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Crystal and Molecular Structure of the Asymmetric Cobaloxime, *trans*-Bis(2,3-butanedione dioximato(1−)-*N*,*N*′)iodopyridinecobalt(III): [Co(Hdmg)$_2$I(py)]

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Synopsis. The three-dimensional structure of the *asymmetric cobaloxime, trans*-bis(2,3-butanedione dioximato)iodopyridinecobalt(III), [Co(Hdmg)$_2$I(py)] (Hdmg$^-$=dimethylglyoximate; py=pyridine), has been determined by X-ray diffraction at ambient temperature. The monoclinic structure ($P2_1/n$) was refined by full matrix least-squares to a final R_w=0.037 for 3233 observed independent reflections. The structure consists of interesting neutral cobaloxime molecules in which the coordination geometry around Co^{III} resembles very closely that observed in cyanocobalamine or vitamin B$_{12}$.

"Cobaloximes" (cobalt complexes based on α,β-dione dioximes as the main ligands) constitute an important class of chemical materials, due to their close relationship to vitamin B$_{12}$.[1] Thus, these materials (especially those based on 2,3-butanedione dioxime or dimethylglyoxime, H$_2$dmg) have been a major focus of systematic studies in past decades, primarily so, in search of a sound understanding of factors and mechanisms that control the biological activity of vitamin B$_{12}$. To provide new systems of this kind, we have recently reported a number of cobaloximes and cobaloximatic salts with glyoxal dioxime (or glyoxime, GH$_2$) as the smallest α,β-dione dioxime ligand.[2,3] Our continuing efforts to prepare a large number of such salts involving considerable intermolecular iodine interactions[3] have now led to the isolation of the neutral cobaloxime, *trans*-bis(2,3-butanedione dioximato)iodopyridinecobalt(III) [Co(Hdmg)$_2$I(py)], which reportedly had been obtained elsewhere by a different preparative procedure.[4] The great scientific and technological attractiveness of this material obviously pertains to its structural nature as an *asymmetric cobaloxime,* closely related to vitamin B$_{12}$. We report here on its full structure.

Experimental

Material Preparation. [Co(Hdmg)$_2$I(py)] was prepared by applying a procedure initially conceived to fabricate the pyridinium salt, (pyH) [Co(Hdmg)$_2$I$_2$].[5] This procedure, therefore, greatly differs from that by which [Co(Hdmg)$_2$I(py)] was obtained previously.[4] A filtered solution of commercial Co(NO$_3$)$_2$·6H$_2$O (3 g, >99% pure), doubly sublimed I$_2$ (1.3 g), and analytical grade pyridinium iodide, pyHI[6] (2.1 g) in absolute methanol (50 ml) was stirred for about 4 h at 50 °C. An equally filtered solution of commercial H$_2$dmg (6.6 g, analytical grade) in absolute methanol (200 ml) was added slowly. The dark-brown mixture was stirred for 30 min, then allowed to concentrate undisturbed to near complete evaporation of the solvent over two weeks at ambient temperature. Elongated, shiny brown crystals were produced. They were separated by filtration, washed with little methanol and air dried between filter papers. The elemental microanalysis was in accord with expectation.

Table 1. Experimental and Computational Details

Crystal shape	Needle
Crystal size/mm^3	0.2×0.28×0.70
Possible indep. reflections	3497
Reflections observed $I \geq 2.5\sigma(I)$	3233
Reflections for ψ-scans	7
2θ range/°	3—60
Min. transmission (max.=1)	0.78
μ (Mo $K\alpha$)/mm^{-1}	2.67
Scan mode	ω
R_{int} (from merging)/%	3.1
Parameters for least-squares	217
R_w, R	0.037, 0.039
Goodness-of-fit	2.28
Max. shift/error	0.01
Extremes in diff. Fourier/eÅ^{-3}	+0.63, −0.58

Structure Determination. A suitable crystal was mounted on top of a glass capillary and analyzed by X-ray diffraction at room temperature. Crystal data were collected on a Syntex R3, four-circle automatic diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71070 Å).

Crystal Data. $C_{13}H_{19}CoIN_5O_4$, M_r=495.17; monoclinic, space group $P2_1/n$ (C^5_{2h}); a=8.834(6), b=14.544(7), c=14.161(6) Å; β=97.59(5)°; V=1803.49 Å^3; Z=4; D_c=1.82 Mg m^{-3}.

Table 1 summarises further experimental and computational details. The structure was solved by the Patterson methods and completed by Fourier syntheses. It was refined by full matrix least-squares, based on F with weight $w=\sigma(|F|)^{-2}$. Nonhydrogen atoms were refined anisotropically, hydrogen atoms were not refined. H atoms bound to carbons were calculated and fixed at C–H=0.960 Å; HH1 and HH2 (involved in intramolecular O-H-O bridgings), however, were located on difference Fourier maps with fixed positions. The final refinement yielded R (R_w)=0.039 (0.037) for 3233 observed independent reflections and 217 parameters. An empirical absorption correction was applied using ψ-scans of 7 reflections (6<2θ<45°). Calculations were carried out on a Microvax II computer with SHELXTL PLUS program[7] which uses scattering factors from the "International Tables"[8] and takes anomalous dispersion into account.[9] Plots were drawn on a Tektronix plotter with SHELXTL PLUS.

Results and Discussion

Atomic coordinates with their equivalent isotropic thermal parameters for [Co(Hdmg)$_2$I(py)] are listed in Table 2, bond lengths and angles in Table 3. Figure 1 displays a molecular perspective view with atom labeling

Table 2. Final Atomic Coordinates ($\times 10^4$) and Their Equivalent Isotropic Thermal Parameters ($\times 10^4$)[a]

Atom	x	y	z	U_{eq}/Å^2
I1	24238(4)[b]	14626(2)[b]	15344(2)[b]	4518(11)[b]
Co1	49808(7)[b]	14139(4)[b]	26518(4)[b]	3091(18)[b]
N1	4517(5)	212(3)	3025(3)	428(14)
N2	5814(5)	758(3)	1687(3)	404(14)
N3	4080(4)	2068(3)	3592(3)	411(14)
N4	5422(5)	2626(3)	2268(3)	406(13)
N10	6970(4)	1356(2)	3481(3)	330(12)
O1	3800(4)	46(3)	3786(3)	587(15)
O2	6426(4)	1184(3)	992(2)	533(13)
O3	3405(4)	1658(3)	4268(3)	562(14)
O4	6159(5)	2797(3)	1531(3)	381(13)
C1	5003(6)	−451(3)	2540(4)	468(18)
C2	5720(6)	−138(4)	1733(4)	457(18)
C3	4812(8)	−1443(4)	2809(5)	834(30)
C4	6254(7)	−755(4)	992(4)	739(26)
C5	4204(6)	2960(4)	3572(4)	490(19)
C6	4964(6)	3282(4)	2789(4)	469(18)
C7	3605(8)	3576(4)	4299(5)	822(29)
C8	5176(8)	4281(4)	2557(5)	743(26)
C11	8269(5)	1472(3)	3118(3)	382(14)
C12	9678(6)	1438(4)	3658(4)	452(17)
C13	9752(6)	1272(4)	4622(4)	501(19)
C14	8397(7)	1158(5)	4999(4)	639(23)
C15	7028(6)	1197(4)	4409(4)	524(20)

a) Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor. Last significant esd digits for each term are given in parentheses.
b) Terms multiplied by 10^5.

scheme. The coordination geometry around Co^{III} is a strongly distorted octahedron. The four N atoms (N1—N4) of the two dioxime ligands lie well within the equatorial chelate plane, though at varying Co-N distances. The iodide ligand and the pyridine N atom

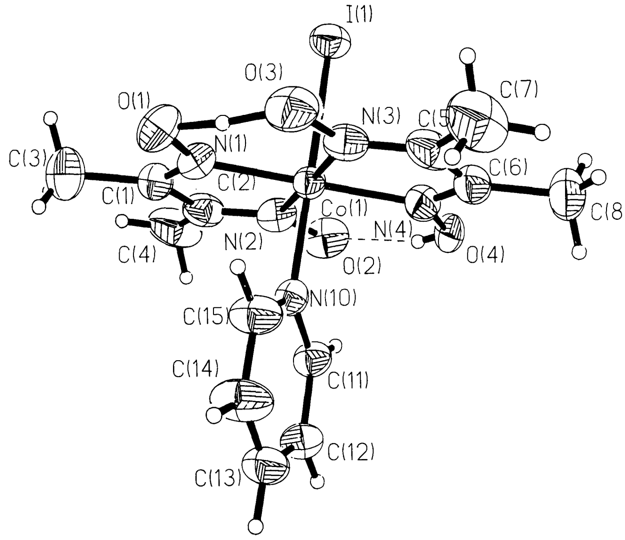

Fig. 1. Perspective view of the asymmetric neutral cobaloxime, [Co(Hdmg)$_2$I(py)], showing the unsymmetrical locations of the hydrogen atoms, HH1 (between O2 and O4), and HH2 (between O1 and O3). Open circles (arbitrary radius) represent H atoms. Ellipsoids have been drawn at 50% probability.

Table 3. Bond Lengths (l/Å) and Angles (θ/°) for $C_{13}H_{19}CoIN_5O_4$

Bond length (l/Å)		Bond angles (θ/°)			
Co1–I1	2.582(1)	I1–Co1–N1	89.6(1)	N1–C1–C3	121.6(5)
Co1–N1	1.887(4)	I1–Co1–N2	87.9(1)	C2–C1–C3	125.1(5)
Co1–N2	1.893(4)	I1–Co1–N3	90.1(1)	N2–C2–C1	112.9(5)
Co1–N3	1.895(4)	I1–Co1–N4	89.7(1)	N2–C2–C4	122.2(5)
Co1–N4	1.900(4)	I1–Co1–N10	178.3(1)	C1–C2–C4	124.9(5)
Co1–N10	1.982(4)	N1–Co1–N2	81.7(1)	Co1–N3–O3	123.2(3)
N1–O1	1.342(6)	N1–Co1–N3	98.1(1)	Co1–N3–C5	116.1(4)
N1–C1	1.290(7)	N1–Co1–N4	179.3(2)	O3–N3–C5	120.6(4)
N2–O2	1.337(6)	N1–Co1–N10	90.2(2)	Co1–N4–O4	122.7(3)
N2–C2	1.308(7)	N2–Co1–N3	178.0(2)	Co1–N4–C6	115.2(4)
N3–O3	1.334(6)	N2–Co1–N4	98.5(2)	O4–N4–C6	122.0(4)
N3–C5	1.301(7)	N2–Co1–N10	90.4(2)	N3–O3–HH2	103.8(3)
O1–HH2	1.337(4)	N3–Co1–N4	81.7(2)	N4–O4–HH1	101.3(5)
O3–HH2	1.168(4)	H3–Co1–N10	91.6(2)	N3–C5–C6	112.8(5)
O4–HH1	0.627(4)	N4–Co1–N10	90.5(2)	N3–C5–C7	122.6(5)
N4–O4	1.325(6)	Co1–N1–O1	122.3(3)	C6–C5–C7	124.6(5)
N4–C6	1.302(7)	Co1–N1–C1	116.3(4)	N4–C6–C5	114.0(5)
C1–C2	1.451(8)	Co1–N2–O2	122.1(3)	N4–C6–C8	121.7(5)
C1–C3	1.508(8)	Co1–N2–C2	115.7(4)	C5–C6–C8	124.3(5)
C5–C6	1.448(8)	O2–Co1–C2	122.2(4)	Co1–N10–C11	120.6(3)
C5–C7	1.512(9)	N1–O1–HH2	104.0(3)	Co1–N10–C15	120.6(3)
C6–C8	1.507(8)	N1–C1–C2	113.3(5)	C11–N10–C15	118.8(4)
C11–C12	1.372(6)				
C12–C13	1.380(7)				
C13–C14	1.383(8)				
C14–C15	1.377(7)				
C11–N10	1.328(6)				
C15–N10	1.329(6)				

(N10) occupy the axial positions, respectively above and below the chelate plane. The segment of line defined by I–Co–N10 is slightly bent by an angle of 178.3°, and so is the segment formed by N3–Co–N2 (178.0°). But the segment defined by N1–Co–N4 is virtually rectilinear (179.3°), quite in accordance with what is usually observed in cobaloximes of this type.[2,3] It is worth noting that the axial Co–N bonding is substancially weaker (the distance Co–N10=1.982 Å being noticeably longer), compared to the equatorial Co–N bondings with bond lengths ranging, as to be expected, from 1.887 to 1.900 Å.

The two intramolecular O–H–O bridges are not equivalent, and this is revealed by the fact that the distances between the bridging H atoms and the corresponding O atoms are different. Whereas, indeed, HH2 may be regarded as being chemically bonded (though unsymmetrically) as well to O1 (O1–HH2=1.337 Å) as to O3 (O3–HH2=1.168 Å), HH1 turns out to be effectively bonded to O4 only (O4–HH1=0.627 Å), the distance O2–HH1=1.878 Å being, by comparison, too large to account for a genuine chemical bonding involving an H atom. Yet, the O···O separations within these bridges (O1···O3=2.479 and O2···O4=2.488 Å) are rather closely comparable, and fall well within the range usually observed in related cobaloximes.[2,3] Furthermore, the remote CH_3 groups of the dimethylglyoxime ligands adopt a conformation which precludes any symmetry relation among themselves. This state of affairs, combined with the unsymmetrical arrangement of the O–H–O bridges, necessarily causes the $[Co(Hdmg)_2I(py)]$ molecule as a whole to possess no symmetry at all. Clearly, one is dealing here with an interesting *asymmetric cobaloxime* which, therefore, appears to offer the doubly attractive potential of being a chemical substance closely related to vitamin B_{12}, and a versatile chiroptical system as well.

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9) Observed and calculated structure factors (12 pages), atomic parameters of hydrogen atoms and anisotropic thermal parameters[10] have been deposited as Document No. 8967 at the Office of the Editor of Bull. Chem. Soc. Jpn.

10) Anisotropic thermal parameters defined as:

$$e^{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+\cdots\cdots+2hka^*b^*U_{12})}.$$