The Crystal and Molecular Structure of Racemic [Bis(ethylenediamine)acetylpyruvato]cobalt(III) Iodide Monohydrate

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The title compound crystallizes in space group $P2_1/c$ with $a = 8 \cdot 467$ (4), $b = 23 \cdot 529$ (12), $c = 8 \cdot 920$ (4) Å, $\beta = 116 \cdot 42$ (6)°, $Z = 4$. The structure has been determined by Patterson and Fourier methods with $R_1 = 0 \cdot 066$, $R_2 = 0 \cdot 070$ from diffractometer data (1624 observed reflexions). The molecule consists of discrete $[Co(en)_2AP]^+$ cations and 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 $Co-O_2N_4$ coordination has $Co-O$ lengths of $1 \cdot 91$ (2) and $1 \cdot 89$ (2) Å, and the averaged $Co-N$ length is $1 \cdot 95$ (2) Å.

Introduction

During a study of the reactions of coordinated acetyl-pyruvic acid and its derivatives (Hughes & O'Connor, 1974) it was found that reaction of the bis(ethylene-diamine)carbonatocobalt(III) ion with the Na salt of acetylpyruvic acid in water at 80°C for 2 h gave pre-dominantly 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).

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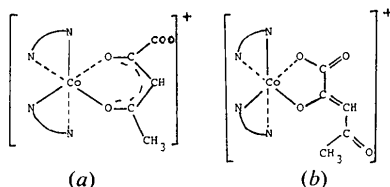
The structure (*a*) was postulated because treatment of the crystalline material under conditions which initially formed the oxalato species caused no further reaction. It might be envisaged that hydrolysis of (*b*) could readily give rise to oxalate formation.

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.

$C_9H_{22}N_4O_5ICo$, $M = 452 \cdot 1$, monoclinic, $a = 8 \cdot 467$ (4), $b = 23 \cdot 529$ (12), $c = 8 \cdot 920$ (4) Å, $\beta = 116 \cdot 42$ (6)°, $U = 1585 \cdot 9$ Å^3. $D_m = 1 \cdot 90$ (1) (by flotation), $D_c = 1 \cdot 89$ g cm^{-3}, $Z = 4$. $F(000) = 224$, $\mu = 31 \cdot 3$ cm^{-1} for Mo $K\alpha$ radiation ($\lambda = 0 \cdot 7107$ Å). Space group $P2_1/c$ from systematic absences: $h0l$, l odd; $0k0$, k odd.

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 $0 \cdot 20 \times 0 \cdot 13 \times 0 \cdot 10$ 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 2θ (Mo $K\alpha$) = 50° by the θ–2θ 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 $2 \cdot 0$ Å^2 gave R_1 and R_2, $0 \cdot 332$ and $0 \cdot 417$ respectively for the 1624 significant reflexions; $R_1 = ||F_o| - |F_c||/\sum|F_o||$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. In all least-squares calculations the function $\sum w(|F_o| - |F_c|)^2$ was minimized.

A difference synthesis at this stage revealed all other non-H atoms and inclusion of these with isotropic

thermal parameters of $3 \cdot 0$ Å^2 gave $R_1 = 0 \cdot 271$. The coordinates of all atoms were refined by full-matrix least squares to give $R_1 = 0 \cdot 186$. Further refinement with isotropic thermal parameter variation gave $R_1 = 0 \cdot 123$.

After additional refinement with anisotropic thermal parameters for I and Co ($R_1 = 0 \cdot 077$, $R_2 = 0 \cdot 085$) a difference synthesis clearly revealed all H atoms except those associated with the water molecule. The H atoms with isotropic thermal parameters of $5 \cdot 0$ Å^2 were included at idealized positions (tetrahedral disposition, C–H $1 \cdot 05$ Å; trigonal disposition, C–H $1 \cdot 0$, N–H $0 \cdot 95$ Å) and refinement of all non-H atom positional and anisotropic thermal parameters by block-diagonal least squares gave convergence with $R_1 = 0 \cdot 066$, $R_2 = 0 \cdot 070$. (For *all* reflexions, $R_1 = 0 \cdot 120$, $R_2 = 0 \cdot 085$.) 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 $2 \cdot 3$ 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)$_2$AP]$^+$ (AP= acetylpyruvate) and I$^-$ ions (Figs. 1 and 2). Relevant

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Table 1. *Final positional parameters* ($\times 10^4$) *and anisotropic thermal parameters of non-hydrogen atoms*

For Co and I, the thermal parameters are $\times 10^3$; for the rest, $\times 10^2$. Estimated standard deviations are given in parentheses. The temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}b^*c^*kl + \ldots)]$.

|	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	1803 (4)	3480 (1)	2756 (4)	30 (2)	22 (2)	23 (2)	3 (2)	16 (2)	0 (2)
I	5020 (2)	1495 (1)	4412 (3)	46 (1)	51 (1)	80 (2)	1 (1)	39 (1)	15 (1)
N(1)	−188 (26)	3105 (8)	991 (25)	4 (1)	3 (1)	4 (1)	1 (1)	3 (1)	0 (1)
N(2)	1926 (26)	3948 (8)	1003 (25)	4 (1)	4 (1)	4 (1)	0 (1)	3 (1)	0 (1)
N(3)	3481 (24)	2916 (8)	2696 (26)	3 (1)	4 (1)	4 (1)	1 (1)	2 (1)	1 (1)
N(4)	3883 (29)	3835 (8)	4563 (26)	5 (1)	3 (1)	3 (1)	−1 (1)	1 (1)	−1 (1)
O(1)	1444 (21)	3055 (6)	4404 (20)	5 (1)	3 (1)	3 (1)	1 (1)	3 (1)	1 (1)
O(2)	265 (21)	4025 (6)	2947 (20)	5 (1)	3 (1)	4 (1)	0 (1)	3 (1)	0 (1)
O(3)	−50 (25)	3127 (7)	5936 (21)	7 (1)	3 (1)	4 (1)	1 (1)	4 (1)	1 (1)
O(4)	−3249 (28)	4951 (9)	4249 (26)	8 (1)	8 (2)	7 (1)	3 (1)	5 (1)	0 (1)
O(H$_2$O)	2962 (26)	5102 (8)	2491 (25)	7 (1)	5 (1)	6 (1)	0 (1)	3 (1)	0 (1)
C(1)	−289 (33)	3264 (11)	−673 (29)	5 (2)	5 (2)	2 (1)	1 (1)	1 (1)	0 (1)
C(2)	253 (34)	3895 (11)	−540 (31)	4 (2)	5 (2)	3 (2)	0 (1)	1 (1)	0 (1)
C(3)	5313 (36)	3070 (13)	3780 (44)	3 (2)	5 (2)	9 (3)	1 (1)	1 (2)	−1 (2)
C(4)	5311 (32)	3382 (16)	5131 (41)	2 (1)	13 (3)	6 (2)	0 (2)	1 (2)	1 (2)
C(5)	413 (31)	3323 (9)	4909 (20)	4 (1)	2 (1)	2 (1)	0 (1)	1 (1)	0 (1)
C(6)	−233 (33)	3888 (10)	4097 (30)	5 (2)	3 (1)	3 (1)	0 (1)	2 (1)	−1 (1)
C(7)	−1345 (34)	4211 (10)	4505 (32)	5 (2)	4 (2)	4 (2)	0 (1)	3 (1)	−1 (1)
C(8)	−2283 (33)	4716 (11)	3702 (33)	4 (2)	4 (2)	5 (2)	1 (1)	3 (1)	0 (1)
C(9)	−2225 (40)	4952 (12)	2166 (36)	7 (2)	4 (2)	6 (2)	1 (1)	4 (1)	1 (1)
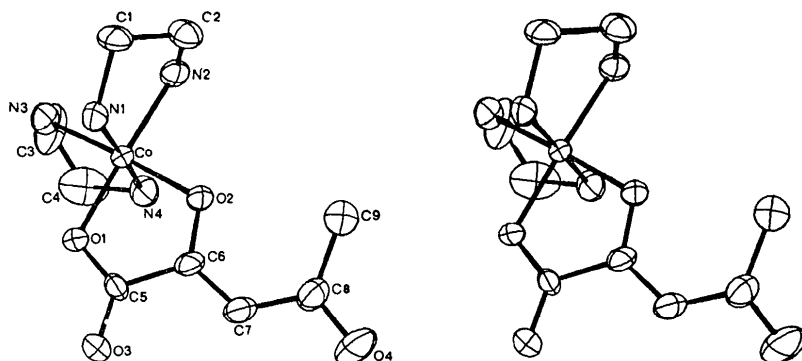
Fig. 1. A stereoscopic view of the molecule showing the labelling scheme. (The water molecule, iodide ion and hydrogen atoms are omitted for clarity.)

bond lengths and angles are given in Tables 3 and 4.

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

Table 2. *Idealized hydrogen atom positions* ($\times 10^3$)

	x	y	z
H(N1)	−66	270	113
H′(N1)	−126	321	103
H(N2)	151	433	92
H′(N2)	308	396	101
H(N3)	322	255	306
H′(N3)	329	287	156
H(N4)	423	417	415
H′(N4)	361	396	545
H(C1)	−28	289	−135
H′(C1)	−148	348	−140
H(C2)	114	308	−56
H′(C2)	−22	362	−169
H(C3)	613	271	420
H′(C3)	581	335	310
H(C4)	509	310	594
H′(C4)	655	358	583
H(C7)	−152	407	550
H(C9)	302	533	178
H′(C9)	−95	505	238
H″(C9)	−277	465	117

Table 3. *Selected bond lengths* (Å) *with estimated standard deviations in parentheses*

Co—O(1)	1·91 (2)	C(4)–N(4)	1·52 (4)
Co—O(2)	1·89 (2)	C(5)–O(1)	1·31 (3)
Co—N(1)	1·93 (2)	C(6)–O(2)	1·31 (4)
Co—N(2)	1·95 (2)	C(5)–O(3)	1·24 (4)
Co—N(3)	1·96 (2)	C(5)–C(6)	1·50 (3)
Co—N(4)	1·97 (2)	C(6)–C(7)	1·38 (4)
C(1)–N(1)	1·49 (4)	C(7)–C(8)	1·42 (3)
C(2)–N(2)	1·48 (3)	C(8)–C(9)	1·50 (5)
C(1)–C(2)	1·55 (4)	C(8)–O(4)	1·25 (4)
C(3)–C(4)	1·41 (5)*	Co—O(H₂O)	3·97 (2)

* Corrected for thermal motion: 1·53 (3).

Table 4. *Bond angles* (°) *with estimated standard deviations in parentheses*

O(1)–Co—O(2)	86 (1)	O(1)–C(5)–C(6)	115 (2)
N(1)–Co—N(2)	87 (1)	O(2)–C(6)–C(5)	115 (2)
N(3)–Co—N(4)	85 (1)	O(2)–C(6)–C(7)	125 (2)
N(1)–Co—N(4)	178 (1)	O(1)–C(5)–O(3)	124 (2)
N(2)–Co—O(1)	174 (1)	C(6)–C(5)–O(3)	122 (2)
N(3)–Co—O(2)	177 (1)	C(5)–C(6)–C(7)	121 (2)
		C(9)–C(8)–O(4)	119 (3)
Co—O(1)–C(5)	112 (1)	O(4)–C(8)–C(7)	119 (3)
Co—O(2)–C(6)	112 (1)	C(7)–C(8)–C(9)	122 (2)

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).

The distorted octahedral arrangement of donor atoms around the Co atom is completed by the two ethylenediamine chelate rings. The Co–N lengths [average 1·95 (2)Å] may be compared with similar systems (Anderson, Buckingham, Gainsford, Robertson & Sargeson, 1975; Aoki, Matsumoto, Ooi & Kuroya, 1973).

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-
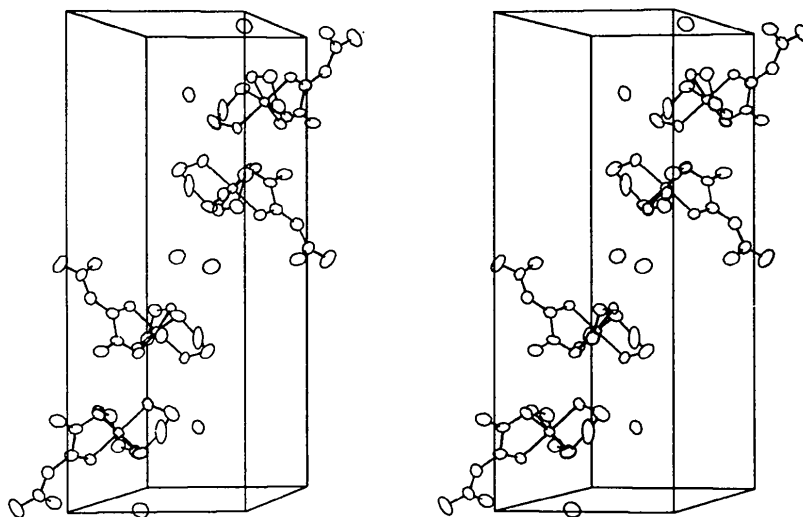

Fig. 2. Stereoscopic packing diagram of bis(ethylenediamine)acetylpyruvatocobalt(III) iodide monohydrate.

dinated ethylenediamine. The N(1)–C(1)–C(2)–N(2) and N(3)–C(3)–C(4)–N(4) torsion angles in these rings are 50·2 and 46·4° respectively.

Table 5. *Equations of least-squares planes and distances of individual atoms (Å) from the planes*

X, Y, Z are orthogonal coordinates related to the fractional coordinates x, y, z in the crystal system by the matrix equation:

$$\begin{pmatrix} 8\cdot4655 & 0 & -3\cdot9678 \\ 0 & 23\cdot529 & 0 \\ 0 & 0 & 7\cdot9872 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$

(I) Plane through Co, O(1), O(2), C(5), C(6)
$$0\cdot4736X + 0\cdot5642Y - 0\cdot6763Z - 3\cdot3145 = 0$$

Co	−0·015 (3)	C(5)	0·00 (2)
O(1)	0·01 (2)	C(6)	−0·02 (3)
O(2)	0·02 (2)		

(II) Plane through O(1), O(2), C(5), C(6)
$$-0\cdot5484X - 0\cdot4531Y - 0\cdot7029Z + 5\cdot4342 = 0$$

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)
$$-0\cdot5320X - 0\cdot4463Y - 7196Z + 5\cdot4471 = 0$$

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
$$-0\cdot7535X + 0\cdot6574Y - 0\cdot0076Z - 5\cdot1151 = 0$$

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
$$0\cdot4376X + 0\cdot5710Y - 0\cdot6946Z - 3\cdot2959 = 0$$

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*

		Symmetry operation[*]
N(2)——O(H₂O)	2·98 (3) Å	
O(H₂O)–O(4')	2·82	$-x, \ 1-y, \ 1-z$
O(H₂O)–O(4'')	2·94	$1+x, \quad y, \quad z$

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

The molecule of water of crystallization is not coordinated to the Co atom [Co–O(H_2O) 3·97 Å] but the bond distances shown in Table 6 and the criteria for hydrogen bonding (Hamilton & Ibers, 1968) indicate that it is involved in hydrogen bonding which links the cations in the unit cell.

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