Crystal Structure and Absolute Configuration of an Isomer of Potassium Carbonatobis(L-valinato)cobaltate(III) Dihydrate

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The crystal structure and absolute configuration of one of the isomers of (+)K[Co(L-valinato)$_2$(CO$_3$)] has been determined, and shown to be Λ(+)-*cis*(N)-*cis*(O)-K[Co(L-valinato)$_2\delta\delta$(CO$_3$)]·2H$_2$O. The crystals are orthorhombic, space group $P2_12_12_1$, with a = 21.41, b = 14.68, c = 5.76 Å, and Z = 4. The structure has been refined to R = 0.087 for 996 reflections.

THERE has been much work on the separation and characterisation of the isomers of bis(amino-acid) complexes of cobalt(III).[1] Electronic absorption and n.m.r. spectroscopic methods have been used extensively in the differentiation of isomers and in structure assignment. The empirical rule of Gillard,[2] subject to the stated limitations, has been used to predict absolute configuration. A structure determination of one of the isomers of K[Co(L-valinato)$_2$(CO$_3$)] has now been undertaken to confirm the absolute configuration assignment on the basis of the Gillard empirical rule.[3]

EXPERIMENTAL

Using the preparative procedure of Shibata *et al.*,[4] one optically pure isomer of carbonatobis(L-valinato)cobaltate(III) is readily isolable. Because of its instability in aqueous solution, the solid was recrystallised from 0.2 mol dm^{-3} K[HCO$_3$], small purple needle-shaped crystals between 1 and 2 mm in length being obtained.

Crystal Data.—C$_{11}$H$_{20}$CoKN$_2$O$_7$·2H$_2$O, M = 426.3, Orthorhombic, a = 21.41(4), b = 14.68(3), c = 5.76(1) Å, U = 1 810 Å^3, D_m = 1.54, Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 888, space group $P2_12_12_1$ from systematic absences, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 100.4 cm^{-1}.

Intensity data were collected from a crystal having approximate dimensions 0.6 × 0.05 × 0.05 mm mounted along the needle axis (c) on a Stoe–Güttinger automated Weissenberg diffractometer using nickel-filtered Cu-K_α radiation. The intensities of 1 001 reflections having $I > 2\sigma(I)$ were obtained from Weissenberg layers hk(0—5), using an ω—2θ scan technique, from all independent reflections having $5 < 2\theta < 150°$. Periodic check reflections showed no significant decline in intensity during each layer. Lorentz and polarisation, but no absorption corrections were applied (the crystal was nearly cylindrical in cross-section, μR = 0.25).

Structure Determination.—All non-hydrogen atoms were located by a Patterson summation and successive cycles of structure-factor and difference-Fourier calculations. The structure was refined by full-matrix least squares, including anisotropic temperature factors for Co and K$^+$ and full anomalous scattering corrections, using the SHELX-76 computer program.[5] A difference-Fourier calculated at this stage showed peaks attributable to several of the hydrogen atoms, so final cycles of refinement included all hydrogen atoms (except those in the water molecules) in calculated positions (C–H, N–H = 1.0 Å), giving a final R factor of 0.087. A weighting scheme of the form $w \propto 1/[\sigma^2(F_o) + 0.002\ 1F_o^2]$ gave a satisfactory distribution of $w\Delta^2$ over F_o, after removal of five reflections with large discrepancies, and R' = 0.085. A final difference Fourier contained no peaks $>$0.6 e Å^{-3}. The correct absolute conformation of the molecule had been chosen fortuitously, as judged by the known absolute configuration of L-valine.[6] As a further check a cycle of least-squares refinement was calculated for the alternative model with the signs of all positional co-ordinates reversed, R was 0.133.

TABLE 1

Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Co	0.014 22(14)	0.077 7(2)	−0.189 1(6)
K	0.417 3(2)	0.099 7(3)	−0.291 7(8)
O(1)	0.001 9(6)	0.137 7(8)	0.100(2)
O(10)	−0.067 0(7)	0.211 5(9)	0.316(3)
O(2)	0.100 6(6)	0.059 4(9)	−0.105(2)
O(20)	0.195 6(8)	0.094 7(11)	−0.235(2)
O(3)	−0.006 3(8)	−0.043 1(9)	−0.096(2)
O(6)	0.019 8(7)	−0.004 0(9)	−0.450(2)
O(9)	0.006 7(8)	−0.152 6(10)	−0.378(2)
O(30)	0.201 2(7)	−0.082 4(12)	−0.027(3)
O(31)	0.317 4(9)	0.126 3(13)	0.003(3)
N(1)	−0.072 5(7)	0.104 2(10)	−0.245(2)
N(2)	0.044 1(6)	0.183 1(9)	−0.353(2)
C(10)	−0.050 9(10)	0.174 7(14)	0.141(3)
C(11)	−0.096 6(10)	0.167 9(13)	−0.072(3)
C(12)	−0.162 7(10)	0.143 6(16)	0.014(4)
C(13)	−0.166 5(14)	0.052 5(18)	0.131(5)
C(14)	−0.209 2(13)	0.146 3(19)	−0.191(5)
C(20)	0.134 7(11)	0.100 7(14)	−0.251(3)
C(21)	0.108 1(10)	0.162 4(13)	−0.432(3)
C(22)	0.146 9(11)	0.244 9(16)	−0.510(4)
C(23)	0.113 1(10)	0.296 6(15)	−0.701(4)
C(24)	0.163 6(12)	0.307 1(17)	−0.308(5)
C(1)	0.005 5(9)	−0.070 0(14)	−0.300(4)

Final positional parameters are given in Table 1. The rather high estimated standard deviations reflect the shortage of reflection data from the weakly diffracting crystal used rather than any systematic errors caused by absorption effects. Bond distances are in Table 2. Observed and

TABLE 2

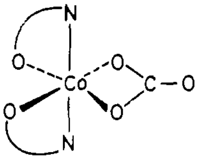
Interatomic distances (Å) with estimated standard deviations in parentheses

Co–N(1)	1.924(21)	C(1)–O(3)	1.26(3)
Co–N(2)	1.921(18)	C(1)–O(6)	1.33(3)
Co–O(1)	1.903(16)	C(1)–O(9)	1.29(3)
Co–O(2)	1.931(18)		
Co–O(3)	1.904(17)		
Co–O(6)	1.924(17)		
C(10)–O(1)	1.28(3)	C(20)–O(2)	1.27(3)
C(10)–O(10)	1.19(3)	C(20)–O(20)	1.31(3)
C(10)–C(11)	1.58(3)	C(20)–C(21)	1.50(3)
C(11)–N(1)	1.46(3)	C(21)–N(2)	1.48(3)
C(11)–C(12)	1.54(4)	C(21)–C(22)	1.54(4)
C(12)–C(13)	1.50(4)	C(22)–C(23)	1.52(4)
C(12)–C(14)	1.55(4)	C(22)–C(24)	1.52(4)

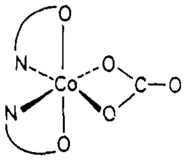
calculated structure factors, hydrogen-atom co-ordinates, and thermal parameters are listed in Supplementary Publication No. SUP 23002 (8 pp.).*

RESULTS AND DISCUSSION

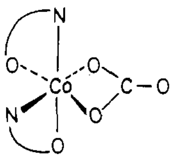
There are six possible isomers of this complex anion; three geometrical isomers (**1**), (**2**), and (**3**), each of which can have a Λ or Δ configuration [7] at the cobalt. The



trans (N)-*cis* (O)
(1)



cis (N)-*trans* (O)
(2)



cis (N)-*cis* (O)
(3)

present *X*-ray study has shown that this complex is the *cis*(N)-*cis*(O) isomer (**3**) with the Λ configuration at the cobalt (see Figure 1), *i.e.* its absolute configuration is related to that of the Λ(+)-[Co(en)$_3$δδδ]$^{3+}$ cation.[8] The structure therefore confirms the configuration predicted from electronic and n.m.r. spectroscopy.[2]

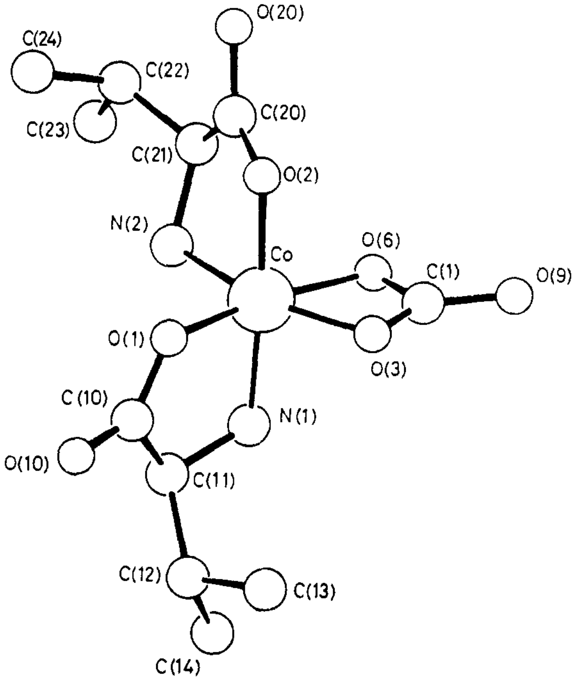


FIGURE 1 Molecular geometry and atomic labelling of the anion [Co(L-valinato)$_2$(CO$_3$)]$^-$, omitting hydrogen atoms

Bond lengths (Table 2) and angles within the complex anion are as expected, within the rather large error limits, which preclude any detailed discussion. The crystal structure is shown as a stereo pair in Figure 2. The potassium ions are in an irregular seven-co-ordinate environment of oxygen atoms from both lattice water molecules, O(2), O(10), and three carbonato-oxygens from different molecules. Besides being co-ordinated to the potassium ion, the two lattice water molecules are weakly hydrogen-bonded to each other, and O(30) is also hydrogen-bonded to O(20).

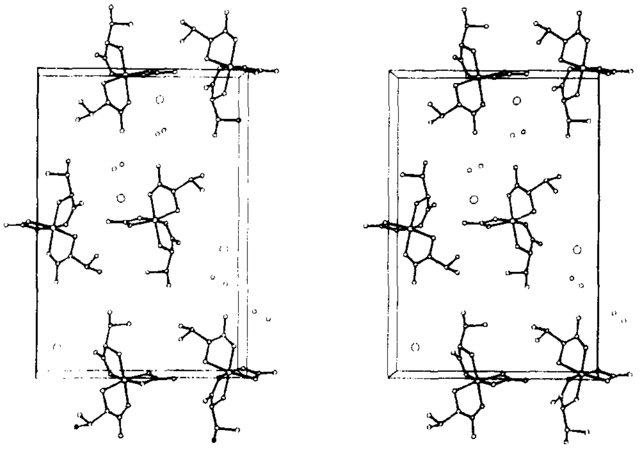


FIGURE 2 A stereoscopic view of the crystal structure of K[Co(L-valinato)$_2$(CO$_3$)]·2H$_2$O along the *x* axis

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.