Pseudo-Polymerization *via* Symmetric O−H−O Bonding of the Cobaloximatic Acid, Hydro-*trans*-Diiodobis(2,3-butanedione dioximato(1−)-N,N′)cobaltate(III). X-Ray Crystal and Molecular Structure

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The structure of hydro-*trans*-diiodobis(2,3-butanedione dioximato)cobaltate(III), $H(CoI_2(dmg)_2)$ (dmg^- = dimethylglyoximate) has been determined by single crystal X-ray diffraction at ambient temperature. The crystals are monoclinic, space group $C2/c$, $C_8H_{15}CoI_2N_4O_4$, M_r = 543.98; a = 15.714(6), b = 7.408(3), c = 13.944(5) Å; β = 107.76(3)°; V = 1545.85 Å^3; Z = 4; D_c = 2.34 Mg m^{-3}. The compound is best visualized as a monobasic acid. The molecules are linked together into two-dimensional network, where linkage parallel to the *ac* plane is effected by weak intermolecular iodine interactions (I···I = 3.826 Å), and linkage along the *b* axis by symmetric intermolecular O−H−O bridges ($O\cdots O_{intermol}$ = 2.499 Å) involving the acidic protons. Each molecule contains two equivalent intramolecular O−H−O bridges ($O\cdots O_{intramol}$ = 2.603 Å). The coordination geometry around Co is a distorted (4+2) octahedron of four chelating equatorial N atoms and two apical iodine atoms. The rectilinear I−Co−I triads are arranged in infinite, faintly zigzagged heteroatomic chains propagating parallel to the *ac* plane.

Introduction

The present work has been carried out in the context of our research program concerned with the preparation and characterization of a wide range of cobaloximes and cobaloximatic salts [1−3]. The main purpose of the research is to provide new model compounds of interest in systematic investigations of molecular parameters and chemical mechanisms that may control the biological activity of cyanocobalamine or vitamin B_{12} [4]. We therefore have set out to fabricate the quinolinium (HQn^+) salt with the anion, *trans*-diiodobis-(2,3-butanedione dioximato)cobaltate(III), $(CoI_2(dmg)_2)^-$. However, instead of the expected salt, $HQn(CoI_2(dmg)_2)$, we obtained the corresponding acid, $H(CoI_2(dmg)_2)$, which reportedly had been isolated earlier by a different preparative procedure [5]. The structure of this acid does not seem to have been established so far, and it turns out, moreover, to present very interesting characteristics, specifically with respect to the extended intermolecular O−H−O bondings and the noticeable interactions between the I atoms of adjacent molecules. We describe the X-ray structure of this acid in the following.

Experimental

Commercial $Co(NO_3)_2\cdot 6H_2O$ (3 g, 10 mmol, >99% pure) and doubly sublimed I_2 (1.3 g, ~10 mmol) were dissolved in absolute methanol (60 ml), and stirred for 30 min at 60 °C. Freshly prepared quinolinium iodide, HQnI (2.6 g, ~10 mmol) [6] was added. A solution of commercial Hdmg (6.6 g, 55 mmol) in absolute methanol (200 ml) was introduced into the red-brown mixture, and stirring at same temperature was pursued over 4 h. A small amount of crystals that had appeared was discarded by filtration. The filtrate was left to stand undisturbed and to concentrate by slow evaporation at room temperature for 10 d. Greenish-brown crystals were collected by filtration, washed with little methanol and air-dried (2.93 g). Recrystallization from saturated methanolic solution yielded crystals suitable for X-ray diffraction.

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Table I. Experimental and computational details for $H(CoI_2(dmg)_2)$.

Crystal shape	block-like
Crystal size	0.28 × 0.40 × 0.48 mm
Possible independent reflections	2386
Reflections observed $I > 2.5\sigma(I)$	2285
Scan mode	ω
2θ range	3–70°
Reflections for ψ-scans	8
Min. transmission (max. = 1)	0.82
R_{merg}	1.8%
μ(MoKα)	5.07 mm^{-1}
Latice parameters	a = 15.714(6) pm
	b = 7.408(3) pm
	c = 13.944(5) pm
	β = 107.76(3)°
	Vol = 1545.85 Å^3
Space group	C_{2h}^6 $C2/c$
Density	2.34 g/cm^3
M_r, F(000), Z	2175.85, 1024, 4

A single crystal (see Table I) was mounted on top of a glass capillary, and data were collected at room temperature on an automatic SYNTEX R3 diffractometer equipped with graphite-monochromatized MoKα radiation (= 0.7107 Å). Lattice parameters were derived from the setting angles of 25 reflections in the range $6 < 2\theta < 28°$. Table I summarizes further experimental and computational details. The structure was solved by Patterson methods and completed by Fourier syntheses. It was refined by full matrix least squares, based on F with weights $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined with fixed isotropic temperature factors, except H1 and H2 involved in O–H–O bridgings, whose positions were taken from a difference Fourier map. Calculations were carried out on a Microwax II computer with the SHELXTL PLUS Program [7] which uses scattering factors from "International Tables" [8] and takes anomalous dispersion into account. Plots were drawn on a Nicolet ZETA plotter with SHELXTL PLUS*.

The final refinement yielded R_w (R) = 3.1 (3.2)%. An empirical absorption correction using ψ-scans of 8 reflections ($6 < 2\theta < 50°$) was applied, and equivalent reflections merged to a set of unique data.

* Lists of observed and calculated structure factors, along with the anisotropic and isotropic thermal parameters have been deposited with the Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG). Copies may be ordered by quoting the deposition number CSD 54745, the authors and the journal reference.

Results and Discussion

The structure clearly reveals that the present compound is adequately formulated as a monobasic acid: $H(CoI_2(dmg)_2)$. For complex formation one of the two dioxime ligands has been ionized (by losing a proton from an OH group) to a dimethylglyoximate (dmg^-), whereas the other ligand has remained a neutral Hdmg (carrying the acidic proton). Thus, the following protolysis equilibrium in aqueous or polar medium may be formulated:

$$CoI_2(dmg)(Hdmg) \rightarrow H^+ + (CoI_2(dmg)_2)^-$$

Final atomic coordinates and their equivalent isotropic thermal parameters are listed in Table II, bond distances and angles in Table III. An ORTEP drawing of two neighbouring molecules with the atomic numbering scheme is given in Fig. 1. It is clear that the arrangement in "infinite" chains extends throughout the structure, parallel to the crystallographic b axis. Co^{III} at the molecular center of symmetry occupies a special position and is surrounded by a regular (4+2) octahedral ligand field of four chelating equatorial N atoms and two

Table II. Final atomic coordinates and equivalent isotropic thermal parameters (× 10^5) for $H(CoI_2(dmg)_2)$.

Atom	x	y	z	U_{eq}*
I1	39297(2)	85335(4)	63820(2)	4045(8)
Co1	75000(0)	25000(0)	50000(0)	2319(17)
N1	30055(19)	51870(37)	49661(20)	2852(85)
N2	19376(20)	71084(40)	60069(20)	2998(90)
O1	28823(19)	37823(31)	55443(18)	3586(87)
O2	19846(23)	55443(39)	65318(22)	4649(113)
C1	64758(24)	33906(48)	62071(25)	3236(109)
C2	64986(23)	50185(45)	56190(25)	2980(101)
C3	60199(30)	67256(55)	57104(34)	4826(160)
H3a	61255(30)	76116(55)	52572(34)	
H3b	62378(30)	71685(55)	63885(34)	
H3c	53903(30)	64940(55)	55420(34)	
C4	59486(30)	32271(59)	69243(31)	4815(160)
H4a	60333(30)	20487(59)	72250(31)	
H4b	53269(30)	34040(59)	65691(31)	
H4c	61430(30)	41264(59)	74408(31)	
H1	75000(0)	−25000(0)	50000(0)	
H2	72586(354)	− 1404(785)	62924(394)	

* Equivalent isotropic U_{eq} are defined as 1/3 of the trace of the orthogonalized U_{ij} tensor. Last significant esd digits for each term are given in parentheses.

Table III. Bond distances and angles for $H(CoI_2(dmg)_2)$.

Bond distances (Å)		Bond angles (°)			
Co1–I1a	2.590(0.000)	I1a–Co1–I1b	180.0(0.0)	O1–N1–C2a	120.1(0.1)
Co1–I1b	2.590(0.000)	I1a–Co1–N1a	90.6(0.1)	Co1–N1–C2a	117.3(0.2)
Co1–N1a	1.895(0.003)	I1a–Co1–N1b	89.4(0.1)	N1–O1–H1a	110.4(0.2)
Co1–N1b	1.895(0.003)	I1a–Co1–N2a	89.4(0.1)	O2–N2–Co1	124.6(0.3)
Co1–N2a	1.896(0.003)	I1a–Co1–N2b	90.6(0.1)	O2–N2–C1a	117.2(0.3)
Co1–N2b	1.896(0.003)	I1b–Co1–N1a	89.4(0.1)	Co1–N2–C1a	118.2(0.3)
N1–O1	1.366(0.004)	I1b–Co1–N1b	90.6(0.1)	N2–O2–H2a	105.3(4.1)
N1–C2a	1.298(0.005)	I1b–Co1–N2a	90.6(0.1)	C2–C1–C4	123.9(0.3)
N2–O2	1.360(0.004)	I1b–Co1–N2b	89.4(0.1)	C2–C1–N2a	112.2(0.4)
N2–C1a	1.277(0.005)	N1a–Co1–N1b	180.0(0.0)	C4–C1–N2a	123.9(0.3)
C1–C2	1.465(0.005)	N1a–Co1–N2a	100.0(0.1)	C1–C2–C3	123.3(0.4)
C1–C4	1.486(0.007)	N1a–Co1–N2b	80.0(0.1)	C1–C2–N1b	112.2(0.3)
C2–C3	1.497(0.006)	N1b–Co1–N2a	80.0(0.1)	C3–C2–N1b	124.5(0.3)
H1–O1a	1.250(0.002)	N1b–Co1–N2b	100.0(0.1)	O1a–H1–O1b	180.0(0.0)
H1–O1b	1.250(0.002)	N2a–Co1–N2b	180.0(0.0)		
H2–O2a	0.801(0.062)	O1–N1–Co1	122.6(0.2)		

apical iodides. There are two kinds of O–H–O bridgings. The *intramolecular* bridges within each molecule are strictly equivalent, with an O1···O2 separation of 2.603 Å. The *intermolecular* bridging involves the acidic proton (H1) which sits *symmetrically* at a center of inversion relative to the adjacent molecules. More interestingly, the latter bridging turns out to be stronger, as judged from the appreciably short O1···O1a separation of 2.499 Å and the angle O1–H1–O1a = 180°.

A projection of the structure down the *b* axis is depicted in Fig. 2. Intermolecular iodine interactions are indicated by broken lines. It is seen that the rectilinear I–Co–I triads are arranged in faintly kinked heteroatomic chains propagating throughout the structure, parallel to the crystallographic *ac* plane. In view of the ionic radius of an iodide at about 2.15 Å, the distance of 3.826 Å separating neighbouring I atoms in these chains may be regarded as a valid argument for ascribing some degree of covalent bonding to these intermolecular iodine contacts. It is worth noting that this state of affairs compares fairly well with that observed recently on a closely related system where the I···I separation is 3.722 Å [1]. The two types of intermolecular interactions observed in the present material are obviously not strong enough to result in dramatic solid state phenomena. Nevertheless, one may anticipate that convenient application of pressure might possibly cause the occurrence of such phenomena. Another structural feature of

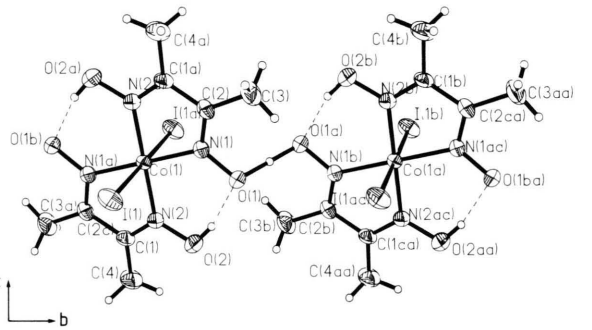

Fig. 1. Perspective ORTEP view of two adjacent $H(CoI_2(dmg)_2)$ molecules with atom labeling, showing the chain arrangement along *b*. The acidic proton, H1, sits at a center of inversion between the two molecules, and acts as "polymerization bridge": O1–H1 = O1a–H1 = 1.250 Å; O1–H1–O1a = 180°.

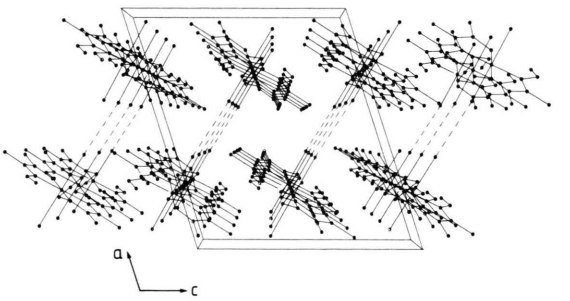

Fig. II. Projection of the structure onto the *ac* plane, showing intermolecular iodine interactions (broken lines), I···I = 3.826 Å, and channel-like matrices running parallel to *b*.

potential interest is the existence of empty channel-like matrices (seen in Fig. 2) which might eventually be used to host guest-species of appropriate size.

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