Acknowledgment. This work was supported by NIH Grant GM 29222 (to L.G.M.). R.C. thanks the NATO Science Fellowships Program for a grant. We also thank the NSF for a departmental grant to Emory toward the purchase of the 360-MHz NMR spectrometer.

Registry No. **1**, 98218-98-5; **2**, 98218-99-6; **3**, 98301-50-9; **4**, 98219-00-2; 6-MP, 50-66-8; $[Ru(6\text{-}MP\text{-}H)_2(P(C_6H_5)_3)_2]$, 98219-01-3; $[RuCl_2(P(C_6H_5)_3)_3]$, 15529-49-4.

Supplementary Material Available: Tables of bond lengths, bond angles, parameters for the hydrogen atoms, thermal temperature factors for the nonhydrogen atoms, observed and calculated structure factors, stacking distances, least-squares planes and dihedral angles between the planes, and hydrogen bonds. Figures of ^1H NMR spectra (downfield region) of $[Ru^{II}(6\text{-}MP)_2(P(C_6H_5)_3)_2]^{2+}$, $[Ru^{II}(6\text{-}MPD)_2(P(C_6H_5)_3)_2]^{2+}$ (6-MPD = 8-deuterated 6-mercaptopurine), and $[Ru^{II}(6\text{-}MP\text{-}H\text{-}8D)_2(P(C_6H_5)_3)_2]$ (6-MP-H-8D = N(9)-deprotonated 8-deuterated 6-mercaptopurine) complexes, the complete atom-labeling scheme for **1**, and the stereoview of the unit cell packing for $[Ru^{II}(6\text{-}MP)_2(P(C_6H_5)_3)_2]Cl_2\cdot 2C_2H_5OH\cdot 2H_2O$ (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322, and Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy

Comparative Structural and Ligand-Exchange Properties of Organocobalt B_{12} Models. Improved Synthetic Procedures for Costa Models and the Structures of Two Pyridine Complexes with Methyl and Neopentyl Ligands

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Several organocobalt complexes containing the uninegative equatorial ligand $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime) ((DO)(DOH)pn) have been prepared. These complexes of the type $[LCo((DO)(DOH)pn)R]X$ (where X = ClO_4, PF_6 and L = H_2O, py) contain several R ligands ($i\text{-}C_3H_7$, *neo*-C_5H_{11}, $CH_2CO_2CH_3$, CH_2CF_3, CH_2Br, and $CH_2Si(CH_3)_3$) which were previously unknown in (DO)(DOH)pn complexes although complexes with $i\text{-}C_3H_7$ and *neo*-C_5H_{11} are known with a related equatorial ligand. The py ligands in $[pyCo((DO)(DOH)pn)R]ClO_4$ complexes dissociate at rates slightly greater than in the comparable cobaloxime complexes in CH_2Cl_2 at 25 °C. The relative dependences on R are almost identical in the two series with identical R but with 4-CN-py as the leaving ligand for the cobaloxime series. The dissociation rate increases by 10^5 across the series $CH_2CO_2CH_3$, CH_2CF_3, CH_2Br, CH_3, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, CH_2CH_3, *neo*-C_5H_{11}, and $i\text{-}C_3H_7$. The three-dimensional structures of $[pyCo((DO)(DOH)pn)R]PF_6$, R = CH_3 (I) and R = *neo*-C_5H_{11} (II), were determined. Crystallographic details follow. I: $C_{17}H_{27}CoF_6N_5O_2P\cdot C_3H_6O$, $P2_1/c$, $a = 7.182$ (3) Å, $b = 12.557$ (3) Å, $c = 29.848$ (6) Å, $\beta = 99.62$ (3)°, D(calcd) = 1.49 g cm^{-3}, $Z = 4$, $R = 0.048$ for 3670 independent reflections. II: $C_{21}H_{35}CoF_6N_5O_2P$, $P2_12_12_1$, $a = 17.154$ (3) Å, $b = 8.011$ (2) Å, $c = 19.726$ (3) Å, D(calcd) = 1.45 g cm^{-3}, $Z = 4$, $R = 0.050$ for 2863 independent reflections. The most unusual feature of the structures is that the py ligand α-H atoms lie over the five-membered $\overline{\text{Co–N–C–C–N}}$ chelate rings. The py ligand probably adopts this orientation to minimize steric interactions with the puckered $\overline{\text{Co–N–C–C–C–N}}$ ring. In I, the central C of the ring is above the plane toward the alkyl group whereas in II it is toward the py ligand. This difference may also arise from a steric effect. Additionally, the Co–N(py) bond distances are slightly longer (0.04 Å) in I and II than in the analogous cobaloximes but the Co–C bond distances appear insensitive to the nature of the equatorial ligand. Finally, the (DO)(DOH)pn ligand deviates from planarity to a much greater extent than cobaloximes and this feature, along with the longer Co–N bonds, makes $[pyCo((DO)(DOH)pn)R]X$ complexes somewhat better than cobaloximes as structural models for coenzyme B_{12}.

Introduction

Recent advances in our understanding of the role of Co–C bond homolysis and of the radicals formed in coenzyme B_{12} dependent processes have been reviewed.[1-6] The B_{12} system itself (i.e. the cobalamins) is comprised of complex molecules with a pseudooctahedral geometry at Co. The equatorial coordination plane is occupied by four corrin N atoms, and the axial positions are occupied by an alkyl group (5′-deoxyadenosyl in coenzyme B_{12}[7] and methyl in the other enzyme cofactor methyl B_{12}[8]). Small organocobalt complexes have played an important role in giving insight into the more complex chemistry of B_{12}.[1-5] Extensive background information is available on the influence of the axial ligands in only one class of B_{12} models, namely cobaloximes where the equatorial ligand system contains two dioximato ligands, such as dimethylglyoximato (DH). We have recently reviewed the extensive solution and structural chemistry of complexes of the type $LCo(DH)_2X$.[3]

However, attempts at obtaining as detailed information on other, perhaps more realistic models, have not been so successful. For example, although information[9] is available on Co–C bond energies on the system pyCo(saloph)R (where saloph = dianion of bis(salicylidene)-*o*-phenylenediamine and py = pyridine), only three such compounds have been structurally characterized.[10,11] There appears to be a clear relationship between the length of the Co–N bond, the Co–C bond energy, and the L ligand dissociation rate.[9,10] Again, the saloph complexes are not particularly tractable because six-coordinate species are difficult to obtain as pure crystalline materials and, furthermore, ligand dissociation is facile and proceeds at rates often too rapid even for evaluation by dynamic NMR methods. Ligand dissociation rates for $LCo(saloph)CH_3$ exceed those for $LCo(DH)_2CH_3$ by a factor of ca. 10^{11} (see ref 11). In contrast, although exact comparisons are not possible,

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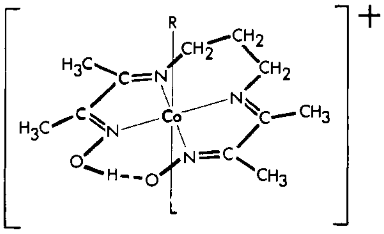
cobalamin dissociation rates exceed $LCo(DH)_2R$ rates by ca. 10^6–10^8 (see ref 10).

Since Schiff base complexes such as LCo(saloph)R appear too reactive and cobaloximes such as $LCo(DH)_2R$ are too unreactive, a mixed Schiff base/oxime system would appear to be worthy of study. Indeed, Costa has explored the chemistry of [LCo((DO)(DOH)pn)R]X complexes,[12,13] where (DO)(DOH)pn is the equatorial ligand in the complex.



Because of solubility problems with this type compound, which limited the synthetic chemistry, Finke has more recently explored the closely related system $[Co((EMO)(EMOH)pn)R]X$.[4,14,15,16] This equatorial ligand, 2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diolato(1−), differs from (DO)(DOH)pn in having ethyl rather than methyl groups at the 3- and 9-positions, i.e. on the oxime C. It has also been abbreviated as C_2(DO)(DOH)pn. With this ligand, a greater diversity of complexes could be prepared compared to the case for the (DO)(DOH)pn system. Evidence is mounting that, compared to other model systems, so called "Costa" complexes of these two equatorial ligands may better reflect the electrochemical behavior of cobalamins and may better promote reactions characteristic of B_{12} enzymes.[14,15,17] In addition, these Costa complexes have an equatorial ligand of the same charge (−1) and pseudosymmetry of the corrin and appear to give the closest ^{59}Co NMR shifts to cobalamins compared to other models.[18]

This intriguing type of B_{12} model is six-coordinate, and it therefore seems worthwhile to investigate its structural properties and ligand-exchange behavior for comparison with the $LCo(DH)_2R$ and the more limited LCo(saloph)R data. The (EMO)(EMOH)pn compounds developed by Finke are more versatile and soluble than the (DO)(DOH)pn compounds of Costa but have proven to be difficult to crystallize. The one successfully crystallized nondisordered compound, $[H_2OCo((EMO)(EMOH)pn)CH_3]PF_6$,[19] has a structure similar to that of $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$,[20] the only other relevant structure on a "Costa" monoalkyl model.

We have now established conditions for preparing a greater diversity of [pyCo((DO)(DOH)pn)R]X complexes and report structural data on two complexes, R = CH_3 and *neo*-C_5H_{11}, and ligand-exchange data for several complexes.

Experimental Section

Reagents. Neopentyl iodide was purchased from Fluka. Trimethyl phosphite (Aldrich) was distilled under vacuum before use. All other reagents were from Aldrich and used without further purification.

Rate Measurements. Ligand substitution reactions were monitored spectrophotometrically with a Perkin-Elmer Lambda 3B instrument equipped with a 3600 Data Station for the slower reactions ($k_{obsd} < 0.1$ s^{-1}) or a Durrum-Gibson D-110 stopped-flow spectrophotometer for the faster reactions. Both instruments were equipped with thermostated cell compartments (25.0 ± 0.04 °C). Visible spectra of several (DO)(DOH)pn complexes in methylene chloride were recorded and then compared with the visible spectra of the same solutions after adding a calculated excess (ca. 10:1) of entering ligand (L′) and allowing sufficient time (as estimated by a similar NMR experiment) for the reactions to reach completion. Suitable wavelengths for following the exchange reactions were in the range 410–590 nm for the complexes (0.0005–0.01 M) studied. Absorbance changes with time were monitored over 3 half-lives with the final absorbance taken at 8 half-lives. At least three data sets were collected for each complex.

Data Analysis. The rate constants are defined as

$$\mathrm{ML} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M} + \mathrm{L}$$

$$\mathrm{M} + \mathrm{L}' \xrightarrow{k_2} \mathrm{ML}'$$

where M = Co((DO)(DOH)pn)R, L = py, and L′ = trimethyl phosphite or tri-*n*-butylphosphine. The experimental absorbance vs. time rate data were treated with the standard integrated expression for a first-order process by a linear least-squares computer program.

Preparation of $[LC((DO)(DOH)pn)R]ClO_4$ Complexes. To avoid cleavage of the Co–C bond, all compounds with Co–C bonds were handled with minimal exposure to light and were not subjected to temperatures above 35 °C.

(DO)(DOH)pn. This ligand was obtained by a procedure reported by Uhlig and Friedrich.[21]

$Co((DO)(DOH)pn)X_2$ (X = Cl, Br) and $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$ were prepared as described by Costa.[12]

$[H_2OCo((DO)(DOH)pn)R]ClO_4$ (R = CH_2CH_3, *i*-C_3H_7, *neo*-C_5H_{11}, CH_2CF_3). A magnetic stir bar and methanol (50 mL) were placed in a 125-mL Erlenmeyer flask containing $Co((DO)(DOH)pn)X_2$ (2 mmol; 0.92 g (X = Br) or 0.74 g (X = Cl) for CH_2CF_3 preparation only). Prepurified nitrogen was continuously bubbled through the stirred suspension. A NaOH solution (5 mmol in 10 mL of H_2O) was added to dissolve the starting material. After 5 min, alkylating agent (4–12 mmol) was added, followed by a solution of $NaBH_4$ (110 mg, 3 mmol in 5 mL of H_2O). Additional alkylating agent was added if the solution was not red after several minutes. After 5 min of stirring, acetone (10 mL) was added to the red solution and the N_2 purging stopped. The solution was diluted with H_2O (50 mL), and $AgNO_3$ (1.19 g, 7 mmol) was added. The resulting suspension was stirred well for 10 min and then filtered through Celite. The clear red filtrate was treated with $NaClO_4$ (2.0 g, 14 mmol in 10 mL of H_2O) and the volume reduced with a rotary evaporator (30 °C) until precipitation began. The solution was evaporated further to yield a powder or cooled overnight (5 °C) to yield a crystalline product.

Yields: R = CH_2CH_3, 650 mg (70%); R = *i*-C_3H_7, 450 mg (48%); R = *neo*-C_5H_{11}, 800 mg (78%); R = CH_2CF_3, 680 mg (68%).

$[H_2OCo((DO)(DOH)pn)R]ClO_4$ (R = $CH_2CO_2CH_3$, $CH_2C_6H_5$, $CH_2Si(CH_3)_3$). The procedure used to prepare these complexes is the same as that listed above with the following exceptions: (1) A magnetic stir bar and 90% methanol (100 mL) were placed in a 125-mL Erlenmeyer flask containing $Co((DO)(DOH)pn)X_2$ (2 mmol; 0.92 g (X = Br) or 0.74 g (X = Cl) for $CH_2CO_2CH_3$ preparation only). (2) After the N_2 purging was stopped, 1 N HNO_3 was used to neutralize the solution before treatment with $NaClO_4$.

Yields: R = $CH_2CO_2CH_3$, 510 mg (52%); R = $CH_2C_6H_5$, 300 mg (30%); R = $CH_2Si(CH_3)_3$, 300 mg (30%).

$[H_2OCo((DO)(DOH)pn)CH_2Br]ClO_4$. This complex could not be synthesized directly as above. A suspension of $Co((DO)(DOH)pn)Br_2$ (3.68 g, 8 mmol) in methanol (200 mL) was treated with *N*-methylimidazole (*N*-MeIMD, 1–2 mL). The resulting red solution was kept under N_2. After 5 min, dibromomethane (1.7 mL, 24 mmol) was added followed by a solution of $NaBH_4$ (440 mg, 12 mmol in 15 mL of H_2O). The solution became bluish green and then turned red. After the solution remained red for 5 min, acetone (20 mL) was added and the N_2 purging stopped. The perchlorate was obtained as above, 3.5 g (76%).

$[(N\text{-MeIMD})Co((DO)(DOH)pn)CH_2Br]ClO_4$ (3.5 g, 6.1 mmol) was dissolved in 80% MeOH (200 mL). Dowex 50X8-100 cation-exchange resin (5 g) was added, and the mixture was stirred for 3 days. Removal of the resin by filtration and evaporation of the filtrate yielded an orange powder (2.4 g, 77%).

$[pyCo((CO)(DOH)pn)R]ClO_4$ (R = CH_3, CH_2CH_3, *i*-C_3H_7, *neo*-C_5H_{11}, CH_2CF_3, $CH_2CO_2CH_3$, CH_2Br, $CH_2C_6H_5$, $CH_2Si(CH_3)_3$). A suspension of $[H_2OCo((DO)(DOH)pn)R]ClO_4$ (300 mg) in CH_2Cl_2 (15 mL) was treated with py (10% excess), producing an orange-yellow solution. Petroleum ether was added until the solution became cloudy.

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Table I. Crystallographic Data for Compounds I and II[a]

	I	II
formula	$CoO_2N_5C_{17}H_{27}PF_6{\cdot}C_3H_6O$	$CoO_2N_5C_{21}H_{35}PF_6$
mol wt	595.5	593.5
a, Å	7.182 (3)	17.154 (3)
b, Å	12.557 (3)	8.011 (2)
c, Å	29.848 (6)	19.726 (3)
β, deg	99.62 (3)	
D(measd), g cm^{-3}	1.48	1.43
D(calcd), g cm^{-3}	1.49	1.45
Z	4	4
space group	$P2_1/c$	$P2_12_12_1$
μ, cm^{-1}	9.2	7.6
cryst dimens, cm^3	0.03 × 0.03 × 0.06	0.02 × 0.03 × 0.05
no. of reflecns measd	8173	4443
no. of indep reflec ($I > 3\sigma(I)$)	3670	2863
max 2θ, deg (Mo Kα)	60	60
R	0.048	0.050
R_w	0.056	0.064

[a] Esd's are given in parentheses.

Acetone was used to dissolve any oil that formed. When the solution was cooled to 0 °C, a crystalline product formed. It was collected and washed with diethyl ether. Yields: R = CH_3, 200 mg (50%); R = CH_2CH_3, 210 mg (64%); R = i-C_3H_7, 190 mg (57%); R = *neo*-C_5H_{11}, 260 mg (77%); R = CH_2CF_3, 190 mg (52%); R = $CH_2CO_2CH_3$, 108 mg (32%); R = CH_2Br, 105 mg (31%); R = $CH_2C_6H_5$, 260 mg (77%); R = $CH_2Si(CH_3)_3$, 145 mg (43%).

[pyCo((DO)(DOH)pn)R]PF$_6$ (R = CH$_3$, *neo*-C$_5$H$_{11}$). An acetone solution of [pyCo((DO(DOH)pn)R]ClO_4 was treated with an aqueous solution of NH_4PF_6 unitl the PF_6 salt precipitated. X-ray-quality crystals were obtained from a clear solution (9:1 acetone–H_2O) left standing unsealed for 2–5 days at 5 °C.

X-ray Methods. Crystal Data. Crystals of [pyCo((DO)(DOH)pn)-CH_3]PF_6 (I) and [PyCo((DO)(DOH)pn)*neo*-C_5H_{11}]PF_6 (II) were grown as above. Cell dimensions determined from Weissenberg and precession photographs were refined on a CAD4 Enraf-Nonius single-crystal diffractometer. Crystal data are given in Table I. The intensity of one check reflection was measured every 100 reflections during data collection. No decay of intensity occurred.

Solution and Refinement of Structures. The structures of I and II were solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares methods to final R values of 0.048 and 0.050, respectively. The contribution of hydrogen atoms, located at calculated positions, was held constant (B = 5 Å^2) in both the structures. The weighting scheme was $w = 1/(\sigma(F) + (pF)^2 + q)$, where p = 0.02 and q = 1.5 for both I and II.

The PF_6^- anion of I was found to be disordered. The disorder was interpreted as due to two anion orientations of about 0.6 and 0.4 (starred symbols of Table II) occupancies differing by a rotation of 30° around the axial direction F(5)–P–F(6). A crystallographically independent acetone of crystallization was found in I. Atomic scattering factors were those given in ref 22. Anomalous dispersion corrections were included for all atoms.

All calculations were done with use of computer programs from the CAD4-SDP suite. Final positional parameters are given in Tables II and III. Anisotropic thermal parameters, hydrogen atom coordinates, and final calculated and observed structure factors are given in the supplementary material. No correction for absorption was applied because of the small size of the crystals used and the small values of the absorption coefficients (Table I).

Results

Synthetic Methods. Cobalt(III) complexes containing the (DO)(DOH)pn equatorial ligand and the related (EMO)-(EMOH)pn ligand have been isolated with 14 different alkyl groups (CH_3, CH_2CH_3, $COCH_3$, CH_2CH_2OH, CH_2CHO, n-C_3H_7, i-C_3H_7, CH_2CHCH_2, n-C_4H_9, *neo*-C_5H_{11}, C_6H_5, $CH_2C_6H_5$, $CHOC(O)OCH_2$, $CH_2C(CH_3)(CO_2CH_2CH_3)_2$).[12,14,15,23-27]

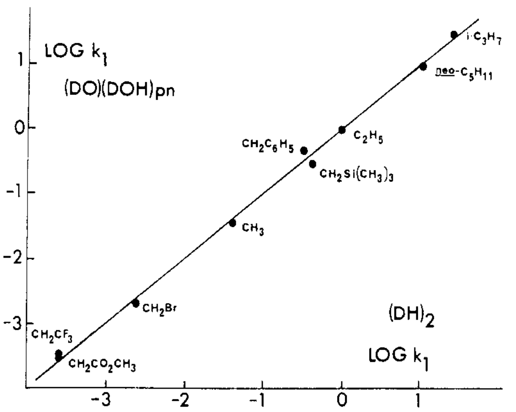

Figure 1. Log k_1 (s^{-1}) for 4-CN-pyCo(DH)$_2$R vs. log k_1 (s^{-1}) for [pyCo((DO)(DOH)pn)R]ClO_4.

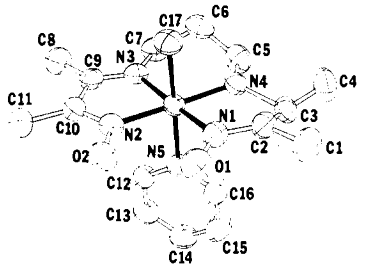

Figure 2. Structure and labeling scheme for the non-hydrogen atoms of I (thermal ellipsoids; 50% probability).

Reports of complexes with bulky alkyl groups such as i-C_3H_7 were absent until BrCo^{III}((EMO)(EMOH)pn)i-C_3H_7 was synthesized from isopropyl bromide by treatment of Co^{I}((EMO)-(EMOH)pn)CO in warm benzene in a drybox (24 h). Following column chromatography, an 8% yield of slightly impure product was isolated.[23] The preparation of Co^{I}((EMO)(EMOH)pn)CO requires an inert atmosphere in the final of three steps beginning with 3-(hydroxyimino)-2-pentanone and 1,3-diaminopropane. To prepare Co((DO)(DOH)pn)Cl_2, only two steps are necessary if one starts with 2,3-butanedione oxime and 1,3-diaminopropane. Syntheses of the [$H_2OCo((DO)(DOH)pn)R]^+$ complexes via the sodium borohydride reduction of basic methanol mixtures, as reported in this paper, required little time (ca. 1 h). The aquo complexes were isolated in good yield and gave acceptable elemental analyses. The yield of the compound with R = i-C_3H_7 was 48%, but this compares to the previous best yield of 8%. The syntheses of [LCo((DO)(DOH)pn)R]$^+$ (R = i-C_3H_7, *neo*-C_5H_{11}, CH_2CF_3, $CH_2CO_2CH_3$, CH_2Br, $CH_2SiC(CH_3)_3$) have not previously been reported.

It should be pointed out that the use of the CO complex, as developed by Finke,[23] has both the advantage of storage of the reactive Co(I) form and of higher yields of primary alkyl complexes. This is particularly important if the alkyl halide is expensive or difficult to synthesize.

Rate Measurements. The py ligand-exchange rate constants (k_1) were determined for the nine [pyCo((DO)(DOH)pn)R]ClO_4 salts in the noncoordinating solvent CH_2Cl_2 (Table IV). Replacement of the ClO_4 anion by PF_6 did not affect the axial ligand-exchange rate for the ethyl complex. Identical ligand-exchange rates were found for the methyl complex with use of trimethyl phosphite or tri-n-butylphosphine as entering ligand at 10- or 100-fold excess concentrations. Therefore, the rate expression is clearly first order, and the S_N1 LIM mechanism describes the exchange reaction. As expected, the stronger elec-

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Table II. Positional Parameters and Their Estimated Standard Deviations for Compound I

atom	x	y	z	atom	x	y	z
Co	−0.01409 (7)	0.17019 (4)	0.12961 (2)	C13	0.2528 (6)	0.0334 (4)	0.0222 (1)
O1	−0.3458 (4)	0.0416 (2)	0.1239 (1)	C14	0.2790 (6)	−0.0707 (4)	0.0341 (2)
O2	−0.3496 (4)	0.1775 (2)	0.06454 (9)	C15	0.2252 (8)	−0.1057 (4)	0.0730 (2)
N1	−0.1727 (4)	0.0633 (3)	0.1468 (1)	C16	0.1437 (7)	−0.0348 (4)	0.0991 (1)
N2	−0.1827 (4)	0.2220 (3)	0.0791 (1)	C17	−0.1394 (6)	0.2696 (3)	0.1678 (1)
N3	0.1337 (4)	0.2873 (3)	0.1149 (1)	P	−0.2404 (2)	0.1614 (1)	0.31729 (4)
N4	0.1474 (4)	0.1196 (3)	0.1831 (1)	F1	−0.359 (1)	0.0610 (5)	0.3093 (3)
N5	0.1148 (4)	0.0670 (3)	0.0884 (1)	F2	−0.069 (1)	0.0986 (8)	0.3253 (4)
C1	−0.2264 (7)	−0.0698 (4)	0.2037 (2)	F3	−0.126 (1)	0.2661 (5)	0.3282 (2)
C2	−0.1132 (6)	0.0117 (3)	0.1840 (1)	F4	−0.427 (1)	0.2290 (7)	0.3113 (3)
C3	0.0782 (6)	0.0442 (3)	0.2044 (1)	F5	−0.2343 (8)	0.1581 (4)	0.3698 (1)
C4	0.1767 (8)	−0.0114 (4)	0.2459 (2)	F6	−0.2489 (7)	0.1610 (4)	0.2654 (1)
C5	0.3398 (6)	0.1624 (4)	0.1972 (2)	F1*	−0.424 (1)	0.101 (1)	0.3133 (3)
C6	0.3507 (6)	0.2793 (4)	0.1885 (2)	F2*	−0.131 (1)	0.0467 (6)	0.3229 (3)
C7	0.3244 (6)	0.3114 (4)	0.1393 (2)	F3*	−0.042 (1)	0.2057 (8)	0.3125 (4)
C8	0.1444 (7)	0.4359 (4)	0.0610 (2)	F4*	−0.320 (2)	0.2666 (8)	0.3110 (5)
C9	0.0566 (6)	0.3425 (3)	0.0802 (1)	OA	0.229 (1)	0.1484 (6)	0.4620 (2)
C10	−0.1300 (6)	0.3055 (3)	0.0585 (1)	CA1	0.2734 (8)	0.1632 (6)	0.4264 (2)
C11	−0.2456 (8)	0.3535 (4)	0.0173 (2)	CA2	0.278 (1)	0.2673 (7)	0.4070 (3)
C12	0.1690 (6)	0.0994 (3)	0.0499 (1)	CA3	0.318 (1)	0.0752 (7)	0.3980 (3)

Table III. Positional Parameters and Their Estimated Standard Deviations for Compound II

atom	x	y	z	atom	x	y	z
Co	0.22203 (4)	0.14449 (8)	0.17564 (3)	C11	0.3487 (4)	0.5229 (9)	0.2703 (3)
O1	0.0777 (2)	0.2985 (5)	0.2039 (2)	C12	0.1554 (4)	0.2798 (8)	0.0430 (3)
O2	0.1937 (2)	0.4561 (5)	0.2386 (2)	C13	0.1507 (5)	0.373 (1)	−0.0156 (3)
N1	0.1137 (2)	0.1595 (6)	0.1819 (2)	C14	0.2126 (5)	0.4660 (8)	−0.0350 (3)
N2	0.2476 (3)	0.3429 (6)	0.2209 (2)	C15	0.2794 (4)	0.4641 (7)	0.0039 (3)
N3	0.3338 (2)	0.1238 (6)	0.1727 (2)	C16	0.2808 (4)	0.3723 (7)	0.0616 (3)
N4	0.1949 (3)	−0.0624 (6)	0.1319 (2)	C17	0.2290 (4)	0.0061 (7)	0.2648 (3)
N5	0.2192 (3)	0.2774 (5)	0.0827 (2)	C18	0.1856 (4)	0.0264 (8)	0.3320 (3)
C1	−0.0145 (4)	0.036 (1)	0.1569 (4)	C19	0.0981 (4)	0.012 (1)	0.3267 (4)
C2	0.0727 (3)	0.0357 (8)	0.1598 (3)	C20	0.2032 (8)	0.186 (1)	0.3658 (4)
C3	0.1214 (4)	−0.0984 (7)	0.1341 (3)	C21	0.2145 (5)	−0.1152 (9)	0.3766 (3)
C4	0.0868 (5)	−0.2607 (9)	0.1153 (4)	P	0.4763 (1)	0.0815 (3)	0.4258 (1)
C5	0.2533 (5)	−0.1779 (8)	0.1052 (4)	F1	0.4553 (4)	0.2614 (7)	0.4051 (3)
C6	0.3263 (4)	−0.0927 (9)	0.0844 (3)	F2	0.5283 (3)	0.1494 (9)	0.4854 (2)
C7	0.3737 (4)	−0.0180 (9)	0.1415 (4)	F3	0.5003 (4)	−0.1011 (8)	0.4463 (4)
C8	0.4553 (4)	0.242 (1)	0.2209 (4)	F4	0.4282 (3)	0.0091 (8)	0.3653 (2)
C9	0.3699 (3)	0.2387 (8)	0.2075 (3)	F5	0.4033 (3)	0.0725 (9)	0.4733 (2)
C10	0.3202 (3)	0.3714 (7)	0.2345 (3)	F6	0.5506 (3)	0.0896 (7)	0.3766 (2)

Table IV. First-Order Rate Constants (s^{-1}) for L Exchange of LCo(chel)R with $P(OCH_3)_3$ in CH_2Cl_2 at 25 °C

R	$[pyCo(DO)(DOH)pnR]ClO_4$	4-CN-pyCo$(DH)_2$R[a]
$CH_2CO_2CH_3$	$(3.09 \pm 0.07) \times 10^{-4}$	$(2.71 \pm 0.2) \times 10^{-4}$
CH_2CF_3	$(3.36 \pm 0.05) \times 10^{-4}$	$(2.7 \pm 0.2) \times 10^{-4}$
CH_2Br	$(2.13 \pm 0.05) \times 10^{-3}$	$(2.6 \pm 0.1) \times 10^{-3}$
CH_3	$(3.63 \pm 0.07) \times 10^{-2}$	$(4.1 \pm 0.3) \times 10^{-2}$
$CH_2Si(CH_3)_3$	$(3.02 \pm 0.19) \times 10^{-1}$	$(4.3 \pm 0.6) \times 10^{-1}$
$CH_2C_6H_5$	$(5.00 \pm 0.14) \times 10^{-1}$	$(3.3 \pm 0.7) \times 10^{-1}$
CH_2CH_3	$(9.78 \pm 0.05) \times 10^{-1}$	$(9.6 \pm 0.1) \times 10^{-1}$
neo-C_5H_{11}	$(1.01 \pm 0.09) \times 10$	$(1.1 \pm 0.03) \times 10$
i-C_3H_7	$(3.34 \pm 0.08) \times 10$	$(2.7 \pm 0.3) \times 10$

[a] From ref 3, 28, and this work for R = $CH_2CO_2CH_3$. Anal. Calcd for $C_{17}H_{23}CoN_6O_6$: C, 43.78; H, 4.97; N, 18.02. Found: C, 43.59; H, 5.00; N, 17.92.

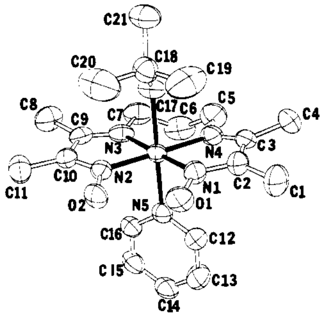

Figure 3. Structure and labeling scheme for the non-hydrogen atoms of II (thermal ellipsoids; 50% probability).

Table V. Bond Lengths (Å) with Estimated Standard Deviations for I and II

	I	II		I	II
Co–N1	1.886 (3)	1.866 (3)	Co–N4	1.918 (3)	1.926 (4)
Co–N2	1.884 (3)	1.875 (4)	Co–N5	2.106 (3)	2.121 (3)
Co–N3	1.908 (3)	1.925 (3)	Co–C17	2.003 (3)	2.083 (4)

Table VI. Selected Bond Angles (deg) for I and II

	I	II
N1–Co–N2	97.2 (1)	98.4 (2)
N1–Co–N3	174.9 (1)	177.6 (2)
N1–Co–N4	81.2 (1)	81.0 (2)
N1–Co–N5	93.7 (1)	90.1 (2)
N1–Co–C17	86.5 (2)	92.1 (2)
N2–Co–N3	81.8 (1)	81.6 (2)
N2–Co–N4	176.8 (1)	178.2 (2)
N2–Co–N5	91.8 (1)	89.5 (1)
N2–Co–C17	87.2 (1)	92.0 (2)
N3–Co–N4	99.5 (1)	98.8 (2)
N3–Co–N5	91.3 (1)	92.3 (2)
N3–Co–C17	88.4 (1)	85.6 (2)
N4–Co–N5	91.1 (1)	92.2 (2)
N4–Co–C17	90.0 (1)	86.3 (2)
N5–Co–C17	178.9 (1)	177.1 (2)
Co–C17–C18		130.4 (3)

tron-donating alkyl groups (e.g. *i*-C_3H_7, *neo*-C_5H_{11}) caused an increase in the py dissociation rate compared to that of the poorer electron-donating groups (e.g. CH_2CF_3, $CH_2CO_2CH_3$). A plot of log k_1 for dissociation of py from [pyCo((DO)(DOH)pn)R]-ClO_4 vs. log k_1 for dissociation of 4-CN-py from 4-CN-pyCo-

Table VII. Relevant Geometrical Data for (DO)(DOH)pn Complexes and for the Analogous Cobaloximes[a]

axial ligands						
R	L	Co–R, Å	Co–L, Å	Co–C–C, deg	α, deg	*d*, Å
			DO(DOH)pn			
CH_3	py[b]	2.003 (3)	2.106 (3)		+6.9	+0.07
neo-C_5H_{11}	py[b]	2.083 (4)	2.121 (3)	130.4 (3)	+14.3	+0.03
CH_3	H_2O[c]	1.977 (4)	2.103 (3)		+2	+0.01
			Cobaloximes			
CH_3	py[d]	1.998 (5)	2.068 (3)		+3.2	+0.04
neo-C_5H_{11}	py[e]	2.060 (6)	2.081 (4)	130.3 (4)	−5.2	0
CH_3	H_2O[f]	1.990 (5)	2.058 (3)		−4.0	0

[a] 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 N4 equatorial donor set is toward L. [b] Present work. [c] Reference 19; the equatorial ligand is (EMO)(EMOH)pn. [d] Bigotto, A.; Zangrando, E.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 96. [e] Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. [f] McFadden, D. L.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1974**, 363.

Table VIII. Relevant Coordination Bond Angles (deg) Involving the Carbon Atom Bonded to Cobalt[a]

	N(1)–Co–C, N(2)–Co–C	N(3)–Co–C, N(4)–Co–C	N(5)–Co–C or O–Co–C	C(6) side
$[pyCo((DO)(DOH)pn)CH_3]PF_6$[b]	86.5, 87.2	88.4, 90.0	178.9	CH_3
$[pyCo((DO)(DOH)pn)$*neo*-$C_5H_{11}]PF_6$[b]	92.1, 92.0	85.6, 86.3	177.1	py
$[H_2OCo((EMO)(EMOH)pn)CH_3]PF_6$[c]	89.3, 89.2	90.4, 89.8	177.4	H_2O

[a] The numbering scheme for N is that of Figures 2 and 3. [b] Present work. [c] Reference 19.

$(DH)_2R$[3,28] is linear with a slope of 0.996 (Figure 1).

Structural Studies. SHELXTL drawings of cations I and II with the atom-numbering scheme are depicted in Figures 2 and 3. In both compounds, cobalt exhibits a distorted-octahedral stereochemistry and the (DO)(DOH)pn ligand occupies the four equatorial positions. Selected bond lengths and angles are reported in Tables V and VI.

The Co(DO)(DOH)pn units are similar within the experimental errors in the two compounds and do not differ significantly from the corresponding figures reported for the $[CH_3Co((EMO)(EMOH)pn)H_2O]^+$ cation[19] and for $[CH_3Co((DO)(DOH)pn)CH_3]$.[29]

However, in I and II, distortions from planarity of the nonhydrogen atoms of the equatorial moiety (excluding the central atom in the propylene bridge) are larger than those reported for the nearly planar Co(EMO)(EMOH)pn unit.[19] The four equatorial N atoms are coplanar within ±0.02 Å (I) and ±0.005 Å (II), and cobalt is displaced (*d*) by 0.07 Å (I) and 0.03 Å (II) from these mean planes toward the axial pyridine ligand. The two chemically equivalent halves of the equatorial macrocycle, with the exclusion of C(6), are approximately planar. These planes have dihedral angles, α, of 6.9° (I) and 14.4° (II) and bend toward the axial alkyl group. The six-membered chelate ring has the expected conformation with the C(6) atom out of the chelate plane on the side of the axial alkyl group in I and of the pyridine ligand in II. The torsional angles around C(5)–C(6) and C(6)–C(7) bonds are +68.6 and −64.9° in I and −67.7 and +68.1° in II, respectively. The position of the central atom of the propylene bridge appears to be determined mainly by the interaction with the axial ligands (see below).

The O···O distances of the oxime bridge are 2.457 (4) Å (I) and 2.454 (5) Å (II). These values are within the experimental error of those of 2.461 (6) Å found for $[CH_3Co((DO)(DOH)pn)CH_3]$[29] and of 2.445 (5) Å found in $[CH_3Co((EMO)(EMOH)pn)H_2O]^+$,[19] but significantly shorter than the mean value of 2.487 (2) Å in cobaloximes.[3] The present data confirm the previous suggestion that the ease of oxime bridge deprotonation of B_{12} models correlates with longer O···O distance.[3] The comparison of α and *d* values with those of cobaloximes, reported in Table VI, shows that the equatorial moiety of (DO)(DOH)pn complexes having py as axial ligand undergoes distortions larger than those reported for the analogous cobaloximes. This result may be mainly attributed to the different orientation of the pyridine ligand with respect to the equatorial moiety in the two series of model complexes (see below).

The relevant data for the py–Co–R fragment are reported in Table VII and compared with those of the corresponding cobaloximes. The Co–C bond lengths are significantly affected by the bulk of the alkyl group as already found in cobaloximes,[3,30] but no significant differences are observed with those found for a given R in the latter complexes. Particularly in compound II, the Co–C–C angle of 130.4° is very close to those reported for cobaloxime neopentyl derivatives. In both model systems, this angle is influenced by the positions of the C(18), C(19), and C(20) atoms, which form a plane nearly parallel to that of the equatorial moiety.

In contrast, the Co–L bond lengths in (DO)(DOH)pn type compounds are about 0.04 Å longer than those found in cobaloximes, for L = H_2O or py (Table VII). Since the lengthening of the Co–L bond appears to be independent of the nature of both the axial ligands in the four relevant structures completed thus far, the cis-influence order appears to be (DO)(DOH)pn > $(DH)_2$. More comparisons are needed to define this order.

Finally, no short intermolecular contacts involving C(6) are detected: C(6) lies on the side of the equatorial plane opposite to that of the bulkier of the axial ligands (Table VIII). However, it should be noted that the C(6)–axial ligand interaction will depend not only on the bulk of the ligand but also on its orientation with respect to the equatorial ligand and on the values of the N(eq)–Co–C bond angles.

Discussion

These compounds allow the first direct comparison between "Costa" organocobalt type complexes and alkylcobalamins. Only two alkylcobalamins have been structurally characterized.[7,8] In both, the Co–N axial bond (between Co and N3 of 5,6-dimethylbenzimidazole) is very long (2.19 Å in methyl B_{12}[8] and 2.24 Å in coenzyme B_{12}[31]). The saloph complexes have Co–N bond distances almost as long[10] whereas the bond length is ca. 0.1 Å shorter in relevant cobaloximes.[3] The Co–N(py) bond of 2.11 Å in I is considerably shorter than the comparable bond in cobalamins. Thus, in this respect, the "Costa" model does not appear to mimic cobalamins as well as saloph compounds, but it is better than the cobaloxime system.

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(31) Recent refinements of coenzyme B_{12} are cited in ref 8.

In a first approximation, the (DO)(DOH)pn and $(DH)_2$ series are very close in both rate and mechanism of ligand-exchange reactions. We can estimate that the exchange rate is 10^6 times slower than in analogous cobalamins.[10] Thus, by this criterion also, the "Costa" model is not a good mimic of the B_{12} system. In previous studies of the ligand-exchange rates of [LCo((DO)(DOH)pn)R] complexes,[32-36] the reaction rates were found to be similar to cobaloximes for comparable L and R. We recently demonstrated a close relationship between relative donor strengths (as exemplified by the trans influence) of R in cobaloximes and in cobalamins.[8] The close relationship found here (although with some different R groups) between "Costa" models and cobaloximes suggests that the relative donor ability of R ligands is nearly independent of the equatorial ligand. A similar finding applies to saloph complexes for more limited data.[11]

The solvent system employed here (CH_2Cl_2) precludes an extensive investigation of the temperature dependence of the ligand-exchange reactions. We are currently searching for a leaving ligand L that would allow direct and accurate comparison of dissociation rates of (DO)(DOH)pn and $(DH)_2$ complexes over a convenient temperature range with a given R group. However, previous limited study of the enthalpy (ΔH^*) and entropy (ΔS^*) of activation for substitution of H_2O in aqueous solution suggests that ΔH^* somewhat favors (1–2 kcal/mol) ligand dissociation in the Costa model and ΔS^* favors ($\sim$5 eu) dissociation in the cobaloxime model.[35] The net result is then a very similar dissociation rate. Our findings in CH_2Cl_2 with py type ligands conform to this relationship. Similarly, the Co–O bond distance is longer for "Costa" compounds than cobaloximes when L = H_2O in the same way that the Co–N bond is longer for the related py compounds (Table VII). The cobaloximes invariably have py oriented so that the two α-H atoms are over the six-membered Co–N–O···H···O–N rings. We have pointed out that this is the sterically favored orientation.[10] In compounds I and II, the α-H atoms are over the five-membered Co–N–C–C–N rings. This orientation should, in itself, lead to greater steric repulsion between py and the equatorial ligand in (DO)(DOH)pn compounds than in $(DH)_2$ compounds. If this were not the case, the Co–N bond could, in fact, be smaller. This orientation may arise because the py avoids the nonplanar Co–N–C–C–C–N ring. Perhaps, then, the (DO)(DOH)pn compound is not really as electron rich as the Co–N bond length suggests. Both the longer Co–N bond and the more rapid dissociation rate in (DO)(DOH)pn compounds compared to that in $(DH)_2$ compounds may be a steric effect. Structural and rate comparisons on complexes with identical axial ligands, with L = nonbulky N-donor, are in progress.

Since the "Costa" models are such good electrochemical mimics of cobalamins,[16] it is puzzling that the ligand dissociation characteristics are so similar to cobaloximes which have reduction potentials which are too negative.[16] The longer axial Co–N bond in the (DO)(DOH)pn compounds could favor the reduction Co(III) → Co(II) since Co–N bond lengths in Co(II) species are expected to be longer than in Co(III) compounds.[37] This is consistent with the available electrochemical data.[16] Alternatively, the greater flexibility of the (DO)(DOH)pn ligand as evidenced by the larger α angles (Table VII) compared to that of cobaloximes and to that of other complexes with the (DO)(DOH)pn ligand,[29,38] may permit the equatorial ligand in the Co(II) form to adopt a nonplanar, perhaps more tetrahedral-like orientation. In this case, a more stable Co(II) form could result. However, at this point we can only speculate as to the reasons for the differences, and additional structural and rate studies on the Costa model are clearly needed.

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Registry No. I, 59691-94-0; I·C_3H_6O, 98541-96-9; II, 98541-98-1; $[H_2OCo((DO)(DOH)pn)$-i-$C_3H_7]ClO_4$, 98541-73-2; $[H_2OCo((DO)(DOH)pn)$-neo-$C_5H_{11}]ClO_4$, 98541-75-4; $[H_2OCo((DO)(DOH)pn)CH_2CF_3]ClO_4$, 98541-77-6; $[H_2OCo((DO)(DOH)pn)CH_2CO_2CH_3]ClO_4$, 98541-79-8; $[H_2OCo((DO)(DOH)pn)CH_2C_6H_5]ClO_4$, 23940-48-9; $[H_2OCo((DO)(DOH)pn)CH_2Si(CH_3)_3]ClO_4$, 98541-81-2; $[H_2OCo((DO)(DOH)pn)CH_2Br]ClO_4$, 98541-83-4; [($N$-MeIMD)Co((DO)(DOH)pn)$CH_2Br]ClO_4$, 98541-85-6; $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$, 23940-46-7; $[pyCo((DO)(DOH)pn)CH_3]ClO_4$, 65805-24-5; $[pyCo((DO)(DOH)pn)CH_2CH_3]ClO_4$, 65805-16-5; $[pyCo((DO)(DOH)pn)$-i-$C_3H_7]ClO_4$, 98541-87-8; $[pyCo((DO)(DOH)pn)$-neo-$C_5H_{11}]ClO_4$, 98577-03-8; $[pyCo((DO)(DOH)pn)CH_2CF_3]ClO_4$, 98541-89-0; $[pyCo((DO)(DOH)pn)CH_2CO_2CH_3]ClO_4$, 98541-91-4; $[pyCo((DO)(DOH)pn)CH_2Br]ClO_4$, 98541-93-6; $[pyCo((DO)(DOH)pn)CH_2C_6H_5]ClO_4$, 65805-20-1; $[pyCo((DO)(DOH)pn)CH_2Si(CH_3)_3]ClO_4$, 98541-95-8; 4-CN-pyCo$(DH)_2CH_2CO_2CH_3$, 98577-04-9; $[pyCo((DO)(DOH)pn)CH_2CH_3]PF_6$, 98541-99-2; Co((DO)(DOH)pn)Br_2, 23917-56-8; Co((DO)(DOH)pn)Cl_2, 23891-55-6; $[H_2OCo((DO)(DOH)pn)CH_2CH_3]ClO_4$, 23940-47-8; B_{12}, 13870-90-1; neo-$C_5H_{11}I$, 15501-33-4; CH_2Br_2, 74-95-3.

Supplementary Material Available: Tables of elemental analyses, anisotropic thermal parameters, hydrogen atom coordinates, complete bond lengths and bond angles, and final calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

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