Crystal Structure and Thermal Study of the Aqua(butyl)cobaloxime/α-Cyclodextrin Inclusion Complex

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(Received February 17, 1999)

The crystal structure of the aqua(butyl)cobaloxime/α-cyclodextrin inclusion complex was determined by single X-ray diffraction. It crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 14.083(3), b = 19.237(4), c = 24.517(5) Å and Z = 4. A thermogravimetric analysis has indicated that the thermal stability of the aqua(butyl) cobaloxime was increased in its α-cyclodextrin inclusion complex.

Organocobalt compounds known as alkylcobaloximes, which have a σ-type cobalt-carbon bond, have been extensively studied as models for coenzyme B_{12}. However, previous investigations were restricted to simple molecules, themselves.[1] Recently, a series of alkyl(aqua)cobaloxime/α-cyclodextrin inclusion complexes have been synthesized and characterized by our research group.[2] Cyclodextrins (CDs) are a class of cyclic oligosaccharide molecules normally comprising six(α), seven(β), and eight(γ) α-(1→4) linked D(+)-glucopyranose units, with a toroidal hydrophobic cavity capable of including a variety of inorganic and organic guest species, and forming rather stable compounds. They have been extensively studied as both molecular receptors and enzyme models.[3] However, there are only a few reports on the crystal structure of inclusion complexes bearing organometallic compounds as guest molecules.[4]

We now report on the crystal structure of [Co(Hdmg)$_2$(n-C_4H_9)H_2O]/α-CD (H_2dmg = dimethylglyoxime) together with its thermogravimetric analysis result. A structural comparison with [Co(Hdmg)$_2$(n-C_3H_7)H_2O]/α-CD and a thermal-stability comparison with [Co(Hdmg)$_2$(n-C_4H_9)-H_2O]/α-CD are also discussed.

Experimental

Synthesis of Compounds. All chemicals were of A.R. or C.P. grade. [Co(Hdmg)$_2$(n-C_4H_9)H_2O] was prepared by a standard reductive alkylation method.[5] Its α-CD inclusion complexes was synthesized by the following procedure.[2b] 1 : 1 molar ratio [Co(Hdmg)$_2$(n-C_4H_9)H_2O] and α-CD were dissolved in water by constant stirring for 30 min at 50 °C. The resulting solution was filtered and the filtrate was stored at 25 °C in the dark. One week later, red crystals were obtained. Anal. Found: C, 42.6; H, 6.80; N, 4.35%. Calcd for $C_{48}H_{87}CoN_4O_{36}$: C, 42.55; H, 6.45; N, 4.15%.

X-Ray Crystallography. The raw intensities for [Co(Hdmg)$_2$(n-C_4H_9)H_2O] were collected on a Rigaku RAXIS-IIC imaging-plate system with a rotating-anode generator powered at 50 kV and 90 mA (Mo $K\alpha$, λ = 0.7103 Å). Details of the crystal data and intensity collection are summarized in Table 1. The structure was solved by direct and difference Fourier methods and refined by full-matrix least-squares calculations using the SHELXS-86[6] and SHELXL-93[7] programs. Hydrogen atoms were treated as riding on their attached atoms, and were refined isotropically. The oxygen

Table 1. Crystal Data and Structure Refinement for [Co(Hdmg)$_2$(n-C_4H_9)H_2O]/α-CD

Empirical formula	$C_{48}H_{85}CoN_4O_{35}\cdot 8H_2O$
Formula weight	1481.26
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a/Å	14.083(3)
b/Å	19.237(4)
c/Å	24.517(5)
α/deg	90
β/deg	90
γ/deg	90
Volume/Å^3	6642(2)
Z	4
Density (calculated)/Mg m^{-3}	1.481
Absorption coefficient/mm^{-1}	0.367
F(000)	3152
Crystal size/mm	0.30 × 0.20 × 0.20
θ range for data collection/deg	1.35 to 26.80
Index ranges	$-17 \le h \le 17$, $0 \le k \le 24$, $-31 \le l \le 31$
Reflections collected	22497
Independent reflections	12829 [R(int) = 0.0255]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12829 / 0 / 874
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0528, $wR2$ = 0.1552
R indices (all data)	$R1$ = 0.0556, $wR2$ = 0.1608
Largest diff. peak and hole/eÅ^{-3}	0.852 and −0.505

atom O16 disordered (O16A and O16B are occupied 0.7 and 0.3, respectively). The complete F_o–F_c data are deposited as Document No. 73029 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Thermogravimetric Analysis. A thermogravimetric analysis was performed on a SDT 2960 simultaneous TGA-DTA instrument. The analysis was carried out at a heating rate of 10 °C min^{-1} in a dynamic nitrogen flow of 100 cm^3 min^{-1}.

Results and Discussion

Crystal Structure. The molecular structure of [Co(Hdmg)$_2$(*n*-C$_4$H$_9$)H$_2$O] is depicted in Fig. 1. The final atomic coordinates and isotropic thermal parameters for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3.

As shown in Fig. 1, the butyl group is inserted into an

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 ×10^3) for [Co(Hdmg)$_2$(*n*-C$_4$H$_9$)-H$_2$O]/α-CD

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Co1	864(1)	5675(1)	−517(1)	33(1)	C42	5434(3)	4039(2)	−73(1)	36(1)
N1	−396(2)	5879(2)	−296(1)	40(1)	C43	4387(3)	3864(2)	−40(1)	35(1)
N2	240(2)	4855(2)	−765(1)	37(1)	C44	4193(3)	3275(2)	364(1)	35(1)
N3	2098(2)	5462(2)	−751(1)	41(1)	C45	4670(3)	3394(2)	910(1)	37(1)
N4	1503(2)	6489(2)	−272(1)	39(1)	C46	4634(4)	2748(2)	1257(2)	53(1)
O1	−651(2)	6473(2)	−16(1)	56(1)	O35	2316(2)	2367(1)	837(1)	50(1)
O2	705(2)	4305(1)	−982(1)	45(1)	O44	3188(2)	3260(1)	438(1)	35(1)
O3	2328(2)	4846(2)	−1002(2)	63(1)	O32	2244(2)	3110(2)	−534(1)	51(1)
O4	1063(2)	6987(1)	14(1)	47(1)	O33	363(2)	3372(2)	−133(1)	46(1)
C1	−1059(3)	5458(2)	−439(2)	43(1)	O36	2269(4)	2540(4)	2031(2)	119(2)
C2	−677(3)	4832(2)	−715(2)	41(1)	C31	2699(3)	2639(2)	346(2)	40(1)
C3	−2084(3)	5572(3)	−340(1)	60(1)	C32	1883(3)	2790(2)	−51(2)	42(1)
C4	−1292(3)	4240(3)	−889(2)	56(1)	C33	1164(3)	3276(2)	208(1)	37(1)
C5	2762(3)	5920(2)	−674(2)	46(1)	C34	842(3)	3018(2)	765(1)	38(1)
C6	2387(3)	6536(2)	−384(2)	44(1)	C35	1709(3)	2853(2)	1120(2)	43(1)
C7	3769(3)	5824(3)	−833(2)	63(1)	C36	1449(4)	2520(3)	1660(2)	75(2)
C8	3003(4)	7136(3)	−235(3)	71(1)	O25	−504(2)	3548(1)	1825(1)	39(1)
C1G	1080(3)	5258(2)	224(2)	50(1)	O34	308(2)	3577(1)	999(1)	37(1)
C2G	2001(5)	5217(4)	469(3)	91(2)	O22	−1381(2)	3837(2)	436(1)	55(1)
C3G	1941(5)	5040(4)	1088(3)	99(3)	O23	−1812(2)	5130(2)	983(1)	50(1)
C4G	2857(6)	4985(6)	1316(4)	127(3)	O26	676(2)	3796(2)	2757(1)	58(1)
O65	2802(2)	7088(1)	2645(1)	38(1)	C21	−573(3)	3447(2)	1255(1)	37(1)
O14	1531(2)	7120(1)	2027(1)	34(1)	C22	−1307(3)	3944(2)	1017(2)	41(1)
O62	2168(2)	8448(1)	1667(1)	44(1)	C23	−1052(2)	4688(2)	1149(1)	36(1)
O63	3942(2)	7976(1)	1267(1)	48(1)	C24	−864(3)	4778(2)	1761(1)	34(1)
O66	4474(2)	6473(2)	3055(1)	58(1)	C25	−172(2)	4232(2)	1976(1)	34(1)
C61	2166(3)	7517(2)	2338(1)	35(1)	C26	−96(3)	4224(2)	2592(1)	45(1)
C62	2748(3)	7981(2)	1963(1)	35(1)	O15	−354(2)	6038(1)	2644(1)	40(1)
C63	3370(3)	7535(2)	1588(1)	34(1)	O24	−463(2)	5469(1)	1810(1)	35(1)
C64	3965(2)	7034(2)	1929(1)	32(1)	O12	−1581(2)	6571(2)	1420(1)	52(1)
C65	3350(2)	6610(2)	2314(1)	33(1)	O13	−205(2)	7656(1)	1571(1)	43(1)
C66	3857(3)	6121(2)	2690(2)	44(1)	O16A	996(5)	5701(3)	3370(2)	80(2)
O55	5873(2)	6032(1)	1754(1)	41(1)	O16B	625(10)	6701(6)	3429(3)	75(4)
O64	4424(2)	6563(1)	1559(1)	34(1)	C11	−903(3)	5942(2)	2168(1)	35(1)
O52	5164(2)	7182(1)	651(1)	51(1)	C12	−1016(2)	6646(2)	1894(1)	36(1)
O53	5737(2)	5947(1)	82(1)	45(1)	C13	−49(2)	6959(2)	1757(1)	33(1)
O56	5833(3)	4829(2)	2436(1)	59(1)	C14	609(2)	6960(2)	2248(1)	34(1)
C51	5420(2)	6608(2)	1502(2)	37(1)	C15	607(2)	6262(2)	2551(1)	36(1)
C52	5663(3)	6622(2)	897(2)	41(1)	C16	1035(3)	6301(3)	3121(2)	59(1)
C53	5390(2)	5940(2)	626(1)	32(1)	O1W	593(2)	6187(2)	−1281(1)	52(1)
C54	5785(2)	5324(2)	938(1)	32(1)	O2W	2084(2)	2224(2)	−1366(1)	49(1)
C55	5572(3)	5369(2)	1546(1)	36(1)	O3W	−3767(3)	4389(2)	−1367(1)	76(1)
C56	6086(3)	4817(2)	1871(2)	49(1)	O4W	−2495(3)	5189(2)	−1935(2)	80(1)
O45	5665(2)	3562(1)	827(1)	39(1)	O5W	811(5)	5921(5)	−2428(3)	186(4)
O54	5299(2)	4724(1)	723(1)	33(1)	O6W	2236(4)	7236(3)	−1635(3)	118(2)
O42	5591(2)	4653(1)	−381(1)	46(1)	O7W	2671(6)	5406(6)	−2174(4)	199(5)
O43	4066(2)	3662(2)	−568(1)	51(1)	O8W	1111(2)	8021(1)	757(1)	51(1)
O46	5018(3)	2876(2)	1779(1)	74(1)	O9W	−1669(5)	3615(3)	−2214(2)	130(2)
C41	5816(3)	4170(2)	506(1)	35(1)					

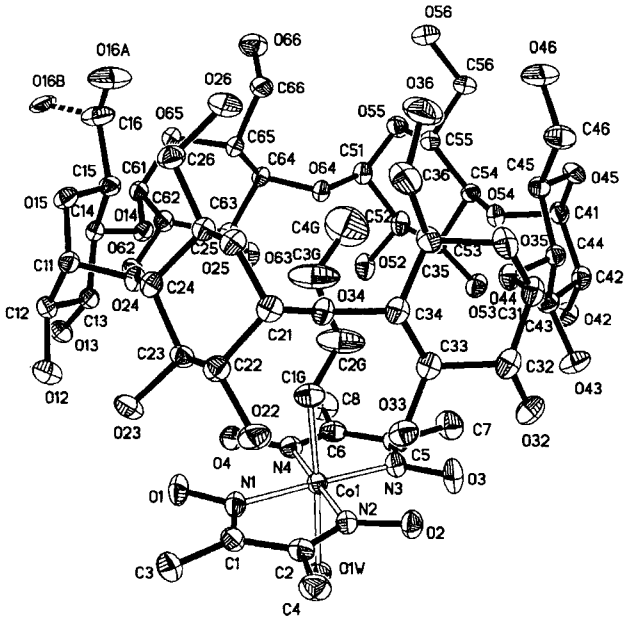

Fig. 1. Molecular structure and atom-labeling scheme for $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD.

α-cyclodextrin cavity from its secondary hydroxyl side, and the $Co(Hdmg)_2H_2O$ moiety is found outside of the cavity and near to the wider opening of α-CD. The C2G, C3G, and C4G (carbon atoms of the axial alkyl group) are 0.192, 1.640, and 2.470 Å, respectively, above the mean plane (plane 1) of the O atoms associated with the twelve secondary OH groups, while the C1G lies 0.664 Å below this plane. The four N atoms in $Co(Hdmg)_2$ are coplanar (plane 2) with a mean deviation from the best plane of 0.007 Å, and the cobalt atom is almost in the plane (0.004 Å). The geometry of $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]$ is characterized by Co1–C1G and Co1–O1W bond lengths of 2.011(4) and 2.148(3) Å, respectively, a C1G–Co1–O1W angle of 175.9(2)° and a $Co–CH_2–C_3H_7$ angle of 122.5(3)°. The Hdmg plane comprising Co1 N1, N2, O1, O2, C1, C2, C3, C4 (plane 3, mean deviation from the best plane is 0.052 Å) makes a dihedral angle of 6.3° with plane 4; the other Hdmg plane comprises Co1, N3, N4, O3, O4, C5, C6, C7, C8 (mean deviation from the plane of 0.032 Å).

Comparing the structure of $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD with its analogous compound, $[Co(Hdmg)_2(n\text{-}C_3H_7)H_2O]/\alpha$-CD,[2b] it has been found that (a) although the α-carbon (carbon atom connected directly to a cobalt atom) of $[Co(Hdmg)_2(n\text{-}C_3H_7)H_2O]/\alpha$-CD is 0.28 Å below the plane comprising twelve secondary OH groups, and that for $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD is 0.66 Å, the terminal carbon for the alkyl of $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]$ inserts into the cavity of α-CD more deeply (2.470 Å above the plane 1) than that of $[Co(Hdmg)_2(n\text{-}C_3H_7)H_2O]$ (2.05 Å above the plane); (b) The bending angle of two Hdmg planes in $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD (6.3°) is smaller than that in $[Co(Hdmg)_2(n\text{-}C_3H_7)H_2O]/\alpha$-CD (10.3°); (c) For $[Co(Hdmg)_2(n\text{-}C_3H_7)H_2O]/\alpha$-CD, the Co atom is pulled out of the plane of four equatorial N atoms toward the propyl by about 0.038 Å, while for $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD, the cobalt atom is almost in the four N plane.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD

Co1–N1	1.897(3)	Co1–N2	1.905(3)
Co1–N3	1.875(3)	Co1–N4	1.903(3)
Co1–C1G	2.011(4)	Co1–O1W	2.148(3)
N1–C1	1.285(5)	N2–C2	1.298(5)
N1–O1	1.378(4)	N2–O2	1.354(4)
N3–C5	1.298(5)	N4–C6	1.278(5)
N3–O3	1.373(4)	N4–O4	1.339(4)
C1–C2	1.483(6)	C1–C3	1.479(5)
C2–C4	1.494(6)	C5–C6	1.481(6)
C5–C7	1.482(6)	C6–C8	1.489(6)
C1G–C2G	1.432(7)	C2G–C3G	1.558(8)
C3G–C4G	1.410(10)		
N3–Co1–N1	178.66(14)	N3–Co1–N4	80.70(14)
N1–Co1–N4	100.45(14)	N3–Co1–N2	98.57(13)
N1–Co1–N2	80.28(13)	N4–Co1–N2	179.24(14)
N3–Co1–C1G	92.7(2)	N1–Co1–C1G	88.0(2)
N4–Co1–C1G	88.3(2)	N2–Co1–C1G	91.5(2)
N3–Co1–O1W	89.96(13)	N1–Co1–O1W	89.39(13)
N4–Co1–O1W	89.06(12)	N2–Co1–O1W	91.15(12)
C1G–Co1–O1W	175.9(2)	C1–N1–O1	118.0(3)
C1–N1–Co1	118.1(3)	O1–N1–Co1	123.8(3)
C2–N2–O2	119.4(3)	C2–N2–Co1	117.2(3)
O2–N2–Co1	123.4(2)	C5–N3–O3	118.6(3)
C5–N3–Co1	118.4(3)	O3–N3–Co1	123.0(2)
C6–N4–O4	120.8(3)	C6–N4–Co1	116.8(3)
O4–N4–Co1	122.4(2)	N1–C1–C2	111.9(3)
N1–C1–C3	124.8(4)	C2–C1–C3	123.3(4)
N2–C2–C1	112.1(3)	N2–C2–C4	125.2(4)
C1–C2–C4	122.6(4)	N3–C5–C6	110.8(3)
N3–C5–C7	124.5(4)	C6–C5–C7	124.6(4)
N4–C6–C5	113.2(3)	N4–C6–C8	124.8(4)
C5–C6–C8	122.0(4)	C2G–C1G–Co1	122.5(3)
C1G–C2G–C3G	111.8(5)	C4G–C3G–C2G	110.7(7)

As for the reason for the conformational difference between $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]$ and $[Co(Hdmg)_2(n\text{-}C_3H_7)H_2O]$ after alkyl is included into the cavity of α-CD, it might be related to steric interactions and the driving force for inclusion between the guest and host. It is supposed that the conformation of $[Co(Hdmg)_2(n\text{-}C_4H_9)H_2O]/\alpha$-CD, i.e. pulling the Co atom out of the 4N plane and a larger bending angle for two Hdmg units, could make the propyl insert into the cavity of α-CD more deeply, therefore experiences stronger van der waals forces and hydrophobic interactions, which are generally accepted to be responsible for the bonding of guest molecules to a CD cavity.[8] It could also be found from our present crystal-structure investigation that, from propyl to butyl, with increasing alkyl chain length the alkyl group inserts into the α-CD cavity more deeply; thus, the interactions for inclusion enhanced. The result is consistent with our former NMR studies,[2b] which showed that the longer is the alkyl chain, the larger are the formation constants (K_a) between α-CD and alkyl(aqua)cobaloxime.

Thermogravimetric Analysis. The curves of the ther-

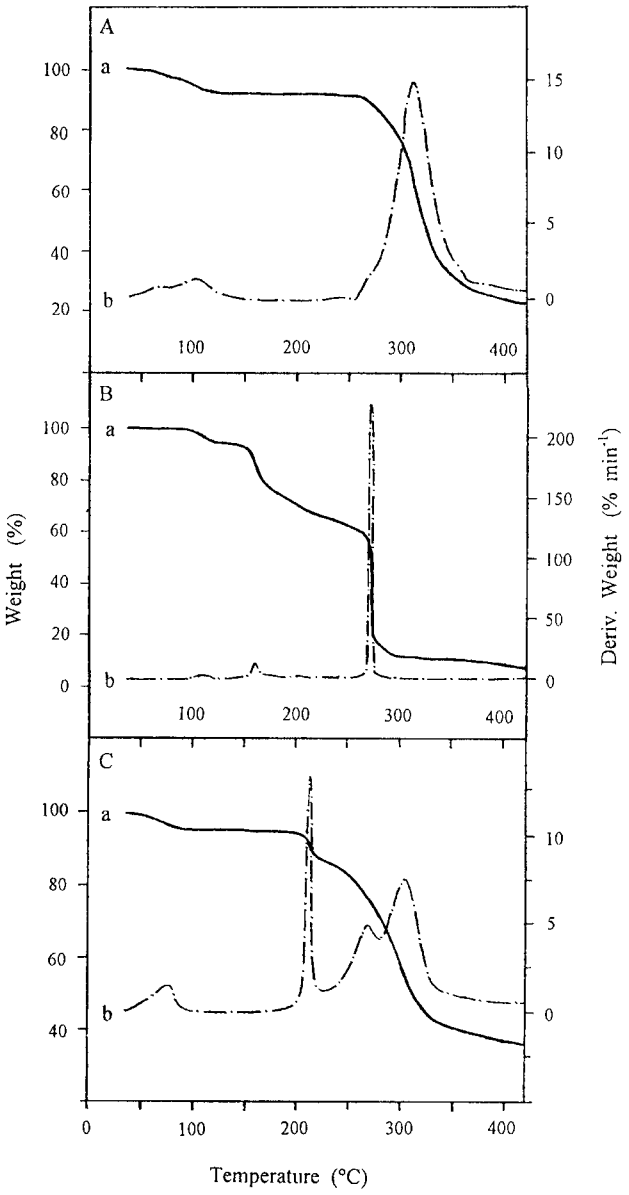

Fig. 2. (a) Thermogravimetric analysis (TGA) and (b) first derivative curves of TG scans (DTG) of (A) α-CD, (B) [Co(Hdmg)$_2$(n-C$_4$H$_9$)H$_2$O], and (C) for n-[Co(Hdmg)$_2$(n-C$_4$H$_9$)H$_2$O]/α-CD.

mogravimetric (TGA) analyses for [Co(Hdmg)$_2$(n-C$_4$H$_9$)-H$_2$O], α-CD, and [Co(Hdmg)$_2$(n-C$_4$H$_9$)H$_2$O]/α-CD are shown in Fig. 2, in which the first-derivation curves of TGA (DTG) are also shown.

It can be seen from Fig. 2b that the thermal decomposition of [Co(Hdmg)$_2$(n-C$_4$H$_9$)H$_2$O] includes three transitions, as interpreted by Brown et al.[9] (a) loss of the axial water ligand coordinated to the cobalt atom (80—125 °C); (b) loss of the axial butyl group (145—175 °C); and (c) finally, decomposition of the equatorial Hdmg ligand (175—300 °C).

In TGA scans of [Co(Hdmg)$_2$(n-C$_4$H$_9$)H$_2$O]/α-CD, there are only two gradually changing transitions. The first one at 40—110 °C is due to a dehydration process. The second transition includes three weight-loss steps according to a DTG scan. They correspond to the loss of a butyl group (180—220 °C), decomposition of the equatorial bis(dimethylglyoxime) ligand (220—280 °C) and the final decomposition of α-CD.

As shown in Fig. 2, the DTG peak temperature of the butyl group loss temperature for the inclusion complex (214 °C) is much higher than that for the guest complex, which is 161 °C. It is generally accepted that a guest compound would be stabilized against, for example, heat, light, oxidizing reagents and acidic conditions by its inclusion into the cyclodextrin cavity.[10] Our thermal analysis gives another example, that CD enhances the thermal stability of Co–C bond in alkyl(aqua)cobaloxime. This result is consistent with our former study,[11] and indicates that the butyl group is tightly included in the cavity of α-CD.

This work was supported by the National Natural Science Foundation of China (No. 29823001).

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