The Reciprocal Influence of Ligands in Diamagnetic Co(do) (doh)pn Complexes. Ground State and Thermodynamic *cis* and *trans* Effects

G. Pellizer*, G. R. Tauszik, G. Tauzher, and G. Costa.

^1H NMR spectra of some $[Co\{(do)(doh)pn\}LL']^x$ complexes (where L and L' are ligands bonded to cobalt through carbon, nitrogen or oxygen) are discussed and their dependence on the ligands is explained in terms of variations of electron density induced through cobalt. Acid-base equilibria at the axial water molecules and at the hydrogen bond are studied and it is pointed out that acidity parallels the variations of electron density reflected by NMR spectra. H-D pH dependent exchanges are reported for the equatorial ligand methyls.

Introduction

The effects of the ligands on the ground state properties of cobalt complexes with tetradentate chelating agents, such as bae, salen, saloph, (dh)₂, (do) (doh)pn,* as well as the thermodynamic and kinetic aspects of the reactivity at the axial positions were recently reviewed.[1-4] As a general result, the reciprocal influence of coordinated groups, i.e., *trans* effect between the axial ligands and *cis* effect of the axial on the equatorial ligand and viceversa, was pointed out. For example in the case of Co(do)(doh)pn complexes, the rate of displacement of the axial water by imidazole and by other molecules increases with decreasing electron withdrawing properties of the organic trans ligand;[5] furthermore, the ^{19}F resonance of m-FC_6H_4 and p-FC_6H_4 in the axial position moves to high fields increasing the basicity of the other axial ligand.[6]

In the research described in this paper it was at first studied the dependence of the ^1H NMR spectra on the nature of the ligands in some series of Co(do)-

(doh)pn complexes. Furthermore, for some of these complexes, it was tested if the deprotonation of the axial water molecules - which has already been reported for $[Co\{(do)(doh)pn\}(H_2O)_2]^{2+}$ and for other $[Co(chel)(H_2O)_2]^x$ complexes[1] - and that of the hydrogen bond - already observed in $[Co-(dh)_2L_2]^{+}$ [7-9]- were detectable through NMR and UV spectroscopy and potentiometric measurements, and if the dependence of acidity on the ligands parallels that of the ground state effects as reflected by NMR spectra.

Results and Discussion

^1H NMR spectra in D_2O - Ground state cis effects. Equatorial protons resonances of some $[Co\{(do)(doh)-pn\}L L']^x$ complexes (Figure 1) in D_2O are reported in Table I. With different axial ligands these peaks move but the spectrum is of the same kind of that shown in Figure 2 except for the structure of the multiplets. In D_2O the two couples of equivalent methyls (*a* and *b* in Figure 1) resonate at different frequencies and show different line widths. The results reported in this paper suggest that the sharper peak has to be assigned to methyls *a*. The propylene bridge protons give two complex multiplets: the higher field one, sometimes obscured by the equatorial methyls, is due to the central methylene. The hydrogen bonded proton resonance cannot be observed for any of these compounds in D_2O because of rapid deuteration, but for $[CH_3Co\{(do)(doh)pn\}H_2O]^{+}$
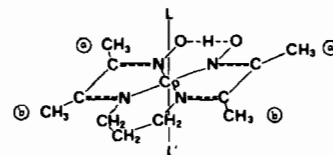

Figure 1. $[Co\{(do)(doh)pn\}L\ L']^x$.

(*) where: bae = N,N'-ethylenebis(acetylacctoneiminato); salen = N,N'-ethylenebis(salicylideneiminato); saloph = o-phenylene-bis(salicylideneiminato); (dh)₂ = bis-dimethylglyoximato; (do)(doh)pn = diacetylmonoximeimino-diacetylmonoximatoimino propane 1,3.

(1) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, G. Tauzher - *Inorg. Chim. Acta Rev. 4,* 41 (1970), and references therein.
(2) H.A.O. Hill - « Corrinoids » In « *Inorganic Biochemistry* » edited by G. Eichorn, Elsevier, Amsterdam, 1972, and references therein.
(3) G. Costa - *Pure and Applied Chemistry 30,* 335 (1972).
(4) G. Costa - *Coord. Chem. Rev. 8,* 63 (1972).
(5) G. Costa, G. Mestroni, G. Tauzher, D.M. Goodall, M. Green, H.A.O. Hill - *Chem. Comm.* 34 (1970).
(6) H.A.O. Hill, K.G. Morallee, F. Cervinca, G. Pellizer - *J. Am. Chem. Soc.,* 94, 277 (1972).

(7) A.V. Ablov, M.P. Filippov - *Russ. J. Inorg. Chem.,* 5, 1311 (1960).
(8) A.V. Ablov, B.A. Bovikin, V.Yu. Zemlyak - *Zh. Neorg. Khim.,* 15, 466 (1970).
(9) Y. Yamano, I. Masuda, K. Shinra - *Inorg. Nucl. Chem. Letters,* 4, 581 (1968).

Table I. Proton δ values in ppm from DSS, in D₂O *.

	Complex	C–CH₃**	N–CH₂	C–CH₂–C	Co-CH₃	
(I)	[Co{(do)(doh)pn}(H₂O)₂](ClO₄)₂	2.88	2.78	(4.26)	2.40	—	a
(II)	[Co{(do)(doh)pn}(H₂O)(OH)]ClO₄	2.73	2.61	(4.17)	2.34	—	b
(I,II)	Co{(do)(doh)pn}(OH)₂	2.63	2.51	(4.04)	(2.28)	—	c
(IV)	[Co{(do)(doh)pn}(NH₃)₂]Br₂	2.66	2.52	4.03	(2.29)	—	d
(V)	[Co{(do)(doh)pn}(NH₂CH₃)₂]Br₂	2.71	2.59	4.01	2.21	—	d
(VI)	[Co{(do)(doh)pn}(NH₂C₂H₅)₂](ClO₄)₂	2.65	2.55	(4.02)	—	—	d
(VII)	[Co{(do)(doh)pn}(NH₂C₄H₉)₂](ClO₄)₂	2.73	2.59	(4.05)	—	—	d
(VIII)	[CH₃Co{(do)(doh)pn}H₂O]ClO₄	2.40	2.28	3.73	—	0.83	e
(IX)	CH₃Co{(do)(doh)pn}OH	—	2.26	(3.86)	—	0.39	f
(X)	[CH₃Co{(do)(doBF₂)pn}H₂O]ClO₄	2.46	2.40	(3.86)	—	1.09	e
(XI)	CH₃Co{(do)(doBF₂)pn}OH	—	(2.37)	(3.84)	—	0.56	f

* reported values are from frequency measurements in internal lock, except those in brackets which are directly read on paper from spectra in external lock. ** the sharper signal, attributed to a methyls, in D₂O is always at higher fields. ᵃ at pD 1.5; ᵇ at pD 6.2; ᶜ at pD 9.8; ᵈ at pD 5; ᵉ in D₂O; ᶠ in strongly alkaline solution.
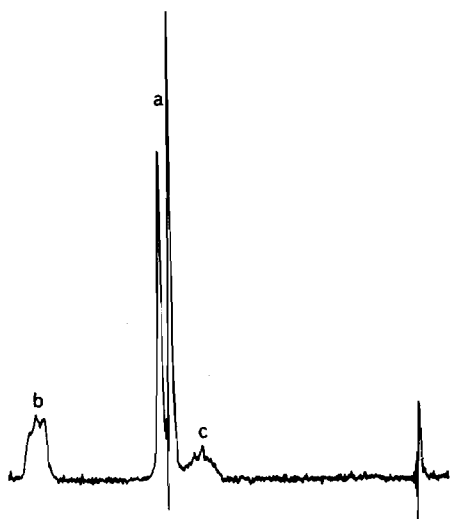
in H₂O it gives a broad peak at about 18.35 ppm from DSS.

Figure 2. ¹H NMR spectrum of [Co{(do)(doh)pn}(H₂O)₂]-(ClO₄)₂ in D₂O at pD 1.5: a) CH₃-C, b) CH₂-N, c) C-CH₂-C.

Changing just one axial ligand, as along the series (I,II,VIII) or (II,III,IX), the equatorial protons resonances move to higher fields in the order H₂O < OH < CH₃ which probably reflects variations in electronic density on the equatorial plane, although in considering differently charged complexes the electric field effect can be relevant. Similar features are observed for the series [Co{(do)(doh)pn}L₂]ˣ were the equatorial methyls resonate at higher fields in the order H₂O < RNH₂ < OH. In the complexes (IV-VII) the magnitude of variations in equatorial protons shifts suggests that electronic density changes on the equatorial plane are small and therefore also other factors (for example the magnetic anisotropy of the axial ligand) must be taken into account to explain the order of observed chemical shifts. Furthermore it is likely that the electronic density on the equatorial plane does not depend only on the basicity of the amine, more basic amines being perhaps more distant because of steric hindrance.

R protons nearest to binding nitrogen in [Co{(do)-

(doh)pn}(RNH₂)₂]²⁺ (where R = methyl, ethyl, n-butyl) are strongly shifted to high fields with respect to the corresponding free amine (Table II). Other R protons are less affected by complexation. Similar shielding effects were already observed for axial ligands in analogous complexes.[10-12]

Nitrogen bonded protons of [Co{(do)(doh)pn}(CH₃-NH₂)₂]²⁺ exchange slowly with deuterium in D₂O and their resonance can be observed as a broad signal centred at 3.31 ppm from DSS. This exchange can be followed also through the evolution of the methyl resonance, which is a triplet for CH₃NH₂-Co, a doublet for CH₃NHD-Co and a singlet for CH₃ND₂-Co (Figure 3). Analogous results were recently reported for CH₃Co(dh)₂NH₂R in CDCl₃.[13]

In the complex (X), where the O - - H - - O is substituted by the O - - BF₂ - - O, all protons resonate at lower fields with respect to (VIII). This could reflect an electron density diminution on the equatorial plane, BF₂ being probably a stronger electron
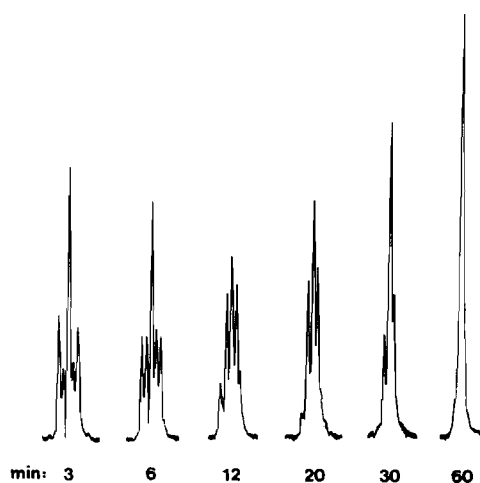

Figure 3. Evolution of axial methyls resonance in [Co{(do)-(doh)pn}(NH₂CH₃)₂]²⁺ in D₂O, during the H-D exchange on NH₂.

(10) G. Pellizer, G.R. Tauszik, G. Costa - J.C.S. Dalton, in press.
(11) H.A.O. Hill, K.G. Morallee - J. Chem. Soc., (A), 554 (1969).
(12) L.M. Ludwick, T.L. Brown - J. Am. Chem. Soc., 91, 5188 (1969).
(13) A. Gaudemer, F. Gaudemer, L. Diep - Bull. Soc. Chim. France, 884 (1972).

acceptor than hydrogen. The different magnitude of the effect on the equatorial methyls is one of the data considered for the above reported attribution of methyls resonances.

RNH₂ protons δ values in ppm from DSS*: (I) for the amine bonded to cobalt in the complex [Co{(do)(doh)pn}-(RNH₂)₂]²⁺ at pD 5, (II) for the free amine in D₂O.

|		(I)	(II)
CH₃NH₂	CH₃	1.54	2.30
C₂H₅NH₂	CH₂	1.93	2.64
	CH₃	0.87	1.05
C₄H₉NH₂	CH₂(1)	1.80	2.62
	CH₃(4)	0.77	0.89

*) measured in external lock.

Table III. pKa values: (I) for hydrogen bond dissociation in the complexes [Co{(do)(doh)pn}(RNH₂)₂]²⁺, (II) for the free amines.

Complex	(I)	(II)*
[Co{(do)(doh)pn}(NH₃)₂]²⁺	8.51	9.25
[Co{(do)(doh)pn}(CH₃NH₂)₂]²⁺	8.15	10.62
[Co{(do)(doh)pn}(C₂H₅NH₂)₂]²⁺	8.09	10.63
[Co{(do)(doh)pn}(C₄H₉NH₂)₂]²⁺	7.96	10.60

* Values in column (II) are from: A. Albert, E.P. Serjeant - Ionization Constants of Acids and Bases, Methuen and Co. Ltd, London 1962.

Acid-base equilibria - Thermodynamic cis and trans effects. Spectral changes with pH in the UV region for [Co{(do)(doh)pn}(RNH₂)₂]²⁺ (IV-VII) are similar to those observed for [Co(dh)₂L₂]⁺ (where L is a nitrogen binding ligand), which undergo hydrogen bond deprotonation;[7] spectra at different pH values show one isosbestic point near 41 kK (Figure 4). This behaviour has to be attributed to the electrolytic dissociation of the hydrogen-bonded hydrogen; acidity
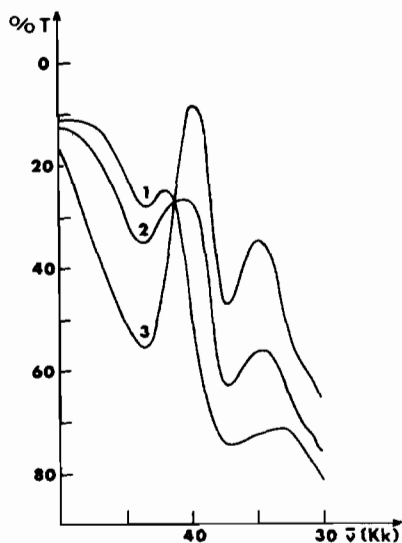
Figure 4. UV spectra of [Co{(do)(doh)pn}(NH₂CH₃)₂](ClO₄)₂ 1×10⁻⁴M: 1) in H₂O; 2) in NaOH 2×10⁻⁴M; 3) in NaOH 5×10⁻⁴M.

constants, measured by potentiometric titrations are reported in Table III. As already observed for dimethylglyoximates,[8] the dissociation constants do not correlate with the basicity of axial ligands; this probably reflects variations of the Co-N geometry, as suggested by the dependence of hydrogen bond acidity on the lenght of the aliphatic chain and by the discussion reported about the equatorial methyls chemical shifts. The NMR spectra of the complexes change when deprotonation occurs (Figure 5), the spectra of the protonated and deprotonated forms—
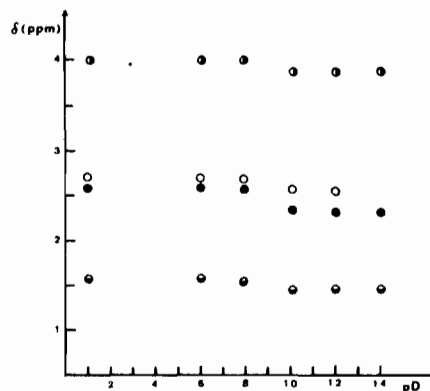
Figure 5. Variations of [Co{(do)(doh)pn}(NH₂CH₃)₂](ClO₄)₂ protons chemical shifts with pD: ◓ : CH₃-N-Co ● : CH₃-C-N-O O : CH₃-C-N-C ◑ : CH₂-N

when alone—being pH independent. Deprotonation has a shielding effect for all protons; the magnitude of this effect on the equatorial ligand seems to depend on the length of the bonds path through which the information is transmitted. The sharper methyls resonance is the most affected and this again suggests that it should be assigned to the a methyls; the observed shifts are of about 0.27 ppm. The other equatorial protons are shifted of about half this value. The high fields shifts for the axial ligands protons are of about 0.12 ppm for CH₃ in (V), 0.08 ppm for CH₂ and 0.06 ppm for CH₃ in (VI). Also the butyl protons of (VII) undergo shielding.

The effects on axial ligands of the deprotonation of the hydrogen bridge, like those of its substitution by an O - - BF₂ - - O bridge, are probably due mainly to variations of electronic charge induced through cobalt. While effects of the axial ligands were already reported for some series of complexes with other tetradentate equatorial ligands,[14] this effect on axial ligands of a variation of charge on the equatorial ligand is the first example of a ground state effect of the in-plane ligand system observed through NMR in the field of B 12 model molecules.

In the complex [Co{(do)(doh)pn}(H₂O)₂]²⁺ the two axial water molecules undergo deprotonation;[1] the effects on NMR spectra are reported in Table I. The UV spectra variations for the complex Co{(do)(doh)pn}(OH)₂ at various pH values higher than 11, being

(14) H.A.O. Hill, K.G. Morallee, G. Costa. G. Pellizer, A. Loewenstein - « Magnetic Resonances in Biological Research, An International Conference » Edited by C. Franconi, Gordon Breach New York, 301, (1971).

Table IV. Proton δ values for CH₃Co{(do)(doh)pn}X in CDCl₃, in ppm from TMS.*

X	Co-CH₃	C-CH₃	N-CH₂	C-CH₂-C
I	0.71	2.24 2.30	—	—
m-FC₆H₄	0.38	2.32	3.56	—
p-FC₆H₄	0.36	2.31	3.53	—
C₆H₅	0.35	2.32	3.56	1.89
CH₃	0.06	2.19 2.22	3.68	—

* measured in internal lock.

similar to those observed for the complexes (IV-VII), suggest that even here the hydrogen bond deprotonation occurs. The NMR spectra are in agreement with this explanation, but show that a fraction of the complex, under these pH conditions, undergoes a slow change, perhaps a *trans-cis* isomerization of the kind observed in dimethylglyoximates.[15]

At pH values higher than 10 also [CH₃Co{(do)-(doh)pn}H₂O]⁺ undergoes deprotonation of the axial water molecule but no evidence for dissociation of hydrogen bond was obtained, even in much more basic solution. As a matter of facts, the axial methyl resonance is strongly shifted to high fields by alkalization (0.44 ppm) but equatorial methyls are almost unaffected (see Table I), i.e. the behaviour is different from that observed for the hydrogen bond deprotonation which causes well observable shifts on equatorial resonances. Furthermore the complex (X), where the O- -H- -O bridge is substituted by O- -BF₂- -O, shows the same NMR spectra dependence on pH changes, the axial methyl resonance being shifted of 0.53 ppm by alkalization, while again equatorial protons are almost unaffected.

On the other hand the pH dependence of NMR spectra of [CH₃Co{(do)(doh)pn}Py]⁺ (XII) and of [CH₃Co{(do)(doh)pn}NH₃]⁺ (XIII) suggests that here the deprotonation of hydrogen bridge occurs to some extent in strongly alkaline solution, all of the protons being shifted to high fields (this is not due to a substitution of the axial ligand in trans to the methyl by OH, as CH₃Co{(do)(doh)pn}OH—if present—gives different peaks on the same spectrum).

The axial water molecule is deprotonated at pH values increasing in the order: [Co{(do)(doh)pn}(H₂O)₂]²⁺ pKₐ=4.17)[1] < [Co{(do)(doh)pn}(H₂O)(OH)]⁺ (pKₐ = 7.70)[1] < [CH₃Co{(do)(doBF₂)pn}H₂O]⁺ < [CH₃Co{(do)(doh)pn}H₂O]⁺; the comparison of acidities for the last two compounds was made following the deprotonation through the movement of the axial methyl resonance, at the same pD values; the determination of acidity constants is not possible by potentiometric titration, their value being too low. A low Kₐ value is observed also for CH₃Co(dh)₂H₂O (XIV), C₆H₅Co(dh)₂H₂O (XV), [C₆H₅Co{(do)(doh)-pn}]H₂O]⁺ (XVI) and CH₃Co(salen)H₂O (XVII).

The deprotonation of hydrogen bridge occurs at pH values increasing in the order [Co{(do)(doh)pn}(RN-H₂)₂]²⁺ < Co{(do)(doh)pn}(OH)₂ < [CH₃Co{(do)-(doh)pn}L]⁺ (where L is a nitrogen binding ligand as in (XII) and (XIII)),being not observable for CH₃Co-{(do)(doh)pn}OH.

In both cases the electron density on oxygen atoms, as reflected by acidity, is consistent with the magnitude of the charge released by the ligand, as reflected by chemical shift variations. I.e. the thermodynamic *trans* effect reflects a strong donation from alkyl to the ligand in *trans*, while the thermodynamic *cis* effect of the axial on the equatorial ligand and viceversa - going from (do)(doBF₂)pn to (do)(doh)pn - shows once more that the charge donated by one ligand is transmitted through cobalt to all other ligands.

Ground state trans effect. The above discussion suggests that the electron density on axial methyl increases on going from H₂O to OH as trans ligand. Therefore the high fields shift observed for methyl protons on *trans* ligand deprotonation is due also to an increase in the local diamagnetic term, even if in this case the through space effects, due to the charge variation, may be relevant. Furthermore considering the series of complexes reported in Table IV, where the charge is constant and the axial methyl chemical shift increases in the order I < mFC₆H₄ < pFC₅H₄ < C₆-H₅ < CH₃, in excellent agreement with the order observed for fluorine resonance in pFC₆H₄-Pt(PEt₃)₂L[16] and in p- and mFC₆H₄Co{(do)(doh)pn}X,[6] it is concluded that also the variations in the shielding constant of the axial methyl protons, observed when the *trans* ligand is changed, reflect variations of electron density induced through cobalt.

H-D exchange reaction on equatorial methyls. During the study of the pH dependence of NMR spectra for Co(do)(doh)pn complexes, it was observed that for some of them the lower field equatorial methyls signal disappears in alkaline D₂O solution. This behaviour could be more accurately pointed out for [CH₃Co{(do)(doh)pn}H₂O]ClO₄ (VIII) and the following results were obtained:

1) when the complex is dissolved in alkaline D₂O, axial water molecule undergoes deprotonation and (IX) is formed; moreover the *b* methyls resonance becomes weaker and weaker, suggesting that a reaction involving those methyl groups is occurring; on the other hand, in alkaline H₂O only the formation of (IX) is observed;

2) on neutralization of the D₂O solution the (VIII) spectrum is restored but the *b* methyls signal does not reappear;

3) the compound (XXIII), obtained by evaporation of the neutralized D₂O solution, when dissolved in

(15) A.V. Ablov, N.M. Samus, O.A. Bologa - *Russ. J. Inorg. Chem.*, 8, 440 (1963).

(16) G.W. Parshall - *J. Am. Chem. Soc.*, 88, 704 (1966).

H_2O has the same visible and NMR (except for the lacking signal) spectra as (VIII); furthermore by addition of iodide to the H_2O solutions of (XXIII) and (VIII), two compounds were precipitated,* which have slightly different IR spectra, the former showing a weak band at 2100 cm^{-1};

4) when (XXIII) is dissolved in H_2O alkaline solution, the b CH_3 resonance reappears.

The above results show that the b methyls hydrogen is substituted by deuterium when (VIII) is dissolved in alkaline D_2O, this giving (XXIII), and that this reaction is reversed when (XXIII) is dissolved in alkaline H_2O. The rate of the exchange H-D is strongly increased by increasing the pH.

The deuteration of b methyls was observed also for (IV-VII,X) and for $[CH_3Co\{(do)(doh)pn\}L]^x$ (where L is pyridine, ammonia or an aminoacid[10]). The deuteration rate, as followed from the diminution of the b methyls NMR signal area, at the same pH value, increases in the order $[CH_3Co\{(do)(doh)pn\}H_2O]^+$ < $[Co\{(do)(doh)pn\}(CH_3NH_2)_2]^{2+}$ < $[CH_3Co\{(do)(doBF_2)pn\}H_2O]^+$.**

Experimental Section

$[Co\{(do)(doh)pn\}(H_2O)_2](ClO_4)_2$ (I),[1] $[Co\{(do)(doh)pn\}(NH_3)_2]Br_2$ (IV),[17] $[CH_3Co\{(do)(doh)pn\}H_2O]ClO_4$ (VIII),[17] $[CH_3Co\{(do)(doBF_2)pn\}H_2O]ClO_4$ (X),[19] CH_3-$Co(dh)_2H_2O$ (XIV),[20] $[C_6H_5Co\{(do)(doh)pn\}H_2O]ClO_4$ (XVI),[17] $CH_3Co(salen)H_2O$ (XVII),[21] $CH_3Co\{(do)(doh)pn\}I$ (XVIII),[17] $(CH_3)(m\text{-}FC_6H_4)Co\{(do)(doh)pn\}$ (XIX),[22] $(CH_3)(p\text{-}FC_6H_4)Co\{(do)(doh)pn\}$ (XX),[22] (CH_3)-$(C_6H_5)Co\{(do)(doh)pn\}$ (XXI)[23] and $(CH_3)_2Co\{(do)$-$(doh)pn\}$ (XXII)[23] were prepared following the procedures described in the references.

$[Co\{(do)(doh)pn\}(CH_3NH_2)_2]Br_2$ (V), $[Co\{(do)$-$(doh)pn\}(C_2H_5NH_2)_2](ClO_4)_2$ (VI) and $[Co\{(do)(doh)pn\}(C_4H_9NH_2)_2](ClO_4)_2$ (VII) were prepared following the same procedure as (IV);[17] ((V): calcd: C, 30.01, H 5.61, N 16.15% - Found: C 29.83, H 5.65, N

15.94%; (VI): calcd: C 30.67, H 5.66, N 14.31% - Found: C 30.45, H 5.45, N 14.16%; (VII): calcd: C 35.46, H 6.42, N 13.06% - Found: C 35.93, H 6.37, N 12.30%).

$[CH_3Co\{(do)(doh)pn\}Py]^+$ (XII) and $[CH_3Co\{(do)$-$(doh)pn\}NH_3]^+$ (XIII) were obtained in water solution adding pyridine and respectively ammonia to the dissolved (VIII).[10]

$C_6H_5Co(dh)_2H_2O$ (XV) was prepared by adding dropwise a THF solution of C_6H_5MgBr (7.5 mmoles) to a suspension of $ClCo(dh)_2H_2O$ (5 mmoles) in anhydrous THF (50 ml), at 0°C. The reaction mixture was stirred for one hour, poured into cold water and neutralized with HCl. The yellow orange solid obtained was filtered and washed with water, ethanol and ether; ((XV): calcd: C 43.75, H 5.50, N 14.58, Co 15.33% - Found: C 43.57, H 5.91, N 14.35, Co 15.21%).

NMR spectra were recorded by a JEOL C 60 HL spectrometer. For measurements in internal lock audiofrequency used to generate the locking signal was measured by a Hewlett and Packard 5216 A 12.5 Mhz electronic counter, accuracy being better than ±1 Hz. Stohler I. C. D_2O (99.8% D), Merck, Sharp and Dohme DSS (sodium 2,2-dimethyl-2-silapantane-5-sulfonate), CIBA CDCl₃ (99% D), NaOD (99% D) and TMS (tetramethylsilane) were used for NMR spectroscopy.

UV spectra were recorded by a UNICAM SP 700 spectrophotometer.

IR spectra were recorded by a Perkin-Elmer 225, from KBr pellets.

For the determination of acidity constants, 1×10^{-3} M solutions of the complexes were titrated at 25°C with 0.1 N NaOH, using an E 353 Metrohm potentiometer equipped with a saturated calomel electrode and a glass electrode. The meter was calibrated with pH 7 phosphate buffer. The pKa values were calculated from the usual plots of pH against log $[A^-]/[AH]$ at the point were $[A^-]=[AH]$. A straight line with a slope equal to one was obtained in each instance.

pD values of the D_2O solutions were measured with the same instrument, adding 0.4 pH units to the instrumental value.[24]

(*) The use of the non charged iododerivative avoids complications due to the strong absorption of the ClO_4^- in the methyl-rocking region.

(**) After H. Yoneda et al.[18] the H—D exchange rate in the CH_3 groups in a series of cobaloximes $Co(dh)_2L$ (L = CH_3NH_2, NH_3, NO_3^-, CN^-) decreases with decreasing effective charge on the metal atom, i.e. increasing donor power of the axial ligand L.

(17) G. Costa, G. Mestroni, E. De Savorgnani - *Inorg. Chim. Acta*, 3, 323 (1969).
(18) H. Yoneda, I. Takagi, Y. Morimoto - *Bull. Chem. Soc. Jap.*, 44, 3493 (1971).
(19) E. Reisenhofer, M. Pillin - Private Communication.
(20) C.N. Schrauzer, R.J. Windgassen - *J. Am. Chem. Soc.*, 88, 3738 (1966).
(21) G. Costa, G. Mestroni, G. Pellizer - *J. Organomet. Chem.*, 11, 333 (1968).
(22) To be published..
(23) G. Costa, G. Mestroni, G. Tauzher - *J. C. S. Dalton*, 450 (1972).

(24) P.K. Glasoe, F.A. Long - *J. Phys. Chem.*, 64, 188 (1960).