New Alkyl−Cobalt(III) Complexes with Tridentate Amino−Oxime Ligands: Synthesis, Structure, and Reactivity

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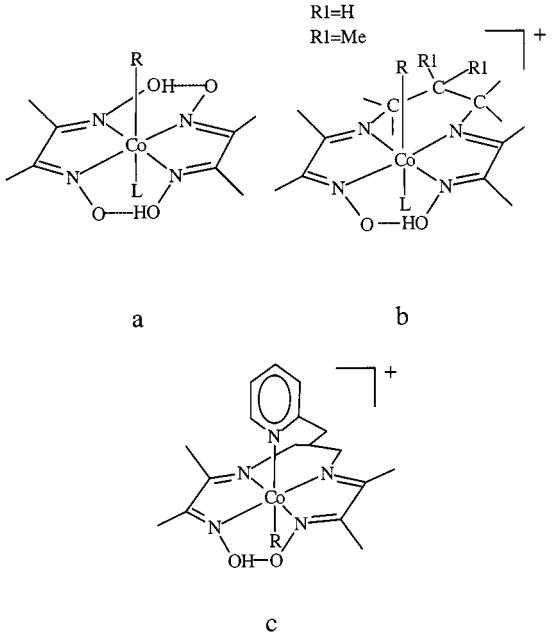
The oxidative addition of alkyl halides to the Co^{I} species generated by the reduction of $[Co^{III}(LNHpy)(HLNHpy)](ClO_4)_2$ (**1**), where HLNHpy is the tridentate 2-(2-pyridylethyl)amino-3-butanone oxime ligand and LNHpy is its conjugate base, led to the formation of a new class of organocobalt complexes of general formula $[RCo^{III}(LNHpy)(HLNHpy)](ClO_4)$ [R = Me (**2a**), Et (**2b**), CH_2CF_3 (**2c**), *n*Bu (**2d**), and CH_2Cl (**2e**)]. All the complexes were characterised by ^1H and ^{13}C NMR spectroscopy. The X-ray structures of **2a**, **2b** and **2c** provide evidence for a pseudo-octahedral configuration, where HLNHpy and LNHpy act as bi- and tridentate ligands, respectively. The axial geometry in **2a** is closer to that found in methylcobalamin than that reported for other models, suggesting steric and electronic *cis* influences of the equatorial ligands close to those of the corrin nucleus. The solution properties and the reactivity show strong analogies with those of the previously known Vitamin B_{12} models.

Introduction

Previous studies on classical models for coenzyme B_{12}, such as alkylcobaloximes $LCo(DH)_2R$ (Scheme 1a, DH = monoanion of dimethylglyoxime, R = alkyl, L = neutral Lewis base), have been aimed at elucidating the factors that affect the properties of the Co−C bond. Experimental evidence shows that steric and electronic factors are both important in this context.[1] The recent structural results on B_{12} enzymes have shown that in some of the enzyme-bound B_{12} coenzymes, the benzimidazole residue is replaced in the coordination to Co by the imidazole moiety of a histidine of the protein chain.[2] This finding has renewed interest in the nature of the Co−L bond in simple models.[3,4,5] The early hypothesis[1] that the Co−L distance is influenced by the orientation of the planar L ligand, measured by the torsional angle φ around that bond, has been confirmed.[6−8] In orientation A (Scheme 2), when φ is close to 0, the Co−L distance is found to be shorter by about 0.03 Å than in orientation B (Scheme 2), corresponding to φ close to 90°. Typically, orientation A is found in cobaloximes, whereas orientation B is found in iminocobaloxime analogues (Scheme 1b). However, in the lariat-type complexes[8] (Scheme 1c), derived from iminocobaloximes, the values of φ and of the Co−py distance are similar to those in the cobaloxime analogues. In fact, in the lariat-type complexes, although derived from iminocobaloximes, orientation A is imposed by the conformational rigidity of the pentadentate ligand.



Scheme 1

Less definitive indications about the influence of the L orientation on the Co−C bond in the ground state has been found so far. In fact, structural (Co−R distance) and spectroscopic (ν_{Co-Me}) evidences have suggested that orientation B may correspond to a weaker Co−C bond than in orientation A.[7] On the other hand, FT-Raman studies did not detect any change in the Co−C force constants even in base-on and base-off cobalamins.[9] Furthermore, recent studies[10] on the interaction of adenosylcobinamides with hindered bases, (1,2-Me_2Im, 2-Mepy and 2,6-Me_2py) have provided evidence for a dominant effect of the axial base on the transition state of the Co−C bond-cleavage process.

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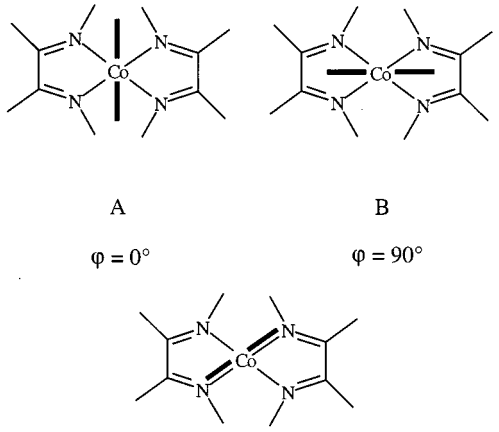
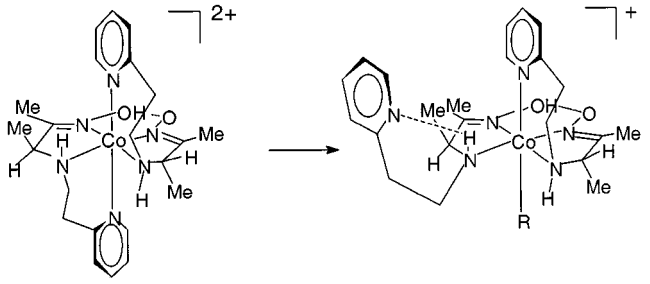


Scheme 2

In order to obtain further insight into the above points, we have synthesised a new class of organocobalt derivatives $[RCo(LNHpy)(HLNHpy)]ClO_4$, (**2**) (HLNHpy = 2-(2-pyridylethyl)amino-3-butanone oxime) derived from $[Co(LNHpy)(HLNHpy)](ClO_4)_2$ (**1**),[11] (Scheme 3). The geometry of **2** is reminiscent of the lariat-type complexes,[8] which combine the corrin-like features of the iminocobaloximes with an appended axial base. However, they differ from the latter by having a more crowded equatorial moiety, owing to the side substituents at the amino C−N fragments. Therefore, complexes **2** could potentially mimic the interactions between axial and equatorial moieties in cobalamins better than previous models.



1 **2**

Scheme 3

The synthesis and NMR characterisation of a series of complexes of type **2** [R= Me (**2a**), Et (**2b**), CH_2CF_3 (**2c**), *n*Bu (**2d**), CH_2Cl (**2e**)], the crystal structure of **2a**, **2b**, **2c** as well as the reactivity of the Me derivative are reported and their ability to model the B_{12} system is discussed.

Results

Synthesis

The organometallic complexes of type **2** were obtained according to Equation (1).

$$[Co^{III}(LNHpy)(HLNHpy)]^{2+} \xrightarrow{NaBH_4, PdCl_2} [Co^{I}(LNHpy)(HLNHpy)]$$
$$[Co^{I}(LNHpy)(HLNHpy)] \xrightarrow{RX} [R\text{-}Co^{III}(LNHpy)(HLNHpy)]^{+} + X^{-} \quad (1)$$

The process involves the oxidative addition of the appropriate alkyl halide to the nucleophilic Co^I species, which may be generated in situ by the reduction of **1** with $NaBH_4$/$PdCl_2$. Similar synthetic routes have been extensively exploited to obtain cobalt complexes containing highly unsaturated equatorial ligands. Generally, the Co^I species are obtained from Co^{III} by the use of $NaBH_4$.[12] We observed[11] that although the reduction of **1** with $NaBH_4$ does not proceed beyond the formation of a Co^{II} species, the complete reduction to Co^I could be achieved by the addition of a catalytic amount of $PdCl_2$ to the reaction mixture. The formation of Co^I is recognisable by its nucleophilic reactivity toward alkyl halides, but the dark brown solutions are extremely sensitive to oxygen and this prevented further characterisation. It is noteworthy that the Co^{II} complex obtained by reduction with $NaBH_4$ is unreactive toward alkyl iodides (see Discussion). Several attempts to synthesise organometallic derivatives with bulky alkyl groups such as iC_3F_7, iC_3H_7, and adamantyl were carried out, but the Co^I species failed to react with the corresponding alkyl halide. Even after several hours, Co^I was unchanged and its presence could be verified by the addition of CH_3I to the reaction mixture, which rapidly led to the formation of the methyl derivative.

Reactivity of the Methyl Derivative 2a

Like alkylcobalamins[13] and synthetic alkylcobalt(III) chelates,[14] complex **2a** is light-sensitive. The photolysis of an aqueous solution of the complex in the presence of oxygen produced formaldehyde and complex **1**. This result may be rationalised by the assumption that the initial step is the homolysis of the Co−C bond, which produces a Co^{II} species and methyl radicals. In the presence of oxygen they are oxidised, giving **1** and formaldehyde, which are the expected products of aerobic photolysis.[13]

The methyl-transfer reaction occurs from complex **2a** to $Co^{II}(DH)_2(H_2O)_2$. The reaction was carried out in the dark under nitrogen. After exposure to air, complex **1** and $CH_3Co^{III}(DH)_2H_2O$ were isolated and identified [Equation (2)].

$$[CH_3Co^{III}(LNHpy)(HLNHpy)]^{+} + [Co^{II}(DH)_2] \longrightarrow$$
$$[Co^{II}(LNHpy)(HLNHpy)]^{+} + [CH_3Co^{III}(DH)_2H_2O] \quad (2)$$
$$[Co^{II}(LNHpy)(HLNHpy)]^{+} \xrightarrow{O_2} [Co^{III}(LNHpy)(HLNHpy)]^{2+}$$

Since the process occurs in the absence of light, it can be formulated as a direct transfer of the methyl radical to the acceptor. The Co^{II} species arising from the dealkylation gives **1** after oxidation in the air. The complex **2a** also

methylates Vitamin B_{12r} under the experimental conditions described above [Equation (3)].

$$[CH_3Co^{III}(LNHpy)(HLNHpy)]^+ + \text{Vit. } B_{12r} \longrightarrow CH_3B_{12} + [Co^{II}(LNHpy)(HLNHpy)]^+ \quad (3)$$

The exchange reaction of the chelate moiety of **2a** has been successfully carried out in one case: A methanolic solution of **2a**, dimethylglyoxime, and pyridine (allowed to stand overnight) produced $CH_3Co^{III}(DH)_2py$ as a product. It seems likely that the reaction proceeds by the stepwise replacement of the two amino oxime ligands by dimethylglyoxime.

X-ray Structures

The ORTEP[15] drawings of **2a**−**2c** are given in Figure 1, crystal data in Table 1. For **2a**, only the ORTEP drawing of one of the two crystallographically nonequivalent molecules (A) is shown. Complexes **2** can formally be described as being derived from parent compound **1**, by substitution of one axial pyridyl moiety with the R group. Complex **1** can

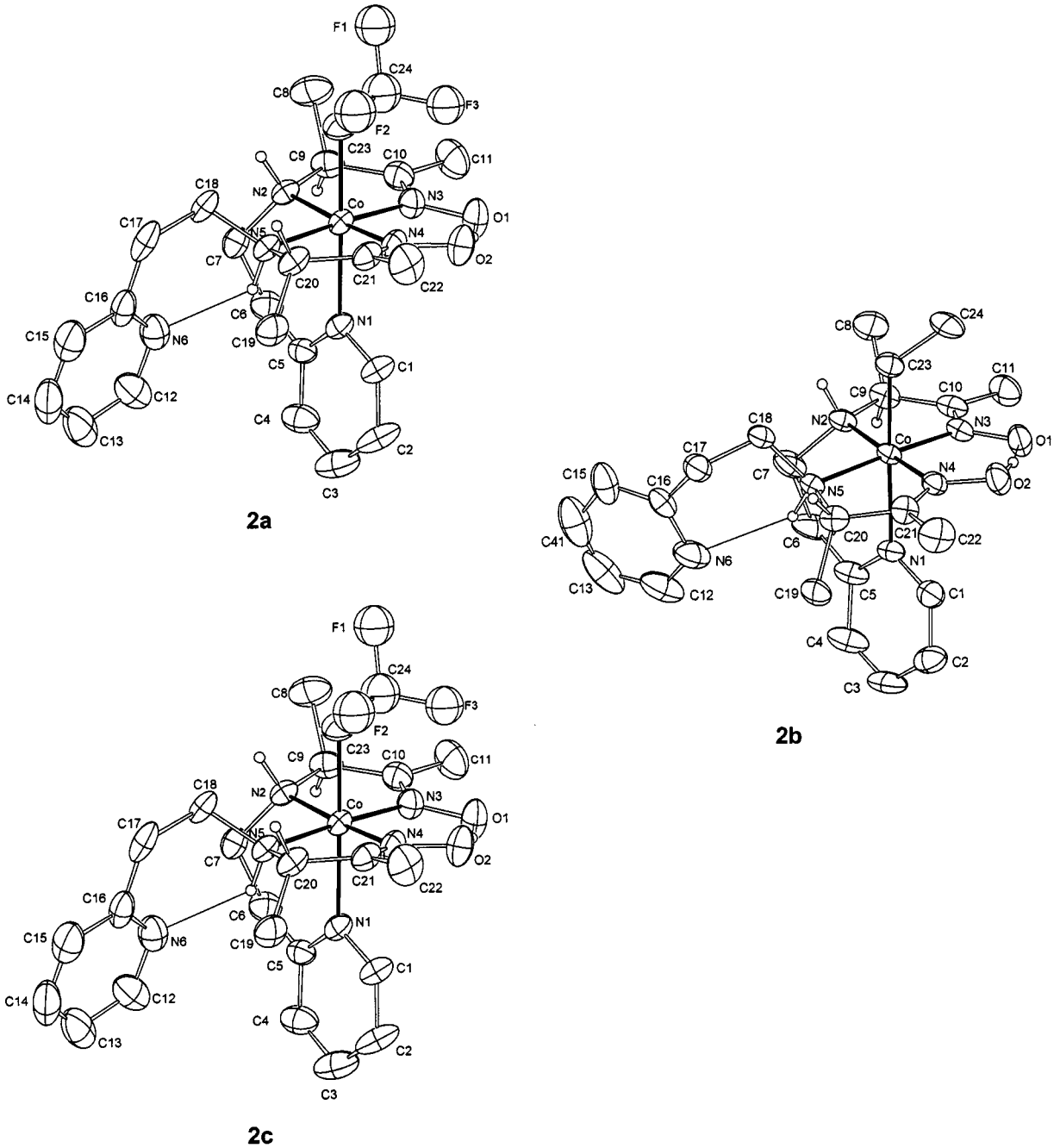


Figure 1. ORTEP diagram with the numbering scheme for the non-hydrogen atoms of one of the two crystallographic independent molecules of **2a**, **2b**, and **2c**

therefore, to a good approximation, be considered as a structural reference for complexes **2** (Scheme 3). The pendant pyridyl group in complexes **2** is anchored through N6 to the N5 amino atom by a short intramolecular hydrogen bond in the range of 2.861(8)−3.020(8) Å (Table 2). The two oximic O atoms of LNHpy and HLNHpy are hydrogen-bonded, with O···O distances ranging from 2.401(7) to 2.432(7) Å (Table 2). The average of the values is shorter by about 0.07 Å than that of 2.487(2) Å, obtained by averaging 140 values found in cobaloximes.[1b] Analysis of the N−O bonds in the three complexes and of the Fourier difference maps did not allow for location of the H oxime bridge, which was assumed to be bonded to O2 (see below), so that LNHpy acts as a tridentate and HLNHpy as a bidentate ligand.

The coordination around N1 is such that the two Co−N1−C angles differ by up to about 10°, the largest value being on the side of the 2-ethylene chain (Table 2). Such an asymmetric coordination of the axial N donor is typical of lopsided ligands, such as Me_3Bzm,[1] and of lariat-type complexes of Scheme 1c.[8]

The axial distances, together with the torsion angle around the Co−N1 bond, φ, are given in Table 3. The Co−N1 distances reflect the notable *trans* influence of the alkyl group in complexes **2**, relative to that of the pyridyl group in **1**. The Co−C bond length in complexes **2** appears to increase with the bulk and to decrease with the electron-withdrawing ability of R, in agreement with previous findings in cobaloximes.[19]

Table 1. Crystal data and structure refinement for complexes **2a**, **2b** and **2c**

Compound	**2a**	**2b**	**2c**
Empirical formula	$C_{24.50}H_{39}ClCoN_6O_{6.50}$	$C_{24}H_{38.50}ClCoN_6O_{6.25}$	$C_{24.50}H_{36}Cl_2CoF_3N_6O_6$
Formula weight	616.00	605.49	697.42
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	monoclinic, $C2/c$
a [Å]	22.581(2)	16.868(4)	16.090(2)
b [Å]	11.907(2)	9.6950(10)	15.165(3)
c [Å]	22.788(3)	17.218(4)	25.837(4)
β [°]	106.370(8)	91.38(2)	105.220(10)
V [Å^3]	5878.7(14)	2814.9(10)	6083(2)
Z, calcd. density [Mg/m^3]	8, 1.392	4, 1.429	8, 1.523
Absorption coefficient [mm^{-1}]	0.724	0.754	0.807
F(000)	2592	1274	2888
Crystal size [mm]	0.3 × 0.6 × 0.9	0.2 × 0.3 × 0.7	0.2 × 0.3 × 0.6
Range for data collect. [°]	2.05 to 27.97	5.01 to 26.02	5.02 to 26.02
Reflections collected/unique	7955/7554 [R(int) = 0.0232]	5675/5494 [R(int) = 0.0287]	6238/5951 [R(int) = 0.0402]
Data/restraints/parameters	7554/0/675	5494/0/347	5951/9/354
Goodness-of-fit on F^2	1.037	0.984	1.037
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0724, $wR2$ = 0.2483	$R1$ = 0.0747, $wR2$ = 0.2044	$R1$ = 0.0877, $wR2$ = 0.2315
R indices (all data)	$R1$ = 0.0724, $wR2$ = 0.2483	$R1$ = 0.1413, $wR2$ = 0.2712	$R1$ = 0.1681, $wR2$ = 0.2760
Largest diff. peak and hole [e.Å^{-3}]	0.903 and −0.930	0.721 and −0.804	0.934 and −0.826

The bending angle, α, between the two equatorial five-membered rings and the displacement, d, of Co out of the four N equatorial donor plane are given in Table 3. The displacement occurs towards the axial pyridyl group in A and B molecules of **2a** and towards R in **2b** and **2c**, and reflects the difference in bulk between R and the *trans*-pyridyl group.[16] In all the complexes, the pyridyl ligand is tilted out of the axial direction and the tilt can be measured by the dihedral angle, γ, between the mean planes of the pyridyl ligand and of the four equatorial N donors. The values of γ in **1** and **2**, (Table 3), are close to those observed in py (82.3°) and 1,5,6-trimethylbenzimidazole (Me_3Bzm) (81.0°) iminocobaloximes with methyl substituents on the propylene bridge (Scheme 1b, R1 = Me).[17]

Equatorial coordination distances and angles in complexes **2** are given in Table 2 together with those of **1**. In complexes **2**, the Co−N4 distances are slightly shorter than those of Co−N3. This supports the previous assignment of the oxime bridge H atom.[18]

NMR Characterisation

The characterisation in solution was performed by ^{1}H and ^{13}C NMR spectroscopy in [D_6]DMSO. The (LNHpy)(HLNHpy) moiety gives rise to strikingly similar ^{1}H NMR spectra for all five complexes. The spectrum of **2c** is described as an example. The CH_3 protons give rise to two doublets at δ_H = 0.66 and 1.32 (CH_3CH) and two singlets at δ_H = 1.78 and 2.05 ($CH_3C{=}N$), each signal integrating for three protons. Ethylenic CH_2 protons generate four partially overlapped multiplets in the range δ_H = 2.88−3.44, the total integration corresponding to eight protons. The signals for the CH protons at δ_H = 3.75 and 3.82 appear as broad multiplets, and those for the NH protons at δ_H = 4.75 and 5.47 as a broad doublet and a broad singlet, respectively; each of these signals integrates for one proton. On addition of D_2O to the DMSO solution, the NH signals did not disappear, indicating a slow exchange on the NMR time scale. In $CDCl_3$ solution, the NH doub-

Table 2. Selected bond lengths [Å] and angles [°] for **1** and **2**

	2a(A)	**2a**(B)	**2b**	**2c**	**1**(A)	**1**(B)
Co−N1	2.134(5)	2.185(5)	2.168(5)	2.160(6)	2.033(4)	2.045(5)
Co−N2	1.996(5)	1.983(5)	1.964(5)	1.991(5)	1.991(5)	1.988(5)
Co−N3	1.888(6)	1.900(6)	1.893(5)	1.903(6)	1.912(5)	1.914(5)
Co−N4	1.888(5)	1.893(5)	1.879(5)	1.887(6)	1.911(5)	1.902(4)
Co−N5	2.018(5)	2.005(5)	2.035(5)	2.021(6)	1.980(5)	1.961(5)
Co−N6	−	−	−	−	2.017(5)	1.983(5)
Co−C23	1.960(7)	1.983(7)	2.015(6)	1.998(8)	−	−
N1−Co−N2	92.2(2)	93.2(2)	90.3(2)	91.8(2)	94.0(2)	94.4(2)
N1−Co−N3	89.2(2)	88.0(2)	89.1(2)	89.2(2)	85.5(2)	83.2(2)
N1−Co−N4	92.1(2)	90.3(2)	91.1(2)	91.6(2)	92.7(2)	91.2(2)
N1−Co−N5	88.7(2)	90.2(2)	87.7(2)	87.6(2)	90.3(2)	90.6(2)
N1−Co−C23	177.3(3)	175.3(3)	177.9(2)	178.7(3)	−	−
N1−Co−N6	−	−	−	−	176.4(2)	174.2(2)
N2−Co−N3	81.9(2)	82.3(2)	81.6(2)	82.2(3)	82.0(2)	81.2(2)
N2−Co−N4	175.6(2)	176.5(2)	178.2(2)	176.6(3)	173.1(2)	174.3(2)
N2−Co−N5	98.4(2)	97.8(2)	98.5(2)	98.7(2)	99.1(2)	97.7(2)
N2−Co−C23	90.4(3)	90.6(3)	91.8(2)	86.9(3)	−	−
N2−Co−N6	−	−	−	−	89.1(2)	89.9(2)
N3−Co−N4	97.5(3)	97.7(2)	97.4(2)	97.7(3)	96.9(2)	97.7(2)
N3−Co−N5	177.9(3)	178.3(2)	176.8(2)	176.7(2)	175.7(2)	173.8(2)
N3−Co−C23	90.5(3)	89.8(3)	90.9(2)	90.7(4)	−	−
N3−Co−N6	−	−	−	−	93.2(2)	93.6(2)
N4−Co−N5	82.4(2)	82.3(2)	82.6(2)	82.0(3)	82.6(2)	83.1(2)
N4−Co−C23	85.3(3)	85.9(3)	86.8(2)	89.7(3)	−	−
N4−Co−N6	−	−	−	−	84.2(2)	84.4(2)
N5−Co−C23	91.6(3)	91.9(3)	92.4(2)	92.6(3)	−	−
N5−Co−N6	−	−	−	−	91.0(2)	92.6(2)
Co−N1−C1	116.9(4)	118.6(4)	117.0(4)	116.6(5)	117.2(3)	116.7(3)
Co−N1−C5	126.4(5)	125.0(4)	125.6(5)	126.1(5)	126.0(4)	124.8(3)
Co−N6−C12	−	−	−	−	116.3(3)	116.2(4)
Co−N6−C16	−	−	−	−	126.9(3)	126.1(3)
O1·····O2	2.402(7)	2.401(7)	2.432(7)	2.408(8)	2.388(7)	2.421(6)
N5·····N6	2.861(8)	2.968(8)	3.020(8)	2.894(8)	−	−

let (belonging to the bidentate ligand) shifts downfield to δ_H = 5.74, whereas the NH singlet shifts upfield to δ_H = 4.60; the different behaviour could be due to the formation of an intramolecular hydrogen bond between the proton of the NH doublet and the nitrogen atom of the noncoordinated pyridine, as found in the solid state. Aromatic protons generate two series of partially overlapped signals, of correct multiplicity and intensity, in the δ_H range 8.41−7.30. The oxime proton resonates at δ_H = 19.6. This value, very close to that found in the lariat-type complexes[8] and shifted remarkably downfield with respect to that of cobaloximes[20] and imino cobaloximes,[21] suggests a strong hydrogen bond.

The main difficulty in the assignment of ^{1}H and ^{13}C NMR spectra of the (LNHpy)(HLNHpy) moiety lied in distinguishing between the resonances of the tridentate and of the bidentate ligands. An almost complete assignment of ^{1}H and ^{13} C signals was performed for **2c** using homonuclear and heteronuclear shift correlation 2D NMR (H,H- and H,C-COSY), HMBC and DIFNOE spectroscopy. Shift assignments for the other alkyl complexes were made according to those of **2c** (Table 4 and 5).

The protons bonded to the α-carbon atom of the axial alkyl groups show a remarkable downfield shift with respect to those of the corresponding cobaloximes (+1.07 ppm for Me, +1.25 ppm for Et, and +1.14 ppm for CH_2CF_3)[20] although a direct comparison is not thoroughly meaningful, because the spectra of the latter were recorded in $CDCl_3$ and the solvent significantly influences the chemical shift of the Cα protons in complexes **2**. The effect is much weaker for protons that are more distant from the metal centre. For R = Et and *n*Bu, the CH_2 resonances in the ^{1}H NMR spectrum are partially buried; for R = CH_2CF_3, the CH_2 protons give rise to a quadruplet owing to coupling with fluorine ($^3J_{HF}$ = 15 Hz). It is noteworthy that in the CH_2Cl derivative, these protons generate an AB spectrum ($^2J_{HH}$ = 5 Hz) owing to the coupling between diastereotopic geminal protons.

Discussion

Complexes **2** are structurally similar to lariat-type complexes, but with some additional features. In fact, the equatorial moiety is more crowded with respect to the latter model, because of the side substituents on the amino C−N, pointing above and below the equatorial plane. Furthermore, the values of φ, found in complexes **1** and **2**, make them "representatives" of the orientation C of Scheme 2, as compared with cobaloximes and lariat complexes, which exhibit orientation A, and iminocobaloximes, which exhibit orientation B. However, the relative flexibility of the ethylene chain bearing the coordinated pyridyl group allows for a rotation, even if limited, of the axial py residue around the Co−N1 bond. This rotation is somewhat less restricted than in lariat-type complexes.[8] In fact, there is clear evid-

Table 3. Axial distance (Å) in some B_{12} models, as well as φ (°), γ (°), and α (°) values; data are from ref.[1], unless otherwise stated

(LNHpy)(HLNHpy)[a] Compound	**1**	**1**	**2c**	**2a**	**2a**	**2b**
R	Py(A)[a]	py(B)[a]	CH_2CF_3[b]	Me(A)[b]	Me(B)[b]	Et[b]
Co−N1/Å	2.033(4)	2.045(5)	2.160(6)	2.134(5)	2.185(5)	2.168(5)
Co−N6/Å	2.017(5)	1.983(5)	−	−	−	−
φ/°	48	44	44	38	48	36
φ′/°	30	28	−	−	−	−
Co−C/Å	−	−	1.998(8)	1.960(7)	1.983(7)	2.015(6)
d/Å	0.022	−0.004	0.002	0.018	0.015	−0.016
α/°	17	13	16	9	14	8
γ/°	81	75	84	82	82	80
γ′/°	86	89	−	−	−	−
$pyCo(DH)_2R$						
R	Cl[b]	CH_2CF_3[c]	Me[c]	Et[c]		
Co−Nax/Å	1.956	2.041(4)	2.068(3)	2.081(3)		
φ/°	6	0	1	0		
Co−R/Å	−	2.010(3)	1.998(5)	2.035(5)		
d/Å	0	0.01	0.05	0.05		
α/°	2	1	3	9.1		
γ/°	89	90	89	90		
$Me_3Bzm[(DO)(DOH)pn]R$[d]						
R	Cl[c]	CH_2CF_3	Me	Et		
Co−N_{ax}/Å	1.993(6)	2.060(3)	2.100(3)	2.105(3)		
φ/°	86	80	115	119		
Co−R/Å	−	2.026(4)	2.011(3)	2.041(4)		
d/Å	0.06	0.06	0.09	0.10		
α/°	13	16.6	13.8	16.7		
γ/°	89	84	88	89		
(C1py)h[e]						
R	Cl	Me(A)	Me(B)			
Co−N_{ax}/Å	1.959(4)	2.06(1)	2.07(1)			
φ/°	0	0	0			
Co−R/Å	2.237(2)	2.05(2)	1.99(2)			
d/Å	0.02	0.02	0.04			
α/°	1.6	−1.8	−4.4			
γ/°	90	90	90			

[a] This work, excluding **1** from ref.[11] − [b] S. Geremia, R. Dreos, L. Randaccio, G. Tauzher, L. Antolini, *Inorg. Chim. Acta* **1994**, *216*, 125. − [c] L = py. − [d] ref.[4] − [e] ref.[8]

Table 4. ^1H NMR chemical shifts of $[RCo(LNHpy)(HLNHpy)]ClO_4$ complexes in $[D_6]DMSO$

R	*ortho*	*meta*[a]		*para*	NH	CH	CH_2-CH_2	CH_3 [b]		O··H··O	axial R
nC_4H_9[c]	8.41 (d)	7.69 (d)	7.54 (t)	8.03 (t)	4.74(bs)	3.60 (bm)	3.32−2.76	1.73 (s)	1.34 (d)	19.40 (s)	CH_3 0.94 (t)
	8.18 (d)	7.31 (d)	7.25 (t)	7.76 (t)	4.50 (bd)	3.73 (bm)	(bm, 8 H)	2.00 (s)	0.84 (d)		CH_2 1.09 (m), 1.44(m), 2.77(m)
C_2H_5 [c]	8.41 (d)	7.69 (d)	7.54 (t)	8.03 (t)	4.70 (bs)	3.58 (bm)	3.31−2.74	1.73 (s)	1.35 (d)	19.41 (s)	CH_3 0.46 (t)
	8.19 (d)	7.31 (d)	7.25 (t)	7.75 (t)	4.44 (bd)	3.72 (bm)	(bm, 8 H)	2.00 (s)	0.84 (d)		CH_2 2.99(q)
CH_3 [c]	8.42 (d)	7.72 (d)	7.55 (t)	8.04 (t)	4.87 (bs)	3.57 (bm)	3.32−2.73	1.72 (s)	1.33 (d)	19.41 (s)	1.89 (s)
	8.29 (d)	7.33 (d)	7.27 (t)	7.77 (t)	4.44 (bd)	3.67 (bm)	(bm, 8 H)	1.99 (s)	0.77 (d)		
CH_2Cl[c]	8.45 (d)	7.75 (d)	7.55 (t)	8.05 (t)	5.08(bs)	3.71 (bm)	3.40−2.84	1.77 (s)	1.39 (d)	19.36 (s)	5.02
	8.34 (d)	7.34 (d)	7.28 (t)	7.78 (t)	4.65 (bd)	3.78 (bm)	(bm, 8 H)	2.04 (s)	0.72 (d)		4.98 ($^2J_{H-H}$ = 5 Hz)
CH_2CF_3 [c]	8.41 (d)	7.76 (d)	7.55 (t)	8.05 (t)	5.47 (bs)	3.75 (bm)	3.44−2.88	1.78 (s)	1.32 (d)	19.60 (s)	2.55 (q)
	8.36 (d)	7.35 (d)	7.30 (t)	7.80 (t)	4.75 (bd)	3.82 (bm)	(bm, 8 H)	2.05 (s)	0.66 (d)		

[a] The first column is for *meta* protons bonded to C4 and C15, the second column for protons bonded to C2 and C13. − [b] The first column is for methyl groups adjacent to C=N, the second column for methyl groups adjacent to CH. − [c] Data in the upper line refer to the tridentate ligand, data in the lower line refer to the bidentate ligand.

ence that the orientation of the py moiety also appreciably influences the length of the Co−N1 bond, so that the expected trend in the *trans* influence with R is modified (see below). Thus, for the same ligand *trans* to N1 (and N6 in **1**) larger φ values correspond to longer Co−N1 distances. In fact, the values of φ and of the Co−N1 distance in mole-

Table 5. ^{13}C NMR chemical shifts of [RCo(LNHpy)(HLNHpy]ClO_4 complexes in [D_6]DMSO

R	C10 C21	C5 C16	C1 C12	C4 C13	C2 C15	C3 C14	C9 C20	C6 C17	C7 C18[a]	C8 C19	C11 C22	axial R group
nC_4H_9[b]	156.75	159.57	150.57	126.55	123.26	138.60	60.94	30.21	45.89	17.17	12.74	CH_3 13.79
	160.54	159.02	148.01	123.77	121.94	137.13	61.50	32.22	49.64	18.87	14.13	CH_2 22.76, 24.30, 33.55
C_2H_5 [b]	156.68	159.53	150.61	126.53	123.24	138.58	60.89	30.21	45.82	17.13	12.73	CH_3 17.06
	160.54	159.00	148.03	123.71	121.92	137.08	61.55	32.25	49.62	18.81	14.12	CH_2 18.05
CH_3 [b]	156.82	159.13	150.78	126.78	123.30	138.74	60.35	30.14	45.06	17.74	12.74	
	169.50	159.06	148.12	123.73	121.96	137.12	61.58	32.21	50.74	18.53	13.89	
CH_2Cl [b]	157.45	160.32	151.30	127.08	123.46	139.05	59.86	30.30	44.54	16.79	13.15	43.08
	160.76	158.96	148.14	123.77	122.07	137.22	61.45	32.02	50.25	18.38	14.32	
CH_2CF_3 [b]	158.63	160.01	151.10	127.31	123.56	139.13	59.09	30.00	43.61	16.25	13.42	CF_3 133 (q)
	161.52	159.06	148.21	123.80	122.14	137.33	61.40	31.92	50.57	18.52	14.55	

[a] Resonances not assigned separately. − [b] Data in the upper line refer to the tridentate ligand, data in the lower line refer to the bidentate ligand.

cule A are smaller than those in molecule B of **2a**. Analogously, the Co−N1 bond is longer than the Co−N6 bond and φ is larger than φ′ in both molecules A and B of **1** (Table 3). This suggests that the φ values of 36° in **2b** and of 44° in **2c** should correspond to a short- and a long-type Co−N1 bond, respectively. Therefore, it appears that the Co−N(py) distance *trans* to the same donor reaches the largest value when φ approaches 50°, which corresponds to orientation C in Scheme 2. That this conformation is the most strained, is also suggested by the increase in the bending α angle when φ approaches 50°, as shown in Figure 2, where the α/φ plot is reported for complexes **1** and **2**.

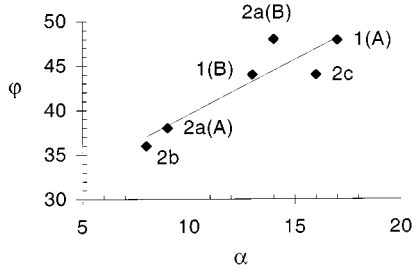


Figure 2. Dependence of the torsion angle φ around the Co−N1 bond on the bending angle α between the two equivalent five-membered rings in complexes **1** and **2**; A and B refer to the two independent molecules of **1** and **2a**

Taking these observations into account, it is of interest to compare the geometry of the axial fragment in complexes **2** with that in the analogous alkylcobaloximes and other related B_{12} models. In the latter series, the Co−N(ax) distance increases with an increase in the σ-donating ability of R, for L ligands with very similar φ values. Thus, in cobaloximes and iminocobaloximes, for which φ ≈ 0 and 90°, respectively, the order of increasing Co−py distances is Cl << CH_2CF_3 < Me < Et. Furthermore, for a given R, the Co−py bond is lengthened, when φ ≈ 90° (in complexes of Scheme 1, b) with respect to that observed when φ ≈ 0° (in complexes of Scheme 1, a and c), irrespective of the type of equatorial moiety. For complexes **2**, the apparently anomalous trends in Co−N(ax) distances with R as well as the differences between the A and B molecules of **2a** (and in the same molecule of **1**) can easily be interpreted if both contributions are considered. In fact, the distance Co−N1 of 2.134(5) Å (R = Me, φ = 38°) in molecule A of **2a**, is shorter than in **2b** [2.168(5) Å] (R = Et, φ = 36°), as is the case with the other B_{12} models. Analogously, the distance of 2.185(5) Å (R = Me φ = 48°) in molecule B of **2a** is longer than in **2c** [2.160(6) Å] (R = CH_2CF_3, φ = 44°). The influence of the torsion angle on the Co−N1 distance can be evaluated in **1**, where the two axial Co−N1 distances (φ ≈ 45°) are longer that those of Co−N6 (φ ≈ 30°). Therefore, the Co−N1 distance is the result of a compromise between the energies involved in the torsion around N1 and in the Co−N1 stretching. These structural features are in agreement with recent molecular mechanics calculations for $LCo(DH)_2Me$ (L is a planar N donor ligand) based on a new approach which also takes the contribution of the electronic *trans* influence into account.[5] These calculations have furnished profiles of the strain energy against the φ angle, which is characterised by a large maximum centred at φ = 90° and a minimum at φ = 0°, the difference in height ranging from 8 to 40 kJ/mol and increasing with the L bulk.[5] In addition, the large maximum at approximately φ = 90° has a fine structure, consisting of two nearly equal maxima at about 55° and 145°, separated by a relative minimum at φ = 90°. This suggested that orientation C (Scheme 2) is energetically even less favoured than orientation B. The corresponding plot of calculated Co−N(ax) distances against φ shows a profile very similar to that of the strain energy with a Co−N bond lengthening at φ = 50° which increases from 0.03 to 0.06 Å depending on the bulk of L. The Co−R distances follow the same trend in all the series of Table 3, reflecting the effects of the bulk and the σ-donating ability of R.[19]

Recent accurate Co−Me and Co−N axial distances of 1.979(4) and 2.162(4) Å, respectively, have been reported in MeCbl.[22] Hence, one of the most interesting structural features of model **2** is that the geometry of the axial N−Co−Me fragment is much closer to that of MeCbl (where the axial N ligand is a benzimidazole residue) than any other previously proposed B_{12} model, as shown by a comparison of the axial distances in several B_{12} models and MeCbl (Table 6).

The present complexes also show many solution properties characteristic of cobalamins and of their synthetic models. Significant parallels include the observation of the

Table 6. Comparison of the axial distances [Å] in MeCbl and in methyl derivatives of several B_{12} models

	Co−Me	Co−Nax
MeCbl	1.979(4)	2.162(4)
2a	1.960(7), 1.983(7)	2.134(5), 2.185(5)
MeCo[(DH)(DOH)pn]py	2.003(3)	2.106(3)
MeCo[(DH)(DOH)pn] Me_3Bzm	2.011(3)	2.100(3)
MeCo(C1py)	1.99(2), 2.05(2)	2.07(1)
MeCo$(DH)_2$py	1.998(5)	2.068(3)
MeCo$(DH)_2Me_3$Bzm	1.989(2)	2.060(2)

Co^{III}/Co^{II} and Co^{II}/Co^{I} redox series, the reactions of the Co^{I} species with alkylating agents to give organocobalt derivatives, the photochemically induced Co−C cleavage and the alkyl-transfer reactions to radical acceptors. On the other hand, there are some distinctive aspects in the chemical behaviour of these novel models which deserve attention. One is the appreciable influence of the steric factors, which is clearly indicated by the anomalous trend in the *trans* influence (see structural results) and by the fact that it is apparently impossible to prepare derivatives with bulky alkyl groups, such as isopropyl, adamantyl and perfluoroisopropyl, which have been reported for previously known models.[1,23] The observed methyl transfer from **2a** to $Co^{II}(DH)_2$ and Vitamin B_{12r} may also be interpreted in terms of steric factors that lower the stability of Co−C bond in these amino−oximato complexes.

The electronic factors appear to be less important in determining the stability of the Co−C bond. In this regard, it should be noted that both alkylcobalamines and their simple models, contain highly unsaturated ligands that allow for an extensive electronic delocalisation over the equatorial plane, while the alkyl−cobalt complexes **2** contain only two unconjugated C=N bonds in their chelating system. It follows that a high extent of unsaturation of the equatorial ligand is not a necessary prerequisite for the formation of stable alkyl−cobalt complexes. This result is not unexpected; at least in a few cases, the synthesis of alkyl−cobalt compounds containing completely saturated polyamine (N4) macrocycles has been successfully achieved.[24−26] On the contrary, electronic factors play a relevant role in stabilising the lowest oxidation state of the metal ion. Thus, both the higher lability of the Co^{I} derivative of the complex (**1**) and the more drastic conditions required for its formation, relative to the formation of the corresponding cobal(I)oximes, may be ascribed to the lower extent of unsaturation present in the equatorial ligand. In at least one case it was unequivocally proved that the Co^{II}/Co^{I} reduction is responsive to the extent of unsaturation present in the ligand; a greater unsaturation causes an anodic shift in the half-wave potentials.[27] This trend justifies, at least qualitatively, the experimental observations reported above.

The last point to stress is the inability of the Co^{II} species derived from **1** to react with alkyl halides to give the corresponding alkyl−cobalt species by means of a free radical process. This behaviour is somewhat unexpected because both photochemical and alkyl-transfer processes involve homolytic cleavage of the Co−C bond, thereby providing clear evidence for the tendency of these complexes to react through radical processes. In addition, the majority of the Co^{II} forms of the Vitamin B_{12} models and Vitamin B_{12r} itself have been found to be reactive toward alkyl halides. On the basis of kinetic studies[28] the following stepwise free-radical mechanism [Equation (4)] has been proposed for these series of compounds:

$$LCo^{II} + RX \longrightarrow LCo^{III}X + R \quad \text{(slow)}$$

$$LCo^{II} + R \longrightarrow LCo^{III}R \quad \text{(fast)} \qquad (4)$$

$$2LCo^{II} + RX \longrightarrow LCo^{III}X + LCo^{III}R$$

Likewise, the lack in reactivity of the Co^{II} form of **1** can be attributed to its inability to abstract the halogen from the alkyl halide in the slow step rather than to its low tendency to trap free alkyl radicals.

Conclusions

Tridentate amino−oxime ligands are effective in stabilising the Co^{III}−C bond, as the analogous tridentate imino−oxime ligands.[29,30] The methyl derivative undergoes photolytic homolysis and is a better methyl donor than methylcobaloxime. These organometallic complexes can therefore be considered as suitable models for the B_{12} system (alkylcobalamin), such as the well-known alkylcobaloximes and other related models.[1] A distinctive feature of this new model is the appreciable influence of steric factors on their chemical behaviour. This is clearly indicated by the anomalous trend in the *trans* influence and by the fact that it is apparently impossible to prepare derivatives with bulky alkyl groups, such as *i*Pr, adamantyl and perfluoroisopropyl, which, on the contrary, have been reported for previously known models. In this respect, they more closely parallel the alkylcobalamin chemistry. Furthermore, the axial distances in the methyl derivative, very close to those recently reported for methylcobalamin, make them a better B_{12} structural model than any other previously reported.[22] Structural evidence is given that this behaviour can be related to the crowded equatorial moiety, which interacts with

the axial ligands more strongly than in cobaloximes. A recent comparison[22] of the structural, spectroscopic and electrochemical properties of alkylcobalamins with those of alkylcobaloximes suggests that the corrin ligand makes more electronic charge available on Co than on the $(DH)_2$ ligand (electronic *cis* influence), and that the longer Co−N axial distances in cobalamins are also due to ring electronic influence. Both the longer Co−N1 bonds and the increased difficulty in the Co^{III}/Co^{I} reduction, relative to alkylcobaloximes, suggests a higher charge density on Co in complexes **2**. The present models are possibly also electronically closer to cobalamins. These compounds therefore seem to offer a better opportunity to study the influence of steric factors on the formation and cleavage of the Co−C bond, than that provided by previous B_{12} models. Finally, the easy substitution of the chelating ligand, which occurs without cleavage of the Co−Me bond, suggests the possibility of preparing new series of otherwise inaccessible organometallic compounds.

Experimental Section

Vitamin B_{12a} and methylcobalamin were purchased from Aldrich. $CH_3Co(DH)_2H_2O$, $CH_3Co(DH)_2py$, and $Co(DH)_2(H_2O)_2$ were prepared by previously reported methods.[12] All other reagents and chemicals were commercial products and were used without further purification. − ^1H and ^{13}C NMR spectra were recorded with a Jeol EX-400 (^1H at 400 MHz and ^{13}C at 100.4 MHz) from [D_6]DMSO solutions with TMS as internal standard. Two-dimensional homonuclear and heteronuclear correlated spectra (H,H and H,C COSY) were obtained using the instrument's automatic programme. The HMBC spectrum of $[CF_3CH_2Co(LNHpy)(HLNHpy)]ClO_4$ in [D_6]DMSO was obtained as a 2048 × 256 data matrix with 64 scans (preceded by 4 dummy scans) per t_1 value and a PDBS (pulse delay between scans) of 1.00 s. An 8.7 μs 90° PW (pulse width) of ^{13}C was used. Values of Δ_1 (the delay between the first 90° proton pulse and the first 90° ^{13}C pulse) and Δ_2 (the delay between the first and the second 90° ^{13}C pulse) were 3.6 and 62.5 ms, respectively.

Syntheses: The same synthetic procedure was followed for all the $[RCo(LNHpy)(HLNHpy)]ClO_4$ complexes (R = Me, Et, *n*Bu, CH_2Cl, CH_2CF_3). − ***CAUTION:*** *Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should only be handled in small quantities!* − The reactions were performed at room temperature, under an inert atmosphere and in the dark. In a typical experiment, a solution of NaOH (0.20 g, 5.00 mmol) in water (2 mL) was added to a suspension of complex **1** (1.00 g, 1.49 mmol) in methanol (150 mL). The resulting clear solution was treated with $NaBH_4$ (0.12 g, 4.70 mmol), dissolved in a minimum volume of water, followed by three drops of $PdCl_2$ solution, prepared by the addition of conc. HCl to a suspension of $PdCl_2$ (1.00 g) in water (20 mL) until complete dissolution had occurred. When the solution assumed a dark brown colour (after 15 min), a solution of the appropriate alkyl iodide (7.45 mmol, i.e. 5 equiv. with respect to the complex) in methanol (10 mL) was added. After about 30 min, the dark brown solution turned to bright orange. At this point, the flow of N_2 was suspended and the methanol was removed in a rotary evaporator at 40 °C. The aqueous suspension was extracted with CH_2Cl_2 (2 × 50 mL) and the residual water removed from the organic phase by treatment with anhydrous Na_2SO_4. After filtration, the solution was concentrated to 10 mL, passed through a chromatographic column of Al_2O_3 and eluted with CH_2Cl_2. A solution of the pure product was obtained (50 mL). The by-products, which were most strongly bound, could eventually be eluted with methanol. Diisopropyl ether was then added until the solution became turbid, and the suspension was allowed to stand overnight. Crystals of the desired product were recovered by filtration and air-dried. In order to obtain crystals suitable for X-ray analysis or for a better purification, the products were treated as follows.

$[CH_3Co(LNHpy)(HLNHpy)]ClO_4·0.5CH_3COCH_3$ (2a): Some drops of water were added to a saturated solution of the complex in acetone, followed by diisopropyl ether, until the solution became turbid. After standing in the dark in a stoppered vessel for 2 d, orange crystals were collected by filtration and air-dried. Yield: 0.31 g (34%). − $C_{24.5}H_{39}ClCoN_6O_{6.5}$ (616.0): calcd. C 47.8, H 6.4, N 13.6; found C 47.9, H 6.4, N 13.6.

$[C_2H_5Co(LNHpy)(HLNHpy)]ClO_4$ (2b): Recrystallised as above; red crystals were obtained. Yield: 0.28 g (31%). − $C_{24}H_{38}ClCoN_6O_6$ (610.0): calcd. C 47.9, H 6.4, N 14.0; found C 48.0, H 6.3, N 13.7.

$[CF_3CH_2Co(LNHpy)(HLNHpy)]ClO_4·0.5CH_2Cl_2$ (2c): Recrystallised by the diffusion of diisopropyl ether stratified over a saturated solution of the complex in dichloromethane. Yellow crystals were collected by filtration and air-dried. Yield: 0.37 g (36%). − $C_{24.5}H_{36}Cl_2CoF_3N_6O_6$ (697.4): calcd. C 42.2, H 5.2, N 12.1; found C 42.5, H 5.2, N 12.2.

[*n*-C_4H_9Co[(LNHpy)(HLNHpy)]ClO_4 (2d): Recrystallised as above; red crystals were obtained. Yield: 0.25 g (27%). − $C_{26}H_{42}ClCoN_6O_6$ (629.1): calcd. C 49.6, H 6.75, N 13.4; found C 49.4, H 6.7, N 12.8.

$[ClCH_2Co(LNHpy)(HLNHpy)]ClO_4$(2e): Recrystallised as above; yellow crystals were obtained. Yield: 0.42 g (45%). − $C_{23}H_{35}Cl_2CoN_6O_6$ (621.4): calcd. C 44.5, H 5.7, N 13.5; found C 44.4, H 5.7, N 13.3.

Substitution of the Chelating System by Dimethylglyoxime: Dimethylglyoxime (0.114 g, 0.98 mmol) and pyridine (0.5 mL) were added to a solution of complex **2a** (0.300 g, 0.49 mmol) in methanol (20 mL). The solution was allowed to stand for 5 h at room temperature in the dark. Water (5 mL) was then added to the solution. After evaporation of the methanol, orange crystals of $CH_3Co(DH)_2py$ were collected by filtration (0.154 g, 82%) and identified by ^1H NMR ($CDCl_3$): δ_H = 0.82 (3 H, CH_3−Co), 2.13 (12 H, CH_3−C), 7.33, 7.73, 8.62 (5 H, C_5H_5N). Following the same procedure, but with exclusion of pyridine, no reaction was observed and the starting complex was recovered. After recrystallisation, the complex was identified by elemental analysis. − $C_{24.5}H_{39}ClCoN_6O_{6.5}$ (616.0): calcd. C 47.8, H 6.4, N 13.6; found C47.6, H 6.3, N 13.3.

Transmethylation Reaction on $Co(DH)_2(H_2O)_2$: A solution of complex **2a** (0.100 g, 0.17 mmol) in methanol (20 mL) was treated with $Co^{II}(DH)_2(H_2O)_2$ (0.055 g, 0.17 mmol, 1 equiv.) under N_2, in the dark at room temperature. After 5 h, the solution was allowed to stand in air, water (5 mL) was added and the methanol was removed in a rotary evaporator. The aqueous residue was extracted with CH_2Cl_2. By evaporation of the solvent, the complex **1** was obtained and identified by ^1H NMR spectroscopy. The aqueous phase, concentrated in air with exclusion of light, gave red crystals of $CH_3(DH)_2H_2O$ identified by ^1H NMR (CD_3OD): δ_H = 0.67 (3 H, CH_3−Co), 2.24 (12 H, CH_3−C).

Transmethylation of Complex 2a on Vitamin B_{12r}: The reaction was carried out under nitrogen, in the dark and at room temperature. A solution of Vitamin B_{12a} (0.050 g) in water (25 mL) was reduced to Vitamin B_{12r} as described in the literature.[14] A solution of the complex **2a** (0.100 g) in methanol (25 mL) was then added and the reaction mixture was allowed to stand overnight. After the evaporation of methanol and the addition of acetone (30 mL), a red microcrystalline precipitate formed slowly. The product (0.030 g, 70%) was collected by filtration, air-dried, and identified as methylcobalamin by comparison of its UV/Vis and ^{1}H NMR spectra in D_2O with those of an authentic sample.

Photolysis of Complex 2a: A solution of $[CH_3Co(LNHpy)(HLNHpy)]ClO_4$ (0.100 g, 0.17 mmol) in water (50 mL) was exposed to sunlight for 1 h. It was then concentrated in air after the addition of a few drops of a saturated solution of $NaClO_4$. Red crystals of complex **1** were collected by filtration and identified by ^{1}H NMR spectroscopy. A solution of **2** (2 mg) in water (1 mL) was photolysed; the formaldehyde present in the filtrate was detected by the chromotropic acid test.[31]

Structure Determination: Single crystals, suitable for X-ray data collection of **2**, were grown as already reported in syntheses. Single-crystal X-ray data were collected at room temperature with a CAD4 Enraf−Nonius diffractometer using graphite-monochromated Mo-K_α radiation (λ= 0.71073 Å). Cell parameters were determined from 25 carefully selected reflections. Data were corrected for Lorentz polarisation effects and for absorption by the ψ-scan technique. Detailed crystallographic data are presented in Table 1. − The structures were solved by Patterson methods followed by Fourier syntheses and refined by full-matrix least-squares cycles. All the calculations were carried out with SHELXS (solution of structures) and SHELXL (refinement of structures) programs.[32] The hydrogen atoms were set in calculated positions and allowed to ride on the atoms to which they are linked. One water molecule at 0.25 occupancy and one acetone molecule at 0.5 occupancy were located in the unit cell of **2b** and **2c**, respectively. Other refinement conditions are given in Table 1. Crystallographic data (excluding structure factors) reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-145122 (**2a**), -145123 (**2b**), and -145124 (**2c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1IZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] N. Bresciani Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers, P. J. Toscano, *Coord. Chem. Rev.* **1985**, *63*, 1−125. − [1b] L. Randaccio, N. Bresciani Pahor, E. Zangrando, L. G. Marzilli, *Chem. Soc. Rev.* **1989**, *18*, 225−250. − [1c] L. Randaccio, *Comments Inorg. Chem.* **1999**, 21, 327−376.

[2] [2a] F. Mancia, N. H. Keep, A. Nakagawa, P. F. Leadlay, S. McSweeney, B. Rasmussen, P. Boske, O. Diat, P. R. Evans, *Structure* **1996**, *4*, 339−350. − [2b] C. L. Drennan, S. Huang, J. T. Drummond, R. G. Mattews, M. L. Ludwig, *Science* **1994**, *226*, 1669−1670. − [2c] R. Reitzer, K. Gauber, C. Jogl, U. G. Wagner, H. Bothe, W. Buckel, C. Kratky, *Biochemistry* **1999**, *38*, 891−902. − [2d] N. Shibata, J. Mesuda, T. Tobimatsu, T. Toraya, K. Suto, Y. Morimoto, N. Yasuoca, *Structure* **1999**, *7*, 997−1007.

[3] J. M. Sirovatka, R. G. Finke, *J. Am. Chem. Soc.* **1997**, *119*, 3057−3067.

[4] [4a] S. M. Polson, R. Cini, C. Pifferi, L. G. Marzilli, *Inorg. Chem.* **1997**, *36*, 314−322. − [4b] S. J. Moore, A. Kutikov, R. J. Lachicotte, L. G. Marzilli, *Inorg. Chem.* **1999**, *38*, 768−776.

[5] S. Geremia, M. Calligaris, L. Randaccio, *Eur. J. Inorg. Chem.* **1999**, 981−992.

[6] R. Cini, S. J. Moore, L. G. Marzilli, *Inorg. Chem.* **1998**, *37*, 6890−6897.

[7] S. Hirota, S. M. Polson, J. M. Puskett, Jr., S. J. Moore, M. B. Mitchell, L. G. Marzilli, *Inorg. Chem.* **1996**, *35*, 5646−5653.

[8] [8a] A. Gerli, M. Sabat, L. G. Marzilli, *J. Am. Chem. Soc.* **1992**, *114*, 6711−6718. − [8b] L. G. Marzilli, A. Gerli, A. M. Calafat, *Inorg. Chem.* **1992**, *31*, 4617−4627.

[9] [9a] S. Dang, R. Padmakumar, N. Maiti, R. Banerjee, T. G. Spiro, *J. Am. Chem. Soc.* **1998**, *120*, 9947−9948 and references therein. − [9b] J. M. Puckett, Jr., M. B. Mitchell, S. Hirota, L. G. Marzilli, *Inorg. Chem.* **1996**, *35*, 4656−4662 and references therein.

[10] J. M. Sirovatka, R. G. Finke, *Inorg. Chem.* **1999**, *38*, 1697−1707.

[11] L. Catalano, R. Dreos, G. Nardin, L. Randaccio, G. Tauzher, S. Vuano, *J. Chem. Soc., Dalton Trans* **1996**, 4269−4274.

[12] B. D. Gupta, S. Roy, *Inorg.Chim.Acta* **1988**, *146*, 209−221.

[13] H. P. C. Hogenkamp, *Biochemistry* **1966**, *5*, 417−422.

[14] G. N. Schrauzer, J. W. Sibert, R. J. Windgassen, *J. Am. Chem. Soc.* **1968**, *20*, 6681−6688.

[15] C. K. Johnson, ORTEP; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, **1976**.

[16] S. Geremia, L. Randaccio, E. Zangrando, L. Antolini, *J. Organomet. Chem.* **1992**, *425*, 131−139.

[17] P. G. Yohannes, N. Bresciani Pahor, L. Randaccio, E. Zangrando, L. G. Marzilli, *Inorg. Chem.* **1988**, *27*, 4738−4744.

[18] L. Randaccio, S. Geremia, R. Dreos-Garlatti, G. Tauzher, F. Asaro, G. Pellizer, *Inorg. Chim. Acta* **1992**, *194*, 1−8.

[19] L. Randaccio, S. Geremia, E. Zangrando, C. Ebert, *Inorg. Chem.* **1994**, *33*, 4641−4650.

[20] H. A. O. Hill and K. G. Morallee, *J. Chem.Soc. A* **1969**, 554−559.

[21] W. O. Parker, Jr., E. Zangrando, N. Bresciani Pahor, L. Randaccio, L. Marzilli, *Inorg. Chem.* **1986**, *19*, 3491−3497.

[22] L. Randaccio, M. Furlan, S. Geremia, M. Slouf, I. Srenova, D. Toffoli, *Inorg. Chem.*, in press.

[23] P. J. Toscano, H. Brand, S. Liu, J. Zubieta, *Inorg. Chem.* **1990**, *29*, 2101− 2105.

[24] T. S. Roche, J. F. Endicott, *Inorg. Chem.* **1974**, *13*, 1575−1580.

[25] T. S. Roche, J. F. Endicott, *J. Am. Chem. Soc.* **1972**, *94*, 8622−8623.

[26] A. Bakac, J. H. Espenson, *Inorg. Chem.* **1987**, *26*, 4353−4355.

[27] A. M. Tait, F. V. Lovecchio, D. H. Busch, *Inorg. Chem.* **1977**, *16*, 2206− 2212.

[28] J. Halpern, *Ann. N. Y. Acad.Sci.* **1974**, *239*, 2−21.

[29] R. Dreos, G. Tauzher, D. H. Trendafilova, G. Nardin, L. Randaccio, *Inorg. Chem.* **1996**, *35*, 2715−2716.

[30] R. Dreos, E. Herlinger, G. Tauzher, S. Vuano, G. Nardin, L. Randaccio, *Organometallics* **1998**, *17*, 2366−2369.

[31] C. E. Bricker, W. A. Vail, *Anal. Chem.* **1950**, *22*, 720−722.

[32] [32a] *SHELXS-86, Program for Structure Solution*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467. − [32b] G. M. Sheldrick, *SHELXL-93, Program for Structure Refinement*; Universität Göttingen, Göttingen, Germany, **1993**.

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