

The Crystal Structure and Absolute Configuration of (+)_D-Tris-[-(-)_D-1-(2-pyridyl)ethylamine]cobalt(III) Perchlorate Dihydrate

EVA BANG

Department I, Inorganic Chemistry, H.C. Ørsted Institute University of Copenhagen,
Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark

The absolute configuration and the conformations of the complex ion in (+)_D-[Co{(-)_D-1-(2-pyridyl)ethylamine}] (ClO₄)₂·2H₂O has been determined to be $\Lambda\delta\delta\delta$ by means of X-ray investigations (MoK α and CuK α). The absolute configuration of the ligand was determined to be *S*. The crystals were monoclinic, space group *P*2₁, $a = 9.416(4)$, $b = 18.122(6)$, $c = 9.129(3)$ Å, $\beta = 92.16^\circ$; $Z = 2$.

The ligand has the pyridine ring tilted against the plane defined by the cobalt atom and the two nitrogen atoms of the ligand. The torsion angles in the 5-membered ring are 20–30°, and the methyl group is close to an equatorial position. The perchlorate ions are disordered. 3438 independent reflexions from diffractometer data were used in the refinement. The final *R*-value was 0.085.

Three different isomers together with their enantiomers of the optically active tris complexes of (-)_D- and (+)_D-[1-2-pyridyl)ethylamine] and Co(III) have recently been isolated.¹ The X-ray structure investigation reported here has been taken up to elucidate the correctness of assignment based upon NMR spectra, circular dichroism spectra and absorption spectra.

EXPERIMENTAL

The crystals were provided by K. Michelsen and belonged to the group described as the first band on the Sephadex column.¹ Thermogravimetric analyses showed two molecules of H₂O per complex.

The crystals were flat, brownish-red needles (*b* needle axis) and were assigned to space group *P*2₁ through Weissenberg and precession photographs. Intensity data were collected on

a Picker FACS-1 diffractometer with graphite-monochromated MoK α (λ 0.7107 Å) radiation. The measurements were carried out in the θ – 2θ mode. The scan rate was 1°/min, the scan range 1.5° and increasing with 2θ . The background counts were made for 20 s at each end of the scan range.

From the 4291 reflexions recorded, 3438 independent reflexions for which $0.06 < \sin \theta/\lambda \leq 0.65$ were retained having $I/\sigma(I) > 1.5$. $\sigma(I)$ is the standard deviation of the intensity calculated from counting statistics. The crystal size was $0.48 \times 0.08 \times 0.12$ mm³. No correction for absorption was applied. Data for centrosymmetric reflexions selected from the Weissenberg diagrams were collected on the diffractometer with monochromatic CuK α (λ 1.5418 Å) radiation and used in the determination of the absolute configuration. The same crystal was used in both diffractometer experiments. The cell dimensions were refined from powder diagrams obtained from a Hägg-Guinier camera and CuK α radiation (λ 1.5405 Å), Si as internal standard.

The X-ray system² was used in the crystal structure analyses and the Ortep II³ for the illustrations.

CRYSTAL DATA

CoC₂₁N₆H₃₄Cl₃O₁₄; Monoclinic, *P*2₁;
 $a = 9.416(4)$, $b = 18.122(6)$, $c = 9.129(3)$ Å, $\beta = 92.16(3)^\circ$, $Z = 2$; $\mu(\text{MoK}\alpha) = 9.2$ cm⁻¹; $D_x = 1.621$, $D_m = 1.61$ gcm⁻³.

SOLUTION OF THE STRUCTURE

The cobalt, three chlorine and two nitrogen atoms were found through a combination of Patterson and direct methods (Multan). The

Table 1. Fractional atomic coordinates ($\times 10^4$), anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$). The anisotropic temperature factor is of the form $T = \exp [-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0539(1)	0000	7178(1)	2.67(7)	2.93(8)	2.12(7)	0.01(6)	0.06(4)	.02(5)
N1	7900(9)	4596(4)	3959(8)	4.1(5)	3.2(5)	2.1(4)	0.1(1)	-0.4(3)	-0.1(3)
N2	0434(9)	4107(5)	3634(10)	3.6(5)	3.3(4)	3.5(4)	-0.1(4)	0.7(4)	-0.0(3)
N3	9652(9)	0584(5)	5613(8)	3.5(4)	3.2(4)	2.4(4)	0.1(4)	-0.1(3)	-0.1(3)
N4	8872(9)	0289(5)	8241(9)	2.9(4)	4.8(5)	2.4(4)	-0.8(4)	0.1(3)	-0.2(4)
N5	1648(9)	0791(5)	8030(9)	3.5(4)	3.5(4)	4.1(5)	2.5(4)	0.1(3)	0.8(4)
N6	8689(9)	4434(5)	1106(9)	4.1(5)	4.1(5)	3.8(5)	2.3(4)	0.0(3)	-0.1(4)
C1	6690(10)	4967(9)	4289(10)	2.9(4)	5.2(5)	3.4(4)	0.0(6)	0.2(3)	0.4(6)
C2	5623(13)	4648(8)	5037(12)	5.1(7)	5.7(8)	3.2(5)	0.6(6)	0.1(5)	0.0(5)
C3	5772(14)	3942(8)	5517(14)	4.9(7)	6.0(8)	5.3(7)	1.0(6)	1.1(6)	0.8(7)
C4	7026(13)	3550(8)	5278(13)	5.0(7)	5.3(7)	4.4(6)	0.8(6)	1.6(5)	0.1(6)
C5	8052(11)	3901(6)	4466(11)	3.7(5)	3.7(6)	3.0(6)	0.8(5)	-0.2(4)	0.1(4)
C6	9422(12)	3521(6)	4030(12)	4.6(6)	3.5(6)	3.5(5)	0.1(5)	0.6(5)	0.2(5)
C7	0064(15)	3024(8)	5275(16)	6.0(8)	4.9(8)	6.9(9)	-1.3(7)	1.0(7)	-1.5(7)
C8	0289(12)	0802(6)	4387(11)	4.6(6)	4.1(6)	2.8(5)	0.3(5)	0.0(4)	-0.6(4)
C9	9565(16)	1223(8)	3292(13)	7.1(9)	5.4(8)	3.2(6)	0.6(7)	-0.6(5)	-0.7(5)
C10	8167(15)	1428(8)	3531(15)	6.4(8)	4.7(7)	5.3(7)	-0.2(6)	-1.8(6)	-1.8(6)
C11	7517(13)	1204(8)	4825(14)	4.6(7)	5.0(8)	5.4(7)	-0.6(6)	-1.1(6)	-1.4(5)
C12	8314(12)	0758(6)	5819(11)	4.0(5)	3.3(5)	3.4(5)	0.0(5)	-0.9(4)	0.1(4)
C13	7628(11)	0431(7)	2835(13)	2.8(5)	5.0(7)	4.4(6)	-0.2(5)	0.1(4)	-0.5(5)
C14	6483(13)	0870(9)	7861(15)	4.1(8)	7.8(9)	5.7(8)	-1.5(7)	1.3(6)	0.9(7)
C15	1917(14)	1438(7)	7426(12)	6.3(8)	3.8(6)	3.9(6)	0.9(6)	0.9(5)	0.7(5)
C16	2802(15)	1965(8)	8093(15)	6.3(8)	4.8(8)	5.6(8)	0.8(6)	1.1(6)	1.3(6)
C17	3483(17)	1901(9)	9480(16)	7.1(9)	6.6(9)	5.9(8)	2.0(8)	0.9(7)	3.1(8)
C18	3138(14)	1145(9)	0110(13)	5.5(7)	6.9(9)	3.7(6)	0.3(7)	-0.0(5)	1.7(6)
C19	2209(12)	0653(7)	9381(12)	3.9(6)	5.1(7)	3.4(5)	0.6(5)	0.6(4)	0.8(5)
C20	1671(11)	0035(9)	0112(10)	5.4(6)	5.6(7)	3.0(5)	0.9(8)	-0.3(4)	-0.1(7)
C21	7343(19)	4631(10)	8698(16)	9.3(9)	8.7(1.0)	4.5(7)	2.2(9)	-2.3(7)	0.4(8)
Cl1	3920(3)	2103(2)	3770(3)	4.8(2)	6.1(2)	4.4(2)	0.5(2)	0.3(1)	-0.9(1)
Cl2	8878(4)	2451(2)	9674(4)	8.3(2)	5.1(2)	4.3(2)	-0.9(2)	1.1(2)	0.0(1)
Cl3	2565(4)	4457(2)	7961(3)	6.4(2)	4.9(2)	3.8(2)	-0.9(2)	0.7(1)	-0.1(1)
<i>U</i>									
O1	2550(12)	3679(6)	1515(12)	7.2(2)					
O2	5907(14)	3728(8)	1534(14)	9.3(3)					
O3	5020(13)	2233(7)	2799(13)	8.3(3)					
O4	3783(18)	1348(10)	3917(18)	12.2(5)					
O5	4298(20)	2330(13)	5044(23)	16.1(7)					
O6	2627(20)	2274(12)	3155(2)	15.2(6)					
O7	9398(12)	1717(6)	9817(12)	7.8(3)					
O8	7672(21)	2547(11)	0584(2)	14.9(6)					
O9	9878(20)	2960(11)	0229(21)	13.8(6)					
O10	8422(21)	2608(12)	8341(22)	15.6(6)					
O11	6453(14)	0048(10)	1692(15)	10.7(4)					
O12	1333(14)	4568(8)	8708(15)	9.6(4)					
O13	2283(11)	4481(6)	6401(11)	6.8(2)					
O14	3226(12)	3786(7)	8342(13)	7.6(3)					

rest of the complex and the water molecules could be located from electron density maps using a weighting scheme for the structure factors according to Sim.⁴ Those oxygen atoms from the perchlorate ions which later showed

good contact to the amine groups were also found in these maps. The rest of the oxygen atoms were taken from difference Fourier syntheses and showed disorder. The structure was refined isotropically to an *R* factor 0.11.

Table 2. Determination of absolute configuration.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
0	2	0	52.2	58.2	1	6	$\bar{2}$	29.9	29.5
0	2	0	50.8	54.7	$\bar{1}$	$\bar{6}$	2	20.8	20.4
0	4	0	78.2	104.1	1	7	$\bar{2}$	12.1	13.4
0	4	0	87.1	115.1	$\bar{1}$	$\bar{7}$	2	4.5	5.2
0	5	2	32.5	31.8	1	10	1	20.8	20.7
0	5	2	34.5	37.2	$\bar{1}$	$\bar{10}$	$\bar{1}$	20.1	20.5
0	6	0	24.5	40.7	1	11	1	11.5	6.2
0	6	0	23.2	37.5	$\bar{1}$	$\bar{11}$	$\bar{1}$	20.9	17.4
0	8	0	57.6	77.6	2	6	1	64.1	61.0
0	8	0	64.5	86.6	$\bar{2}$	$\bar{6}$	$\bar{1}$	70.8	66.2
0	9	$\bar{1}$	14.5	6.6	4	5	1	41.0	29.6
0	9	1	19.8	15.4	$\bar{5}$	$\bar{5}$	$\bar{1}$	36.5	27.4
0	10	0	13.3	22.1	4	11	0	30.8	30.9
0	10	0	23.1	26.8	$\bar{4}$	$\bar{11}$	0	23.2	25.5
0	12	0	4.5	9.2	6	2	0	21.2	16.5
0	12	0	16.5	16.5	$\bar{6}$	$\bar{2}$	0	26.4	21.4
0	14	$\bar{3}$	17.6	18.3	7	1	0	32.5	26.1
0	14	3	22.3	23.0	$\bar{7}$	$\bar{1}$	0	33.9	28.3
1	6	2	73.8	70.2					
$\bar{1}$	$\bar{6}$	$\bar{2}$	80.3	77.9					

After refining anisotropically for all atoms except the oxygens the *R* factor was 0.085.

No further refining or determination of the hydrogen positions were attempted because of the disorder of the perchlorate ions. Atomic parameters are given in Table 1. A list of ob-

served and calculated structure factors can be obtained from the author on request.

The intensity measurements with CuK α -radiation determined the choice of absolute configuration. A list of observed and calculated structure factors for these calculations is given in Table 2.

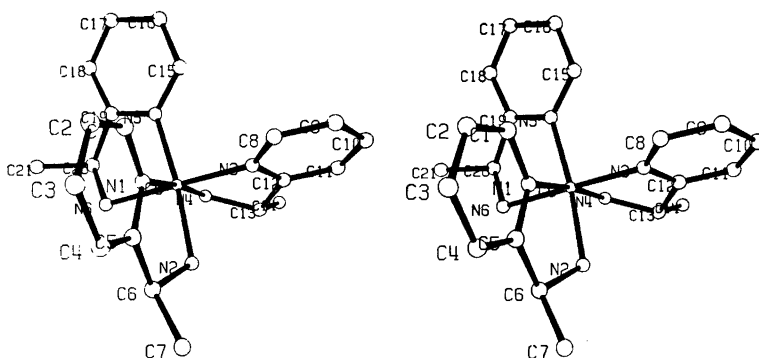


Fig. 1. Stereoscopic view of the complex ion (+)_D(Co(-)_D{1-(2-pyridyl)ethylamine}₃.

Table 3. Bond lengths (Å).

Co-N1	1.972(8)	N5-C15	1.323(15)
Co-N2	1.989(9)	N5-C19	1.346(14)
Co-N3	1.941(8)	C15-C16	1.392(18)
Co-N4	1.948(8)	C16-C17	1.428(16)
Co-N5	1.922(9)	C17-C18	1.366(22)
Co-N6	1.987(9)	C18-C19	1.400(18)
		C19-C20	1.510(20)
N1-C1	1.366(13)	C20-N6	1.500(20)
N1-C5	1.348(14)	C20-C21	1.527(16)
C1-C2	1.364(16)		
C2-C3	1.358(20)	C11-O3	1.408(12)
C3-C4	1.402(19)	C11-O4	1.383(18)
C4-C5	1.394(17)	C11-O5	1.271(19)
C5-C6	1.527(15)	C11-O6	1.358(19)
C6-N2	1.481(14)		
C6-C7	1.555(18)	C12-O7	1.423(12)
		C12-O8	1.443(19)
N3-C9	1.348(13)	C12-O9	1.400(19)
N3-C12	1.319(13)	C12-O10	1.306(19)
C8-C9	1.413(17)		
C9-C10	1.392(19)	C13-O11	1.442(16)
C10-C11	1.411(20)	C13-O12	1.383(14)
C11-C12	1.410(17)	C13-O13	1.440(10)
C12-C13	1.528(15)	C13-O14	1.404(12)
C13-N4	1.521(18)		
C13-C14	1.501(13)		

DESCRIPTION OF THE STRUCTURE

As expected the complex ion is facial and the configuration is $\Lambda\delta\delta\delta$ (Fig. 1) in accordance with the assumptions made in Ref. 1. The absolute chirality of the ligand $(-)_D$ -1-(2-pyridyl)ethylamine is *S*. The atomic distances and angles are given in Tables 3 and 4.

The distances from the atoms in each pyridine ring to the best plane through the ring do not exceed 0.02 Å. The distances from the cobalt atom to these planes vary from 0.03 to 0.15 Å. For each ligand the pyridine ring is tilted to the same side against the plane of the cobalt atom and the two nitrogen atoms of the ligand. The tilt angles, characterized by the nitrogen atom of the pyridine ring to which they belong, are: N1 15°, N3 16°, N5 13°. The carbon atoms of the five-membered rings are both on the same side of the cobalt-nitrogen plane defined above. The methyl groups are not far from being equatorial. The distances from the plane are: C5, 0.26, C6 0.56, C7-0.04 Å; C12 0.27, C13 0.61, C14 0.32 Å; C19 0.19, C20 0.61, C21 0.30 Å. The angles between the normal to the cobalt nitrogen plane and the C-C bond to

Table 4. Selected angles (°).

N1-Co-N2	81.0(3)	C8-N3-C12	120.4(9)
N1-Co-N3	97.1(3)	N3-C8-C9	121.8(10)
N1-Co-N4	173.1(4)	C-C9-C10	117.8(11)
N1-Co-N5	94.9(3)	C9-C10-C11	119.8(12)
N1-Co-N6	88.0(4)	C10-C11-C12	117.8(11)
N2-Co-N3	89.4(4)	C11-C12-N3	122.2(10)
N2-Co-N4	92.1(4)	C11-C12-C13	120.6(9)
N2-Co-N5	173.6(4)	N3-C12-C13	117.2(9)
N2-Co-N6	91.4(4)	C12-C13-N4	104.3(8)
N3-Co-N4	83.6(3)	C12-C13-C14	117.8(10)
N3-Co-N5	95.9(4)	N4-C13-C14	111.3(9)
N3-Co-N6	174.9(4)		
N4-Co-N5	91.9(4)	C15-N5-C19	118.2(9)
N4-Co-N6	91.4(3)	N5-C15-C16	123.1(12)
N5-Co-N6	83.6(3)	C15-C16-C17	119.1(12)
		C16-C17-C18	116.6(13)
C1-N1-C5	117.6(9)	C17-C18-C19	120.6(12)
N1-C1-C2	122.5(12)	N5-C19-C20	115.6(10)
C1-C2-C3	119.5(12)	C18-C19-N5	122.2(11)
C2-C3-C4	120.3(12)	C18-C19-C20	121.9(10)
C3-C4-C5	117.2(12)	N6-C20-C21	112.8(13)
C4-C5-N1	122.8(10)	C19-C20-C21	115.9(11)
N1-C5-C6	114.3(9)	C19-C20-N6	105.8(8)
C4-C5-C6	122.8(10)		
C5-C6-N2	107.3(8)		
C5-C6-C1	110.9(9)		
N2-C6-C7	112.3(9)		

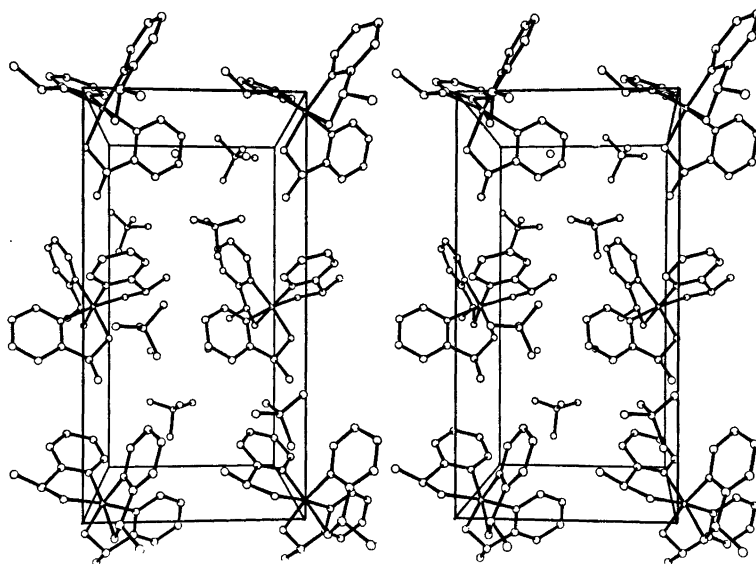


Fig. 2. Stereoscopic view of the cell perpendicular to the *ab* plane.

Table 5. Relevant interatomic distances less than 3.30 Å outside the complex cation.

O1-N2	2.93(1)	O2-N1	3.25(1)	N2-O13	3.09(1)
O1-N4	3.22(1)	O2-N6	2.95(2)	N3-O13	3.23(1)
O1-O2	3.16(2)	O2-O3	3.07(2)	N4-O7	2.99(2)
O1-O6	2.95(2)	O2-O8	2.86(2)	N5-O7	3.20(1)
O1-O9	3.03(2)			N6-O9	3.02(2)
O1-O12	3.20(2)				
O1-O14	3.00(2)				

the methyl group are for C6-C7 67°, for C13-C14 77° and for C20-C21 78°.

The torsion angles for the five-membered rings are N1-C5-C6-N2 20°, N3-C12-C13-N4 26° and N5-C19-C20-N6 31°. The octahedral angles in the five-membered rings are 81-84°, between bonds to pyridine rings 94-97° and the rest 88-92°.

The unit cell is shown in Fig. 2, the intermolecular distances in Table 5 and the distances for the perchlorate ions in Table 3. The oxygens of the perchlorate ions are as mentioned partly disordered and the variations in distances and angles found here are not unusual. We find from a survey of 22 structures of perchlorate salts published in recent years that more than 50 % of these showed perchlorate ion disorder.

CONCLUSIONS

The theoretical work of Corey and Bailar⁵ indicated that the most stable conformation of the coordinated 1,2-propanediamine in *tris* complexes is that with the methyl group in the equatorial position. This is in accord with the stereospecificity displayed by optically active propanediamine in the formation of such complexes.⁶ An equatorial methyl group was found in the structures of the facial species of (+)₅₈₉-[Co(Rpn)₃][Co(CN)₆·2H₂O and (-)₅₈₉-[Co(Rpn)₃][Br₃],^{7,8} and the angles between the bonds to the methyl groups and the normal to the cobalt nitrogen plane varied from 74 to 81°.

These investigations were followed up on Co(III) complexes^{9,10} where optically active

propanediamine forms a part of a more complex ligand, and in one such species one of the methyl groups was found to be axial. It follows that an equatorial orientation of the methyl group cannot automatically be assumed in structure assignment, especially not in the case of a rather inflexible ligand such as 1-(2-pyridyl)ethylamine.

The meridional form of *tris*(1-(2-pyridyl)ethylamine)cobalt(III) theoretically occurs as 16 isomers for each of the two enantiomeric ligands. In the case of the facial complex only eight isomers are possible for each enantiomeric ligand. This therefore gives the possibility of 24 ($\times 2$) isomers in the crystalline state.

As mentioned previously only three ($\times 2$) isomers could be prepared.¹ In the spectroscopic assignment of a facial structure to one of these the existence of a 3-fold axis was also assumed. However, the 3-fold symmetry is absent in the crystalline state. The $\Delta S\delta\delta\delta$ structure was assigned on the basis of spectral data in agreement with the X-ray results. The assignment of $\Delta S\lambda\lambda\lambda$ configuration to the second isolated facial isomer then followed automatically.

The configurational assignment of the third isomer is more problematical. If we assume the same general features for the ligands as found in the present structure we then have the $\Delta\lambda\lambda\lambda$ and $\Delta\delta\delta\delta$ structures for the meridional case with no great differences in steric interactions. The stability may be improved if the methyl group can adopt the axial orientation. It appears that these problems can only be solved satisfactorily by further X-ray investigations.

REFERENCES

1. Michelsen, K. *Acta Chem. Scand. A* 28 (1974) 428.
2. Stewart, J. M. *et al.*, *The X-RAY System 1972*, Technical Report 92, Computer Science Center, University of Maryland.
3. Johnson, C. K. *Ortep: A Fortran Ellipsoid Plot Program for Crystal Structure Illustrations*, Report ORNL-3794, Sec. Rev., Oak Ridge National Laboratory, Oak Ridge 1970.
4. Sim, G. A. *Acta Crystallogr.* 13 (1960) 511.
5. Corey, E. J. and Bailar, J. C. *J. Am. Chem. Soc.* 81 (1959) 2620.
6. Harnung, S. E., Kallesøe, S., Sargeson, A. M. and Schäffer, C. E. *Acta Chem. Scand. A* 28 (1974) 385.

7. Kuroda, R. and Saito, Y. *Acta Crystallogr. B* 30 (1974) 2126.
8. Kuroda, R., Shimanouchi, N. and Saito, Y. *Acta Crystallogr. B* 31 (1975) 931.
9. Kobayashi, A., Marumo, F. and Saito, Y. *Acta Crystallogr. B* 30 (1974) 1495.
10. Toriumi, K. and Saito, Y. *Acta Crystallogr. B* 31 (1975) 1247.

Received February 23, 1977.