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Vitamin B_{12} Model Compounds: Influence of Neutral Ligand Orientation on the Co–N Axial Bond Length

NEVENKA BRESCIANI PAHOR, LUCIO RANDACCIO* and ENNIO ZANGRANDO

Dipartimento di Scienze Chimiche, Universita' di Trieste, 34127 Trieste (Italy)

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Abstract

The crystal structures of two complexes of the type $[L(Co(DO)(DOH)pn)Me]PF_6$ where (DO)(DOH)pn = N^2,N^{2}-propanediylbis(2,3-butanedione 2-imine 3-oxime) and L = 1-methylimidazole, 1-MeImd (**1**) and 1,2-dimethylimidazole, 1,2-Me_2Imd (**2**) have been determined. Both compounds crystallize in the space group $P2_1/c$ with cell parameters $a = 7.104(2)$, $b = 23.110(5)$, $c = 15.224(2)$ Å, $\beta = 99.29(2)°$ for **1** and $a = 8.072(2)$, $b = 12.290(2)$, $c = 23.704(4)$ Å, $\beta = 95.41(2)°$ for **2**. The two structures were solved by Patterson and Fourier methods and refined by least-squares methods to final R values of 0.053 (**1**) and 0.043 (**2**) using 4190 (**1**) and 2782 (**2**) independent reflections. The axial N–Co–C fragment is characterized by Co–N and Co–C distances of 2.042(2) and 2.001(3) Å in **1** and 2.100(4) and 2.003(5) Å in **2**, respectively.

A comparison with the structure of the analogous cobaloximes shows that the nature of the equatorial ligand affects significantly the orientation of py with respect to the equatorial moiety as well as the Co–N(axial) distance. No significant variation is observed in the Co–C bond length. The relationship between the Co–N axial bond lengths and the rate constants for the reaction of displacement of the planar neutral ligand, L, is discussed.

Introduction

It is widely believed that structural and conformational changes in coenzyme B_{12} lead to an acceleration in Co–C bond cleavage and the role of 5,6-dimethylbenzimidazole has been considered primarily in terms of its *cis* steric interaction with the corrin ring [1]. The benzimidazole ligand lies over the corrin six-membered chelate rings [2] and the Co–N(benzimidazole)–C angles are unsymmetrical to avoid short contacts of the benzimidazole six-membered ring with the corrin. Any distortion which moves the benzimidazole with respect to the equatorial ligand could induce a change in corrin pucker which could weaken (lengthen) the Co–C bond by enhancing repulsive interactions between corrin and the 5'-deoxyadenosyl group.

In simple models, we have termed this type of transmission of steric effects between axial ligands as steric *trans* effect [3]. Evidence of such effect has been reported for cobaloximes having neutral ligand with different bulk [4]. On the other hand, recent attention has been focused on the chemistry of the so called Costa complexes, $[L(Co(DO)(DOH)pn)R]PF_6$ [5–7]. In these new B_{12} model complexes the planarity of the equatorial ligand is disrupted by the pucker of a propylene group which formally substitutes one of the oxime O–H···O bridges of the $Co(DH)_2$ moiety.

Preliminary data suggested that changing of the equatorial moiety induces a different orientation of the planar axial ligand and a variation of the corresponding axial distance [7, 8].

In order to obtain further insight into this feature, which has been termed steric *cis* effect, we report the structural determination of $[L(Co(DO)(DOH)pn)Me]PF_6$ with L = 1-MeImd and 1,2-Me_2Imd.

Experimental

Crystal Data

Crystals of $[L(Co(DO)(DOH)pn)Me]PF_6$ where L = 1-MeImd (**1**) and 1,2-Me_2Imd (**2**) were obtained as previously reported [5]. Cell dimensions determined from Weissenberg and precession photographs, were refined from 25 reflections in the θ range 12–17° on a CAD4 Enraf Nonius single crystal diffractometer equipped with graphite monochromator and Mo Kα radiation ($\lambda = 0.7107$ Å). Intensities of three standard reflections were measured during the data collection and did not show any systematic variation throughout the data recording. Reflections having intensities $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors and for anomalous dispersion and were used in the subsequent refine-

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*Author to whom correspondence should be addressed.

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TABLE 1. Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$CoO_2N_6C_{16}H_{28}PF_6\cdot CH_4O$	$CoO_2N_6C_{17}H_{30}PF_6$
Molecular weight	572.4	554.4
a (Å)	7.104(2)	8.072(2)
b (Å)	23.110(5)	12.290(2)
c (Å)	15.224(2)	23.704(4)
β (°)	99.29(2)	95.41(2)
D (meas.) (g cm^{-3})	1.53	1.57
D (calc.) (g cm^{-3})	1.54	1.57
Z	4	4
F(000)	1184	1144
Space group	$P2_1/c$	$P2_1/c$
μ (cm^{-1})	8.3	8.7
Crystal dimensions (cm^3)	0.03 × 0.03 × 0.06	0.04 × 0.04 × 0.05
2θ max (Mo Kα)	56	56
No. reflections measured	6312	6037
No. independent reflections $I > 3\sigma(I)$	4190	2782
No. varied parameters	361	352
R	0.053	0.043
R_w	0.063	0.051

ment. No absorption correction was included because of the small size of the crystals used and the low values of the absorption coefficients.

The crystallographic data are summarized in Table 1.

Solution and Refinement of the Structures

The two structures were solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares methods. After anisotropic refinements, the calculated positions of the hydrogen atoms all occurred in positive electron density regions. The final cycles with the fixed contribution of hydrogen atoms ($B = 5.0$ Å^2) converged to final R and R_w values reported in Table 1. The final weighting scheme [9] was $w = 1/(\sigma(F)^2 + (pF)^2 + q)$ where $p = 0.01$ and 0.02 and $q = 4$ and 3 for **1** and **2**, respectively, chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and ($\sin \theta/\lambda$). In both structures the PF_6^- anions were found to be disordered. This fact was interpreted as due to two anion orientations of about 0.5 occupancy factors for structure **1** and of about 0.7 (F1–6) and 0.3 (F19–69) for **2**. All fluorine atoms occupancies were fixed on the basis of the respective electron density of the peaks in the Fourier maps. A crystallographically independent molecule of methanol was found in **1**. Atomic scattering factors were those of ref. 10. All calculations were carried out using the SDP-CAD4 programs on a PDP11-44 computer. Final positional parameters of non-hydrogen atoms and their B_{eq} (Å^2) are given in Tables 2 and 3. See also 'Supplementary Material'.

Description of the Structures

ORTEP drawings of cations **1** and **2** with the atom numbering scheme are depicted in Figs. 1 and 2. In both compounds, the (DO)(DOH)pn ligand occupies the four equatorial positions in a distorted octahedral stereochemistry around the Co atom. Selected bond lengths and angles of the cations are reported in Table 4. The Co(DO)(DOH)pn units are similar within experimental error in the two compounds. The four equatorial N atoms are coplanar within ±0.014(4) (**1**) and ±0.049(4) (**2**) Å and the cobalt atom is displaced by 0.053 (**1**) and 0.104 (**2**) Å from their respective

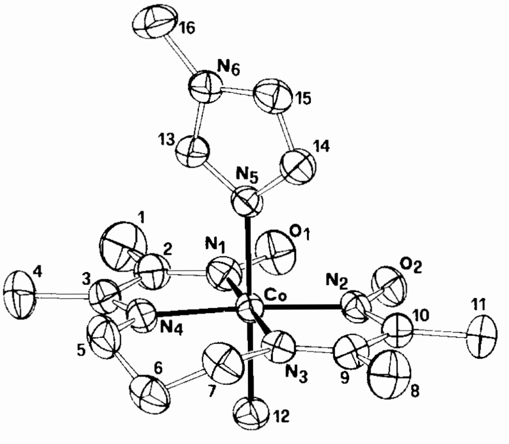

Fig. 1. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for non-hydrogen atoms of cation **1**. Carbon atoms are labeled only by their ordering number in the coordinate list.

TABLE 2. Atomic positional parameters of non-hydrogen atoms with e.s.d.s in parentheses for [1-MeImd(Co(DO)(DOH)pn)Me]PF_6 (**1**)

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
Co	0.05114(7)	0.36159(2)	0.31559(3)	2.212(8)	C12	0.1828(6)	0.3024(2)	0.2512(3)	3.10(8)
O1	0.3697(4)	0.4356(1)	0.3136(2)	4.00(7)	C13	−0.1605(6)	0.4710(2)	0.3445(3)	3.12(8)
O2	0.3978(4)	0.3681(1)	0.4380(2)	3.38(6)	C14	−0.1259(6)	0.4216(2)	0.4647(3)	3.24(9)
N1	0.2009(5)	0.4178(2)	0.2705(2)	3.04(7)	C15	−0.2236(6)	0.4696(2)	0.4790(3)	3.42(9)
N2	0.2260(4)	0.3430(1)	0.4182(2)	2.56(6)	C16	−0.3470(8)	0.5555(2)	0.3831(4)	5.0(1)
N3	−0.0917(4)	0.3017(2)	0.3616(2)	2.63(6)	OMe	−0.0398(7)	0.1590(2)	0.1675(3)	7.7(1)
N4	−0.1153(5)	0.3774(2)	0.2063(2)	2.96(7)	CMe	−0.194(1)	0.1279(3)	0.1894(5)	7.9(2)
N5	−0.0855(5)	0.4223(2)	0.3797(2)	2.68(6)	P	0.3285(2)	0.12215(7)	0.3876(1)	5.52(4)
N6	−0.2455(5)	0.5010(2)	0.4022(2)	3.08(7)	F1	0.444(2)	0.1213(7)	0.3176(8)	15.7(5)
C1	0.2396(9)	0.4843(3)	0.1477(4)	5.6(1)	F2	0.197(2)	0.1121(6)	0.4612(9)	14.0(4)
C2	0.1362(7)	0.4398(2)	0.1926(3)	3.46(9)	F3	0.237(2)	0.0709(4)	0.3264(6)	10.3(3)
C3	−0.0517(7)	0.4153(2)	0.1563(3)	3.48(9)	F4	0.222(2)	0.1713(6)	0.3471(9)	16.2(5)
C4	−0.1528(9)	0.4373(3)	0.0688(3)	5.5(1)	F5	0.436(1)	0.1711(4)	0.4440(6)	10.8(3)
C5	−0.3055(6)	0.3513(2)	0.1842(3)	4.1(1)	F6	0.425(2)	0.0648(5)	0.4464(8)	11.8(4)
C6	−0.3096(6)	0.2901(2)	0.2196(3)	3.8(1)	F19	0.335(1)	0.1472(4)	0.2847(6)	9.2(3)
C7	−0.2858(6)	0.2858(2)	0.3200(3)	3.8(1)	F29	0.332(2)	0.1084(6)	0.4824(7)	13.2(4)
C8	−0.0988(8)	0.2359(2)	0.4905(3)	4.8(1)	F39	0.148(1)	0.1613(5)	0.3782(6)	10.4(3)
C9	−0.0112(6)	0.2797(2)	0.4365(3)	2.99(8)	F49	0.150(2)	0.0823(7)	0.355(1)	18.5(5)
C10	0.1795(6)	0.3024(2)	0.4695(3)	2.94(8)	F59	0.514(2)	0.0912(6)	0.3860(8)	15.2(4)
C11	0.3064(7)	0.2811(2)	0.5504(3)	4.0(1)	F69	0.492(2)	0.1631(8)	0.4188(9)	19.4(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\Sigma_i\Sigma_j a_i a_j \beta(i,j)$.

TABLE 3. Atomic positional parameters of non-hydrogen atoms with e.s.d.s in parentheses for [1,2-Me_2Imd(Co(DO)(DOH)pn)Me]PF_6 (2)

Atom	*x*	*y*	*z*	*B* (Å^2)	Atom	*x*	*y*	*z*	*B* (Å^2)
Co	0.26425(7)	0.17789(5)	0.16063(2)	2.284(9)	C12	0.2191(6)	0.2965(4)	0.2151(2)	3.5(1)
O1	0.5994(4)	0.1908(3)	0.2074(2)	4.21(8)	C13	0.3819(5)	−0.0404(4)	0.1043(2)	2.94(9)
O2	0.5295(4)	0.2983(3)	0.1213(1)	3.87(7)	C14	0.2547(7)	0.0714(4)	0.0445(2)	3.9(1)
N1	0.4497(4)	0.1460(3)	0.2118(2)	2.90(8)	C15	0.2928(7)	−0.0161(5)	0.0154(2)	4.5(1)
N2	0.3652(5)	0.2829(3)	0.1177(2)	2.77(7)	C16	0.4322(8)	−0.1944(5)	0.0385(3)	5.3(1)
N3	0.0709(4)	0.2298(3)	0.1165(2)	2.74(7)	C17	0.4592(7)	−0.0965(4)	0.1554(2)	4.2(1)
N4	0.1621(4)	0.0770(3)	0.2081(2)	2.69(7)	P	0.0406(2)	0.2248(1)	0.38638(6)	4.37(3)
N5	0.3102(5)	0.0579(3)	0.1010(2)	2.91(8)	F1	0.1715(7)	0.3051(5)	0.3663(3)	9.0(2)
N6	0.3733(5)	−0.0862(3)	0.0528(2)	3.69(9)	F2	−0.0972(8)	0.3100(5)	0.3679(3)	10.0(2)
C1	0.5557(7)	0.0673(5)	0.3031(2)	4.9(1)	F3	−0.1036(8)	0.1497(5)	0.4056(3)	8.7(2)
C2	0.4263(6)	0.0866(4)	0.2555(2)	3.03(9)	F4	0.172(1)	0.1356(6)	0.4043(4)	11.9(2)
C3	0.2566(6)	0.0427(4)	0.2512(2)	3.08(9)	F5	0.0102(9)	0.1733(6)	0.3262(2)	9.4(2)
C4	0.2066(8)	−0.0387(5)	0.2929(2)	4.8(1)	F6	0.064(1)	0.2727(7)	0.4463(3)	12.9(3)
C5	−0.0124(6)	0.0424(4)	0.1989(2)	3.6(1)	F19	0.187(2)	0.195(1)	0.3503(6)	8.8(4)
C6	−0.0891(6)	0.0681(4)	0.1397(2)	3.6(1)	F29	−0.035(2)	0.117(1)	0.3779(9)	11.3(5)
C7	−0.0947(5)	0.1874(5)	0.1250(2)	3.8(1)	F39	−0.079(2)	0.271(2)	0.4233(8)	16.2(6)
C8	−0.0403(7)	0.3770(4)	0.0530(2)	4.4(1)	F49	0.153(2)	0.329(1)	0.4038(8)	9.9(5)
C9	0.0937(6)	0.3122(4)	0.0849(2)	3.04(9)	F59	−0.051(2)	0.280(1)	0.3356(7)	11.4(5)
C10	0.2684(6)	0.3426(4)	0.0829(2)	3.03(9)	F69	0.151(2)	0.180(1)	0.4372(6)	8.3(4)
C11	0.3323(8)	0.4293(5)	0.0471(2)	4.6(1)					

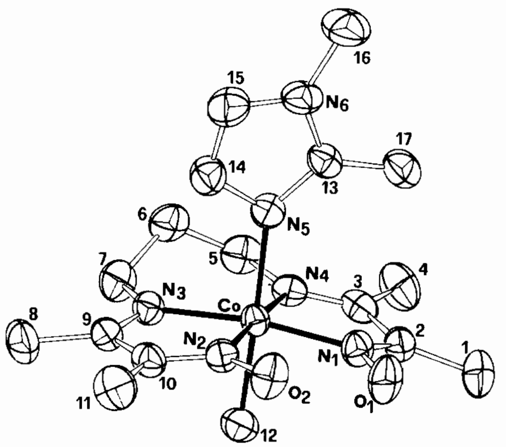

Fig. 2. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for non-hydrogen atoms of cation 2.

TABLE 4. Selected bond lengths (Å) and angles (°) with e.s.d.s for compounds 1 and 2

	1	2
Co–N1	1.878(2)	1.877(4)
Co–N2	1.881(2)	1.876(4)
Co–N3	1.915(2)	1.905(4)
Co–N4	1.914(2)	1.912(4)
Co–N5	2.042(2)	2.100(4)
Co–C12	2.001(3)	2.003(5)
N1–Co–N2	97.1(1)	97.7(2)
N1–Co–N3	177.2(1)	170.7(2)
N1–Co–N4	81.8(1)	81.2(2)
N1–Co–N5	92.3(1)	96.2(2)
N1–Co–C12	87.5(1)	85.3(2)
N2–Co–N3	81.3(1)	81.2(2)
N2–Co–N4	175.8(1)	176.6(2)
N2–Co–N5	93.51(9)	90.3(2)
N2–Co–C12	87.3(1)	87.9(2)
N3–Co–N4	99.6(1)	99.4(2)
N3–Co–N5	90.07(9)	93.1(2)
N3–Co–C12	90.1(1)	85.5(2)
N4–Co–N5	90.55(9)	93.1(2)
N4–Co–C12	88.6(1)	88.8(2)
N5–Co–C12	179.2(1)	177.8(2)
Co–N5–C13	125.7(2)	134.2(3)
Co–N5–C14	129.1(2)	120.4(3)
C13–N5–C14	105.2(2)	105.3(4)

mean planes towards the imidazole ligand. The two chemically equivalent halves of the equatorial macrocycle with the exclusion of C(6), are approximately planar. These planes bend towards the alkyl ligand and make a dihedral angle, α, of 4.8° in **1**, but the (DO)(DOH)pn unit is significantly distorted from planarity with an umbrella shape conformation. In **2** the α value is 19.7°. The six-membered chelate ring has the expected conformation with the C(6) atom out of the chelate plane on the side of the less bulkier axial methyl group in **1** and of substituted imidazole in **2**, respectively. The torsion angles around C(5)–C(6) and C(6)–C(7) bonds are –68.6 and 69.2° in **1**, –61.7 and 72.6° in **2**. The O...O distances of the oxime bridges are 2.436(3) Å in **1** and 2.451(5) Å in **2**, and fall within the range reported in other octahedral (DO)(DOH)pn cobalt complexes [5–7], but are significantly shorter than the mean value of 2.487(2) Å in cobaloximes [3]. The Me–Co–L fragment is characterized by a C–Co–N angle of 179.2(1) (**1**) and 177.8(2)° (**2**). In the two compounds, the Co–C bond lengths (≈2.0 Å), reported in Table 4, are similar within experimental error. The Co–N distance lengthens with the increasing bulk of the neutral ligand, from 2.042(2) Å in **1** to 2.100(4) Å in **2**. As in B_{12} coenzyme, the coordination of 1,2-Me_2Imd is characterized by a strong 'asymmetry' in the two Co–N–C angles which are 134.2(3)° on the side of the methyl substituent in position 2, and 120.4(3)° on the opposite side [6]. The imidazole residues are planar (±0.015 Å in **1** and ±0.018 Å in **2**) and lie over the five-membered Co–N–C–C–N chelate rings, making dihedral angles of 86.0 and 88.1° for **1** and **2**, respectively, with the equatorial coordination plane. The orientation of the neutral ligand in (DO)(DOH)pn, imposed by the propylene bridge, is sketched in Fig. 3. In compound **1** the oxygen atom of methanol is involved in weak hydrogen bonds with F4 (3.06(2) Å) and F19 (2.97(1) Å).

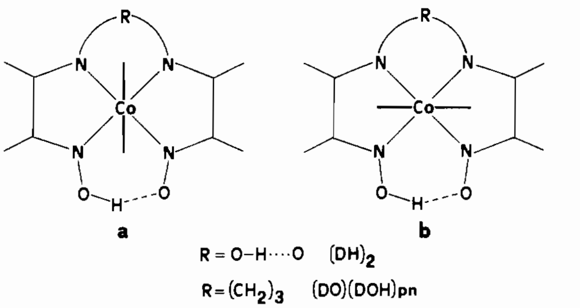

Fig. 3. Orientation of the neutral ligand L with respect to the equatorial plane in LCo(chel)R complexes.

Discussion

Some structural and kinetic data for $(DH)_2$ and (DO)(DOH)pn series are compared in Table 5. Although this Table is far from complete for a quantitative analysis, the comparison clearly indicates that log *k* values and Co–N(axial) bond lengths are influenced by the following properties of the axial ligands:

(1) The σ-donor power of the alkyl group strongly influences the *trans* Co–N(axial) bond. This point has been well established in numerous series of cobaloximes [3]. In addition, comparison of Me and iPr

TABLE 5. Comparison of Co–N axial bond lengths (Å), log k^a (s^{-1}) and α angles (°) in LCo(chel)R complexes[b], with L = planar neutral ligand

L	R = Me			R = iPr		
	Co–N	log k	α	Co–N	log k	α
chel = $(DH)_2$ (orientation of L as in Fig. 3a)[c]						
Imd	2.019		+1.8			
1-MeImd	2.058	−3.75	+4.4		−0.80	
Me_3Bzm	2.060	−2.38	+4.7	2.097	0.56	+4.0
py	2.068	−2.10	+3.2	2.099	0.48	+4.0
1,2-Me_2Imd	2.086	−1.96	+3.4	2.121	1.04	+7.3
2-NH_2py		0.54		2.194	too fast	+5.2
chel = (DO)(DOH)pn (orientation of L as in Fig. 3b)						
1-MeImd (**1**)	2.042	−4.00	+4.8			
Me_3Bzm	2.100	−2.36	+13.8		1.60	
py	2.106	−1.47	+6.9		1.52	
1,2-Me_2Imd (**2**)	2.100	−1.23	+19.7			
2-NH_2py		0.89				

[a] First order rate constant for L exchange of LCo(chel)R in CH_2Cl_2 at 25 °C. Data from refs. 3, 5 and 11. [b] Crystallographic data from refs. 3 and 4. α is the interplanar angle between the two chemically equivalent moieties of the equatorial ligand; a positive sign indicates a bending towards the alkyl group. [c] With exception of 1-MeImdCo$(DH)_2$Me, where it is *b*.

derivatives shows an increase of log k of about 3 units and a corresponding increase of the Co–N bond length of about 0.03 Å.

(2) The Co–N distances are influenced by the kind of N donor atom (pyridine or imidazole) and by the bulk of the N ligand. The substituted imidazole complexes show Co–N bond lengths shorter than those of corresponding py analogues from 0.04 to 0.07 Å. Correspondingly, log k values are lower by 1.7 to 2.5 units. Such a difference may be attributed to the narrower C–N–C angle in imidazole derivatives (theoretical value of 105°) with respect to that in pyridine analogues (120°) [7]. This decreases, in the former, the interaction of the side H atoms of the neutral ligand with the equatorial one. The increase of the bulk, mainly originated from the 2-NH_2 group in pyridine derivatives and from the 2-methyl side group in imidazoles, provokes a lenghtening of the Co–N bond in the range from 0.06 to 0.1 Å with respect to the parent compounds and an increase of 2–3 units in log k.

(3) The nature of the equatorial ligand, $(DH)_2$ or (DO)(DOH)pn, determines differences in the Co–N(axial) bond lengths from 0.02 to 0.04 Å and in the α bending (Table 5) significantly larger in Costa models. Correspondingly, differences in log k not larger than 1 unit are observed.

(4) Comparison of the 1-MeImd and Imd cobaloximes derivatives, which have different orientations a and b (see Fig. 3 and Table 5), illustrates clearly that a lengthening of the Co–N distance is to be expected in going from orientation a to b.

Furthermore, comparison of Me(Co(DO)(DOH)pn)L^+ derivatives with L = py and 1-MeImd gives further support to the hypothesis that Co–N bond lengths, in the imidazole derivatives, are to be expected significantly shorter than those of the py analogues, when the orientation of the neutral ligand is the same. Since in the (DO)(DOH)pn derivatives the orientation [6, 7] imposed by the propylene bridge is b, it may be supposed that a large amount of the lengthening observed in these complexes when compared with the analogous cobaloximes should be attributed to the different orientation.

Finally, data of Table 5 suggest that all the above influences, which determine the Co–N bond length and the log k values, are almost independent. Both Co–Me and Co–iPr for complexes of Table 5 do not change significantly with the nature of the N ligand, ranging from 1.985(3) to 2.009(7) Å and from 2.085(3) to 2.097(6) Å, respectively. Therefore, it may be concluded that the nature and the orientation of the N ligands in the Costa models mainly influence the Co–N bond length and the pucker of the equatorial ligand, particularly enhanced in the (DO)(DOH)pn derivatives.

Supplementary Material

Hydrogen atom coordinates, anisotropic thermal parameters, bond lengths and angles and tables of calculated and observed structure factors are available from the authors on request.

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