acid catalysis, will be necessary in order to prepare poly(carbophosphazenes) with organic groups attached to phosphorus from the corresponding ring systems.

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Supplementary Material Available: Listings of hydrogen atom parameters, thermal parameters, bond distances, bond angles, torsion angles, and crystallographic parameters (14 pages); a table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Molecular Structure of a Cobalt(I) Complex Lacking a Carbonyl Ligand. A Unique Example of Co–N Bond Shortening

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The following compound, $[(CH_3)_4N][Co(dmgBF_2)_2py]$, where py = C_5H_5N and $(dmgBF_2)_2^{2-}$ = bis[(difluoroboryl)dimethylglyoximato], was crystallized and its molecular structure determined by X-ray diffraction. The distances between Co(I) and the nitrogen of the macrocycle are unusually short (1.839 Å), even shorter than the corresponding bond (1.878 Å) in the cobalt(II) analogue. The cobalt atom is displaced 0.257 Å above the axial plane toward pyridine. Reasons for this unusual Co–N bond shortening are discussed along with the electronic structure of the d^8 cobalt(I) anion.

Introduction

It is well-known that vitamin B_{12} (=cyanocobalamin) and its derivative B_{12a} (aquocobalamin) can be reduced by one electron to B_{12r} (=cobalt(II) cobalamin) and by two electrons to B_{12s}.[1] The crystal structure of B_{12r} was also determined recently.[2] Vitamin B_{12s} exists in solution as the cobalt(I) complex, although at higher acidities it is in equilibrium with its conjugate acid, HCo(corrin), with pK_a = 1.[3-5] In a localized valence formalism, the latter is referred to as a hydridocobalt(III). The B_{12} model complexes $Co(dmgH)_2py^-$ and $HCo(dmgH)_2py$ are also known; here the acidity is lower (pK_a = 9),[6-9] and the rate of acid–base interconversion, sufficiently low that the two forms undergo separate and not always identical chemical reactions.[9-12]

We have now succeeded in isolating single crystals of a closely related model complex that is an example of a nonporphyrin cobalt(I) macrocycle, and that lacks a carbonyl or phosphine ligand. The compound studied is $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$ crystallized from acetonitrile. It contains the anion $Co(dmgBF_2)_2py^-$ (py = C_5H_5N; $(dmgBF_2)_2^{2-}$ = bis[(difluoroboryl)dimethylglyoximato]), which was first prepared by Schrauzer.[13] Not only is this of interest because of the biological role of B_{12} but also, aside from species containing carbonyl, phosphine, or porphyrin ligands,[14-20] it is the first cobalt(I) macrocyclic complex to be so characterized. Moreover, the structure is of interest in its own right because of the considerable variations in distances, angles, and displacements that are found in it, compared to those in the cobalt(II) analogue. Cobalt(I) macrocycle complexes are often short-lived owing to high reactivity with protic solvents or to internal metal–ligand decompositions. The species examined here is moderately stable, even more so than the cobaloxime parent, $Co(dmgH)_2py^-$. In general cobalt(I) complexes are strong nucleophiles[2,12,13,21-24] and Bronsted (as well as Lewis) bases.[6-9,24] As expected from inductive effects, the complex $Co(dmgBF_2)_2py^-$ is much less nucleophilically reactive than the $(dmgH)_2$ and B_{12s} analogues.[13] Several catalytic reactions of cobalt(I) macrocycles are known.[23-25]

Table I. Crystallographic Data for $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$

chem formula	$C_{18}H_{29}B_2NO_4F_4Co\cdot CH_3CN$	γ, deg	103.72 (2)
		V, Å^3	1280.9 (7)
fw	579.02	Z	2
space group	$P\bar{1}$	T, °C	−75 (1)
a, Å	12.492 (4)	λ, Å	0.71073
b, Å	12.883 (3)	d_{calc}, g cm^{-3}	1.501
c, Å	8.996 (3)	μ(Mo Kα), cm^{-1}	7.338
α, deg	99.39 (2)	$R(F_o)$	0.045
β, deg	109.25 (2)	$R_w(F_o^2)$	0.061

Results and Discussion

The pentacoordinated structure of the cobalt(I) monoanion $Co(dmgBF_2)_2py^-$ is depicted in the ORTEP diagram given in Figure 1. The structure is square-pyramidal. The closest analogues are cobalt(I) porphyrins.[26,27] Most often cobalt(I) needs to be stabilized by CO (or phosphine) coordination.[25-30]

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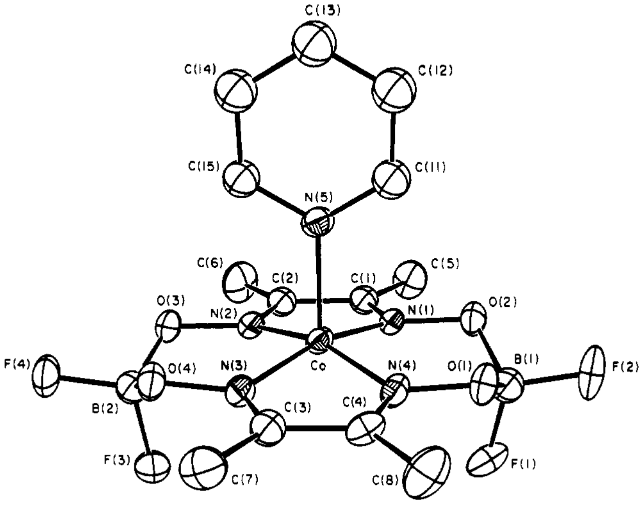

Figure 1. ORTEP view of the monoanion, $Co^{I}(dmgBF_2)_2py^-$.

Table II. Positional Parameters of $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Co(1)	0.21545 (4)	0.27016 (4)	0.00770 (6)	1.61 (1)
F(1)	0.0133 (2)	0.1333 (2)	−0.3952 (3)	3.04 (7)
F(2)	−0.0705 (2)	0.2693 (2)	−0.4501 (3)	3.70 (8)
F(3)	0.3714 (2)	0.0810 (2)	0.1245 (3)	2.80 (6)
F(4)	0.4863 (2)	0.1802 (2)	0.3886 (3)	3.06 (7)
O(1)	0.1290 (2)	0.3214 (2)	−0.3003 (3)	2.41 (7)
O(2)	−0.0258 (2)	0.2426 (2)	−0.1963 (3)	2.29 (7)
O(3)	0.2955 (2)	0.1829 (2)	0.2852 (3)	2.30 (7)
O(4)	0.4527 (2)	0.2749 (2)	0.1923 (3)	2.31 (7)
N(1)	0.0515 (3)	0.2176 (2)	−0.0673 (4)	1.78 (8)
N(2)	0.2002 (3)	0.1897 (3)	0.1554 (4)	1.85 (8)
N(3)	0.3732 (3)	0.2853 (2)	0.0492 (4)	1.95 (8)
N(4)	0.2232 (3)	0.3081 (3)	−0.1772 (4)	2.01 (8)
N(5)	0.2407 (3)	0.4225 (3)	0.1407 (4)	2.04 (9)
C(1)	0.0036 (3)	0.1653 (3)	0.0208 (5)	2.0 (1)
C(2)	0.0939 (3)	0.1493 (3)	0.1560 (4)	2.0 (1)
C(3)	0.4198 (4)	0.3299 (3)	−0.0478 (5)	2.2 (1)
C(4)	0.3286 (4)	0.3424 (3)	−0.1843 (5)	2.2 (1)
C(5)	−0.1269 (4)	0.1254 (4)	−0.0178 (5)	3.1 (1)
C(6)	0.0686 (4)	0.0932 (4)	0.2772 (6)	3.5 (1)
C(7)	0.5496 (4)	0.3617 (4)	−0.0176 (6)	3.1 (1)
C(8)	0.3494 (4)	0.3843 (4)	−0.3207 (5)	3.4 (1)
C(11)	0.1794 (4)	0.4875 (3)	0.0770 (5)	2.8 (1)
C(12)	0.1921 (4)	0.5909 (4)	0.1644 (6)	3.7 (1)
C(13)	0.2732 (5)	0.6304 (4)	0.3261 (6)	3.7 (1)
C(14)	0.3386 (4)	0.5654 (4)	0.3915 (5)	3.3 (1)
C(15)	0.3200 (4)	0.4621 (3)	0.2966 (5)	2.6 (1)
B(1)	0.0136 (4)	0.2400 (4)	−0.3348 (5)	2.4 (1)
B(2)	0.3993 (4)	0.1795 (4)	0.2435 (5)	2.2 (1)
N(6)	0.3308 (3)	−0.0035 (3)	−0.3228 (4)	2.34 (9)
C(21)	0.2385 (4)	0.0515 (4)	−0.3199 (6)	3.3 (1)
C(22)	0.3144 (4)	−0.1002 (4)	−0.2514 (5)	3.0 (1)
C(23)	0.4528 (4)	0.0766 (4)	−0.2291 (6)	3.5 (1)
C(24)	0.3165 (4)	−0.0436 (4)	−0.4972 (5)	3.0 (1)
N(7)	0.8121 (6)	0.3497 (6)	0.2190 (9)	9.0 (3)
C(31)	0.9116 (6)	0.3823 (6)	0.2816 (8)	5.8 (2)
C(32)	1.0392 (6)	0.4204 (6)	0.3562 (9)	6.7 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as follows: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Bond Distances ($\times 10^{-10}$ m) and Their Standard Deviations of $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$[a]

Co(1)–N(1)	1.842 (3)	N(4)–C(4)	1.312 (6)
Co(1)–N(2)	1.844 (4)	N(5)–C(11)	1.337 (6)
Co(1)–N(3)	1.836 (3)	N(5)–C(15)	1.349 (4)
Co(1)–N(4)	1.834 (4)	C(1)–C(2)	1.443 (5)
Co(1)–N(5)	2.019 (3)	C(1)–C(5)	1.488 (6)
F(1)–B(1)	1.393 (6)	C(2)–C(6)	1.479 (7)
F(2)–B(1)	1.385 (6)	C(3)–C(4)	1.436 (5)
F(3)–B(2)	1.407 (5)	C(3)–C(7)	1.494 (6)
F(4)–B(2)	1.393 (5)	C(4)–C(8)	1.491 (7)
O(1)–N(4)	1.392 (4)	C(11)–C(12)	1.375 (6)
O(1)–B(1)	1.468 (5)	C(12)–C(13)	1.394 (6)
O(2)–N(1)	1.384 (4)	C(13)–C(14)	1.373 (7)
O(2)–B(1)	1.481 (6)	C(14)–C(15)	1.380 (6)
O(3)–N(2)	1.398 (4)	N(6)–C(21)	1.495 (7)
O(3)–B(2)	1.472 (6)	N(6)–C(22)	1.495 (6)
O(4)–N(3)	1.392 (4)	N(6)–C(23)	1.490 (5)
O(4)–B(2)	1.472 (6)	N(6)–C(24)	1.506 (6)
N(1)–C(1)	1.317 (6)	N(7)–C(31)	1.12 (1)
N(2)–C(2)	1.309 (5)	C(31)–C(32)	1.43 (1)
N(3)–C(3)	1.330 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg) and Their Standard Deviations of $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$[a]

N(1)–Co(1)–N(2)	80.7 (1)	N(2)–C(2)–C(6)	124.9 (4)
N(1)–Co(1)–N(3)	164.4 (1)	C(1)–C(2)–C(6)	124.2 (4)
N(1)–Co(1)–N(4)	96.6 (1)	N(3)–C(3)–C(4)	110.9 (4)
N(1)–Co(1)–N(5)	98.5 (1)	N(3)–C(3)–C(7)	124.1 (4)
N(2)–Co(1)–N(3)	96.9 (2)	C(4)–C(3)–C(7)	125.1 (4)
N(2)–Co(1)–N(4)	162.4 (1)	N(4)–C(4)–C(3)	111.2 (4)
N(2)–Co(1)–N(5)	99.7 (1)	N(4)–C(4)–C(8)	124.1 (4)
N(3)–Co(1)–N(4)	81.0 (2)	C(3)–C(4)–C(8)	124.7 (4)
N(3)–Co(1)–N(5)	97.0 (1)	N(5)–C(11)–C(12)	122.9 (4)
N(4)–Co(1)–N(5)	97.9 (1)	C(11)–C(12)–C(13)	118.8 (5)
N(4)–O(1)–B(1)	113.0 (3)	C(12)–C(13)–C(14)	118.7 (4)
N(1)–O(2)–B(1)	111.9 (3)	C(13)–C(14)–C(15)	119.1 (4)
N(2)–O(3)–B(2)	112.8 (3)	N(5)–C(15)–C(14)	122.6 (4)
N(3)–O(4)–B(2)	111.9 (2)	F(1)–B(1)–F(2)	110.7 (3)
Co(1)–N(1)–O(2)	124.7 (3)	F(1)–B(1)–O(1)	110.7 (4)
Co(1)–N(1)–C(1)	118.0 (2)	F(1)–B(1)–O(2)	109.5 (4)
O(2)–N(1)–C(1)	116.5 (3)	F(2)–B(1)–O(1)	105.6 (4)
Co(1)–N(2)–O(3)	124.9 (2)	F(2)–B(1)–O(2)	104.7 (4)
Co(1)–N(2)–C(2)	118.3 (3)	O(1)–B(1)–O(2)	115.4 (3)
O(3)–N(2)–C(2)	116.0 (3)	F(3)–B(2)–F(4)	109.5 (4)
Co(1)–N(3)–O(4)	124.2 (3)	F(3)–B(2)–O(3)	110.4 (3)
Co(1)–N(3)–C(3)	117.5 (3)	F(3)–B(2)–O(4)	109.6 (4)
O(4)–N(3)–C(3)	117.0 (3)	F(4)–B(2)–O(3)	104.5 (4)
Co(1)–N(4)–O(1)	125.1 (3)	F(4)–B(2)–O(4)	106.0 (3)
Co(1)–N(4)–C(4)	118.2 (3)	O(3)–B(2)–O(4)	116.5 (4)
O(1)–N(4)–C(4)	115.8 (3)	C(21)–N(6)–C(22)	109.9 (4)
Co(1)–N(5)–C(11)	121.1 (2)	C(21)–N(6)–C(23)	110.3 (3)
Co(1)–N(5)–C(15)	121.1 (3)	C(21)–N(6)–C(24)	108.8 (3)
C(11)–N(5)–C(15)	117.8 (3)	C(22)–N(6)–C(23)	109.9 (3)
N(1)–C(1)–C(2)	111.1 (4)	C(22)–N(6)–C(24)	109.2 (3)
N(1)–C(1)–C(5)	124.1 (4)	C(23)–N(6)–C(24)	108.8 (4)
C(2)–C(1)–C(5)	124.7 (4)	N(7)–C(31)–C(32)	177.5 (9)
N(2)–C(2)–C(1)	111.0 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The structural refinement of $Co(dmgBF_2)_2^-$ establishes that the imine nitrogens, methylene carbons, and oxygens of the $(dmgBF_2)_2^{2-}$ macrocycle constitute a base planar ($\chi^2 = 4105$) entity made rigid by the sp^2 C═N hybridization. The cobalt atom is displaced 0.257 Å toward pyridine above the macrocyclic plane. The aromatic plane of pyridine bisects the equatorial plane through the two boron atoms; the two BF_2 units are displaced below the equatorial plane, away from the coordinated pyridine. The molecule of CH_3CN is located in the crystal lattice near the axial pyridine but does not appear to interact with it. Crystallographic data are summarized in Tables I and II.

Selected bond lengths and angles are given in Tables III–V. Table V also contains data for analogous compounds. The bond distance between cobalt(I) and a nitrogen atom of the equatorial ligands, 1.839 (4) Å, is significantly shorter than other Co^I–N_{eq} single bonds (ca. 2.1 Å, Table V). Moreover the distance is

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(30) The structurally characterized compound $CoPC_{25}H_{45}N_5O_4$ was reported as a cobalt(I) complex (Adams, W. W.; Lenhart, P. G. *Acta Crystallogr.* **1973**, *B24*, 2412), but it is actually a cobalt(III) derivative.

Table V. Comparison of Selected Bond Distances ($\times 10^{-10}$ m)

complex	coord no.	$Co-N_{eq}$	N-C(methylene)	C-C	$Co-N_4$ plane	ref
$Co^{II}(dmgBF_2)_2(CH_3OH)_2$	6	1.878 (4)	1.270 (7)	1.473 (7)	0	31
$Co^{I}(dmgBF_2)_2py^-$	5	1.839 (4)	1.317 (6)	1.443 (5)	0.257 (1)	this work
$Co^{II}[Me_6[14]dieneN_4]Cl_2$	6	1.976 (6)	1.282 (9)		0	29
$Co^{I}(CO)(Me_6[14]dienN_4)^+$	5	2.158 (5)	1.271 (8)		0.57	29
$Co^{II}(bpy)_3{}^{2+}$	6	2.128 (8)				*a*
$Co^{I}(bpy)_3{}^+$	6	2.11 (2)				*a*
$Co^{I}(CO)(C_{10}H_{17}N_8)$	5	1.873 (5)	1.335 (3)			28
$Co^{I}(HDP)$	4	1.91				27

[a] Szalda, D. J.; Creutz, C.; Mahajan, D.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 2372.

unmistakably shorter than the average $Co^{II}-N_{eq}$ distance of 1.878 (4) Å in the cobalt(II) complex, $Co(dmgBF_2)_2(CH_3OH)_2$. In fact, the $Co^{I}-N_{eq}$ distance in the anion is the shortest distance so far reported.

The short $Co^{I}-N_{eq}$ bond distance relative to $Co^{II}-N_{eq}$ contradicts what one might have presumed: a considerable bond lengthening should attend reduction of cobalt(II) to cobalt(I). The displacement of cobalt(I) above the N_4 equatorial plane is therefore not to be attributed to the larger size of the low-valent cobalt ion. Correspondingly, to accommodate the change of the Co–N bond distance, the O–N–C(methylene) and N–C(methylene)–C(methylene) bond angles in the cobalt(I) anion are smaller (averaging 116.3 (3) and 111.0 (4)°, respectively) than those in the cobalt(II) compound (averaging 119.76 (39) and 112.72 (42)°, respectively).[31]

It is interesting to note that the addition of one extra electron to the d_{z^2} orbital in the cobalt(II) complex is not only accompanied by a reduction in coordination number but also by a decrease in the $Co-N_{eq}$ bond distances. Strengthening of a M–CO bond attending an increase of electron density at the metal center is well-known, as it is often reflected by the decrease of ν_{CO}.[32] Similar shortening of the $Co-N_{eq}$ bond in macrocycles is rare, the only example being the carbonyl-containing species $[Co(CO)(C_{10}H_{17}N_8)]$,[28] where π-back-bonding to the equatorial ligand was invoked to account for short Co–N bonds. Our example is a particularly clear one since no carbonyl group is involved and since the same $Co(dmgBF_2)_2$ unit has been structurally characterized in both cobalt(I) and -(II) oxidation states. We need to ask whether the same explanation might apply. Also, we must consider why there is a bond alternation within the macrocyclic ligand itself for Co(I) as compared to the Co(II) complex. We shall consider each of these issues in turn.

The suggested[13] electron configuration at cobalt is $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^2$. This is supported by short $Co^{I}-N_{eq}$ bonds, the absence of a sixth axial ligand in the crystal, and the diamagnetism of the complex. The diamagnetism of the low-spin d^8 $(Co(dmgBF_2)_2py^-$ is consistent with its having a normal ^1H NMR spectrum and no ESR signal. The diamagnetism of similar cobalt(I), rhodium(I), and iridium(I) compounds is well documented.[13,33-36] There is no evidence of axial hydrogen coordination from the difference Fourier map and refinement.

The axial displacement of cobalt may significantly decrease the repulsion between the electron lone pairs of nitrogen atoms in the $(dmgBF_2)_2$ ligand and the filled d_{z^2} orbital of the cobalt as the upward displacement of the cobalt from the basal plane results in the nitrogen lone pairs approaching the nodal plane of the d_{z^2} orbital of cobalt. This diminishing antibonding repulsion may contribute to the shortening of the $Co^{I}-N_{eq}$ bonds.

The electrons in the doubly populated d_{z^2} orbital in the cobalt(I) complex not only allow back-donation[37] but also increase the energy level of the d_{z^2} orbital, making back-bonding more energetically favorable compared to the situation for cobalt(II). That is not to say this is the transition responsible for the intense bands in the absorption spectrum—indeed, they are properly accommodated by d–d transitions for quite a range of Co(I) complexes of N_4 macrocycles[13]—but rather that it allows for a shift of electron density to the equatorial ligand in the electronic ground state of the molecule.

A reviewer suggested the possibility that this complex might really be formulated as a cobalt(III) complex. That is, if electron donation to ligands were carried to the extreme, the result would be $[Co^{III}(dmgBF_2)_2{}^{4-}py]^-$ or $[Co^{III}(dmgBF_2)_2{}^{2-}py^{2-}]^-$. But we do not believe such an assignment of Co(III) oxidation state to $[Co(dmgBF_2)_2]^-$ to be appropriate. This is because of the following. (1) The deep blue color of $[Co(dmgBF_2)_2]^-$ is known to be associated with the Co(I) oxidation state. Relevant inorganic Co(III) macrocyclic complexes are known to be yellow (e.g., $ClCo(dmgBF_2)_2P(C_4H_9)_3$) or brown (e.g., $ClCo(dmgBF_2)_2py$).[38] (2) All the known inorganic Co(III) complexes of bis(dimethylglyoximato) and bis[(difluoroboryl)dimethylglyoximato] are hexacoordinated to satisfy the 18e rule.[38-41] No precedent is found in these groups of Co(III) complexes where cobalt is only pentacoordinated.

Displacement of cobalt above the N_4 equatorial plane toward pyridine seems necessary to make such a short $Co^{I}-N_{eq}$ bond. Indeed, the bonding interaction with pyridine may pull the cobalt out of the equatorial plane. Such a displacement is also noticed in $Co(CO)(C_{10}H_{17}N_8)$,[28] where a short Co–N bond was observed. On the other hand, consider the case of $Co^{I}(HDP)$ (HDP = 2,2,3,3,7,7,8,8,12,12,13,13,17,17,18,18-hexadecamethyl-10,20-diazaoctahydroporphinato),[27] where such a displacement is absent and cobalt is coplanar with the four nitrogen atoms of the equatorial ligand. Even though the ligand contains a more highly conjugated π-system (and is therefore a better electron acceptor) the $Co^{I}-N$ bond is still relatively long, 1.91 Å.[27] This comparison suggests upward displacement of the cobalt is necessary for shortening of the $Co-N_{eq}$ distance.

As shown in Table V, the bond distances between imine nitrogens and adjacent carbons and those between the pair of adjacent methylene carbons change with oxidation state, such that $N-C(Co^{I}) > N-C(Co^{II})$ and $C-C(Co^{I}) < C-C(Co^{II})$. This bond length alternation may arise from donation of electron density to the $(dmgBF_2)_2$ macrocycle. The BF_2 units certainly serve to stabilize the cobalt(I) oxidation state via an inductive effect, but no unambiguous comparison can be made on the basis of the structural data.

Experimental Section

Crystal Growth. The formation of the macrocyclic monoanion $Co(dmgBF_2)_2py^-$ is recognized by the intense blue coloration[38,42] that de-

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velops. It can be generated either by controlled potential reduction of its parent neutral compound $Co(dmgBF_2)_2(H_2O)_2$ in acetonitrile in the presence of one equivalent of pyridine at −0.44 V (vs NHE) or by decomposition of alkyl-$Co(dmgBF_2)_2py^{2-}$ in acetonitrile. Formation of n-$C_3H_7Co(dmgBF_2)_2py^{2-}$ can be achieved by controlled potential electrolysis of n-$C_3H_7Co(dmgBF_2)_2py$ at −1.90 V (vs NHE) in 0.06 M $(CH_3)_4NBF_4$ acetonitrile solution. An air-free electrocell with a mercury pool working electrode, a platinum plate auxiliary electrode, and an Ag/AgCl reference electrode was used to conduct the electrolysis. Owing much to the higher solubility of n-$C_3H_7Co(dmgBF_2)_2py$ over $Co(dmgBF_2)_2(H_2O)_2$ in acetonitrile, the second method was adopted to obtain a crystal for this study. A three layer solution system in a test tube was employed for the crystal to grow. Diethyl ether was allowed to diffuse slowly from the top layer through a C_5H_{12} middle layer into the bottom layer of the dark blue acetonitrile solution containing the title compound, all at 0 °C. The middle layer, which is immiscible with the blue acetonitrile solution on the bottom, functions as a spacer to slow the diffusion of diethyl ether into the acetonitrile solution and ensure the quality of crystals for the diffraction study. Anaerobic conditions are required owing to the extreme sensitivity of $Co(dmgBF_2)_2py^-$ solution toward oxygen. The deep blue crystal of $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$ is less air-sensitive.

X-ray Data Collection. A dark blue crystal of the title compound was taken from a nitrogen-filled test tube and attached to the tip of a glass fiber. The crystal was then moved into the cold stream of the low-temperature device on the diffractometer and slowly cooled to −75 °C. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table I.

A total of 4741 reflections were collected in the $\pm h,+k,\pm l$ hemisphere. Lorentz and polarization corrections were applied. An absorption correction based on a series of ψ-scans was applied, and equivalent reflections were averaged.

Determination and Refinement of the Structure. The choice of the centric triclinic group was indicated initially by intensity statistics and later confirmed by the successful refinement of the structure. The positions of all of the non-hydrogen atoms of the complex and the associated counterion were found by an automatic Patterson interpretation method.[43] One molecule of acetonitrile was later located in a difference Fourier map. In the final stages of refinement, the non-hydrogen atoms were refined with anisotropic temperature factors, and hydrogen atoms were added in idealized positions. A common isotropic temperature factor was refined for each of these groups of hydrogen atoms: one for the methyl hydrogens of the complex, one for the pyridinyl hydrogens, and one for the methyl hydrogen atoms on the $[(CH_3)_4N]^+$ and CH_3CN moieties.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX-II computer using the SHELX-76 programs.[44]

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Supplementary Material Available: A full table of crystal data and a table of anisotropic temperature factors (4 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Reduction-Induced Cleavage of the Cobalt–Carbon Bond in Macrocyclic Organocobalt Complexes

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The one-electron reduction of $RCo(dmgBF_2)_2A$ ($dmgBF_2$ = (difluoroboryl)dimethylglyoximato, A = pyridine or H_2O, R = CH_3, C_2H_5, C_3H_7, $C_6H_5CH_2$, or 4-$XC_6H_4CH_2$) yields $RCo(dmgBF_2)_2A^-$ as transients. The ESR parameters (R = 4-$BrC_6H_4CH_2$, $g_\parallel = 2.23$, $A_\parallel = 111 \times 10^{-4}$ cm^{-1}, $g_\perp = 2.07$, $A_\perp = 54 \times 10^{-4}$ cm^{-1}) indicate that the unpaired electron resides in the $d_{x^2-y^2}$ orbital of the cobalt. The reduced complexes hydrolyze in H_2O to yield the alkanes RH and $Co(dmgBF_2)_2(H_2O)_2$. In acetonitrile the decomposition mode depends on the availability of β-hydrogens. For R = C_2H_5 and 1-C_3H_7, the final products are the corresponding alkenes and a cobalt(II) complex of a modified macrocycle. The benzyl and substituted benzyl complexes yield the hydrolysis products 4-$XC_6H_4CH_3$ and the unchanged cobalt(II) macrocycle. The kinetics of the reduction of $RCo(dmgBF_2)_2A$ by *R,S,-R,S*-Ni(tmc)$^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in H_2O, pH 12, are biphasic for R = benzyl and substituted benzyl and monophasic for the primary alkyl complexes, consistent with the expected effect of the organic group on the lifetimes of the $RCo(dmgBF_2)_2A^-$ transients.

Introduction

Reduction-induced cleavage of cobalt–carbon bonds in organocobalt macrocyclic complexes presents challenging questions. Detailed mechanistic and kinetic information is still insufficient to understand fully the roles of vitamin B_{12} in catalysis of reactions such as skeletal 1,2-rearrangements,[1,2] reduction of ribonucleoside triphosphates,[3-5] and biosynthesis of methionine,[6,7] methane,[8-11] and acetate.[10,12-14] Studies of the "partial-strength" M–C σ-bonds[15] should provide additional insight into the mechanism of these reactions.

With some exceptions,[16] the electrochemcial reduction of alkylcobalt(III) complexes yields unstable alkylcobalt species that decompose by cleavage of the cobalt–carbon bond. Several decomposition pathways have been reported.[17-19] In the case of

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