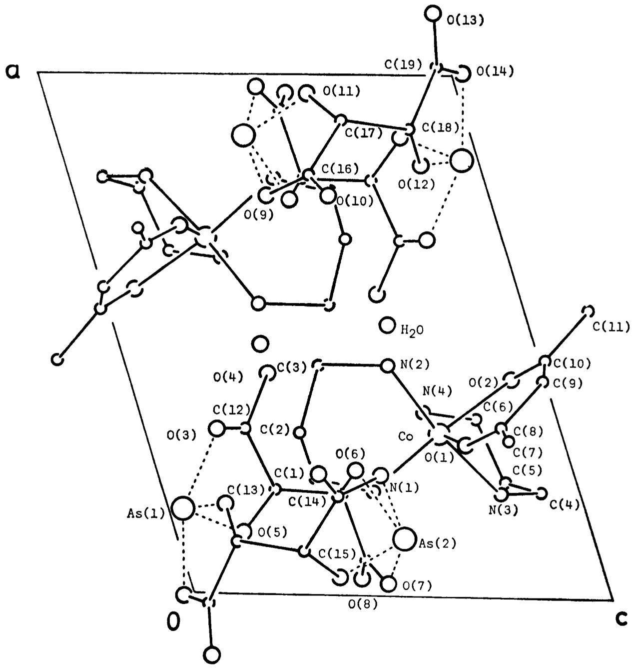

Fig. 1. Projection of the absolute structure of $(-)_{589}$-$[Co\ acac\ tn_2][As\text{-}(+)\text{-}tart]H_2O$ along the *b* axis.

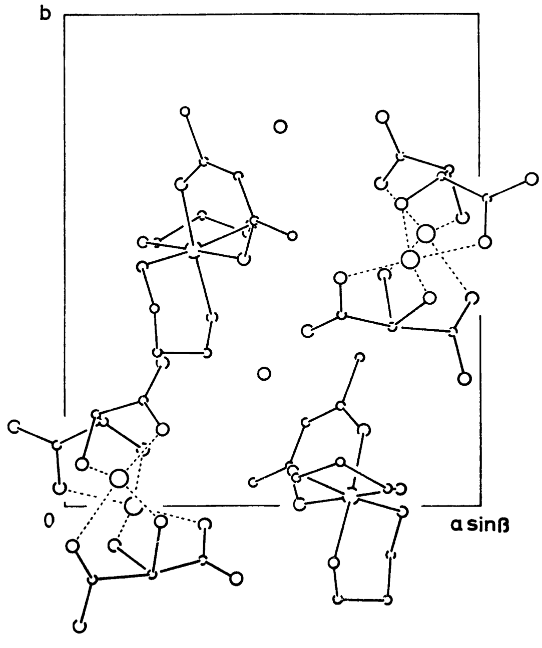

Fig. 2. The *c* projection of the absolute structure.

92°. Therefore, both hydrogen atoms of the water molecule seem to take part in the O–H···O hydrogen-bond formation.

A perspective view of the complex cation is shown in Fig. 3. The cobalt atom is octahedrally coordinated by the four nitrogen atoms of the two trimethylenediamine molecules and the two oxygen atoms in the enolate chelate of acetylacetone. The complex cation has no two-fold axis, in contrast with the case of the $(-)_{589}$-$[Co(NCS)_2tn_2]^+$ complex.[14]

Table 2. Possible hydrogen bonds

N	O	N···O	H···O	Angle around H
$N(1)^{I}$	$O(7)^{II}$	3.00 Å	2.02 Å	158°
$N(2)^{I}$	H_2O^{I}	3.01	2.06	152
$N(3)^{I}$	$O(11)^{III}$	3.01	2.23	131
$N(3)^{I}$	$O(13)^{III}$	3.04	2.05	160
$N(4)^{I}$	$O(10)^{IV}$	2.96	1.99	156
$N(4)^{I}$	$O(4)^{IV}$	3.03	2.01	170
O	O	O···O		
H_2O^{I}	$O(4)^{I}$	2.86		
H_2O^{I}	$O(10)^{I}$	3.10		

I x, y, z II $-x, 1/2+y, 1-z$
III $1-x, y, z$ IV $1-x, 1/2+y, 1-z$

The positions of the hydrogen atoms were computed on the assumption that the $>NH_2$ groups have the tetrahedral geometry and the N-H bond distances are 1.03 Å.

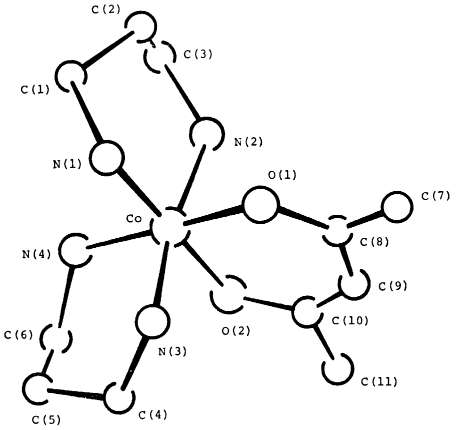

Fig. 3. Perspective view of the complex cation.

It was previously indicated that the rotational strengths of the E_a transitions of $\Delta(-)_{589}$-$[Co\ en_3]^{3+}$ and $\Delta(+)_{589}$-$[Co\ tn_3]^{3+}$ are negative in sign,[1-3] that the $(-)_{589}$-$[Co\ acac\ en_2]^{2+}$ complex shows a single CD band with a negative sign in the visible region, and that it is mainly derived from the dominant E_a component of $(-)_{589}$-$[Co\ en_3]$.$^{3+}$[8] On this basis, the $(-)_{589}$-$[Co\ acac\ en_2]^{2+}$ complex was concluded to have the Δ configuration.[8] Likewise, the Cotton effect of $(-)_{589}$-$[Co\ acac\ tn_2]^{2+}$ in the first-absorption-band region is negative in sign (Fig. 4), suggesting that the Δ configuration should be assigned to it; actually, this has been found to be the case. Thus, the spectral assignment for $(+)_{589}$-$[Co\ tn_3]^{3+}$ made by several workers[1-3] is quite compatible with the results of the present X-ray study.

However, Judkins and Royer identified the positive CD band of $\Delta(+)_{589}$-$[Co\ tn_3]^{3+}$ in the region of the octahedral T_{1g} transition as E_a component.[4] If their assignment of the CD peak is correct, the Λ configuration should be given to $(-)_{589}$-$[Co\ acac\ tn_2]^{2+}$; this is inconsistent with our result. Piper's model for optical activity is not supported in this case, either.[15]

---

[14] K. Matsumoto, M. Yonezawa, H. Kuroya, H. Kawaguchi, and S. Kawaguchi, This Bulletin, **43**, 1269 (1970).

[15] K. R. Butler and M. R. Snow, *Chem. Commun.*, **1971**, 550; K. Matsumoto and H. Kuroya, This Bulletin, **45**, 1755 (1972).

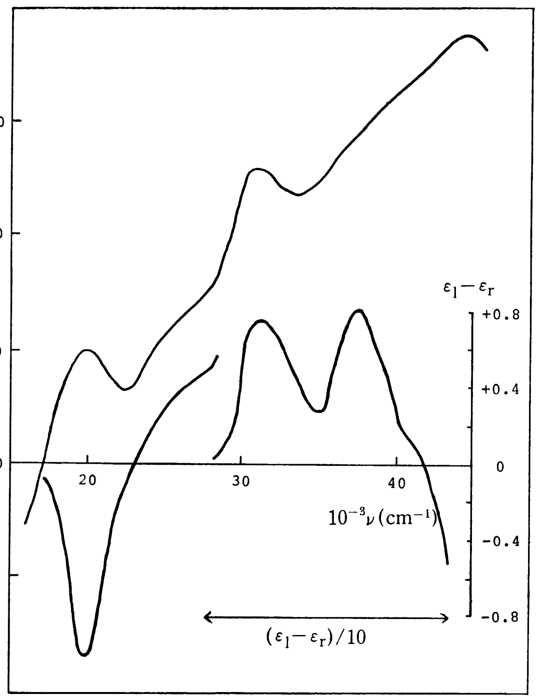

Fig. 4. Absorption and circular dichroism spectra of $(-)_{589}$-[Co acac tn$_2$]$^{2+}$ in water.

Recent conformational analyses of the chelate ring formed by trimethylenediamine (tn) provide an interesting basis for the interpretation of the CD spectrum of $(+)_{589}$-[Co tn$_3$]$^{3+}$. Those who computed its conformational preference derived significantly different results from one another,[16–18] but they all joined in suggesting that the energy difference between the tris-chair form and the tris-lel-skew-boat form is quite small. It seems that, in soluton, a conformational equilibrium involving significant amount of two or more conformers prevails, as has been pointed out by Woldbye.[18,19] This is possibly the case with $\Delta(-)_{589}$-[Co acac tn$_2$]$^{2+}$, whose CD spectrum shows a single negative peak in the visible region. Though such a conformational equilibrium is to be expected in solution, the absolute configuration of $\Delta(-)_{589}$-[Co acac tn$_2$]$^{2+}$ was found to be related to that of $\Delta(+)_{589}$-[Co tn$_3$]$^{3+}$ in terms of Mason's rule.[8] Therefore, the CD spectrum of $\Delta(+)_{589}$-[Co tn$_3$]$^{3+}$ in water should have a negative peak in the region of $A_{1g} \rightarrow E_a$ transition.[20]

The two six-membered diamine chelate rings of $(-)_{589}$-[Co acac tn$_2$]$^{2+}$ assume the chair form in the crystal. The coordination angles in both chelate rings are 96°, slightly larger than those (94°) found in $(-)_{589}$-[Co tn$_3$]$^{3+}$.[21] The Co-acac chelate ring is almost planar, the maximum deviation from the best

Table 3. Bond distances and angles with their estimated standard deviations in parentheses

Co–N (1)	1.98 (2) Å	As (2)–O (11)	1.82 (2)	N (1)–Co–N (2)	96 (1) °	O (9)–As (2)–O (11)	85 (1) °
Co–N (2)	2.01 (2)	O (3)–C (12)	1.28 (3)	N (3)–Co–N (4)	96 (1)	As (2)–O (6)–C (14)	121 (2)
Co–N (3)	2.00 (3)	O (4)–C (12)	1.23 (4)	Co–N (1)–C (1)	121 (2)	As (2)–O (7)–C (15)	112 (2)
Co–N (4)	1.98 (2)	C (12)–C (13)	1.55 (4)	Co–N (2)–C (3)	121 (2)	As (2)–O (9)–C (16)	113 (2)
N (1)–C (1)	1.52 (4)	O (5)–C (13)	1.42 (3)	Co–N (3)–C (4)	117 (2)	As (2)–O (11)–C (17)	115 (2)
N (2)–C (3)	1.50 (4)	C (13)–C (14)	1.48 (4)	Co–N (4)–C (6)	116 (2)	O (3)–C (12)–O (4)	126 (3)
N (3)–C (4)	1.50 (4)	O (6)–C (14)	1.49 (4)	N (1)–C (1)–C (2)	110 (3)	O (3)–C (12)–C (13)	117 (2)
N (4)–C (6)	1.51 (4)	C (14)–C (15)	1.58 (5)	N (2)–C (3)–C (2)	109 (3)	O (4)–C (12)–C (13)	118 (2)
C (1)–C (2)	1.55 (5)	O (7)–C (15)	1.31 (4)	N (3)–C (4)–C (5)	112 (3)	C (12)–C (13)–C (14)	108 (2)
C (2)–C (3)	1.52 (5)	O (8)–C (15)	1.23 (4)	N (4)–C (6)–C (5)	113 (3)	C (12)–C (13)–O (5)	111 (2)
C (4)–C (5)	1.53 (5)	O (9)–C (16)	1.31 (4)	C (1)–C (2)–C (3)	113 (3)	O (5)–C (13)–C (14)	111 (2)
C (5)–C (6)	1.58 (5)	O (10)–C (16)	1.22 (4)	C (4)–C (5)–C (6)	107 (3)	C (13)–C (14)–O (6)	109 (2)
Co–O (1)	1.89 (2)	C (16)–C (17)	1.54 (5)	O (1)–Co–O (2)	96 (2)	C (13)–C (14)–C (15)	110 (3)
Co–O (2)	1.88 (2)	O (11)–C (17)	1.48 (4)	Co–O (1)–C (8)	127 (2)	O (6)–C (14)–C (15)	106 (3)
O (1)–C (8)	1.31 (3)	C (17)–C (18)	1.54 (4)	Co–O (2)–C (10)	121 (2)	C (14)–C (15)–O (8)	117 (3)
O (2)–C (10)	1.33 (3)	O (12)–C (18)	1.42 (3)	O (1)–C (8)–C (9)	122 (3)	C (14)–C (15)–O (7)	117 (3)
C (7)–C (8)	1.50 (4)	C (18)–C (19)	1.53 (4)	O (2)–C (10)–C (9)	129 (3)	O (7)–C (15)–O (8)	126 (3)
C (8)–C (9)	1.39 (4)	O (13)–C (19)	1.23 (4)	O (1)–C (8)–C (7)	119 (3)	O (9)–C (16)–O (10)	127 (3)
C (9)–C (10)	1.33 (4)	O (14)–C (19)	1.32 (4)	O (2)–C (10)–C (11)	108 (2)	O (9)–C (16)–C (17)	115 (3)
C (10)–C (11)	1.57 (4)			C (7)–C (8)–C (9)	119 (3)	O (10)–C (16)–C (17)	119 (3)
				C (9)–C (10)–C (11)	123 (3)	C (16)–C (17)–O (11)	110 (2)
				C (8)–C (9)–C (10)	126 (3)	C (16)–C (17)–C (18)	104 (2)
As (1)–O (3 (	2.11 (2)			O (3)-As (1)–O (5)	84 (1)	O (11)–C (17)–C (18)	110 (2)
As (1)–O (5)	1.83 (3)			O (12)–As (1)–O (14)	87 (1)	C (17)–C (18)–O (12)	112 (2)
As (1)–O (12)	1.77 (2)			As (1)–O (3)–O (12)	110 (2)	C (17)–C (18)–C (19)	106 (2)
As (1)–O (14)	1.99 (2)			As (1)–O (5)–C (13)	117 (2)	O (12)–C (18)–C (19)	110 (2)
As (2)–O (6)	1.79 (2)			As (1)–O (12)–C (18)	117 (2)	C (18)–C (19)–O (13)	125 (3)
As (2)–O (7)	2.06 (2)			As (1)–O (14)–C (19)	111 (2)	C (18)–C (19)–O (14)	115 (3)
As (2)–O (9)	2.01 (2)			O (6)–As (2)–O (7)	85 (1)	O (13)–C (19)–O (14)	120 (3)

---

16) R. J. Geue and M. R. Snow, *J. Chem. Soc.*, *A*, **1971**, 2981.

17) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **11**, 156 (1972).

18) S. R. Niketić and F. Woldbye, *Acta Chem. Scand.*, in press.

19) P. G. Beddoe, M. J. Harding, S. F. Mason, and B. J. Peart, *Chem. Commun.*, **1971**, 1283.

20) K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971).

21) T. Nomura, F. Marumo, and Y. Saito, This Bulletin, **42**, 1016 (1969).

plane being 0.08 Å. The average Co–O bond distance is 1.89 Å, and the O–Co–O angle is 96°. The important bond distances and angles within the complex cation and anion are listed in Table 3.

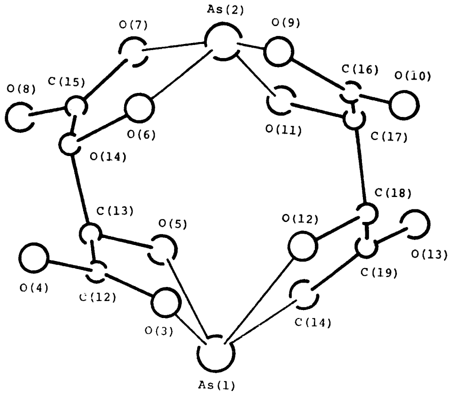

Fig. 5. Coordination about the two arsenic atoms.

A perspective view of $[\mathrm{As}\text{-}(+)\text{-tart}]_2^{2-}$ is given in Fig. 5. The shape of the complex anion is identical with that of $[\mathrm{Sb}\text{-}(+)\text{-tart}]_2^{2-}$.[14,22] The dimeric structure is built up of the two tetradentate tartrate ions and the two arsenic atoms. Two kinds of As–O distances are found, as in the case of $[\mathrm{Sb}\text{-}(+)\text{-tart}]_2^{2-}$; one, As–O(alcoholic), is 1.80 Å, and the other, As–O (carboxylic), 2.04 Å.

The authors wish to express their thanks to Mr. Ken Hirotsu and Mr. Masayuki Hinamoto, who adapted the HBLS-4 and the RSSFR-3 computer programs to the FACOM 270-30 computer at Osaka City University. This research was aided in part by a Scientific Research Grant from the Ministry of Education, to which also the authors' thanks are due.

---

22) R. E. Tapscott, R. L. Belford, and I. C. Paul, *Coord. Chem. Rev.*, **4**, 323 (1969); J. G. Forrest and C. K. Prout, *J. Chem. Soc.*, *A*, **1967**, 1312.