The Crystal Structure of Di-μ-hydroxobis[bis{(S)-1-(2-pyridyl)-ethylamine}chromium(III)] Dithionate Dihydrate and the Absolute Configuration of the Cation

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The crystal structure of the title compound has been determined by X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$, Z = 4 with unit cell dimensions a = 16.945 Å, b = 23.393 Å and c = 10.452 Å. The structure was solved and refined from diffractometer data to a final R-value of 0.055. The complex cations, the dithionate ions and the water molecules are interlinked by hydrogen bonds in the crystal. The complex ion has almost C_2 symmetry with the pyridine nitrogen atoms in a *trans* configuration. The interplanar angle between the pyridine rings attached to the same chromium atom is 50° indicating strain within this binuclear complex. The absolute configuration was found to be ΛΛ. The four ligands have identical conformations, δ, with the methyl groups in an equatorial position.

The interesting magnetic and structural properties of binuclear chromium(III) complexes with two hydroxo groups as the bridging ligands (diols) have recently attracted considerable attention.[1−9] Many of the diols studied are complexes with bidentate chelates which can be characterized structurally as optically active or *meso* forms. Preparing diols with an asymmetric bidentate ligand introduces additional possibilities for geometrical isomers. Michelsen has prepared and characterized spectroscopically diols of the latter type with 2-pyridylmethylamine (picomeam) and 1-(2-pyridyl)ethylamine (picoetam) as ligands.[6,8] Despite the possibility of many isomers, Michelsen found that the preparation yielded only one isomer of a diol which can be resolved into optical antipodes. From model building[8] it was suggested that the

geometrical isomer formed was the one with the pyridine nitrogen atoms in a *trans* configuration and from absorption and circular dichroism spectra it was concluded that the diol resulting from the preparation with (S)-1-(2-pyridyl)-ethylamine has the absolute configuration ΛΛ. This last assignment was based on empirical rules for mononuclear complexes since all the previously reported structure analyses of chromium(III) diols have been of either *meso* forms or racemates. The present structure determination was undertaken to see if the structural conclusion mentioned above is correct. Also, by establishing the absolute configuration for a chromium(III) diol, we hope to provide a reference structure for future investigations.

EXPERIMENTAL

A sample of di-μ-hydroxobis[bis{(S)-1-(2-pyridyl)ethylamine} chromium(III)] dithionate dihydrate was kindly supplied by Michelsen. The compound crystallizes as red-violet prismatic needles. X-Ray diffraction photographs showed that the crystals are orthorhombic. The space group is uniquely determined to be $P2_12_12_1$ from the systematically absent reflections. A single crystal with the approximate dimensions 0.15 × 0.2 × 0.2 mm was used for the data collection performed on a Picker FACS-1 diffractometer using CuKα radiation monochromated by a graphite crystal. The intensities were measured at 22 °C, operating the diffractometer in a θ, 2θ scan mode at a rate of 2° min⁻¹ in 2θ. The scan range was symmetrical, $\Delta 2\theta$ = 2.2° + 0.286 tanθ, and background counts were made for 20 s at each end of the scan range. The experimental stability was checked by measuring 6

standard reflections after every 60 reflections. The intensities were measured in the hemisphere (h ≥ 0) in the range $2.4° \leq 2\theta \leq 125°$. The data were corrected for Lorentz, polarization and absorption effects. After averaging of the reflections related by the crystal class symmetry 222, 5999 independent reflections were obtained. Of these, 5269, which had

Table 1. Final fractional coordinates with estimated standard deviations. The first number in the number of C, N atoms differentiate between the different ligands (see Fig. 2 and Fig. 3).

Atom	x	y	z
Cation			
Cr1	0.56586(6)	0.81912(4)	0.63272(9)
Cr2	0.45394(6)	0.91864(4)	0.66419(9)
O1	0.5313(3)	0.87432(17)	0.7598(4)
O2	0.4877(2)	0.86279(17)	0.5376(4)
N11	0.6605(3)	0.8679(2)	0.5719(5)
N12	0.6532(3)	0.7879(2)	0.7488(5)
C11	0.7236(4)	0.8683(3)	0.6511(6)
C12	0.7867(4)	0.9046(3)	0.6289(8)
C13	0.7850(5)	0.9397(3)	0.5216(8)
C14	0.7231(5)	0.9361(3)	0.4379(7)
C15	0.6608(4)	0.9008(3)	0.4673(6)
C16	0.7194(4)	0.8293(3)	0.7670(6)
C17	0.7972(4)	0.7980(3)	0.7937(8)
N21	0.4863(3)	0.7578(2)	0.6875(5)
N22	0.5791(3)	0.7602(2)	0.4874(5)
O21	0.4649(4)	0.7218(3)	0.5946(6)
C22	0.4029(5)	0.6829(3)	0.6148(9)
C23	0.3669(5)	0.6815(4)	0.7336(10)
C24	0.3941(5)	0.7162(3)	0.8313(8)
C25	0.4530(4)	0.7546(3)	0.8064(6)
C26	0.5049(4)	0.7284(3)	0.4679(7)
C27	0.5199(5)	0.6703(4)	0.3999(8)
N31	0.5313(3)	0.9813(2)	0.6054(5)
N32	0.3866(3)	0.9626(2)	0.5324(5)
C31	0.5113(4)	1.0091(3)	0.4972(6)
C32	0.5575(5)	1.0538(3)	0.4522(7)
C33	0.6239(5)	1.0689(3)	0.5182(8)
C34	0.6445(4)	1.0409(3)	0.6278(7)
C35	0.5966(4)	0.9975(3)	0.6705(6)
C36	0.4390(4)	0.9865(3)	0.4318(6)
C37	0.3957(5)	1.0308(3)	0.3501(7)
N41	0.3572(3)	0.8741(2)	0.7316(5)
N42	0.4240(3)	0.9660(2)	0.8235(5)
C41	0.3339(4)	0.8866(3)	0.8528(7)
C42	0.2707(5)	0.8600(4)	0.9081(8)
C43	0.2295(5)	0.8189(4)	0.8373(10)
C44	0.2523(5)	0.8070(3)	0.7172(8)
C45	0.3161(4)	0.8354(3)	0.6632(7)
C46	0.3842(4)	0.9296(3)	0.9210(6)
C47	0.3405(6)	0.9666(4)	1.0164(8)

Table 1. Continued.

	x	y	z
Dithionate ions			
S1	0.62469(12)	0.61464(8)	0.76869(19)
S2	0.72625(12)	0.63789(8)	0.6645(2)
O11	0.6509(4)	0.5656(2)	0.8388(7)
O12	0.6081(5)	0.6644(3)	0.8444(7)
O13	0.5664(4)	0.6005(3)	0.6758(7)
O21	0.7058(3)	0.6895(2)	0.5940(5)
O22	0.7482(5)	0.5917(3)	0.5875(7)
O23	0.7830(4)	0.6519(3)	0.7682(7)
S3	0.40562(14)	0.42023(9)	0.39890(18)
S4	0.36149(15)	0.33663(9)	0.38773(19)
O31	0.3592(6)	0.4564(3)	0.3199(6)
O32	0.4057(4)	0.4337(2)	0.5335(5)
O33	0.4872(4)	0.4163(3)	0.3492(8)
O41	0.2779(4)	0.3449(4)	0.4192(7)
O42	0.4027(4)	0.3048(3)	0.4802(6)
O43	0.3774(4)	0.3173(2)	0.2582(4)
Water oxygens			
O3	0.0647(4)	0.1627(3)	0.8036(5)
O4	0.4838(5)	0.1907(4)	0.4233(7)

intensities with $I/\sigma(I) \geq 2.0$, were classified as observed and used in the structure analysis.

Determination and refinement of the structure. The structure was solved and refined by conventional methods. The positions of the heavier atoms (Cr and S) were found by direct methods using the program system MULTAN[10] and the remaining non-hydrogen atoms were located by Fourier syntheses. The refinement was performed by the method of least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$. Due to the large number of parameters (524), a block diagonal refinement was used. A difference Fourier calculated after an anisotropic refinement of the heavier atoms showed the hydrogen atoms of the cation. In the region around the oxygen atoms of the water molecules only diffuse density could be observed. With their positional parameters fixed according to their idealized positions and isotropic temperature factors identical to the refined isotropic temperature factor of the atom to which they are bonded, the contribution from the hydrogen atoms was included in the final cycles of least squares refinement. The weights used follow the expression $w^{-1} = 7.5 - 0.18F + 0.0028F^2$. In the last cycle of the least squares refinement the maximum shift was 0.52σ and the unit weighted and weighted residuals, R and R_w, were 0.055 and 0.065 respectively.

The final atomic coordinates are listed in Table 1.

In order to establish the absolute configuration of the complex the mirror image of the structure was also refined. The residuals following this refinement

were $R = 0.102$ and $R_w = 0.125$, so the latter configuration can be rejected.

The following computer programs were used: The Vanderbilt system for diffractometer operations,[11] a data reduction program of local origin, ORTEP II [12] for the illustrations, and the X-Ray System [13] for the crystal structure analysis. The atomic scattering factors were taken from Cromer and Mann [14] for C, N, O, S and Cr and from Stewart et al.[15] for H. The anomalous dispersion corrections added to the scattering factor of Cr and S were those calculated by Cromer and Liberman.[16]
Listings of observed and calculated structure amplitudes, the hydrogen parameters and the anisotropic thermal parameters may be obtained from the authors.

CRYSTAL DATA

Di-μ-hydroxobis[bis{(S)-1-(2-pyridyl)ethylamine}-chromium(III)] dithionate dihydrate; Cr_2C_{28}-$H_{46}O_{16}N_8S_4$, $M = 982.97$. Orthorhombic, $a = 16.945(4)$ Å, $b = 23.393(5)$ Å, $c = 10.452(2)$ Å; $V = 4140.6$ Å³; $D_m = 1.57$ g/cm³; $Z = 4$; $D_x = 1.577$ g/cm³. $\mu(CuK\alpha) = 69.19$ cm⁻¹. $F(000) = 2040$. Space group $P2_12_12_1$. The prismatic crystals are elongated along c, developed forms {110}, {120}, {010}, {011}, {101} and {111}.

Description and discussion of the structure. It can be seen from the stereo pair shown in Fig. 1 that the structure consists of binuclear [Cr(2-picetam)₂(OH)]₂ cations, $S_2O_6^{2-}$ anions and water molecules held together by an extensive system of hydrogen bonds. Judging from the interatomic

Table 2. Hydrogen bond distances (Å).

N12−O21	2.952(7)	N32−O11	2.833(8)
N12−O42	3.012(8)	N32−O22	2.947(9)
N22−O21	2.930(8)	N42−O11	3.149(8)
N22−O43	2.986(7)	N42−O13	3.152(9)
O1−O32	2.781(7)	O2−O3	2.670(6)
O3−O23	2.700(9)	O4−O12	2.950(11)
O3−O33	2.773(9)	O4−O42	3.060(11)

distances listed in Table 2, all the possible donor atoms appear to be involved in the hydrogen bonding system.

The complex ion. The stereochemistry of the cation is illustrated by the ORTEP drawing in Fig. 2. This drawing also shows the labelling of the ligands. The absolute configuration of the binuclear complex is ΛΛ in agreement with the predictions made from absorption and circular dichroism spectra. There are 7 theoretically possible geometrical isomers. However, only the one isomer, which is studied here, is found; and it has the pyridine nitrogen atoms in a *trans* configuration. This was predicted by Michelsen and Pedersen [8] from (Dreiding) model building.

The angle between the planes of the pyridine rings attached to the same chromium atom is 50° for Cr1 and 52° for Cr2 making the pyridine rings of ligands 1 and 3 and consequently also for 2 and 4 almost parallel. In the related mononuclear complex *cis*-aquahydroxobis(2-pyridylmethylamine)chromium(III) dithionate [17] the pyridine planes are
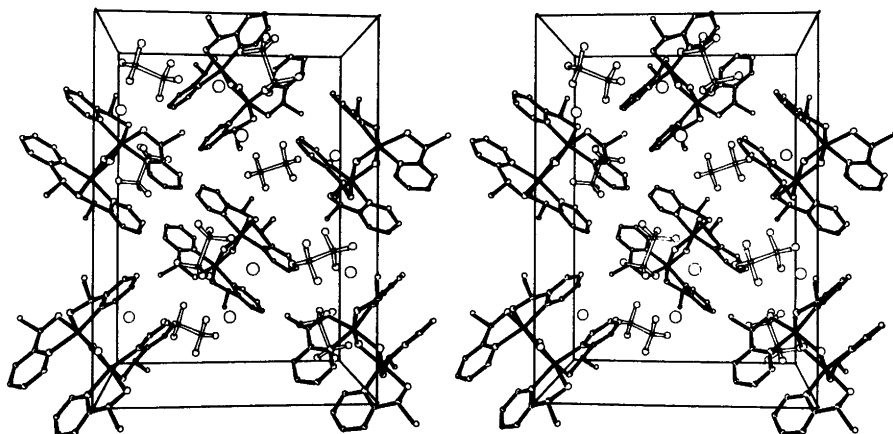

Fig. 1. Stereo pair viewed along the *c*-axis.

Table 3. Bond distances (Å) and bond angles (°) with e.s.d.'s.

|			
Cr1−O1	1.943(4)	Cr2−O2	1.946(4)
Cr1−O2	1.946(4)	Cr2−O1	1.947(4)
Cr1−N11	2.068(5)	Cr2−N31	2.059(5)
Cr1−N12	2.048(5)	Cr2−N32	2.062(5)
Cr1−N21	2.050(5)	Cr2−N41	2.065(5)
Cr1−N22	2.064(5)	Cr2−N42	2.063(6)
N11−C11	1.352(8)	N31−C31	1.349(8)
C11−C12	1.385(9)	C31−C32	1.388(10)
C12−C13	1.389(11)	C32−C33	1.367(12)
C13−C14	1.369(11)	C33−C34	1.364(11)
C14−C15	1.374(10)	C34−C35	1.374(10)
C15−N11	1.338(8)	C35−N31	1.353(9)
C11−C16	1.518(9)	C31−C36	1.498(9)
C16−C17	1.534(11)	C36−C37	1.530(10)
C16−N12	1.493(9)	C36−N32	1.487(8)
N21−C21	1.336(8)	N41−C41	1.359(9)
C21−C22	1.405(11)	C41−C42	1.367(10)
C22−C23	1.384(14)	C42−C43	1.399(12)
C23−C24	1.385(13)	C43−C44	1.342(13)
C24−C25	1.368(11)	C44−C45	1.387(11)
C25−N21	1.367(9)	C45−N41	1.348(9)
C21−C26	1.496(10)	C41−C46	1.499(10)
C26−C27	1.556(11)	C46−C47	1.513(11)
C25−N22	1.474(9)	C46−N42	1.488(9)
Cr1−O1−Cr2	101.9(2)	Cr1−O2−Cr2	101.8(2)
O1−Cr1−O2	78.2(2)	O1−Cr2−O2	78.1(2)
O1−Cr1−N11	94.4(2)	O1−Cr2−N31	95.9(2)
O2−Cr1−N11	94.6(2)	O2−Cr2−N31	95.0(2)
O1−Cr1−N21	94.3(2)	O1−Cr2−N41	95.2(2)
O2−Cr1−N21	93.6(2)	O2−Cr2−N41	97.3(2)
N11−Cr1−N12	79.5(2)	N31−Cr2−N32	78.4(2)
N21−Cr1−N22	79.0(2)	N41−Cr2−N42	78.5(2)
N12−Cr1−N22	96.9(2)	N32−Cr2−N42	97.8(2)
C15−N11−C11	119.5(5)	C35−N31−C31	119.4(5)
N11−C11−C12	120.8(6)	N31−C31−C32	120.4(6)
N11−C11−C16	116.6(5)	N31−C31−C36	114.7(5)
C12−C11−C16	122.6(6)	C32−C31−C36	124.9(6)
C11−C12−C13	118.8(7)	C31−C32−C33	119.3(7)
C12−C13−C14	119.6(7)	C32−C33−C34	120.6(7)
C13−C14−C15	118.9(7)	C33−C34−C35	118.4(7)
C14−C15−N11	122.1(6)	C34−C35−N31	121.8(6)
C11−C16−C17	113.1(6)	C31−C36−C37	114.0(5)
C11−C16−N12	108.9(5)	C31−C36−N32	107.3(5)
C17−C16−N12	111.0(6)	C37−C36−N32	111.3(6)
C25−N21−C21	120.9(5)	C45−N41−C41	119.2(6)
N21−C21−C22	120.2(6)	N41−C41−C42	121.6(6)
N21−C21−C26	117.0(6)	N41−C41−C46	115.0(6)
C22−C21−C26	122.6(6)	C42−C41−C46	123.4(6)
C21−C22−C23	118.7(7)	C41−C42−C43	118.7(7)
C22−C23−C24	120.0(8)	C42−C43−C44	119.6(7)
C23−C24−C25	119.2(8)	C43−C44−C45	120.3(7)
C24−C25−N21	120.7(6)	C44−C45−N41	120.6(7)
C21−C26−C27	112.8(6)	C41−C46−C47	114.8(6)
C21−C26−N22	108.5(5)	C41−C46−N42	108.3(5)
C27−C26−N22	111.4(6)	C47−C46−N42	110.3(6)
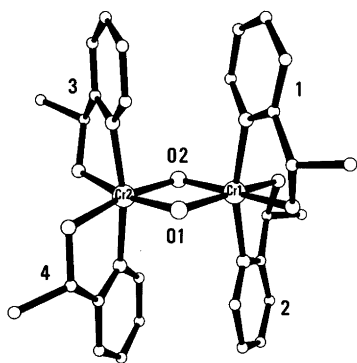
Fig. 2. ORTEP drawing of the cation di-μ-hy-droxobis{bis[(*S*)-1-(2-pyridyl)ethylamine]chro-mium(III)], showing the relative numbering of the ligands.
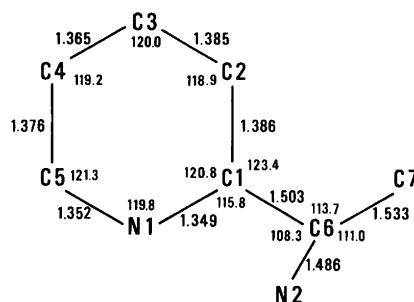

Fig. 3. Schematic drawing of 1-(2-pyridyl)ethylamine illustrating the atomic labelling and the averaged molecular dimensions.

almost perpendicular, the angle being 86°. This indicates that there is considerable steric strain within the binuclear complex.

The bond lengths and bond angles are given in Table 3. The Cr—Cr separation is 3.021 (1) Å. The four independent Cr—O distances are essentially identical $\langle$Cr—O$\rangle$ = 1.946 Å and there is no difference between the Cr—N(amino) and Cr—N(pyridine) bond lengths $\langle$Cr—N$\rangle$ = 2.059 Å. These values are consistent with those reported for similar di-μ-hydroxochromium complexes with ethylenediamine, glycine and 1,10-phenanthroline as bidentate ligands.[1-4,7,9] The hydrogens of the hydroxo bridge were both found in the coordinate plane (Cr1, Cr2, O1, O2). The configuration around the chromium atoms appears to deviate from regular octahedral symmetry. This is illustrated by Table 4 which lists distances to the plane formed by Cr1, Cr2, O1 and O2 for selected atoms. These deviations are probably caused by the steric strain introduced by placing the pyridine rings so close to each other.

This structure determination confirms that the absolute configuration of (—)$_D$-1-(2-pyridyl)ethyl-amine is *S*. The four independent ligands each have a

δ conformation. The dihedral angle N1—C1—C6—N2 (see Fig. 3) takes the values 4.2(8)°, 20.1(8), 30.2(7) and 24.9(7)°, respectively, for the ligands 1, 2, 3 and 4. This conformation is probably influenced by the methyl groups which are all in an equatorial position. There are no significant deviations from planarity in any of the pyridine rings. The molecular geometry is virtually identical for the four ligands. The averaged molecular dimensions are shown in Fig. 3 which also illustrates the atomic labelling. All these structural characteristics of (*S*)-1-(2-pyridyl)ethylamine acting as a bidentate ligand are in agreement with the ones previously observed in the structure of tris[(*S*)-1-(2-pyridyl)ethylamine]-cobalt(III) perchlorate.[18] Summarizing the structural description of the [Cr(2-picetam)$_2$(OH)]$_2^{4+}$ it has an absolute configuration which can be described as $\Lambda\Lambda$ $\delta\delta\delta\delta$ and it is apparent that the molecular symmetry does not deviate considerably from C_2.

The dithionate ions. The bond lengths and bond angles are given in Table 5. The S—S bond lengths observed in the two independent ions agree internally well, $\langle$S—S$\rangle$ = 2.103 Å, but are slightly shorter than the values found in previous works where S—S = [2.127—2.140 Å].[7,19-22] The S—O bonds show rather large variations in this structure [1.397—1.486 Å]. The average value 1.441 Å is, however, consistent with the values reported in other structures containing this ion.[7,19-22] The conformation of the ions is staggered, the dihedral angles O12—S1—S2—O22 and O33—S3—S4—O41 are 179.5(4) and —171.7(4)°, respectively. In previous works the symmetry of the dithionate ion approximates $\bar{3}m$, even if the crystallographic symmetry is 1. From the results of this structure

Table 4. Distances (Å) from the least squares plane defined by the atoms marked with.*

Cr1*	0.005	N12	0.245
Cr2*	0.005	N22	—0.241
O1*	—0.005	N32	0.245
O2*	—0.005	N42	—0.167

Table 5. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses for the dithionate ions.

S1−S2	2.108(3)	S3−S4	2.097(3)
S1−O11	1.432(6)	S3−O31	1.420(8)
S1−O12	1.434(7)	S3−O32	1.441(5)
S1−O13	1.424(7)	S3−O33	1.479(8)
S2−O21	1.457(5)	S4−O41	1.467(7)
S2−O22	1.397(7)	S4−O42	1.406(7)
S2−O23	1.486(7)	S4−O43	1.453(5)
O11−S1−S2	102.6(3)	O31−S3−S4	109.0(3)
O12−S1−S2	103.6(3)	O32−S3−S4	104.9(3)
O13−S1−S2	105.9(3)	O33−S3−S4	104.8(3)
O11−S1−O12	115.4(4)	O31−S3−O32	116.0(4)
O11−S1−O13	112.2(4)	O31−S3−O33	110.5(5)
O12−S1−O13	115.3(4)	O32−S3−O33	110.8(4)
O21−S2−S1	106.3(2)	O41−S4−S3	102.0(3)
O22−S2−S1	108.4(3)	O42−S4−S3	106.2(3)
O23−S2−S1	102.0(3)	O43−S4−S3	106.0(3)
O21−S2−O22	114.4(4)	O41−S4−O42	113.3(4)
O21−S2−O23	109.9(4)	O41−S4−O43	115.4(4)
O22−S2−O23	114.8(4)	O42−S4−O43	112.6(4)

investigation there is no indication that the ions have higher symmetry than 1.

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