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Notes

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X-ray Crystallographic Investigation of the Bonding Changes Accompanying a New, Reversible Cobalt-to-Carbon Alkyl Migration Reaction

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Introduction

We recently reported a reversible and unprecedented alkyl migration in the coenzyme B_{12} model complex $C_6H_5CH_2Co^{III}[C_2(DO)(DOH)_{pn}]I$ (**1**).[1,2] An X-ray crystallographic structure analysis of the isomeric rearrangement product (*SP*-5-15)-[2-[[3-[[2-(hydroxyamino)-1-methyl-2-(phenylmethyl)butylidene]amino]propyl]imino]-3-pentanone oximato(2−)-*N*,*N′*,*N″*,*N‴*]iodocobalt(III) (**2**) demonstrated that the benzyl migration occurs to carbon (eq 1),[3] not nitrogen, as others had speculated previously. A detailed mechanistic investigation[2] demonstrated that this reversible migration is a *highly selective, intermolecular* free-radical reaction; the selectivity is due to the buildup of ca. 10^{-7} M $\cdot Co^{II}[C_2(DO)(DOH)_{pn}]I$, which directs ≥99% of the reaction to **2** and thus away from the "expected" product, bibenzyl.[4,5] The mechanistic investigation also revealed the presence of a low carbon–benzyl bond dissociation energy of 25 ± 3 kcal/mol in **2**.[2,6]

Because of the novelty of this system, we felt it is of interest to probe the bonding changes that occur in the rearrangement of **1** to **2**. Reported herein is a single-crystal X-ray structural analysis of **1** which in turn allows a precise comparison of the distance and thus bonding changes in the two isomers, **1** vs **2** (see Figure 1 for the ORTEP diagram of **1** and Table I for the X-ray crystallographic parameters for **1**).

Results and Discussion

As indicated in greater detail in the Experimental Section, single crystals of **1** were grown from an O_2-free benzene solution of **1** in vapor contact with hexanes; the solution was sealed in a Schlenk tube in the dark to prevent the photochemically induced rearrangement of **1** to **2**. Once dried, the crystals are not air- or light-sensitive and so were mounted without protection. The structure was solved by the heavy-atom method without complications and refined to $R = 0.056$ and $R_w = 0.062$. The structure of **1** is unexceptional in light of the many cobaloxime, Costa, and other similar B_{12} model structures now reported in the literature,[7] although it becomes invaluable in a direct comparison to **2** when evaluating the bonding changes that occur upon migration of the benzyl group. (Figure 2 and Table II contain the relevant data to accompany the analysis and discussion which follow.)

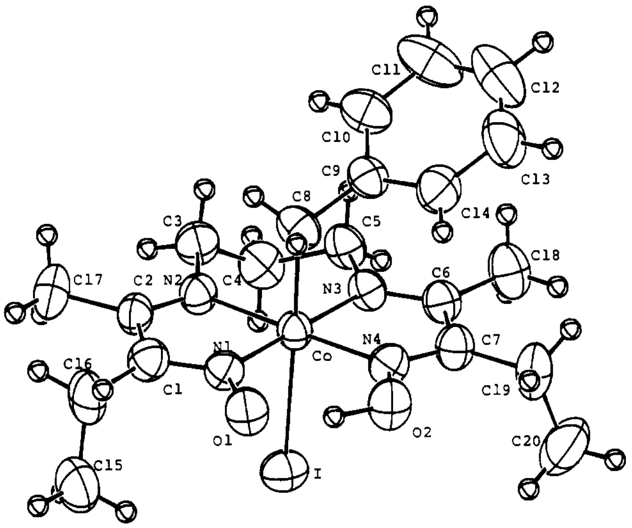

Figure 1. ORTEP diagram of **1**.

Table I. Crystallographic Data

composition: $C_{20}H_{30}CoIN_4O_2$ (**1**)	$Z = 2$
fw = 544.3	$d_{calc} = 1.590$ g cm^{-3}
space group: $P\bar{1}$	$T = 18$ °C
$a = 7.864$ (3) Å	λ(Mo Kα) = 0.71069 Å
$b = 9.968$ (4) Å	$\mu = 21.2$ cm^{-1}
$c = 14.893$ (5) Å	rel trans cft: 0.71–1.00 (4)
$\alpha = 97.46$ (3)°	no. obsd rfclns: 2944 [$I \geq 3\sigma(I)$]
$\beta = 96.66$ (3)°	$R^a = 0.056$
$\gamma = 97.67$ (3)°	$R_w{}^b = 0.062$
$V = 1137$ (2) Å^3	

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

As expected, a number of bonds in the equatorial chelating ligand, in the vicinity of the alkyl migration, have changed;[8] a close analysis of the bond distances in **1** vs **2** indicates that only those which change by more than ±0.02 Å merit discussion in what follows. The most dramatic change has occurred in the N(4)–C(7) bond length. The +0.18 (2) Å change (going from **1** to **2**)[9] from 1.305 (10) to 1.489 (13) Å clearly indicates the decrease in bonding between N(4) and C(7). Comparison to literature values for N—C and N═C bonds (Table II) shows, as expected, that the N(4)═C(7) double bond in the starting material **1** has been replaced by an N(4)—C(7) single bond in the product. The adjacent C(6)–C(7) bond has also lengthened +0.04 (2) Å from 1.459 (11) to 1.505 (13) Å upon migration, but is still shorter than an average C–C bond. The lengthening of this bond can

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(8) For the purpose of comparison, the atom labels for **2** in Figure 2 have been changed from the way they appear in our previous publications[1,2] in order to conform to the labels employed for **1** in this publication.

(9) Changes in bond lengths are written as + for an increase in length (decrease in bond order) and − for a decrease in length (increase in bond order) going in the direction **1** to **2**.

(10) Because **1** has a noncrystallographic mirror plane, average bond lengths for chemically equivalent bonds are used.

(11) Macgillavry, C. H., Rieck, G. D., Lonsdale, K., Eds. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1962; Vol. III, p 270.

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Table II. Selected Bond Length Comparisons in **1** vs **2** and Their Comparison to Selected Literature (Average) Bond Lengths

bond	length, Å		Δ(length) (**1** → **2**), Å	lit.[11] bond lengths bond (av length, Å)
	1[10]	**2**		
Co–I	2.681 (2)	2.697 (2)	+0.016 (3)	
O(1)–O(2)	2.437 (8)	2.473 (9)	+0.04 (1)	
Co–N(2)	1.908 (6)	1.936 (8)	+0.03 (1)	
Co–N(4)	1.871 (6)	1.781 (7)	−0.09 (1)	
N(1)–O(1)	1.335 (8)	1.378 (10)	+0.04 (1)	N—O (1.47); N=O (1.18)
N(4)–O(2)	1.335 (8)	1.277 (10)	−0.06 (1)	
N(4)–C(7)	1.305 (10)	1.489 (13)	+0.18 (2)	C—N (1.47); C=N (1.27)
C(6)–C(7)	1.459 (11)	1.505 (13)	+0.04 (2)	C—C (1.54); C=C (1.34)
C(7)–C(19)	1.493 (12)	1.546 (15)	+0.05 (2)	

be rationalized by the loss of conjugation in N(3)–C(6)–C(7)–N(4) in **2**. The +0.05 (2) Å lengthening of the single C(7)–C(19) bond from 1.493 (12) to 1.546 (15) Å following the migration is the expected result in going from sp^2 to sp^3 hybridization at the C(7) carbon.

Dramatic bonding changes have also occurred between N(1)–O(1) and N(4)–O(2) in going from **1** to **2**. The N(4)–O(2) bond has shortened −0.06 (1) Å from 1.335 (8) to 1.277 (10) Å. This decrease in length represents a significant increase in double bond character between N(4) and O(2). By comparison, the N(1)–O(1) bond has increased in length by almost the same amount. This "compensation effect" has increased the N(1)–O(1) bond length +0.04 (1) Å from 1.335 (8) to 1.378 (10) Å, giving this bond substantially more single-bond character, presumably due to increased bonding between O(1) and the bridging H in **2** [and decreased O(2)··H (bridging) bonding]. Supporting this, a valence sums treatment[12] on O(1) and O(2) shows that in **1** the bond orders between N(1)–O(1) and N(4)–O(2) are 1.35 and 1.30 respectively. Assuming that the bond order for a hydrogen equally bonded between two oxygens would be about 0.5 implies that the valence bond sum around either oxygen is ≈1.8–1.9. In contrast, the N(1)–O(1) and N(4)–O(2) bond orders in **2** are 1.16 and 1.57, respectively. To fulfill equivalent valence bond sums around these two oxygens in **2** requires the bridging hydrogen to lie much closer to O(1) (at least in this predominant tautomer[2] of **2**). The O(1)–O(2) interatom distance has also increased +0.04 (1) Å in length, from 2.437 (8) to 2.473 (9) Å, but is still within the range of values reported in the literature.[7]

Perhaps the most interesting and unusual bonding changes that have occurred as a result of this alkyl migration are the resultant differences between the Co–N(4) and Co–N(2) bonds in going from **1** to **2**. The Co–N(4) bond has decreased in length dramatically, −0.09 (1) Å, from 1.871 (6) to 1.781 (7) Å. This new value is well below the average value for Co—N bonds in chelating compounds such as **1**[7] and presumably represents an increase in Co=N double bond character. In interesting contrast, the opposing, trans Co–N(2) bond length has increased +0.03 (1) Å from 1.908 (6) to 1.936 (8) Å. The comparative increase in length of this bond and decrease in length of the Co–N(4) bond is an excellent example of the trans influence.

The examples discussed above are the most significant changes in bonding to occur within the equatorial ligand following the rearrangement of **1** to **2**. Shifting to the axial iodine atom, changes in bonding have occurred here as well. The Co–I bond has increased +0.016 (3) Å from 2.681 (2) to 2.697 (2) Å in going from **1** to **2**. This increase in length and thus decrease in bonding is consistent with the increase in ·Co^{II}-containing resonance structures in **2**.[2] The decrease in bonding also explains our earlier observation[2] of increased conductivity (I$^-$ dissociation) in CH$_3$CN of **2** compared to ICo^{III}[C$_2$(DO)(DOH)$_{pn}$]I.

Conclusions

The determination of the X-ray diffraction crystal structure of **1**, and its comparison to that for **2** provides a detailed picture of both the individual and the overall bonding changes that have occurred in the formation of the novel cobalt-to-carbon alkyl migration product, **2**. The bond distance changes, which generally parallel the changes in bond strengths, indicate that the formation of a C(7)–benzyl bond and strengthening of the Co–N(4) and N(4)–O(2) bonds drive the reaction enthalpically, whereas the loss of the Co–benzyl bond and weakening of the N(4)–C(7),

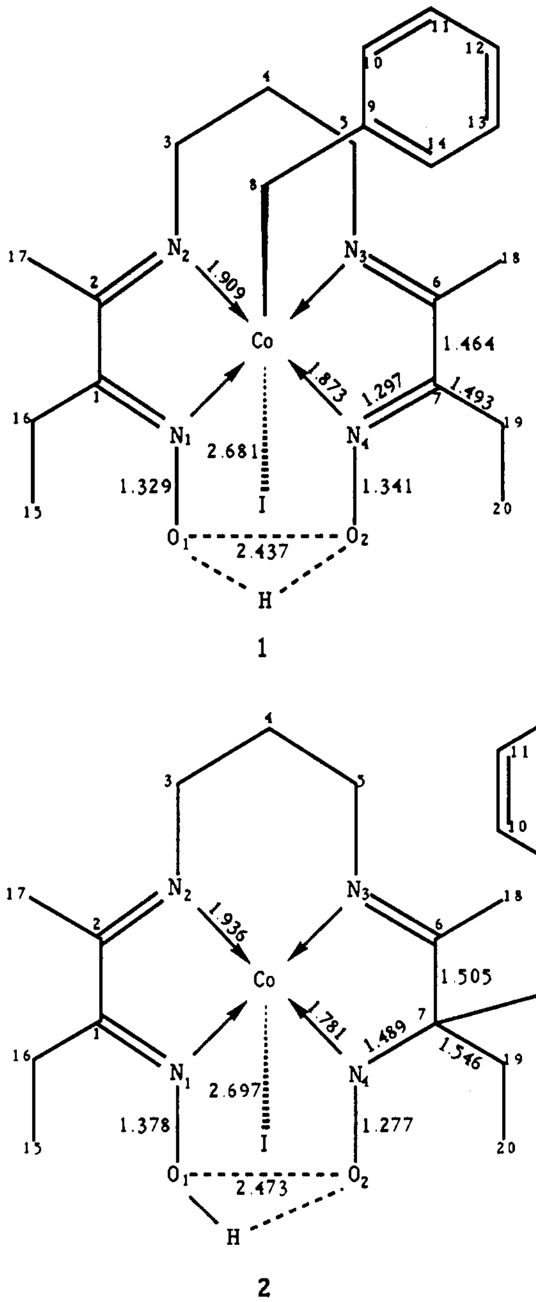

Figure 2. Schematic representations of **1** and **2** showing relevant bond lengths for comparison. All other directly comparable bond lengths were unchanged within ±0.02 Å and, hence, are not shown.

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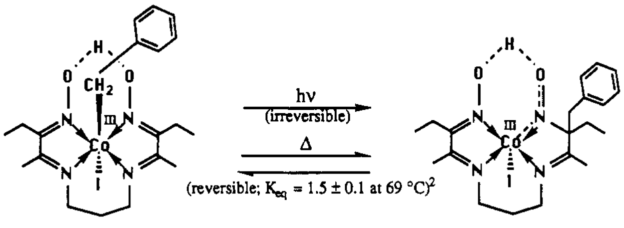
C(7)–C(19), Co–N(2), and Co–I bonds oppose the reaction. These compensating bond changes are consistent with our finding that the overall reaction is enthalpically thermoneutral, $\Delta H^\circ \approx 0$.[2] The results indicate considerable flexibility within the macrocycle ligand system as it accommodates the alkyl migration reaction and bonding changes shown schematically in eq 1.



1 **2**

(1)

One additional crystal structure of interest is that of the migration intermediate, $^\bullet Co^{II}[C_2(DO)(DOH)_{pn}]I$, formed upon cobalt–carbon bond homolysis in **1** or carbon–carbon bond homolysis in **2**. The structure of this homolysis product would allow insight into the bonding changes following Co–C or C–C cleavage (in **1** or **2**, respectively). This compound has been synthesized independently, and we are presently attempting to crystallize it and determine its exact structure.

Experimental

Preparation of $C_6H_5CH_2Co^{III}[C_2(DO)(DOH)_{pn}]I$ (1) and (*SP*-5-15)-[2-[[3-[[2-(Hydroxyamino)-1-methyl-2-(phenylmethyl)butylidene]amino]propyl]imino]-3-pentanone oximato(2−)-*N,N′,N″,N‴*] iodocobalt(III) (2). Complex **1** was prepared via our method reported in detail elsewhere.[2] This compound was characterized by ^1H NMR spectroscopy, visible spectroscopy, elemental analysis, and mass spectroscopy; the results obtained matched identically those obtained from previous reports.[13] A detailed method for the preparation of **2** is also available to the interested reader.[2]

Equipment. X-ray crystallographic data were collected on a Rigaku AFC6R diffractometer. All air-sensitive compounds were manipulated either by the Schlenk technique or in an inert atmosphere, double-length, nitrogen-containing glovebox (Vacuum Atmospheres). Oxygen levels averaged 0.3 ppm and did not exceed 2 ppm. Light-sensitive compounds were protected from light by wrapping their containers in foil or electrician's tape or by sealing them in metal canisters.

X-ray Crystal Structure Determination. 1. Dark red laths were obtained from an air-free benzene solution of the compound in vapor contact with hexanes. They were vacuum-dried and found to be air-stable when dry. A crystal of dimensions 0.12 × 0.07 × 0.45 mm was glued to a fiber, mounted on the diffractometer with its long axis at *ca.* 20° to the ϕ axis and the orientation matrix and cell dimensions determined from the setting angles of 25 centered reflections in the range $11^\circ \le 2\theta \le 17^\circ$. Improved values were found by refinement of 25 reflections selected after rapid data collection in the shell $20^\circ \le 2\theta \le 25^\circ$. A summary of relevant crystal data is given in Table I and a full table including particulars of data collection and refinement is given in the supplementary materials. The value of $|F_0|$ for each of three standard reflections varied *randomly* over a range of ca. ±2% during data collection, although there was no *systematic* change; this variation was subsequently traced to small fluctuations in the vacuum at the rotating anode. The consequent noise in the data appears to account for the somewhat high *R* factor; note, however, that a similar *R* factor and slightly *larger* standard deviations in bond lengths were obtained for the photoproduct **2** although the above problem was not encountered. The positions of the iodine and cobalt atoms were obtained from the Patterson function. A cycle of DIRDIF[14] then showed all the O, N, and C atoms. The data were corrected for absorption by use of DIFABS[15] and after isotropic refinement of the non-hydrogen atoms. The stronger peaks (maximum 1.0 e Å^{-3}) in a difference synthesis after anisotropic refinement lay near the heavy atoms, but a number of hydrogen atoms were also apparent, including that of the –O··H··O– hydrogen bond. The latter was included without refinement in the last cycles of refinement, and all other H atoms were placed at "riding" positions. No solvent of crystallization was present. The TEXSAN program suite,[16] incorporating atomic scattering factors from ref 17, was used in all calculations.

2. For a detailed discussion of the X-ray structure determination of **2**, see refs 1 and 2. A full table of crystal data, including particulars of the data collection and refinement, is given in the supplementary materials of refs 1 and 2.

Acknowledgment. Support of this work from NIH Grant DK 22614 is gratefully acknowledged.

Registry No. 1, 8719-52-6.

Supplementary Material Available: Details of the X-ray structural analysis of **1** including an ORTEP diagram and tables of crystallographic data, refined atomic coordinates, bond lengths and angles, calculated hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, intermolecular contacts, torsion angles, and least-squares mean planes (15 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Triply Bridged Diruthenium Complexes with $[Ru^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}$ and $[Ru^{IV}Ru^{III}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{3+}$ Cores: Synthesis, Spectra, and Electrochemistry

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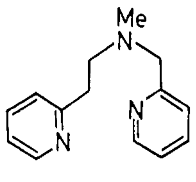
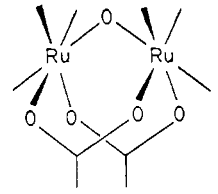
Recently there has been a great deal of interest[1,2] in oxo-bridged dinuclear complexes of Fe(III) because of the discovery of diiron sites in an emerging class of oxo-bridged non-heme iron proteins and enzymes. This has stimulated discovery[3] of a fast growing series of triply bridged iron(III) complexes. The present work originated from our search for $[M_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]^{2+}$ (M = Ru, Fe)[4] cores using MeL as a facially capping ligand. Here we present the rich redox chemistry of the diruthenium complexes of the bridging type as shown in the diagram.



MeL



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