The Crystal Structure of s-facial-Bis(diethylenetriamine)cobalt(III) Bromide, s-facial-[Co(dien)₂]Br₃

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The crystal structure of s-facial-[Co(dien)₂]Br₃ has been determined from three dimensional X-ray diffraction data. The crystal is monoclinic with space group $C2/c$ and the cell dimensions are $a = 12\cdot686$, $b = 10\cdot330$, $c = 12\cdot577$ Å and $\beta = 100\cdot7°$. There are four formula units in the cell. The structure was solved by the heavy-atom method and refined by the anisotropic block-diagonal least-squares method to an R value of 0·074 for the 1021 observed reflexions. Each dien molecule acts as a tridentate ligand with the terminal nitrogen atoms in *cis* positions. The conformations of the two independent chelate rings are enantiomeric with each other. The complex cation has approximately the symmetry C_{2h}.

Introduction

There are three different ways in coordinating two diethylenetriamine ($NH_2CH_2CH_2NHCH_2CH_2NH_2$:dien) molecules to a cobalt(III) ion as illustrated in Fig. 1 (Keene, Searle, Yoshikawa, Imai & Yamasaki, 1970). Among three geometric isomers, the *u-facial-* and *mer*-isomer are optically active and have pairs of enantiomers respectively, whereas the *s-facial*-isomer is optically inactive. All the geometric and optical isomers in this system were isolated, and the geometric configurations were as signed for the optically active isomers from the difference in racemization behaviour of the optically active *u-facial-* and *mer*-isomer by Keene *et al.* (1970). The *s-facial*-isomer can be distinguished from the others, since it is the only isomer which has no optically active form.

As a part of the systematic study on the structures of the complex cation in the [Co(dien)₂]³⁺ system, the structure determination of the *s-facial*-[Co(dien)₂]Br₃ has been undertaken with the intention of confirming the geometry of the *s-facial*-isomer and obtaining the configurational details.

Experimental

Reddish-orange crystals of [Co(dien)₂]Br₃ were kindly supplied by Professor K. Yamasaki of Nagoya University. They are usually short, prismatic in habit, somewhat flattened parallel to (11Ī) and elongated along [101]. Sometimes they show a platy habit. The cell dimensions were determined from Weissenberg photographs taken with Fe $K\alpha$ radiation, and refined with reflexion data collected on the Rigaku automated four-circle diffractometer utilizing Mo $K\alpha$ radiation monochromatized with a LiF crystal. The possible space groups deduced from the systematic absences, $h + k =$

$2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, are Cc and $C2/c$. The true space group was found in the course of the structure determination to be $C2/c$. The density was measured by the flotation method. The crystal data are:

$C_8H_{26}N_6Br_3Co$, monoclinic with the space group $C2/c$,
$a = 12\cdot686 \pm 0\cdot003$, $b = 10\cdot330 \pm 0\cdot002$,
$c = 12\cdot577 \pm 0\cdot003$ Å,
$\beta = 100\cdot71 \pm 0\cdot03°$, $U = 1619\cdot3$ Å³,
$D_m = 2\cdot0$ g.cm⁻³, $D_x = 2\cdot02$ g.cm⁻³, $Z = 4$,
linear absorption coefficient for Mo $K\alpha$ radiation = 89·4 cm⁻¹.

A crystal having dimensions of about $0\cdot07 \times 0\cdot07 \times 0\cdot14$ mm was used for the intensity measurement on the Rigaku automated four-circle diffractometer equipped with a scintillation counter and a pulse-height discriminator. The crystal was mounted on the goniometer-head with the b axis roughly parallel to the φ axis. The symmetrical A setting (Arndt & Willis, 1966) was adopted for the geometry of measurement and the $\omega-2\theta$ scan was employed with the scanning speed of $2\theta = 1°/$min. The scanning range was determined according to the formula $A + B \tan \theta$ proposed by Alexander & Smith (1964) with $A = 1\cdot00°$ and $B = 0\cdot45°$. The radiation used was Mo $K\alpha$ monochromatized with a LiF crystal. Backgrounds were counted both at the beginning and at the end of each scan for 10 sec. Reflected X-rays were attenuated with an absorber when the peak intensity exceeded 6000 counts/sec. The measurement
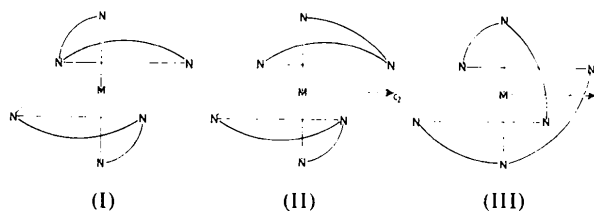

Fig. 1. Schematic drawings of (I) *s-facial-*, (II) *u-facial-* and (III) *mer*-isomer of the [Co(dien)₂]³⁺ complex cation.

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Table 1. *Final atomic parameters* ($\times 10^4$) *for non-hydrogen atoms*

Standard deviations given in parentheses are for least significant figures. The temperature factor expression used was
$$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\,\beta_{12}+2hl\,\beta_{13}+2kl\,\beta_{23})]$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	2500 (0)	2500 (0)	5000 (0)	21 (2)	35 (2)	20 (2)	−3 (2)	−9 (1)	−1 (2)
Br(1)	0 (0)	748 (2)	2500 (0)	38 (1)	60 (2)	25 (1)	0 (0)	−5 (1)	0 (0)
Br(2)	1171 (2)	3907 (2)	1303 (2)	52 (1)	79 (2)	49 (1)	−24 (1)	−22 (1)	15 (1)
N(1)	2369 (9)	3152 (12)	6440 (10)	13 (7)	54 (13)	35 (9)	−7 (8)	−6 (6)	−15 (9)
N(2)	1204 (10)	1505 (12)	5040 (10)	28 (8)	53 (13)	20 (8)	−15 (8)	−15 (6)	0 (8)
N(3)	3318 (10)	997 (12)	5678 (10)	24 (18)	42 (12)	30 (8)	5 (8)	−16 (6)	2 (8)
C(1)	2568 (13)	21 (15)	5991 (14)	34 (10)	40 (14)	44 (12)	4 (10)	−10 (9)	4 (10)
C(2)	1481 (13)	2528 (19)	6842 (12)	38 (10)	85 (17)	18 (9)	4 (12)	10 (7)	1 (11)
C(3)	1552 (14)	96 (16)	5235 (13)	45 (12)	49 (15)	29 (10)	−13 (11)	−1 (9)	−1 (10)
C(4)	647 (13)	2111 (17)	5856 (12)	32 (11)	83 (18)	21 (9)	−13 (11)	7 (8)	5 (10)

was carried out up to $2\theta = 55°$. There are about 1900 reflexions in this range, of which 1021 reflexions gave enough intensities to produce reliable structure amplitudes and these were used for the structure determination.

The measured intensities were corrected for the Lorentz and polarization factors assuming the monochromator crystal to be an ideal mosaic. No corrections were made for the absorption factors in view of the small μr value of 0·35. The structure amplitudes obtained were put on an absolute scale by comparison with the calculated values at a later stage.

Determination and refinement of the structure

The three-dimensional Patterson function was calculated. If the space group is $C2/c$, the Co and one of the Br atoms must be on fourfold special positions. There are two kinds of fourfold positions for the space group $C2/c$, one being on a set of centres of symmetry and the other on twofold rotational axes. On the other hand, all the atoms should be at general positions, if the space group is Cc. On the Patterson maps, there are high peaks at the positions (0·00, 0·50, 0·50), (0·00, 0·14, 0·50) and (0·25, 0·18, 0·25). These are explained if two heavy atoms are allocated to the positions (d) (0·25, 0·25, 0·50) and (e) (0·00, y, 0·25) of the space group $C2/c$ with $y = 0·07$. All the remaining prominent peaks in the maps can also be interpreted by locating the remaining Br atoms at a set of appropriate general positions of the same space group. From consideration of the peak heights, it was revealed that the maps fitted better with the model having the Co atom on the centre of symmetry (d). A three dimensional Fourier synthesis, phased by the heavy atoms derived thus, revealed the positions of all the N atoms, with which the diethylenetriamine molecules are coordinated to the Co atom. The structure factors calculated at this stage gave an R value of 0·29, and $C2/c$ was confirmed to be the true space group of the crystal. All the atoms were found with the second Fourier synthesis except the hydrogen atoms.

The structure was refined by a block-diagonal least-squares program, *HBLS*-4 (Ashida, 1967), with isotropic temperature factors for all the atoms. Then the

R value was reduced to 0·17. Further cycles of refinement, carried out with anisotropic temperature factors, reduced the R value to 0·080. The difference Fourier maps were synthesized at this stage with the intention of determining the positions of the hydrogen atoms. Of the thirteen independent hydrogen atoms, nine were recognized in the maps. The positions of the remaining four hydrogen atoms, H(1), H(4), H(8) and H(10), were evaluated by assuming sp^3 hybrid bonds around the relevant C and N atoms and C(N)–H distances of 1·08 Å. The final refinement of parameters except those of the hydrogen atoms was carried out including the hydrogen atoms in the structure factor calculation. The temperature factor of each hydrogen atom was assumed to be the same as the isotropic temperature factor of the atom to which the hydrogen atom is bonded. The final R value was 0·074. The following weighting scheme was adopted at a later stage of the refinement: $w = 1$ when $F_{\text{obs}} < 145$, $w = 145/|F_{\text{obs}}|$ otherwise. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The values for neutral Co and Br atoms were used. The anomalous dispersion effects were taken into account for the Br and Co atoms.

The final atomic parameters of non-hydrogen and hydrogen atoms are given in Tables 1 and 2 respectively. The observed structure amplitudes are listed in Table 3 together with the calculated ones for comparison.

Table 2. *Final atomic parameters for hydrogen atoms*

Values of positional parameters are multiplied by 10^4

	x	y	z	B
H(1)	2446	220	6813	2·0 Å²
H(2)	2899	−942	5981	2·0
H(3)	1586	−367	4476	1·9
H(4)	907	−411	5573	1·9
H(5)	1124	3192	7342	1·9
H(6)	1171	1688	7329	1·9
H(7)	92	1421	6101	2·6
H(8)	194	2946	5509	2·6
H(9)	2226	4188	6393	1·6
H(10)	3109	2976	7002	1·6
H(11)	3888	1305	6383	1·3
H(12)	3762	562	5108	1·3
H(13)	679	1578	4257	1·4

Table 3. *The observed and calculated structure amplitudes*

Results and discussion

The projection of the crystal structure along the a axis is shown in Fig. 2. The arrangement of the complex cations can be best approximated to the cubic closest packing. Each bromide anion has two $Br^- \cdots$ HN contacts closer than 3·6 Å as seen in Table 4. According to the criterion given by Hamilton & Ibers (1968), these contacts can be considered as weak hydrogen bonds. The distances between the bromide anions and the probable positions of the relevant hydrogen atoms are much shorter than the sum of the van der Waals radii, 3·15 Å, having the values 2·38 Å for
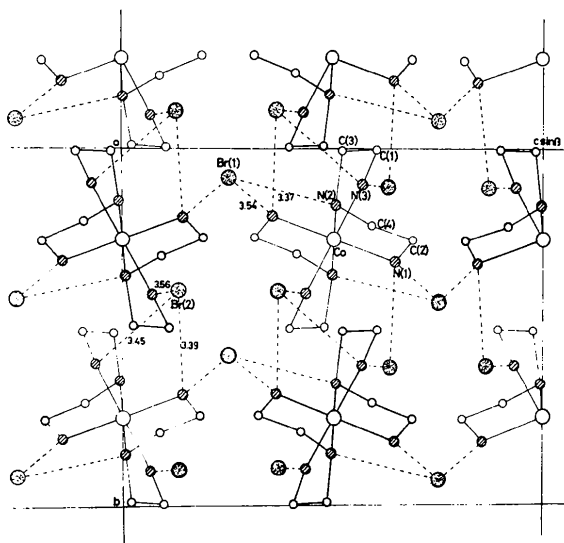

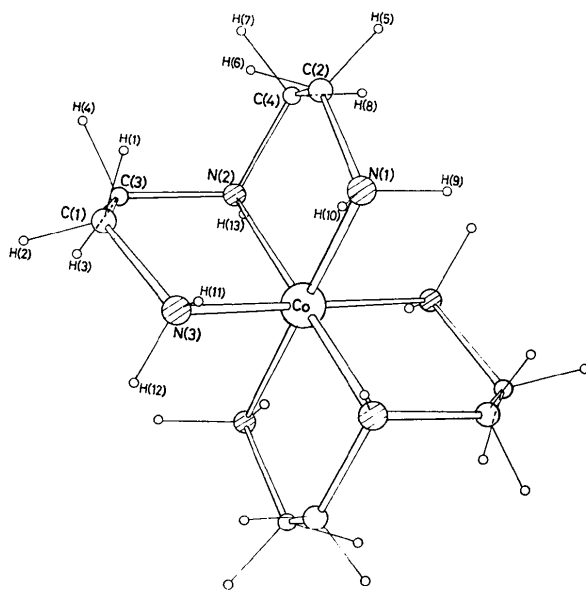Fig. 2. The projection of the crystal structure along the a axis.

Fig. 3. A perspective drawing of the $[Co(dien)_2]^{3+}$ complex cation.

$Br(1)\cdots H(13)$, 2·37 Å for $Br(2)\cdots H(9)$ and 2·48 Å for $Br(2)\cdots H(12)$. Besides these contacts, several short distances are observed between bromide anions and nitrogen atoms, ranging from 3·54 to 3·75 Å. The $Br^-\cdots H$ distances are, however, longer than 2·70 Å, suggesting much weaker interactions in these contacts than in the former three.

Table 4. *Intermolecular contacts less than* 3·6 Å

	Distances	Symmetry operation applied to second atom
Br(1)–N(2)	3·37 Å	1
Br(1)–N(1)	3·54	2
Br(2)–N(1)	3·39	3
Br(2)–N(3)	3·45	4
Br(2)–N(3)	3·56	5

Key to symmetry operations

	x	y	z
1	x	y	z
2	$0\cdot5-x$	$0\cdot5-y$	$1\cdot0-z$
3	x	$1\cdot0-y$	$-0\cdot5+z$
4	$0\cdot5-x$	$0\cdot5+y$	$0\cdot5-z$
5	$-0\cdot5+x$	$0\cdot5-y$	$-0\cdot5+z$

A perspective drawing of the complex cation is presented in Fig. 3. The cobalt atom is surrounded octahedrally by six nitrogen atoms from two dien molecules, which act as tridentate ligands with the terminal amine groups in *cis* positions. The complex cation has an exact centre of symmetry owing to the symmetry of the crystal. It also has an approximate mirror plane as seen in Fig. 3. Accordingly the approximate symmetry of the complex cation is C_{2h}.

The bond distances and angles in the complex cation are given in Table 5 together with the estimated standard deviations. The C–C and the C–N distances are in agreement, within experimental error, with the normal values for the single bond distances. All the Co–N distances are also normal for cobalt(III) complexes of linear aliphatic polyamines. The central nitrogen atom is at a slightly shorter distance (1·95 Å) from the cobalt atom than the terminal nitrogen atoms (1·97 Å). Though the difference is almost within the experimental errors in the present case, the same tendency has been observed in the structures of cobalt(III) complexes with the tridentate ligand of a dien molecule in the meridional position (Yamaguchi, Ōhi, Ōhkawa & Kuroya, 1970). Also, the shortest two Cu–N distances are those to the central nitrogen atoms in the structures of *trans*-bis(diethylenetriamine)copper(II) bromide monohydrate (Stephens, 1969a) and of *trans*-bis(diethylenetriamine)copper(II) nitrate (Stephens, 1969b), which have tetragonally distorted octahedral environments around the copper atoms. The N–Co–N angles in the five-membered chelate rings are both smaller than 90°, having the values 86·6 and 87·2°. The bond angle C(3)–N(2)–C(4) of 116·0° is somewhat larger than the tetrahedral angle. This strain must be caused by non-bonding hydrogen–hydrogen repulsions.

Table 5. Bond lengths and angles within the complex cation

Standard deviations given in parentheses are for least significant figures

	Bond lengths
Co—N(1)	1·97 (1) Å
Co—N(2)	1·95 (1)
Co—N(3)	1·97 (1)
N(1)–C(2)	1·47 (2)
N(2)–C(4)	1·49 (2)
N(2)–C(3)	1·52 (2)
N(3)–C(1)	1·49 (2)
C(1)–C(3)	1·48 (2)
C(2)–C(4)	1·54 (2)

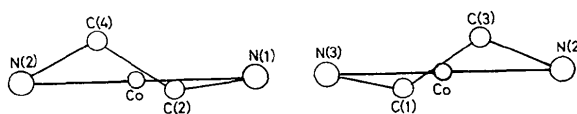|	Bond angles
N(1)–Co—N(2)	86·6 (5)°
N(2)–Co—N(3)	87·2 (5)
N(1)–Co—N(3)	89·5 (5)
Co—N(1)–C(2)	111·6 (10)
N(1)–C(2)–C(4)	107·7 (12)
C(2)–C(4)–N(2)	109·9 (12)
C(4)–N(2)–Co	107·9 (10)
C(3)–N(2)–Co	108·1 (10)
C(3)–N(2)–C(4)	116·0 (12)
C(1)–C(3)–N(2)	109·4 (13)
N(3)–C(1)–C(3)	109·5 (13)
Co—N(3)–C(1)	109·7 (10)

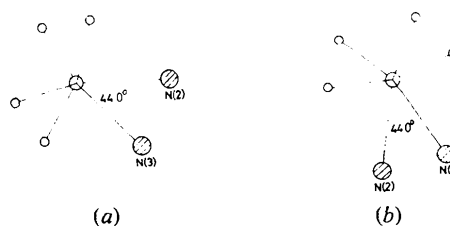Fig. 4. Conformations of the chelate rings.

(a)   (b)

Fig. 5. Newman projections along the bonds (a) C(1)–C(3) and (b) C(2)–C(4). The angles indicated are the torsional angles.

Both of the two independent five-membered chelate rings have an unsymmetrical skew conformation. The C(2) and C(4) atoms are off the plane defined by the cobalt and the two nitrogen atoms in the same ring at distances of −0·11 and 0·49 Å respectively. The corresponding deviations of the C(1) and C(3) atoms are −0·18 and 0·40 Å. The conformations of the two rings are, however, opposite, as seen in Fig. 4. The Newman projections along the C–C bonds are shown in Fig. 5. The dihedral angles between the planes N(1)–C(2)–C(4) and C(2)–C(4)–N(2) and between the planes N(2)–C(3)–C(1) and C(3)–C(1)–N(3) are both 44·0°. The value is much smaller than that in a typical gauche structure, but a little larger than those observed in cis-α and cis-β isomers of the dinitro(L-3,8-dimethyl-triethylenetetramine)cobalt(III) complex cation (Ito, Marumo & Saito, 1970, 1972).

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