

appreciable axial V → π*(CN) transfer, the π-bonding system thus being delocalized to embrace both axial ligands. This difference between [V(CN)₆NO]⁴⁻ and the pentacyanonitrosyl ions may perhaps be due in part to the difference in symmetry. Further investigation involving X-ray photoelectron spectroscopy and *ab initio* FSGO calculations is in progress.

The mean equatorial V—C and C—N bond lengths may be compared with those in other cyanovanadates (Table 3). Although such a comparison is not strictly relevant, since V is seven-coordinated in two of the complexes but six-coordinated in the remaining three, it is seen that, if [V(CN)₆NO]⁴⁻ is excluded, there is a trend towards a shorter V—C distance as the formal oxidation state of V increases. This has been interpreted (Jagner, 1975) in terms of a negligible π contribution to the V—C bond, the trend simply reflecting an increase in σ-bond strength with the increasing formal oxidation state of V. The mean equatorial V—C bond in [V(CN)₆NO]⁴⁻ is seen to be more consistent with V^{III} or V^{IV} than V^I. The strong axial V → π*(ligand) transfer must thus result in a formal oxidation state effectively higher than +I with respect to the equatorial ligands and a consequent increase in σ-bond strength. As in the other complex ions cited in Table 3, π contributions to the equatorial V—C bonds in [V(CN)₆NO]⁴⁻ are undoubtedly slight.

The K—N and K—O contacts range from 2.740 (6) to 3.461 (5) Å for K(1) and from 2.841 (5) to 3.061 (5) Å for K(2). K(2) is surrounded by a distorted trigonal prism of four N and two O atoms, while the coordination polyhedron about K(1) may be described as a tricapped trigonal prism composed of six N and three O atoms. The Na ion is surrounded by a distorted octahedron of four N and two O atoms at distances of 2.380 (5)–2.621 (5) Å.

The shortest contacts involving the water molecule O(2) are O(2)···Na, 2.380 (5), and O(2)···K(2), 2.841 (5) Å, while the shortest contact to a N or O atom is O(2)···N(3), 2.989 (6) Å.

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trans,cis,cis-abc, fed-Bis[(*S*)-2,4-diaminobutyrate-*O,N,N'*]cobalt(III) Bromide Hydrate

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Abstract. Co(C₄H₉N₂O₂)₂Br·1.71H₂O, *M_r* = 403.97, orthorhombic, *C*222₁, *a* = 14.164 (10), *b* = 9.809 (5), *c* = 10.719 (4) Å, *V* = 1482.86 Å³, *D_o* = 1.79, *D_c* (*Z* = 4) = 1.81 g cm⁻³. Purple crystals of the title compound were prepared from optically pure (*S*)-2,4-diaminobutyric acid, separated from other isomers by

ion-exchange, and recrystallized from water. Each amino-acid residue serves as a tridentate ligand; the complex ion consists of two fused-ring systems related by a crystallographic twofold axis passing through the cobalt atom. The approximately octahedral complex has donor oxygen atoms *trans*, 2-nitrogen donor atoms

cis and 4-nitrogen donor atoms *cis*. The bromide counter-ions are disordered about the special position 2(b).

Introduction. Preliminary precession photographs showed orthorhombic symmetry and the systematic absences hkl for $h + k$ odd and $00l$ for l odd. The orthorhombic space group $C222_1$ was thus indicated. A prismatic crystal with a roughly regular hexagonal base was used for intensity data collection. Its dimensions were approximately 0.22 mm by 0.27 mm (minimum and maximum) across the base by 0.35 mm in height. It was mounted on a Picker FACS-1 computer-controlled four-circle diffractometer. The crystal was accurately centered and aligned with [110] coincident with the φ axis of the diffractometer. To determine the severity of the absorption problem the 440 reflection was measured (by repeated $\theta-2\theta$ scans) at $\chi = 90^\circ$ and at 10° intervals from $\varphi = 0^\circ$ to $\varphi = 350^\circ$. The variation in intensity as a function of φ (defined as maximum - minimum/average) was

Table 1. *Experimental data for the X-ray diffraction study*

(A) Measurement of intensity data

Radiation: Mo $K\alpha$

Filter(s): Nb foil at counter aperture (~47% transmission of Mo $K\alpha$)

Attenuators: Cu (inserted when $I > 10^4$ counts s^{-1})

Take-off angle: 3.0°

Detector aperture: 10 mm \times 10 mm

Crystal-detector distance: 330 mm

Crystal orientation: mounted on [110]

Reflections measured: $h,k,\pm l$ (rejecting $h + k = 2n + 1$)

Maximum 2θ : 45°

Scan type: coupled θ (crystal)- 2θ (counter)

Scan speed: $2.0^\circ \text{ min}^{-1}$

Scan length: $\Delta(2\theta) = (2.0 + 0.692 \tan \theta)$, starting 1.0° below the Mo $K\alpha$ peak

Background measurement: stationary crystal, stationary counter, 20 s each at beginning and end of 2θ scan

Standard reflections: three remeasured after every 48 reflections; r.m.s. deviations (after application of anisotropic linear decay correction) were 1.09% for 400, 1.29% for 020, and 0.44% for 004

Reflections collected: 1171 independent measurements; of these 181 were duplicate or equivalent measurements (averaged into primary data set), 12 were systematic absences

(B) Treatment of intensity data

Conversion to $|F_o|$ and $(w|F_o|)$: as in Churchill & DeBoer (1973), using an 'ignorance factor' of $p = 0.03$

(C) Details of refinement

Unique data used: 978

Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$, by full-matrix least squares

Final number of variables: 132 independent, 35 dependent (for 'riding' hydrogen atoms)

Final error in observation of unit weight: 2.064

Final R_p : 5.24

Final R_{wF} : 5.77

18.0%. This variation represents a maximum or near-maximum effect of absorption in this crystal since the maximum variation in the thickness of the crystal lay perpendicular to [110]. The final model of the structure was fitted to data uncorrected for absorption.

Data-collection procedures and computer programs for the reduction of the data, for application of an empirical correction to take account of absorption by the β filter, and for solution and refinement of the structure were as described by Churchill & DeBoer (1973). All details pertinent to this structure are summarized in Table 1.

Calculations were performed on an IBM 370/158 computer. The structure was solved by the heavy-atom method. A complete trial structure was readily found from the usual combination of Patterson and Fourier maps. It was noted that the intensity of the Br-Br vectors in the Patterson map was less than half that of the Co-Co vectors. This observation is suggestive of the disordered Br atom included in the final model.

Atomic scattering factors for neutral non-hydrogen atoms were taken from Cromer & Waber (1965), and for hydrogen from Stewart, Davidson & Simpson (1965).

Refinement included the use of anisotropic thermal parameters for all non-hydrogen atoms and insertion of riding H atoms in idealized positions [based on $d(\text{C-H}) = 0.95$, $d(\text{N-H}) = 0.87$ Å, as suggested by Churchill (1973)]. These H atoms had shifts in positional parameters held equal to the shifts of their attached atoms.

The single independent H atom of one of the water molecules of crystallization [O(3)] was located and its positional parameters varied independently. The one independent H atom of the other water of crystallization [O(4)] was not located. Independent isotropic

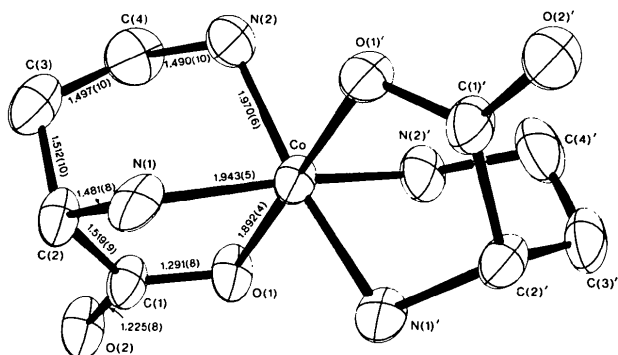


Fig. 1. Perspective drawing of the complex ion in the title compound. Hydrogen atoms are omitted; interatomic distances are in Å. E.s.d.'s are shown in parentheses and are right-justified to the last digit of the preceding number. Their calculation includes the effect of all elements of the positional covariance matrix as well as the uncertainties in the unit-cell dimensions. No corrections have been applied for the effects of thermal motion.

thermal parameters were used for each of the 10 H atoms included in the final model.

Both the real and imaginary components of anomalous dispersion were included throughout the refinement for all non-hydrogen atoms, using the values of Cromer & Liberman (1970). During the final stages of refinement a reversal of handedness to the enantiomeric coordinates gave significantly higher discrepancy indices. The absolute configuration of the molecule was thus determined to be that given in Fig. 1 and Table 2.

Table 2. *Final positional parameters and, for H atoms, isotropic thermal parameters*

Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and were derived from the inverse of the final least-squares matrix.

	<i>x</i>	<i>y</i>	<i>z</i>	
Br*	0.0207 (2)	0.1104 (2)	-0.2298 (4)	
Co	0.32562 (8)	0	0	
O(1)	0.3214 (3)	0.0037 (5)	-0.1764 (3)	
O(2)	0.2834 (4)	0.1357 (5)	-0.3367 (4)	
N(1)	0.2329 (4)	0.1458 (5)	-0.0132 (5)	
N(2)	0.4217 (4)	0.1445 (6)	0.0177 (6)	
C(1)	0.2861 (5)	0.1133 (7)	-0.2243 (6)	
C(2)	0.2563 (5)	0.2201 (7)	-0.1295 (5)	
C(3)	0.3387 (6)	0.3158 (6)	-0.1082 (6)	
C(4)	0.4310 (6)	0.2445 (8)	-0.0862 (8)	
O(3)	0.6015 (6)	0	0	
O(4)†	0.0637 (9)	0	0	
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(N11)	0.1760 (4)	0.1120 (5)	-0.0186 (5)	2.8 (14)
H(N12)	0.2362 (4)	0.1997 (5)	-0.0511 (5)	2.8 (14)
H(N21)	0.4765 (4)	0.1046 (6)	0.0259 (6)	2.8 (15)
H(N22)	0.4086 (4)	0.1898 (6)	0.0853 (6)	3.8 (19)
H(C2)	0.2036 (5)	0.2725 (7)	-0.1566 (5)	4.7 (19)
H(C31)	0.3247 (6)	0.3711 (6)	-0.0378 (6)	3.1 (13)
H(C32)	0.3451 (6)	0.3719 (6)	-0.1801 (6)	4.6 (17)
H(C41)	0.4497 (6)	0.1983 (3)	-0.1601 (8)	4.3 (19)
H(C42)	0.4777 (6)	0.3102 (8)	-0.0648 (8)	7.9 (28)
H(O3)	0.628 (6)	-0.035 (10)	0.045 (10)	5.6 (26)

* The bromine atom is disordered about the special position (0, $\frac{1}{2}$, $\frac{1}{2}$).

† Occupancy of this oxygen atom was varied during refinement. The final value was 0.357 (13).

The final conventional R_p [defined as $(\sum |F_o| - |F_c|)/\sum |F_o| \times 100\%$] was 5.24%.*

In the final cycle of refinement the largest change in any non-hydrogen-atom parameter was 0.013 σ . The highest electron density in a difference Fourier map after the refinement was 0.68 e Å⁻³ in the vicinity of the cobalt atom.

Discussion. This compound was originally prepared and characterized as part of a study of the effect of varying chelate ring size and conformation upon the circular dichroism of cobalt(III) complexes. It is one of the nine geometrical or optical isomers that are possible when the racemic amino acid serves as a tridentate ligand. When pure *S* or *R* amino acid is used, as was the case in the synthesis (Freeman & Liu, 1970) of the title compound, only three of these isomers should result. Because of the large number of possible isomers, one purpose of this X-ray crystallographic study was to check prior conclusions about the identity of the isomer. The mode of coordination, geometrical isomerism (oxygen atoms *trans*, 2-nitrogen atoms *cis*, 4-nitrogen atoms *cis*), and absolute configuration found in this study (see Fig. 1) all in fact confirm what was previously concluded on the basis of visible-ultra-violet, circular dichroism and PMR spectrometry (Freeman & Liu, 1970) and chemical correlation of (*S*)-2,4-diaminobutyric acid with (*S*)-glutamic acid (Adamson, 1939).

The structure consists of discrete bis[(*S*)-2,4-diaminobutyrate]cobalt(III) ions. As would be expected, all of the hydrogen atoms on the nitrogen atoms appear to enter into hydrogen bonds; the complex ion is hydrogen-bonded to two different waters of crystallization and also to neighboring complex ions (all possible hydrogen bonds are summarized in Table 3). With four molecules per unit cell in the eightfold space group *C*222₁, the cobalt atoms and bromine atoms are in special positions and the asymmetric unit contains one amino-acid residue. In the trial model the cobalt

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32996 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Possible A—H...B hydrogen bonds*

<i>A</i>	<i>H</i>	<i>B</i>	<i>A—H</i>	<i>H...B</i>	<i>A...B</i>	$\angle A—H...B$
N(1)	H(N11)	O(4)	0.8700 Å	1.938 (12) Å	2.786 (12) Å	168.4 (2)°
N(1)	H(N12)	O(2)($\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$)	0.8700	2.032 (6)	2.868 (6)	160.9 (2)
N(2)	H(N21)	O(3)	0.8700	2.059 (10)	2.911 (10)	166.0 (2)
N(2)	H(N22)	Br($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$)	0.8700	2.956 (7)	3.591 (7)	131.5 (1)
O(3)	H(O3)	O(2)($-x, -y, \frac{1}{2} + z$)	0.70(9)	2.04 (9)	2.733 (7)	175 (7)
O(4)	H(O4)	Br	—	—	2.758 (5)	—
		Br($-x, y, \frac{1}{2} - z$)			3.313 (5)	

atom was placed in special position 2(a) ($x, 0, 0$) and the bromine atom in special position 2(b) ($0, y, \frac{1}{4}$). From a study of the difference Fourier synthesis during refinement it was soon evident that the bromine atom is in fact disordered about the twofold axis at this special position and this feature was included in the final model.

The complex ion, because of the cobalt atom's location at a special position, is required crystallographically to possess symmetry 2. Thus, in this cation the cobalt atom is coordinated to two twofold-related tridentate amino-acid residues. The coordination geometry of the cobalt atom is approximately octahedral. The angles of the ligating atoms at the cobalt atom and the other bond angles are given in Table 4. The former show the distortion exerted upon the nominal octahedral geometry by the chelate ring formation.

From a study of the difference Fourier synthesis during refinement it was clear that there are two distinct water molecules of crystallization in the asymmetric unit. This fact and the results of the elemental analysis, which restricts the proportion of water to at most two molecules per cobalt atom, mean that both the waters of crystallization must lie in special positions. Both are found on the x axis. One [oxygen atom O(3)] is hydrogen-bonded to the two equivalent N(2) donors and to another complex ion's carbonyl oxygen. The other [oxygen atom O(4)] is hydrogen-bonded to the two equivalent N(1) donors and also to the bromide ion.

The coordinated tridentate ligand in this complex ion presents a fused-ring system of stereochemical interest. It is composed of one five-membered α -amino acid ring, one six-membered propylenediamine chelate ring and one seven-membered γ -amino acid ring. In the crystal structure the five-membered α -amino acid ring is in a puckered conformation of absolute configuration λ . The dihedral angle defined by the planes O(1)–C(1)–C(2) and C(1)–C(2)–N(1) in this ring is $27.0(3)^\circ$ [within the range found in other X-ray structural studies (Freeman, 1967)].

In the six-membered chelate ring both boat and chair conformations are conceivable. This is in contrast to the homologous fused-ring system formed by tridentate coordination of (S)-2,3-diaminopropionic acid to cobalt(III) where a rigid ring system is expected. Liu & Ibers (1969) have reported the crystal structure of one of the isomers of this related complex ion. Comparison of bond distances and bond angles with the current case is worthwhile. Insertion of the extra 'backbone' carbon atom in this ion leaves the angles O(1)–Co–N(1) and N(1)–Co–N(2) unchanged from their values in the comparison structure [$83.8(1)$ versus $83(1)^\circ$ and $86.6(2)$ versus $85(1)^\circ$ respectively]. The result of the increased ring size is rather exhibited wholly at the angle O(1)–Co–N(2) which expands from $87(1)$ to $96.0(2)^\circ$. All of the bond distances involving the cobalt atom are essentially unchanged between the two complex ions. Within the chelate ring system the C–N and C–C distances are unexceptional in the (S)-2,4-diaminobutyrate complex; a significant difference between the two C–N bond distances, found in the comparison structure, vanishes here. The results of this study show that in the crystal the chair conformation is preferred. The six-membered chelate ring is, however, distorted from the exact non-chiral chair conformation. The bond vectors C(2)–N(1) and C(4)–N(2) form angles of $68.8(2)$ and $53.9(4)^\circ$ respectively to the plane defined by C(2), C(3) and C(4). An analysis of values of coupling constants from the PMR spectra of the complex ion and its isomers had indicated that in solution the ring is in rapid equilibrium between the boat and chair conformations (Freeman & Liu, 1970).

The final model of the structure includes both a disordered Br atom and partial occupancy by one of the waters of crystallization, O(4). Since this water of crystallization is within hydrogen-bonding distance of the Br atom it is possible that these observations have a single cause: for example, partial dehydration of the crystal could allow introduction of the disorder in the Br atom position.

Table 4. Bond angles ($^\circ$)

O(1)–Co–N(1)	83.8 (1) ^(b)	N(1)–C(2)–C(1)	106.6 (5)
O(1)–Co–N(2)	96.0 (2)	N(1)–C(2)–C(3)	110.5 (5)
N(1)–Co–N(2)	86.6 (2)	C(2)–C(1)–O(1)	114.5 (5)
O(1)–Co–N(1) ^(a)	93.8 (2)	C(2)–C(1)–O(2)	121.7 (6)
O(1)–Co–N(2)'	86.5 (2)	C(2)–C(3)–C(4)	113.7 (6)
O(1)–Co–O(1)'	176.4 (3)	C(3)–C(4)–N(2)	110.4 (6)
N(1)–Co–N(1)'	95.4 (3)	C(4)–N(2)–Co	117.6 (5)
N(2)–Co–N(2)'	93.1 (4)	Co–O(1)–C(1)	115.2 (4)
N(2)–Co–N(1)'	170.2 (3)	O(2)–C(1)–O(1)	123.5 (6)
Co–N(1)–C(2)	105.8 (4)	C(3)–C(2)–C(1)	108.4 (6)

(a) Primed atoms refer to the twofold-related ligand in the same complex ion.

(b) See legend of Fig. 1 for an explanation of the computation of the e.s.d.'s.

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