The Crystal and Molecular Structure of Racemic
[Bis(ethylenediamine)acetylpyruvatocobalt(III) Iodide Monohydrate

BY B. M. GATEHOUSE
Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia
AND M. J. O’CONNOR
Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

(Received 10 April 1976; accepted 15 May 1976)

The title compound crystallizes in space group \(P2_1/c\) with \(a = 8.467(4)\) \(\text{Å}\), \(b = 23.529(12)\) \(\text{Å}\), \(c = 8.920(4)\) \(\text{Å}\), \(\beta = 116.42(6)\)°. The structure has been determined by Patterson and Fourier methods with \(R_1 = 0.066\), \(R_2 = 0.070\) from diffractometer data (1624 observed reflections). The molecule consists of discrete \([	ext{Co(en)}_2\text{AP}]^+\) cations and \(\text{I}^-\) anions. The acetylpyruvate ion is bonded in the keto carboxylate form with the \(O\) of the acetyl group involved in intermolecular hydrogen bonding. The slightly distorted octahedral Co–O,N\(_4\) coordination has Co–O lengths of 1.91 (2) and 1.89 (2) \(\text{Å}\), and the averaged Co–N length is 1.95 (2) \(\text{Å}\).

Introduction

During a study of the reactions of coordinated acetylpyruvic acid and its derivatives (Hughes & O’Connor, 1974) it was found that reaction of the bis(ethylenediamine)carbonatocobalt(III) ion with the Na salt of acetylpyruvic acid in water at 80°C for 2 h gave predominantly the bis(ethylenediamine)oxalatocobalt(III) species.

However, when this reaction was carried out at room temperature, an orange-red crystalline product containing the acetylpyruvate ion was isolated. The structure of this material could be reasonably considered to be either (a) or (b) (N–N=ethylenediamine).

The structure (a) was postulated because treatment of the crystalline material under conditions which initially formed the oxalato species caused no further reaction. It might be envisaged that hydrolysis of (b) could readily give rise to oxalate formation.

The present study was initiated to obtain structural information on the compound.

Experimental

Crystal data

Well formed orange tabular crystals (Hughes & O’Connor, 1974) were obtained by slow crystallization from a warm aqueous solution.

\[
\begin{align*}
\text{C}_9\text{H}_{12}\text{N}_4\text{O}_4\text{ICo}, & \quad M = 452.1, \text{monoclinic}, \quad a = 8.467(4) \text{Å}, \\
b = 23.529(12) \text{Å}, & \quad c = 8.920(4) \text{Å}, \quad \beta = 116.42(6)\text{°}.
\end{align*}
\]

The standard Philips PW1100 X-ray diffractometer computer program was used to determine the cell parameters.

Intensity measurements

Intensities were collected from a single crystal 0.20 \(\times\) 0.13 \(\times\) 0.10 mm on the diffractometer with Mo K\(\alpha\) radiation. The crystal was mounted on a quartz fibre and centred from selected high-angle data obtained from an initial rapid data collection. A unique data set of 2776 reflexions was collected out to \(2\theta\) (Mo K\(\alpha\)) = 50° by the 0–2\(\theta\) scan technique. 1624 reflexions satisfied the condition \(I > 3\sigma(I)\) and were used in subsequent calculations. Three standard reflexions measured at intervals of 2 h showed insignificant intensity variation.

The data were processed with a program written for the PW1100 diffractometer (Hornstra & Stubbe, 1972). Values of \(I\) and \(\sigma(I)\) were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The coordinates of the I and Co atoms were determined from an unsharpened Patterson synthesis. A structure-factor calculation based on these atomic positions with an isotropic thermal parameter of 2.0 \(\text{Å}^2\) gave \(R_1\) and \(R_2\), 0.332 and 0.417 respectively for the 1624 significant reflexions; \(R_1 = \frac{|F_o| - |F_c|}{|F_o|/|F_c|}\) and \(R_2 = \frac{|\Sigma w(F_o) - |F_c|\Sigma w|F_c|^2}{|w|F_o|^2}\). In all least-squares calculations the function \(\Sigma w(F_o) - |F_c|\Sigma w|F_c|^2\) was minimized.

A difference synthesis at this stage revealed all other non-H atoms and inclusion of these with isotropic
thermal parameters of 3.0 Å² gave R₁ = 0.271. The
coordinates of all atoms were refined by full-matrix
least squares to give R₁ = 0.186. Further refinement with
isotropic thermal parameter variation gave R₁ = 0.123.

After additional refinement with anisotropic thermal
parameters for I and Co (R₁ = 0.077, R₂ = 0.085) a dif-
gerence synthesis clearly revealed all H atoms except
those associated with the water molecule. The H
atoms with isotropic thermal parameters of 5.0 Å²
were included at idealized positions (tetrahedral dis-
position, C–H 1.05 Å; trigonal disposition, C–H 1.0,
N–H 0.95 Å) and refinement of all non-H atom
position and anisotropic thermal parameters by
block-diagonal least squares gave convergence with
R₁ = 0.066, R₂ = 0.070. (For all reflections, R₁ = 0.120,
R₂ = 0.085.) Scattering factors for non-H atoms were
those of Cromer & Waber (1965); those of Ibers (1962)
were used for the H atoms.

A final difference synthesis showed no significant
features except for one peak (maximum 2.3 e Å⁻³)
which was associated with the I atom. The final param-
eters are given in Table 1* and the numbering system in
Fig. 1. (The water molecule, I⁻ ion and H atoms are
omitted.) The idealized positions for H atoms are
given in Table 2.

The major programs used during refinement were
modified versions of ORFLS (Busing, Martin & Levy,
1962), a block-diagonal least-squares program by
Shiono (1968) and the Fourier summation program of
White (1965) (see also Rollett, 1961). The diagrams
were drawn with ORTEP (Johnson, 1965).

**Results and discussion**

The structure consists of discrete [Co(en)₂AP⁺]⁺ (AP =
acetylpyruvate) and I⁻ ions (Figs. 1 and 2). Relevant

* A list of structure factors has been deposited with the
British Library Lending Division as Supplementary Publica-
tion No. SUP 31898 (14 pp., 1 microfiche). Copies may be ob-
tained through The Executive Secretary, International Union
of Crystallography, 13 White Friars, Chester CH1 1NZ,
England.

Table 1. Final positional parameters (× 10⁴) and anisotropic thermal parameters of non-hydrogen atoms
For Co and I, the thermal parameters are × 10³; for the rest, × 10². Estimated standard deviations are given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₂</th>
<th>U₂₃</th>
<th>U₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1803</td>
<td>3480</td>
<td>2756</td>
<td>30</td>
<td>22</td>
<td>23</td>
<td>3</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>5020</td>
<td>1495</td>
<td>4412</td>
<td>46</td>
<td>51</td>
<td>80</td>
<td>1</td>
<td>39</td>
<td>15</td>
</tr>
<tr>
<td>N(1)</td>
<td>3481</td>
<td>2916</td>
<td>2696</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>N(2)</td>
<td>3883</td>
<td>3835</td>
<td>4563</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>N(3)</td>
<td>1444</td>
<td>3055</td>
<td>4404</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>N(4)</td>
<td>265</td>
<td>4025</td>
<td>2947</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>N(5)</td>
<td>50</td>
<td>3127</td>
<td>5936</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>O(1)</td>
<td>-3249</td>
<td>4951</td>
<td>4249</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>3</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>O(2)</td>
<td>2962</td>
<td>5102</td>
<td>2491</td>
<td>7</td>
<td>5</td>
<td>6</td>
<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>C(1)</td>
<td>-289</td>
<td>3264</td>
<td>-673</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>C(2)</td>
<td>253</td>
<td>3855</td>
<td>3540</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>C(3)</td>
<td>5313</td>
<td>3570</td>
<td>3780</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>C(4)</td>
<td>5311</td>
<td>3382</td>
<td>5131</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>C(5)</td>
<td>413</td>
<td>3323</td>
<td>5009</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>C(6)</td>
<td>-233</td>
<td>3888</td>
<td>4097</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>C(7)</td>
<td>-1345</td>
<td>4211</td>
<td>4505</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>C(8)</td>
<td>-2283</td>
<td>4716</td>
<td>3702</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>C(9)</td>
<td>-2225</td>
<td>4952</td>
<td>2166</td>
<td>7</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 1. A stereoscopic view of the molecule showing the labelling scheme. (The water molecule, iodide ion and hydrogen atoms
are omitted for clarity.)
The acetylpyruvate ion is bonded to Co in the keto carboxylato form represented as (b) in the Introduction. The Co-O lengths, Table 3, are similar to those found in several oxalatocobalt(III) species (Butler & Snow, 1971; Couldwell, House & Penfold, 1975). Bond lengths and angles within the O(1)-C(5)-O(3)-C(6)-O(2) unit are in agreement with those normally found in coordinated oxalate groups (Lethbridge, Glasser & Taylor, 1970; Stephens, 1969; Couldwell, House & Penfold, 1975). The chelate ring containing the Co and coordinated O atoms is almost planar (Table 5, planes I and II).

There is appreciable thermal motion of C(3) and C(4) (Fig. 1) which is responsible for the rather short bond length observed (1.41 Å). Correction for thermal motion gives a value of 1.53 Å which is similar to the corresponding length in the other ethylenediamine ring.

The ethylenediamine rings have opposite conformations and the results shown in Table 5, planes IV and V, indicate that C(2) and C(4) are displaced 0.59 and −0.52 Å respectively from the mean plane through the chelate rings containing the Co atom and coor-
Table 5. Equations of least-squares planes and distances of individual atoms (Å) from the planes

\[
x, y, z = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} 8.4965 & 0 & -3.9678 \\ 0 & 23.529 & 0 \\ 0 & 0 & 7.9872 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}
\]

(I) Plane through Co, O(1), O(2), C(5), C(6)

\(-0.4736X + 0.5642Y - 0.6763Z - 3.3145 = 0\)

Co -0.015 (3) C(5) 0.00 (2) O(1) -0.01 (2) C(6) -0.02 (3)

(II) Plane through O(1), O(2), C(5), C(6)

\(-0.5484X - 0.4531Y - 0.7029Z + 5.4342 = 0\)

O(1) -0.01 (2) C(5) 0.01 (2) O(2) 0.01 (2) C(6) -0.01 (3) Co -0.060 (3)

(III) Plane through O(1), O(2), C(5), C(6), C(7), O(3)

\(-0.5320X - 0.4463Y - 7.196Z + 5.4471 = 0\)

O(1) -0.01 (2) C(7) -0.01 (3) O(2) 0.03 (2) O(3) 0.03 (2) C(5) -0.01 (2) Co -0.022 (3) C(6) -0.02 (3)

(IV) Plane through N(1), N(2), C(1), Co

\(-0.7535X + 0.6574Y - 0.0076Z - 5.1151 = 0\)

N(1) 0.10 (2) C(1) -0.08 (3) N(2) 0.06 (2) Co -0.075 (4) C(2) 0.59 (3)

(V) Plane through N(3), N(4), C(3), Co

\(-0.4376X + 0.5710Y - 0.6946Z - 3.2959 = 0\)

N(3) -0.05 (2) C(3) 0.04 (3) N(4) -0.03 (2) Co 0.039 (3) C(4) -0.52 (3)

Table 6. Bond lengths between atoms involved in hydrogen bonding of the water molecule

<table>
<thead>
<tr>
<th></th>
<th>Symmetry operation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)---O(H₂O)</td>
<td>2.98 (3) Å</td>
</tr>
<tr>
<td>O(H₂O)---O(4')</td>
<td>2.82 -x, 1-y, 1-z</td>
</tr>
<tr>
<td>O(H₂O)---O(4'')</td>
<td>2.94 1+x, y, z</td>
</tr>
</tbody>
</table>

* To transform O(4) to O(4') and O(4'').