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Synthesis and Crystal Structures of A New Series of Intramolecular Bridged Alkylcobaloxime Complexes

Kaian Yao, Xin Zhang, Huilan Chen,* Yuhua Mei, and Yizhi Li*

Department of Chemistry, Coordination Chemistry State Key Laboratory, Nanjing University, Nanjing 210093, China

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A new series of intramolecular bridged alkylcobaloxime complexes were prepared by heating a solution of aqua-(3-bromopropyl)cobaloxime (**1**) through an intramolecular nucleophilic substitution. They are characterized by EA, ESI-MS, and ^{1}H NMR. Crystal structures of Br(O–C_3H_6–(dmgH))(dmgH)Co^{III} (**2**), [H_2O(O–C_3H_6–(dmg))($dmgH_2$)-Co^{III}]ClO_4 (**3**), [Py(O–C_3H_6–(dmg))($dmgH_2$)Co^{III}]ClO_4 (**4**), [Bzm(O–C_3H_6–(dmg))($dmgH_2$)Co^{III}]ClO_4 (**5**), and Im(O–C_3H_6–(dmg))(dmgH)Co^{III} (**6′**) were determined by X-ray diffraction. It is revealed that an intramolecular tri-methylene bridge exists between cobalt and one of the equatorial oxime oxygens forming a six-membered ring in the complexes. Additionally, the axial bases have some influences in their structure parameters, for example, Co–L bond lengths; folding angles in equatorial ligands; hydrogen atom positions in O–H–O bridge; and the orientations of those L planes with respect to the equatorial planes.

Introduction

Coenzyme B_{12} (5′-dexoyadenosylcobalamin, Adocbl) is one of the known organometallic complexes in nature. It serves as a cofactor for certain enzymatic reactions in biological systems, i.e., the intramolecular rearrangements or the reduction of nucleotide acid.[1] The widely accepted mechanism for the coenzyme B_{12} catalytic rearrangement reaction is that homolytic dissociation of the Co−C bond of coenzyme B_{12} generates Cob(II)alamin and a 5′-deoxyadenosyl radical ($AdCH_2$•). This radical then abstracts a hydrogen atom from the substrate to produce a substrate radical and 5′-deoxyadenosine ($AdCH_3$). Next, an electronegative group migrates to an adjacent carbon atom in the substrate radical, and the product radical recaptures a hydrogen atom from the $AdCH_3$. Finally, the produced $AdCH_2$• recombines with Co(II) to complete the catalytic circle. The key step of the above reactions is the cleavage of Co−C bond to produce a 5′-deoxyadenosyl radical, which is initiated by the distortion of corrin ring and plane folding of the cofactor induced by the interaction between substrate and enzyme.[2] Previous investigations had shown that the rate of homolytic cleavage of the Co−C bond in the enzyme-bond cofactor is about 10^{11-13} times larger than that in the absence of a cofactor.[3,4] Recently, the X-ray data for methylmalonyl-CoA mutase,[5,6] glutamate mutase,[7] and diol dehydratase[8] revealed that distances from the Co to the radical centers on substrate and product are 6−8 Å in the three B_{12} enzymes. Further, the former model investigations had provided evidence that, in the absence of Co(II), such kinds of radical did not isomerize.[9,10] Accordingly, it is of interest to mimic the situation of the holo-enzyme where the C-center radical formed from homolysis of the Co−C bond stays in the proximity of a Co(II) and allows the cobalt intermediate to assist in group migration.[11,12] Therefore, the synthesis and investigation of the intramolecular bridged organo-cobalt B_{12} models were performed, in which an alkyl

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* Authors to whom correspondence should be addressed. E-mail: hlchen@nju.edu.cn (H.C.); llyyjz@nju.edu.cn (Y.L.).

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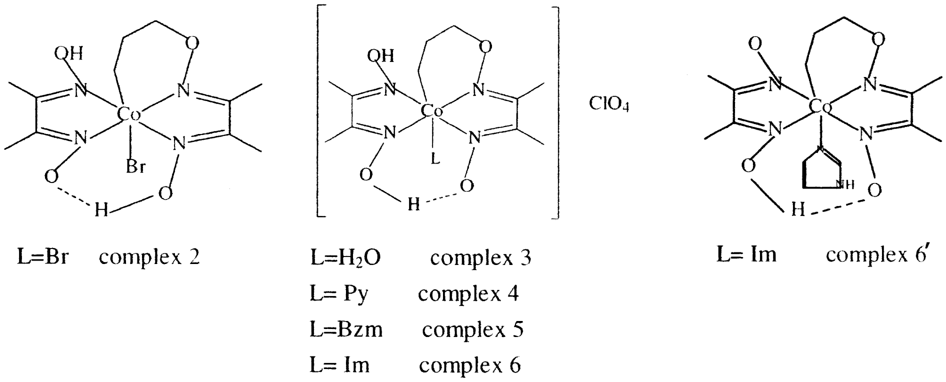

Figure 1. Schematic representation of the intramolecular bridged alkylcobaloxime complexes.

ligand links to the equatorial plane and the carbon radicals that came from homolysis of the Co−C bond will be retained in the proximity of the Co^{II}-complex. Comparing the structure and properties of these species to those of the nonbridged models might help to understand the role of the Co(II) in B$_{12}$-catalyzed 1,2-exchange. In past years, several hundreds of coenzyme B$_{12}$ models have been synthesized and investigated.[13−16] However, only a few of cobaloxime, Cocosta, and Cosalen complexes with bridged structures have been reported.[17−22] To our knowledge, very few of them have crystal structures that were determined. In our present work, a new series of intramolecular bridged alkylcobaloxime complexes with different L groups (Br, H$_2$O, Py, Bzm, Im) were prepared and characterized (Figure 1). Their crystal structures were studied by X-ray diffraction. Influences of the L ligand on the structures and comparison of the structural features with those of ordinary alkylcobaloximes were addressed.

Experimental Section

*Caution: The perchlorates are potentially explosive. Only a small amount of material should be prepared at one time, and it should be handled with care. All manipulations were performed in the dark to avoid Co−C bond cleavage. All chemicals used were of analytical reagent grade unless stated otherwise. Aqua-(3-bromopropyl)cobaloxime **1** was prepared by reductive alkylation as described in the literature.*[23]

Preparation of Bromo(*O*-trimethylene-dimethyloxime)(dimethylglyoximato)cobalt(III), Br(O−C$_3$H$_6$−(dmgH)(dmgH))-Co^{III} (Complex 2). A 1 g portion of **1** was dissolved in 500 mL water and heated at 80 °C with stirring for 1 h. The solution was filtered, and the filtrate was rotary evaporated under reduced pressure until some precipitation occurred. The products were recrystallized from methanol−water (4:1), and two weeks later, dark red crystals (0.37 g, 39%) were obtained. Anal. Calcd for C$_{11}$H$_{20}$-BrCoN$_4$O$_4$: C, 32.13; H, 4.90; N, 13.62. Found: C, 32.22; H, 5.07; N, 13.52. UV−vis (methanol/water, nm): 419.0, 452.8. Positive-ion ESI-MS: *m/z* at 331.0, [M$_2$ − Br]$^+$. ^{1}H NMR (D$_2$O) ppm: 4.75 (m, 1H, H(9)) behind in water peak; 3.92 (m, 1H, H(9)); 2.59 (m, 1H, H(11)); 2.48 (s, 3H, C(1)H$_3$); 2.34 (s, 3H, C(4)H$_3$); 2.33 (s, 3H, C(8)H$_3$); 2.25 (s, 3H, C(5)H$_3$); 1.91 (m, 1H, H(11)); 1.66 (m, 1H, H(10)); 0.526 (m, 1H, H(10)).

Preparation of Perchlorate Aqua(*O*-trimethylene-dimethyloximato)(dimethylglyoxime)cobalt(III) [H$_2$O (O−C$_3$H$_6$−(dmg)-(dmgH$_2$)Co^{III})]ClO$_4$ (Complex 3). A 1 g portion of **2** (2.4 mmol) was dissolved in 400 mL water, and then, a 20 mL aqueous solution which contained 0.4 g AgNO$_3$ (2.4 mmol) was added. The resulting suspension was stirred well for 1 day and filtered. The clear red filtrate was treated with 10 mL of aqueous solution containing 0.3 g NaClO$_4$ (2.4 mmol). After stirring for 0.5 h, the volume of this solution was reduced by a rotary evaporator until precipitation occurred. The products were recrystallized form methanol−water (4:1), and two weeks later, we obtained dark red crystals, 0.45 g. The yield is about 42%. Anal. Calcd for C$_{11}$H$_{22}$CoN$_4$O$_9$Cl: C, 29.44; H, 4.94; N, 12.48. Found: C, 29.42; H, 4.87; N, 12.56. UV−vis (methanol/water, nm): 419.8, 450.8. Positive-ion ESI-MS: *m/z* at 331.0, [M$_3$ − ClO$_4$ − H$_2$O]$^+$. ^{1}H NMR (D$_2$O) ppm: 4.78 (m, 1H, H(9)) behind in water peak; 3.93 (m, 1H, H(9)); 2.60 (m, 1H, H(11)); 2.49 (s, 3H, C(1)H$_3$); 2.35 (s, 3H, C(4)H$_3$); 2.34 (s, 3H, C(8)H$_3$); 2.27 (s, 3H, C(5)H$_3$); 1.92 (m, 1H, H(11)); 1.68 (m, 1H, H(10)); 0.53 (m, 1H, H(10)).

Preparation of Perchlorate Pyridine-(*O*-trimethylene-dimethyloximato)(dimethylglyoxime)cobalt(III), [Py(O−C$_3$H$_6$−(dmg))(dmgH$_2$)Co^{III}]ClO$_4$ (Complex 4). This complex was prepared following the preceding procedures by using pyridine as axial L. We obtained dark red crystals, 0.58 g. The yield is about 47%. Anal. Calcd for C$_{16}$H$_{25}$CoN$_5$O$_8$Cl: C, 37.69; H, 4.94; N, 13.73. Found: C, 37.71; H, 4.90; N, 13.59. UV−vis (methanol/water, nm): 416.6, 449.6. Positive-ion ESI-MS: *m/z* at 331.0, [M$_4$ − ClO$_4$ − C$_5$H$_5$N]$^+$ and 409.9, [M$_4$ − ClO$_4$]$^+$. ^{1}H NMR (DCCl$_3$) ppm: 8.41 (d, 2H, H(12), H(16)); 7.89 (t, 1H, H(14)); 7.54 (m, 2H, H(13), H(15)); 4.98 (m, 1H, H(9)); 4.08 (m, 1H, H(9)); 2.52 (s, 3H, C(1)-H$_3$); 2.34 (s, 3H, C(4)H$_3$); 2.27 (s, 3H, C(8)H$_3$); 2.14 (s, 3H, C(5)-H$_3$); 1.72 (m, 3H, C(11)H$_2$, H(10)); 1.08 (m, 1H, H(10)).

Preparation of Perchlorate Benzimidazole-(*O*-trimethylene-dimethyloximato)(dimethylglyoxime)cobalt(III), [Bzm(O−C$_3$H$_6$−(dmg))(dmgH$_2$)Co^{III}]ClO$_4$ (Complex 5). This complex was prepared following the preceding procedures by using bezimidazole

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as axial L. We obtained orange crystals, 0.6 g. The yield is about 45%. Anal. Calcd for $C_{18}H_{26}CoN_6O_8Cl$: C, 39.39; H, 4.77; N, 15.31. Found: C, 39.52; H, 4.69; N, 15.47. UV−vis (methanol/water, nm): 416.4, 448.4. Positive-ion ESI-MS: *m/z* at 331.0, $[M_5 - ClO_4 - C_7H_6N_2]^+$ and 448.9, $[M - ClO_4]^+$. ^1H NMR ($DCCl_3$) ppm: 8.144 (s, 1H, H(12)); 7.70 (d, 1H, H(17)); 7.47 (d, 1H, H(14)); 7.31 (q, 1H, H(16)); 7.26 (q, 1H, H(15)); 4.99 (m, 1H, H(9)); 4.09 (m, 1H, H(9)); 2.462 (s, 3H, $C(1)H_3$); 2.36 (s, 3H, $C(4)H_3$); 2.30 (m, 1H, H(11)); 2.17 (s, 3H, $C(8)H_3$); 2.06 (s, 3H, $C(5)H_3$); 1.91 (m, 1H, H(11)); 1.64 (m, 1H, H(10)); 1.15 (m, 1H, H(10)).

Preparation of Perchlorate Imidazole-(*O*-trimethylene-dimethyloximato)(dimethylglyoxime)cobalt(III) $[Im(O-C_3H_6-(dmg))(dmgH_2)Co^{III}]ClO_4$ (Complex 6) and Imidazole-(*O*-trimethylene-dimethyloximato)(dimethylglyoximato)cobalt(III) $Im(O-C_3H_6-(dmg))(dmgH)Co^{III}$ (Complex 6′). The complexes were prepared following the preceding procedures by using imidazole as axial L. We obtained orange solid **6** (0.42 g, yield 35%) and a small amount of orange crystals **6′**. Anal. Calcd for $C_{14}H_{24}CoN_6O_8Cl$ (**6**): C, 33.71; H, 4.85; N, 16.85. Found: C, 33.73; H, 4.94; N, 16.83. UV−vis (methanol/water, nm): 406.4. Positive-ion ESI-MS: *m/z* at 398.9, $[M_6 - ClO_4]^+$ and 331.1, $[M_6 - ClO_4 - C_3H_4N_2]^+$. Anal. Calcd for $C_{14}H_{23}CoN_6O_4$ (**6′**): C, 42.22; H, 5.82; N, 21.10. Found: C, 42.18; H, 5.72; N, 21.27. UV−vis (methanol/water, nm): 415.2. Positive-ion ESI-MS: *m/z* at 398.8, $[M_{6'} + H]^+$ and 330.9, $[M_{6'} + H - C_3H_4N_2]^+$. ^1H NMR ($DCCl_3$) ppm: 8.15 (s, 1H, H(14)); 7.70 (d, 1H, H(12)); 7.48 (d, 1H, H(13)); 5.00 (m, 1H, H(9)); 4.15 (m, 1H, H(9)); 2.46 (s, 3H, $C(1)H_3$); 2.35 (s, 3H, $C(4)H_3$); 2.28 (m, 1H, H(11)); 2.16 (s, 3H, $C(8)H_3$); 2.05 (s, 3H, $C(5)H_3$); 1.92 (m, 1H, H(11)); 1.72 (m, 1H, H(10)); 1.15 (m, 1H, H(10)).

X-ray Structure Determination. Intensity data were collected at 293 K on a Bruker SMART CCD area detector diffractometer operating in the $\omega-2\theta$ scan mode with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

The structure was solved by direct methods using the program SHELXTL.[24] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures.[25] The two bridging oxime protons were found in difference Fourier map, while the other hydrogen atom positions were fixed geometrically at a calculated distance and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless.

Results and Discussion

Synthesis. Usually the reactions of cobalt(III) intermediates and the pendant ω-alkenyl side chain or an interligand nucleophilic addition were involved in preparation of the intramolecular alkylated Cosalen[19] or Cocosta complexes.[22] In our previous investigation, heating a solution of aqua-(3-bromopropyl)cobaloxime and β-cyclodextrin, a novel β-cyclodextrin inclusion complex crystal with bridged aqua-cobaloxime has been found in addition to the normal inclusion complex.[26] To obtain the bridged cobaloxime compound, one of the methods is to remove the β-cyclodextrin by using methanol extraction with the product undergoing further purification. The above route and removing β-cyclodextrin to prepare bridged cobalt complex are tedious and of low yield. After careful examination of the thermolysis behavior of aqua-(3-bromopropyl)cobaloxime (complex **1**), we found that in the absence of β-cyclodextrin simply heating the solution of **1** will also cause the cyclization to form the bridged cobaloxime complex **2**.[27] Further investigation revealed that the above reaction was accelerated through increasing both temperature and polarity of the solvent.[28] In this study, complex **2** was prepared by heating an aqueous solution of aqua(3-bromopropyl)cobaloxime (complex **1**) at 80 °C. This improved method is a little different from a previous published method by Song, et al.,[27] in which **1** was dissolved in methanol/water(v/v 4:1) and heated at 50 °C. Complexes **3**−**6** were fabricated through removing the axial bromine atom of complex **2** and then adding a different L group. The synthetic route with its possible mechanism is presented in Scheme 1. It is observed that, during the heating process, complex **1** lost its axial H_2O ligand first.[29] An intramolecular nucleophilic substitution reaction then follows, in which elimination of an HBr molecule is accompanied with ring formation. Last, the Br^- occupied the axial position, and complex **2** came into being. For complexes **3**−**6**, the axial ligand Br of complex **2** was removed through addition of $AgNO_3$ first. Next, the L ligands (L = H_2O for **3**, L = Py for **4**, L = Bzm for **5**, L = Im for **6**) were introduced for coordination with Co(III). Finally, the intramolecular bridged cobaloxime cation combined with the ClO_4 anion to give the relevant complexes.

X-ray Diffraction Structure Analysis. Crystal data for **2**−**6′** are listed in Table 1. The selected bond lengths (Å) and angles (deg) are listed in Table 2. The ORTEP drawings with atomic numbering for **2**−**6′** are shown in Figure 2. It should be noted that crystal **6′** is neutral without perchlorate anion because there are two oximes with charge −1.

It can be seen from Figure 2 that the five bridged complexes are similar in structure. Their molecules have octahedral configuration around the cobalt with one alkyl C; one Br, O, or N atom from L as the axial ligands; and four N atoms of two oxime units as the equatorial ligands, respectively. One of the oxygens in dimethylglyoxime displaced from the four N mean plane of the oxime formed a six-membered ring with the axial alkyl and cobalt.

For comparison, we summarized the structure parameters of them in Table 3. It can be seen that the four N atoms in the equatorial ligands have a greater displacement from the mean plane. And due to forming six-membered rings, all the O1 atoms deviate from the N1N2N3N4 planes (0.4−0.6 Å), which are obviously larger than those in the nonbridged alkylcobaloximes. Also, the N−O bond lengths related to the rings in the complexes are longer than those in the equatorial ligand. It is noted that the angles of C−Co−L deviate from 180°. The $Co-C_{11}-C_{10}$ and $C_9-C_{10}-C_{11}$ angles involving the bridge are all larger than that of ideal

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Scheme 1. Possible Mechanism for Formation of Bridged Complex **2** (a) and **3**−**5** (b)

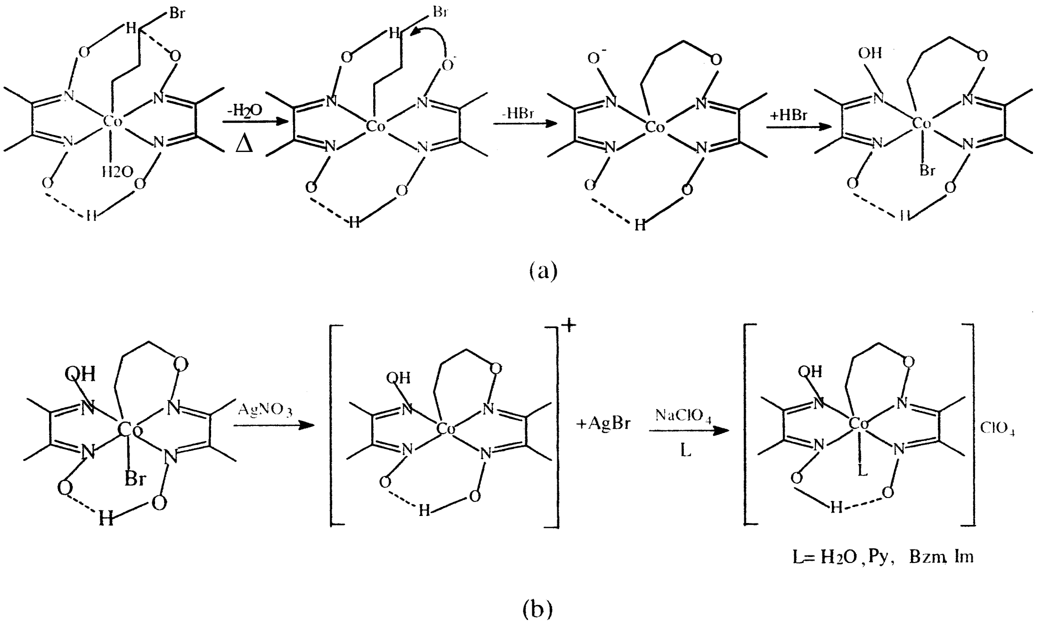

Table 1. Crystal Data for Complexes **2**−**6′**

	2	**3**	**4**	**5**	**6′**
formula	$C_{11}H_{20}Br$-CoN_4O_4	$ClO_4C_{11}H_{22}$-CoN_4O_5	$ClO_4C_{16}H_{25}$-CoN_5O_4	$C_{18}H_{26}CoN_6O_4$-ClO_4, H_2O	$C_{14}H_{23}Co$-N_6O_4, H_2O
fw	411.14	448.71	509.79	566.84	416.33
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	7.2651(8)	6.3450(10)	8.3150(10)	7.6630(10)	8.6522(9)
b [Å]	10.4394(12)	13.1610(10)	11.8120(10)	12.6790(10)	8.9895(9)
c [Å]	20.293(2)	21.071(2)	22.357(2)	13.3530(10)	23.872(2)
V [$Å^3$]	1539.1(3)	1747.3(3)	2184.9(4)	1260.4(2)	1834.0(3)
α [deg]	90	90	90	91.770(10)	90
β [deg]	90	96.770(10)	95.710(10)	101.750(10)	98.976(2)
γ [deg]	90	90	90	96.390(10)	90
Z	4	4	4	2	4
D(calcd) [g/cm^3]	1.774	1.706	1.550	1.494	1.508
μ(Mo Kα) [mm]	3.731	1.190	0.960	0.845	0.974
F(000)	832	928	1056	588	872
cryst size [mm^3]	0.12 × 0.15 × 0.20	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
θ min−max [deg]	2.0, 25.0	1.8, 25.0	2.0, 25.0	2.2, 25.0	2.4, 25.0
hkl ranges	−8 to 8 −11 to 12 −24 to 15	−7 to 6 −15 to 15 −25 to 24	−9 to 9 −14 to 14 −22 to 26	−9 to 8 −15 to 14 0 to 15	−9 to 10 −8 to 10 −28 to 23
total data	7689	8780	10922	6467	9141
unique data	2717	3071	3839	4366	3235
R_{int}	0.040	0.043	0.031	0.042	0.030
obsd data [$I > 2.0\ \sigma(I)$]	2220	2296	2966	3471	2603
N_{ref}, N_{par}	2717, 194	3071, 241	3839, 292	4366, 358	3235, 239
R	0.0356	0.0417	0.0526	0.0558	0.0401
wR2	0.0613	0.0948	0.1511	0.1485	0.1028
S	0.90	0.95	1.05	1.01	0.99
min and max resd dens [e/$Å^3$]	−0.32, 0.70	−0.44, 0.48	−0.38, 0.83	−0.41, 0.76	−0.25, 0.52

sp^3 tetrahedral (109.5°). In addition, there are some different structural features among these five complexes, which we summarized in the following paragraphs.

(a) The Deformation of the Co(DH)$_2$ Units. Generally, for alkylcobaloxime complexes, the Co(DH)$_2$ unit may undergo geometrical deformations, which may be represented by the displacement of the cobalt out of the plane of 4-nitrogen equatorial donors (*d*) and by the bending angle between the two DH units (α).[13−16] These two parameters appear to be influenced by the electronic and steric properties of the axial ligands. Usually, the positive values of α and *d* indicate that the bending of the equatorial ligand is toward the alkyl group and that the displacement of Co out of the 4N equatorial donor set is toward L. From Table 3, we can see that the Co atoms deviate 4N planes and the folding exists in the two (DH)$_2$ units. It is worth noting that only the α and *d* values of complex **3** (L = H_2O), which has smaller water molecule as an axial ligand, are presumed to be negative. This indicates that distortions of the Co(DH)$_2$ moiety are related to the relative bulk extent of the axial

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2**−**6′**

	2 (L = Br1)	**3** (L = O5)	**4** (L = N5)	**5** (L = N5)	**6′** (L = N5)
L−Co1	2.5164(8)	2.092(2)	2.086(3)	2.058(3)	2.0391(19)
Co1−N1	1.859(3)	1.857(3)	1.869(3)	1.860(4)	1.8902(18)
Co1−N2	1.884(4)	1.893(3)	1.884(3)	1.881(3)	1.911(3)
Co1−N3	1.882(3)	1.900(3)	1.887(3)	1.888(4)	1.8841(19)
Co1−N4	1.892(4)	1.917(3)	1.903(3)	1.894(3)	1.9267(18)
Co1−C11	2.020(4)	2.000(4)	2.013(4)	2.023(4)	2.008(2)
O1−N1	1.416(5)	1.403(4)	1.404(4)	1.394(5)	1.399(3)
O2−N2	1.325(5)	1.315(4)	1.331(4)	1.323(5)	1.320(3)
O3−N3	1.340(5)	1.356(4)	1.353(5)	1.344(5)	1.363(3)
O4−N4	1.373(5)	1.379(4)	1.385(4)	1.366(5)	1.323(3)
L-Co1−N1	93.79(12)	92.28(11)	93.91(11)	94.78(15)	94.58(8)
L-Co1−N2	89.06(11)	87.41(11)	87.85(12)	88.11(15)	88.63(8)
L-Co1−N3	91.83(11)	90.47(11)	90.47(13)	89.80(15)	94.57(8)
L-Co1−N4	88.24(11)	88.78(11)	89.17(12)	92.13(15)	86.80(8)
Co1−C11−C10	113.2(3)	113.5(3)	113.0(3)	113.0(3)	115.82(19)
Co1−N1−C2	118.2(3)	118.8(3)	118.9(2)	118.8(3)	118.18(17)
Co1−N1−O1	122.0(3)	121.7(2)	121.9(2)	121.3(3)	125.02(13)
Co1−N2−C3	116.8(3)	116.4(3)	117.5(3)	118.2(3)	116.4(2)
Co1−N2−O2	123.2(2)	122.3(2)	122.3(2)	122.2(3)	122.65(19)
Co1−N3−O3	123.8(3)	123.9(2)	122.7(2)	123.4(3)	123.91(18)
Co1−N3−C6	117.2(3)	118.1(3)	119.1(3)	119.2(3)	118.3(2)
Co1−N4−O4	127.7(3)	126.6(2)	127.1(2)	126.1(3)	124.31(14)
Co1−N4−C7	117.5(3)	115.7(3)	117.8(3)	118.8(3)	115.11(16)
N1−Co1−N2	80.62(15)	80.63(13)	79.81(12)	80.19(15)	79.77(10)
N1−Co1−N3	173.83(16)	176.78(13)	174.88(13)	175.03(17)	169.98(8)
N1−Co1−N4	101.99(15)	102.16(13)	103.05(12)	102.69(15)	103.73(8)
N1−Co1−C11	82.95(16)	83.41(14)	84.11(14)	83.94(18)	84.80(10)
N2−Co1−N3	96.96(15)	97.83(13)	97.74(14)	98.07(15)	96.38(11)
N2−Co1−N4	176.37(14)	175.37(12)	176.01(11)	177.08(16)	174.44(9)
N2−Co1−C11	93.68(16)	93.46(14)	93.28(14)	91.81(18)	94.09(10)
N3−Co1−N4	80.70(15)	79.56(13)	79.63(13)	79.02(15)	80.87(9)
N3−Co1−C11	91.58(16)	93.88(14)	91.57(15)	91.48(18)	86.26(10)
N4−Co1−C11	89.17(16)	90.54(14)	89.81(14)	88.02(18)	90.56(9)
L-Co1 −C11	175.34(12)	175.40(13)	177.51(14)	178.71(16)	177.06(9)
C9−C10−C11	116.6(4)	116.4(3)	115.1(4)	116.1(5)	116.1(3)

ligands in some degree. In fact, the displacement *d* is toward and the bending is away from the bulkier of the two axial ligands.

(b) Distances and Angles around the Cobalt. As shown by the values of the σ cobalt−carbon bond lengths in Table 3, there is only a little difference among complex **2**−**6′**, and they are all 1.99−2.0 Å.[13] This indicates that the trans influence of the L ligand to the Co−R bond length is similar.

For our complexes with N atom as axial base, the Co−L bond distances have the following order: **4** (L = Py) > **5** (L = Bzm) > **6′** (L = Im). They are in accord with the base strength of the L groups (pK_a values: Py(5.25) < Bzm(5.53) < Im(6.95)). According to previous reports, for a given R ligand the length of the Co−L distance is dependent on both steric and electronic effects of the L ligand.[13−16] In this study, the bond length is increased with the base strength of the L groups, i.e., the increasing σ-donating power of the L. Therefore, the main influence on the Co−N bond length of the series of bridged complexes is not due to the bulk, but to the electronic effect of the L. The length of the Co−Br bond in complex **2** is the longest one in five bridged complexes. The reason for that probably is due to both the bulk and a poor σ-donor of the Br ligand.

(c) Intermolecular H Bonding in the Equatorial Ligand. The main hydrogen bonds in our complexes (**2**−**5**) are O−H−O bridges in the equatorial plane; the hydrogen bond between oxygen in dimethylglyoxime and axial ligand L or nitrogen in another dimethylglyoxime; the hydrogen bond between axial ligand L and perchlorate (see Tables 4−7). From previous reports, there are two types of the O−H−O bridge that form in the equatorial plane: (a) the two acidic protons are asymmetrically located between the dioxime oxygen atoms (form A in Figure 3), and (b) both localized protons are attached to one of the two dimethylglyoxime ligands, yielding one neutral ligand ($dmgH_2$) and one dianion (dmg^{2-}) (form B in Figure 3). It was proposed that the localization of the two protons on one dimethylglyoxime ligand is primarily stimulated and stabilized by the presence of extra interligand hydrogen bonds, where one of the oxime oxygen atoms in the equatorial plane acts as the acceptor.[30] In our case, the extra hydrogen bond involves another ligand and one of the oxygen (O2) in the dimethyloximato group which forms a O1-trimethylene bridged six-membered ring with the cobalt. For example, the extra hydrogen bond in complex **5** is O4−H4···O2 (see Table 7); in complex **3**, it is O5−H5OA···O2 (see Table 5), which comes from the oxime oxygen O2 and axial ligand water. There is also an extra hydrogen bond involving O3 (O4−H4···O3) in complex **3**, but from the data in Table 5, we can see that it is weaker than that of O5−H5OA···O2. Hence, in these two complexes, the proton shifted, and two protons are attached to one dimethylglyoxime ligand. In complexes **2** and **4** (see Tables 4 and 6), neither of the oxygens in different oxime ligands has an extra hydrogen bond with the other ligand. So in these two complexes the hydrogen atom in O−H−O is positioned close to the middle of the bridge. Because there is only one hydrogen bond in the equatorial plane in complex **6′**, it was not considered in this discussion.

(d) The Orientation of the L Plane. The orientation of the L plane with respect to the equatorial plane can be

Table 3. Comparison of the Structure Parameters

	2	**3**	**4**	**5**	**6′**
complex	L = Br	L = H_2O	L = Py	L = Bzm	L = Im
N1N2N3N4[a] (Å)	0.0677	0.0540	0.0601	0.0349	0.1128
d(Co)[b] (Å)	0.0242	−0.0086	0.0122	0.0415	0.0366
α[c] (deg)	7.8	−11.0	11.4	5.1	12.2
d(O1)[d] (Å)	0.4905	0.4637	0.4829	0.4261	0.5992
Co−C bond distances (Å)	2.020(4)	2.000(4)	2.013(4)	2.023(4)	2.008(2)
Co−L bond distances (Å)	2.5164(8)	2.092(2)	2.086(3)	2.058(3)	2.0391(19)
$\angle L-Co-C_{11}$ (deg)	175.34(12)	175.40(13)	177.51(14)	178.71(16)	177.06(9)
$\angle Co-C_{11}-C_{10}$ (deg)	113.2(3)	113.5(3)	113.0(3)	113.0(3)	115.82(19)
$\angle C_9-C_{10}-C_{11}$ (deg)	116.6(4)	116.4(2)	115.1(4)	116.5(5)	116.1(2)

[a] Mean deviation from the equatorial plane of four donor atoms N1N2N3N4. [b] Displacements of Co atom from the N1N2N3N4 plane. [c] Angle between the two oxime planes. [d] Displacements of O1 atom from the N1N2N3N4 plane.

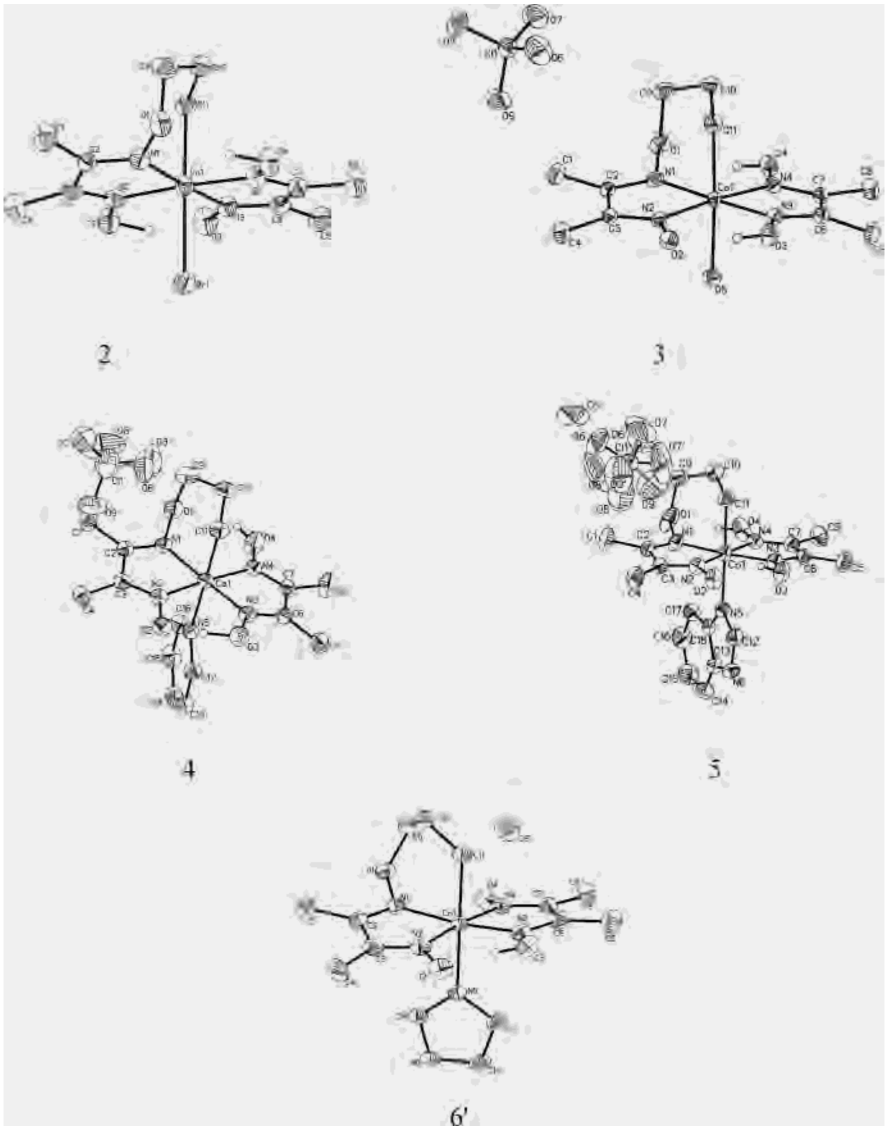

Figure 2. Structures and numberings of complexes **2**−**6′**.

Table 4. Hydrogen Bonds for Complex **2**

A−H···B	*d*(A−H)	*d*(H···B)	*d*(A−B)	∠(A−B)
O2−H2···O3	1.0412	1.4656	2.458(4)	157.13
O2−H2···N3	1.0412	2.1135	2.940(5)	134.60
O4−H4···O1	1.0188	1.8564	2.817(4)	155.77
O4−H4···N1	1.0188	2.4230	3.209(5)	133.34

Table 5. Hydrogen Bonds for Complex **3**

A−H···B	*d*(A−H)	*d*(H···B)	*d*(A−B)	∠(A−B)
O5−H5OA···O2[a]	0.8499	1.8864	2.727(3)	169.92
O5−H5OB···O8[b]	0.8503	2.0497	2.881(4)	165.74
O3−H3···O2	0.8200	1.7077	2.493(4)	159.77
O4−H4···O1	0.8209	2.0907	2.792(4)	143.21
O4−H4···O3[c]	0.8209	2.4787	2.960(4)	118.49

[a] Symmetry transformation: $-x, 1 - y, -z$. [b] Symmetry transformation: $-^1/_2 + x, ^3/_2 - y, -^1/_2 + z$. [c] Symmetry transformation: $1 + x, y, z$.

Table 6. Hydrogen Bonds for Complex **4**

A−H···B	*d*(A−H)	*d*(H···B)	*d*(A−B)	∠(A−B)
O3−H3···O2	1.13(6)	1.33(6)	2.456(4)	170(5)
O4−H4···O1	0.7891	2.1427	2.865(4)	152.26
O4−H4···O9[a]	0.7891	2.5883	2.867(5)	102.70

[a] Symmetry transformation: $-x, -^1/_2 + y, ^1/_2 - z$.

Table 7. Hydrogen Bonds for Complex **5**

A−H···B	*d*(A−H)	*d*(H···B)	*d*(A−B)	∠(A−B)
O3−H3···O2	0.8262	1.7413	2.474(5)	146.75
O3−H3···O4[a]	0.8262	2.4569	2.878(5)	112.70
O3−H3···N2	0.8262	2.3573	2.986(5)	133.37
O4−H4···O1	0.8189	2.0188	2.761(6)	150.55
O4−H4···O2[b]	0.8189	2.2983	2.692(5)	110.10
N6−H6···O5[c]	0.8603	1.9821	2.814(8)	162.29
O5−H50A···O9′[b]	0.8597	2.5932	3.453(19)	179.63
O5−H50B···O8′	0.8573	2.4793	3.08(3)	128.29

[a] Symmetry transformation: $1 + x, y, z$. [b] Symmetry transformation: $-1 + x, y, z$. [c] Symmetry transformation: $x, y, -1 + z$.

described by the torsion angle φ (C_{12}−N5−Co−N*; where N* is the midpoint between N_2 and N_3).[31] When φ is 0°, it is in an eclipsed orientation (A in Figure 4) and 90° in the staggered orientation (B in Figure 4). In the three complexes **4**−**6′** which contain various planar N-donor ligands, the

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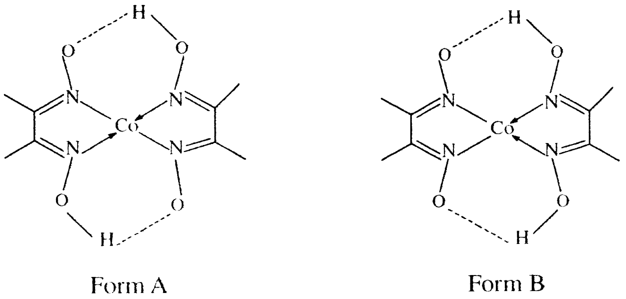

Figure 3. Two forms of H bonded structure in the equatorial plane of the cobaloxime.

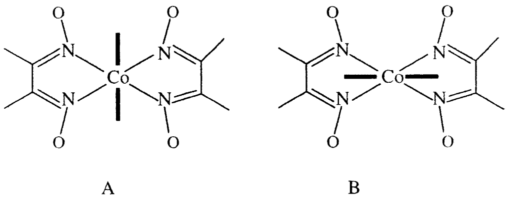

Figure 4. Orientation of the L plane.

absolute values of φ changed as follows: Bzm (7.6°) < Py (15.2°) < Im (74.3°). This means that the orientation of the L plane was close to A when L = benzimidazol, whereas an orientation close to B was found in the less bulky imidazole ligand. While L = pyridine, the φ is between them. It was proposed that the torsion angles increase with the decrease of the bulkiness of ligand L.[15] In fact, in more than 50 cobaloximes, the L ligands assume orientation A with respect to the equatorial moiety. However, orientation B is quite rare and has been found only in two cobaloximes, i.e., *N*-MeImCo(DH)$_2$Me (φ = 66.2) and *N*-MeImCo(DH)$_2$CH$_2$CH$_2$CN (φ = 67.0).[32] Apparently, our complex **6′** is one of the other examples but with a larger φ value.

Conclusion

Using a convenient improved way, a new series of intramolecular bridge alkylcobaloxime complexes have been synthesized and characterized. Their interesting features in structures, which apparently lead to the novel properties in their Co−C bond, are discussed and compared. Further investigations are in progress.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**, **3**, **4**, **5**, and **6′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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