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Syntheses, Structures and Ligand Dissociation Kinetics of Vitamin B_{12} Model Compounds with Exceptionally Poor Electron Donating Groups, $LCo(DH)_2CHX_2$ (X = Cl or Br)

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Abstract

The syntheses and ligand dissociation kinetics of vitamin B_{12} model compounds $LCo(DH)_2CHX_2$ with X = Cl and Br and L = different neutral N- and P-ligands are reported together with the crystal structures of the $CHCl_2$ derivatives with L = py (**1**) and 1,5,6-trimethylbenzimidazole, Me_3Bzm (**2**). Compound **1** crystallizes in the space group $P2_1/n$ with cell parameters $a = 9.617(1)$, $b = 12.601(2)$, $c = 15.586(2)$ Å, $\beta = 95.44(1)°$; **2** crystallizes in the space group $P1$ with cell parameters $a = 8.867(2)$, $b = 10.719(2)$, $c = 13.345(2)$ Å, $\alpha = 94.81(2)$, $\beta = 90.89(1)$, $\gamma = 105.63(2)°$. The two structures were solved by Patterson and Fourier methods and refined by least-squares methods to final R values of 0.037 (**1**) and 0.036 (**2**), using 3474 (**1**) and 4435 (**2**) independent reflections.

The axial N–Co–C fragment is characterized by Co–N and Co–C distances of 2.045(2) and 1.995(2) Å in **1** and 2.043(2) and 1.983(2) Å in **2**, respectively. The Co–C bond lengths have the smallest values so far reported in both py and Me_3Bzm alkylcobaloximes.

The displacement of the L ligand followed SN1 LIM behaviour and the corresponding rate constants depend upon the nature of L and vary in $CHCl_2$ derivatives from 2.42×10^{-1} s^{-1} for 2-aminopyridine to 1.99×10^{-5} s^{-1} for $P(OMe)_3$. For fewer $CHBr_2$ analogs the rate constants were smaller.

Kinetic results confirm previous findings that the donating ability of $CHBr_2$ is less than that of $CHCl_2$, although the electronegativity of Cl and Br species would suggest an opposite trend. Some relationships between kinetic and structural properties are discussed.

Introduction

Alkyl cobaloximes, $LCo(DH)_2R$, where DH = monoanion of dimethylglyoxime, L = neutral ligand and R = alkyl group, are widely studied as models for B_{12} coenzymes [1]. On the other hand, this class of compounds is particularly suitable for studying the interrelationship between steric and electronic influences [1].

Correlations between molecular structure and solution properties have been established for many good electron-donor R groups, but only recently have data been reported [2] relative to R groups with electron-withdrawing substituents. In particular, it has been shown that R groups, such as CH(CN)Cl, exert a weak *trans*-influence on the L neutral ligand as indicated by the Co–py distance of 2.017(2) Å in $pyCo(DH)_2CH(CN)Cl$ [2], compared with that of 2.068(3) Å in the methyl analog [1]. This corresponds to values of the first order rate constant for the dissociation reaction of L of about 3 orders of magnitude less for the CH(CN)Cl derivative than that for the methyl derivative [2]. On the other hand, the Co–C bond length of 2.015(3) Å [2] in the CH(CN)Cl derivative is the shortest bond to Co found in a 'secondary' alkyl group. Indeed, it is only slightly longer than that of 1.998(5) Å in $pyCo(DH)_2Me$ [1].

These results should be compared with those obtained for bulky R groups substituted with electron-donors, such as i-Pr (Co–py 2.099(2) Å and Co–C 2.085(3) Å) [3], and with bulky electron-withdrawing groups, such as $CH(CN)CH_2CN$ (Co–Me_3Bzm 2.031(2) Å and Co–C 2.061(3) Å) [4]. These data suggest that Cl substituents at the α-C largely affect its electronic properties and could have an effect on the overall bulk of R comparable to or less than that of a hydrogen atom.

Finally, the influence exerted by R groups, such as CH_2X where X = Cl, Br, I on the dissociation rate of the neutral ligand was found to be opposite to that

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expected on the basis of the electronic properties of X [1].

In order to obtain further insight into the above problems, a systematic study of $LCo(DH)_2CHX_2$ (X = Cl, Br, I and L = neutral ligand) was undertaken. We report the synthesis and kinetics of the series with X = Cl and Br and the X-ray structures of $pyCo(DH)_2CHCl_2$ (1) and $Me_3BzmCo(DH)_2CHCl_2$ (2).

Experimental

Reagents

Aniline was distilled under vacuum before use in the preparations. Dicyclohexylphenylphosphine was purchased from Strem. All other reagents were from Aldrich and used without further purification.

Instrumentation

Ligand substitution reactions were monitored spectrophotometrically with a Perkin-Elmer Lambda 3B UV–Vis spectrophotometer equipped with a Perkin-Elmer C570-0701 digital temperature controller thermostated at 25.00 ± 0.04 °C (for slow reactions of $k_1 < 5 \times 10^{-1}$ s^{-1}) or a Durrum-Gibson D-110 stopped-flow spectrophotometer (for faster reactions) equipped with a MGW LAUDA RC 3 B-2 temperature controller thermostated at 25.00 ± 0.1 °C.

Rate Measurements

For each compound the visible spectrum of a methylene chloride solution was scanned and then compared with the visible spectrum obtained after addition of a calculated excess (>20:1 mole ratio) of entering ligand ($L' = P(OMe)_3$ or, for $P(OMe)_3Co(DH)_2CHCl_2$, 1-methylimidazole) and allowing sufficient time for the reaction to reach completion. The optimum wavelengths used to monitor the reaction rates were selected in the range 400–430 nm for solutions (2.00×10^{-3} M) of the complexes studied. Absorbance data were collected continuously over at least three half-lives with final absorbance readings taken at about eight half-lives. The experimental absorbance *versus* time rate data were treated with the standard integrated expression for the first order reaction using linear least-squares analysis as previously described [5] and yielded classical SN1 LIM behaviour.

Preparations

$PhNH_2Co(DH)_2CHCl_2$

A NaOH solution (1 pellet in 10 ml H_2O) was added to 200 ml of 80% (*v*/*v*) $MeOH/H_2O$. $PhNH_2(DH)_2Cl$ (2 g) was added to the solution under N_2. The mixture was stirred for 10 min. Soon thereafter, a 1.3-fold excess of $NaBH_4$ (0.24 g) dissolved in 10 ml of H_2O was slowly added. A 6-fold excess of $CHCl_3$ (2.3 ml) was slowly added. When the bubbling stopped, acetone (25 ml) was added and the solution was stirred for 10 min. The volume was reduced by rotoevaporation until some solid particles appeared on the side of the round-bottom flask. About 3 ml of Et_2O were added. The mixture was kept at 5 °C overnight. The fine red–orange crystals collected were washed with H_2O petroleum ether. Yield 32%.

$2\text{-}NH_2pyCo(DH)_2CHCl_2$ ($2\text{-}NH_2py$ = 2-aminopyridine)

$PhNH_2Co(DH)_2CHCl_2$ (1.0 g) and Dowex 50X8-100 cation exchange resin (1.0 g) were stirred overnight in 80% $MeOH/H_2O$ (*v*/*v*) (100 ml). The solids were removed by filtration and the wine-colored filtrate was reduced to 20 ml to yield an orange precipitate which was collected and washed with a little water and with CH_2Cl_2. Yield of $H_2OCo(DH)_2CHCl_2$ 76%.

A mixture of $H_2OCo(DH)_2CHCl_2$ (0.64 g), a 1.5-fold excess of $2\text{-}NH_2py$ (0.23 g) and CH_2Cl_2 (50 ml) was stirred for at least 2 h. The resulting solution was filtered and taken to dryness on a rotary evaporator. The residue, a red–brown powder, was collected and washed with petroleum ether and Et_2O.

$AnisCo(DH)_2CHCl_2$ (anis = $4\text{-}MeO\text{-}C_6H_4NH_2$)

$Anis(DH)_2Cl$ (1.74 g) was suspended in MeOH (174 ml) under N_2. Half of a pellet of NaOH dissolved in 5 ml H_2O was added to the stirred solution. A 1.3-fold excess of $NaBH_4$ (0.18 g) dissolved in H_2O (10 ml) was added. Immediately thereafter, but slowly, a 5-fold excess of $CHCl_3$ (1.7 ml) was added. When the bubbling stopped, acetone (10 ml) was added. After 5 min, the solution volume was reduced with a rotary evaporator until some solid particles appeared. The brown powder was collected and washed with H_2O and petroleum ether. Yield 40%.

$PPh_3Co(DH)_2CHCl_2$

$PhNH_2(DH)_2CHCl_2$ (1 g) and a 1.5-fold excess of PPh_3 (0.84 g) were dissolved in acetone (20 ml). Next, H_2O (5 ml) was added. Enough acetone was added to make a clear solution. The orange powder which formed was collected and washed with Et_2O. Yield 62%.

$PPhChx_2Co(DH)_2CHCl_2$ (Chx = $c\text{-}C_6H_{11}$)

$PhNH_2Co(DH)_2CHCl_2$ (0.64 g) and a 1.2-fold excess of $PPhChx_2$ (0.45 g) were suspended in MeOH (6 ml). Acetone (10 ml) was added to dissolve all the solid. The solution was filtered, placed in a tightly covered container and laid aside in a hood overnight. The next day, flat hexagonal, red–orange crystals had formed. The container was kept at 5 °C overnight. The crystals were collected and dried in air. Yield 40%. After 48 h at 5 °C, a second crop of crystals was obtained from the filtrate (18%).

4-CNpyCo(DH)$_2$CHCl$_2$

A solution of $PhNH_2Co(DH)_2CHCl_2$ (0.65 g) and a 5-fold excess of 4-CNpy (0.73 g) in $CHCl_3$ (25 ml) was stirred overnight. An HCl solution (10 ml, pH 3) was added. The solution was concentrated under vacuum until a copious precipitate appeared. A yellow–brown powder was collected and then washed with H_2O and petroleum ether. Yield 90%.

pyCo(DH)$_2$CHCl$_2$

$pyCo(DH)_2Cl$ (3 g) was suspended in MeOH (300 ml). Three pellets of NaOH dissolved in H_2O (10 ml) were added. The solution was stirred and purged with N_2. A 2-fold excess of $NaBH_4$ (0.56 g) dissolved in H_2O (5 ml) and then a 4-fold excess of $CHCl_3$ (2.38 ml) were added carefully to avoid vigorous bubbling. When the bubbling stopped, acetone (5 ml) was added. A precipitate had formed. The stirring was continued for 5 min. Most of the solvent was removed by rotoevaporation. More water was added. The mixture was put in a refrigerator overnight. An orange–red powder was collected and washed with H_2O and then petroleum ether. Yield 59%.

DEACo(DH)$_2$CHCl$_2$ (DEA = dimethoxyethylamine)

A solution of $PhNH_2Co(DH)_2CHCl_2$ (0.75 g) and a 1.5-fold excess of DEA (0.27 ml) in acetone (20 ml) was set aside in a hood overnight. The solution volume was reduced to about 5 ml under vacuum. Petroleum ether (5 ml) was added. The red–brown precipitate formed was collected and washed with dilute aqueous acetic acid (pH 2.7), H_2O, and petroleum ether. Yield 80%.

Me$_3$BzmCo(DH)$_2$CHCl$_2$

A solution of Me_3Bzm (0.32 g) and a 1.1-fold excess of $PhNH_2Co(DH)_2CHCl_2$ (0.85 g) in acetone (10 ml)/MeOH (5 ml) was stirred for 2.5 h. Then water (15 ml) was added to induce nearly complete precipitation. The yellow–red powder was collected and washed with H_2O until the filtrate appeared colorless and then with Et_2O. Yield 78%.

P(OMe)$_3$Co(DH)$_2$CHCl$_2$

$PhNH_2Co(DH)_2CHCl_2$ (0.73 g) and a 1.5-fold excess of $P(OMe)_3$ (0.28 ml) were dissolved in a mixture of acetone (22 ml) and H_2O (2 ml). The solution was set aside in a hood overnight and then reduced in volume under vacuum to 5 ml. A precipitate appeared. To induce complete precipitation, aqueous acetic acid (20 ml, pH 2.7) was added. The yellow powder was collected and washed with H_2O and then petroleum ether. Yield 82%.

PPh$_2$EtCo(DH)$_2$CHCl$_2$

A solution of $PhNH_2Co(DH)_2CHCl_2$ (0.5 g) and a 1.1-fold excess of PPh_2Et (0.3 ml) in MeOH (15 ml) was stirred overnight. Then H_2O (15 ml) was added and the mixture stirred for 15 min. The yellow precipitate which formed on addition of H_2O was collected and washed with H_2O and Et_2O. Yield 71%.

PhNH$_2$Co(DH)$_2$CHBr$_2$

12.5 ml of NaOH solution (1.63 g of NaOH/100 ml of H_2O) and $PhNH_2Co(DH)_2Cl$ (5 g) were added to MeOH (500 ml). The mixture was stirred for 10 min under N_2. A 1.3-fold excess of $NaBH_4$ (0.6 g) dissolved in 20 ml H_2O was added, followed quickly by 1 equivalent of $CHBr_3$ (1.1 ml). When the bubbling stopped, acetone (25 ml) was added. The solution was stirred for 10 min then reduced in volume by rotoevaporation until some solid particles appeared. Absolute Et_2O (3 ml) was added and the mixture was kept tightly covered at 5 °C overnight. The red–brown powder was collected, then washed with H_2O and petroleum ether. Yield 67%.

PPh$_3$Co(DH)$_2$CHBr$_2$

$PhNH_2Co(DH)_2CHBr_2$ (0.5 g) and a 5-fold excess of PPh_3 (1.18 g) were suspended in acetone (2 ml)/H_2O (5 ml). Enough acetone was added to dissolve the solids completely. The solution was stirred overnight then reduced in volume by rotoevaporation until a copious precipitate appeared. More H_2O was added. The mixture was kept at 5 °C overnight. A solid (0.3 g) was collected and washed thrice with Et_2O (3 ml). It contained about 1/7 of the starting material (by ^1H NMR). It was dissolved in $CHCl_3$ (5 ml) containing PPh_3 (0.4 g). The solution was set aside in a hood overnight in a tightly sealed container. The container was uncovered and allowed to evaporate in the hood until many large needles appeared. The red–brown crystals were collected and washed with H_2O and Et_2O. Yield 34%.

4-CNpyCo(DH)$_2$CHBr$_2$

A solution of $PhNH_2Co(DH)_2CHBr_2$ (1.53 g) and 4-CNpy (1.43 g, a 5-fold excess) in acetone (60 ml) was stirred overnight. Aqueous acetic acid (30 ml, pH 2.7) was added. The solution was reduced in volume to 30 ml by rotoevaporation. The yellow–brown precipitate was collected and washed with H_2O and then Et_2O. It contained about 1/7 of starting material (by ^1H NMR), so it was dissolved in CH_2Cl_2 (15 ml) containing 4-CNpy (0.3 g) and the process described above was repeated.

Preparation of Single Crystals

pyCo(DH)$_2$CHCl$_2$

$pyCo(DH)_2CHCl_2$ was dissolved in a mixture of CH_2Cl_2 and MeOH (2:1) and filtered. The filtrate was put in a refrigerator (5 °C). Large crystals formed over several days.

TABLE I. Crystallographic Data for $pyCo(DH)_2CHCl_2$ (1) and $Me_3BzmCo(DH)_2CHCl_2 \cdot H_2O$ (2)

Formula	$CoCl_2O_4N_5C_{14}H_{20}$	$CoCl_2O_4N_6C_{19}H_{27} \cdot H_2O$
Molecular weight	452.2	551.4
a (Å)	9.617(1)	8.867(2)
b (Å)	12.601(2)	10.719(2)
c (Å)	15.586(2)	13.345(2)
α (°)		94.81(2)
β (°)	95.44(1)	90.89(1)
γ (°)		105.63(2)
D(meas.) (g cm^{-3})	1.60	1.49
D(calc.) (g cm^{-3})	1.60	1.51
Z	4	2
Space group	$P2_1/n$	$P\bar{1}$
μ (cm^{-1})	12.3	9.6
Crystal dimensions (cm^3)	0.05 × 0.04 × 0.06	0.04 × 0.04 × 0.07
No. reflections measured	4896	4635
No. independent reflections $I \geqslant 3\sigma(I)$	3474	4435
2θ max (°) (Mo Kα)	56	56
R	0.037	0.036
R_w	0.050	0.049

$Me_3BzmCo(DH)_2CHCl_2$

$Me_3BzmCo(DH)_2CHCl_2$ was dissolved in a mixture of H_2O and acetone (1:4) and filtered. The filtrate was kept at 5 °C. After four days, many beautiful crystals of similar size had formed.

Elemental Analyses

C, H, N analyses were performed by Atlantic Microlabs, Inc. (Atlanta, Ga.). See 'Supplementary Material'.

Crystal Data

Unit cell parameters were determined from Weissenberg and precession photographs and refined on a CAD4 automated single crystal diffractometer. The results are given in Table I.

The intensity data were collected by the $\omega/2\theta$ scan technique using graphite-monochromated Mo Kα radiation. Three standard reflections, measured every 60 min, showed no systematic variation throughout the data collection. The intensities with $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption (Table I).

Solutions and Refinement of the Structures

Structures of both 1 and 2 were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods.

For compound 2 the Fourier maps revealed the presence of an additional peak, interpreted as the oxygen atom of a crystallization water with occupancy factor 1.0. In the final cycles the contribution of hydrogen atoms at calculated positions, held constant at $B = 5$ Å^2, and the anisotropic temperature factors for non-hydrogen atoms were included. The oxime bridge hydrogen atoms for both structures and the crystallization water hydrogen atoms for 2 were located on the difference Fourier map. Final R values are given in Table I. The final weighting scheme was $1/(\sigma^2(F) + (0.02F)^2 + 1)$ for both 1 and 2, chosen so as to mantain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $\sin\theta/\lambda$. Atomic scattering factors were those given in ref. 6. All the calculations were done by using the computer programs from the CAD4-SDP package. Final positional parameters for non-hydrogen atoms are given in Table II. See also 'Supplementary material'.

Results and Discussion

Description and Discussion of the Structures

The ORTEP drawings with the atom numbering schemes are given in Figs. 1 and 2.

In 2, each crystallization water molecule bridges two $Me_3BzmCo(DH)_2CHCl_2$ through hydrogen bonds between O(4) of the complex molecule at x, y, z (2.915(3) Å) and O(1) of that at $1-x, 1-y, 1-z$ (2.818(3) Å).

In both compounds, cobalt exhibits the usual distorted octahedral stereochemistry [1]. The four equatorial N atoms are coplanar within ±0.04 (1) and ±0.02 Å (2) and cobalt is displaced by 0.02 (1) and 0.008 Å (2) from these mean planes towards C(9) and N(5), respectively. The two chemically equivalent equatorial halves are approximately planar. Their mean planes in 1 make a dihedral angle, α, of 7.6° and bend towards the axial neutral ligand. In 2 the $Co(DH)_2$ unit is essentially planar ($\alpha = 1.5°$).

The structural features of the bonding of the $CHCl_2$ group to cobalt are very similar in both compounds. The C–Cl bond lengths and the Co–C–Cl

TABLE II. Atomic Parameters[a] of $pyCo(DH)_2CHCl_2$ (1) and $Me_3BzmCo(DH)_2CHCl_2 \cdot H_2O$ (2)

Atom	x	y	z	B (Å²)	Atom	x	y	z	B (Å²)
$pyCo(DH)_2CHCl_2$									
Co	0.00673(3)	0.08420(3)	0.23081(2)	2.052(5)	C2	0.2300(3)	0.1517(2)	0.1499(2)	2.64(5)
Cl1	−0.0508(1)	−0.16380(6)	0.19061(5)	5.04(2)	C3	0.1096(3)	0.2090(2)	0.1086(2)	2.69(5)
Cl2	−0.14862(8)	−0.01594(7)	0.05957(5)	3.81(1)	C4	0.1187(4)	0.2904(3)	0.0396(2)	3.70(6)
O1	0.2956(2)	0.0275(2)	0.2544(1)	3.46(4)	C5	−0.3595(3)	0.0177(3)	0.3445(2)	4.15(7)
O2	−0.1275(2)	0.2293(2)	0.1099(1)	3.26(4)	C6	−0.2152(3)	0.0253(2)	0.3167(2)	2.73(5)
O3	−0.2849(2)	0.1336(2)	0.2024(1)	3.42(4)	C7	−0.0932(3)	−0.0260(2)	0.3629(2)	2.67(5)
O4	0.1443(2)	−0.0475(2)	0.3605(1)	3.27(4)	C8	−0.1021(4)	−0.0960(3)	0.4387(2)	3.77(6)
N1	0.1969(2)	0.0875(2)	0.2095(1)	2.48(4)	C9	−0.0162(3)	−0.0360(2)	0.1474(2)	2.81(5)
N2	−0.0067(2)	0.1828(2)	0.1386(1)	2.46(4)	C10	0.1605(3)	0.2183(2)	0.3652(2)	3.12(5)
N3	−0.1837(2)	0.0794(2)	0.2509(1)	2.56(4)	C11	0.1871(3)	0.3020(3)	0.4214(2)	3.60(6)
N4	0.0219(2)	−0.0065(2)	0.3277(1)	2.43(4)	C12	0.0894(4)	0.3812(3)	0.4242(2)	4.15(7)
N5	0.0410(2)	0.2100(2)	0.3130(1)	2.43(4)	C13	−0.0321(4)	0.3743(3)	0.3702(2)	4.44(7)
C1	0.3757(3)	0.1683(3)	0.1274(2)	3.83(6)	C14	−0.0532(3)	0.2876(2)	0.3164(2)	3.42(6)
$Me_3BzmCo(DH)_2CHCl_2 \cdot H_2O$									
Co	0.43080(3)	0.26289(3)	0.18023(2)	2.141(5)	C5	−0.0194(3)	0.0096(3)	0.1573(3)	4.53(7)
Cl1	0.2822(1)	0.49906(7)	0.15032(7)	4.84(2)	C6	0.1267(3)	0.1160(3)	0.1816(2)	3.01(5)
Cl2	0.27987(9)	0.32227(8)	−0.02311(5)	4.42(2)	C7	0.1474(3)	0.2133(2)	0.2677(2)	3.07(5)
O1	0.5963(2)	0.4867(2)	0.3059(1)	3.34(4)	C8	0.0183(4)	0.2288(4)	0.3333(3)	4.85(7)
O2	0.5350(2)	0.1416(2)	0.0082(1)	3.40(4)	C9	0.3822(3)	0.3896(2)	0.0935(2)	3.00(5)
O3	0.2569(2)	0.0438(2)	0.0517(1)	3.40(4)	C10	0.5838(3)	0.1419(2)	0.3511(2)	2.40(4)
O4	0.3279(2)	0.3814(2)	0.3566(1)	3.69(4)	C11	0.6415(3)	0.2461(2)	0.4233(2)	2.88(5)
N1	0.6048(2)	0.4004(2)	0.2288(2)	2.53(4)	C12	0.7285(3)	0.2287(3)	0.5056(2)	3.20(5)
N2	0.5732(2)	0.2381(2)	0.0824(2)	2.53(4)	C13	0.8026(4)	0.3446(3)	0.5791(2)	4.92(7)
N3	0.2531(2)	0.1287(2)	0.1311(2)	2.62(4)	C14	0.8499(4)	0.0881(3)	0.6080(2)	4.70(7)
N4	0.2887(2)	0.2872(2)	0.2793(2)	2.72(4)	C15	0.7536(3)	0.1054(3)	0.5184(2)	3.33(5)
N5	0.5001(2)	0.1313(2)	0.2592(2)	2.55(4)	C16	0.6948(3)	0.0017(2)	0.4477(2)	3.14(5)
N6	0.5470(3)	−0.0593(2)	0.2798(2)	3.13(4)	C17	0.6126(3)	0.0225(2)	0.3644(2)	2.77(5)
C1	0.8796(3)	0.5144(3)	0.2089(3)	4.16(7)	C18	0.5535(4)	−0.1930(3)	0.2572(3)	4.71(7)
C2	0.7329(3)	0.4108(2)	0.1808(2)	2.83(5)	C19	0.4833(3)	0.0102(2)	0.2206(2)	2.99(5)
C3	0.7156(3)	0.3122(2)	0.0954(2)	2.71(5)	O5	0.2335(4)	0.3080(3)	0.5564(2)	8.13(9)
C4	0.8455(3)	0.2978(3)	0.0303(2)	4.06(6)					

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\alpha)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\gamma)\beta_{23}]$. e.s.d.s given in parentheses.

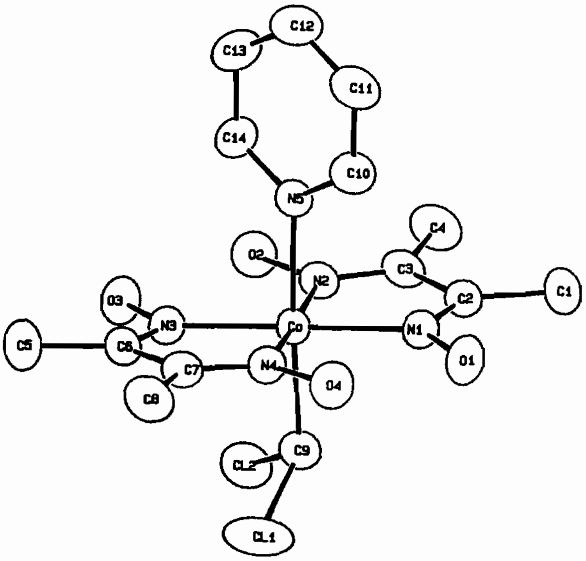

Fig. 1. ORTEP drawing of 1.

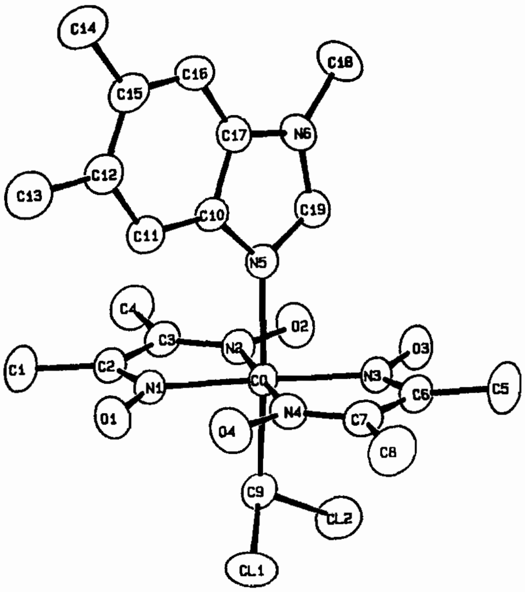

Fig. 2. ORTEP drawing of 2.

angles average to 1.792(2) (1) and 1.783(2) Å (2) and to 116.1(1) (1) and 115.8(1)° (2), respectively. The neutral ligands are essentially planar and their planes nearly coincide with the ideal mirror plane which crosses the oxime bridges of the $Co(DH)_2$ unit. The L–Co–C fragment is characterized by Co–N and Co–C distances of 2.045(2) and 1.995(2) Å in 1 and 2.043(2) and 1.983(2) Å in 2, respectively, with a C–Co–N angle of 176.52(8)° in 1 and 173.72(8)° in 2.

The axial Co–C and Co–N bond lengths in some py and Me_3Bzm alkylcobaloximes containing R groups with electron-withdrawing substituents are given in Table III. The Me, i-Pr and CH_2SiMe_3 derivatives are reported for comparison. The data show that the Co–C bonds in Me_3Bzm derivatives are slightly shorter than those in the py analogues [7] and that the Co–C distance is mainly determined by steric interactions of R with the equatorial moiety. Furthermore, the substitution of α-C hydrogens with chlorine atoms leads to a small decrease of the Co–C bond lengths. The $CHCl_2$ derivatives have the shortest $Co–C(sp^3)$ bond lengths so far reported suggesting that the $CHCl_2$ group interacts with the $Co(DH)_2$ moiety to an extent close to or even less than that of Me. This point is supported by the comparison of the C–Cl distance of 1.827(2) Å in $pyCo(DH)_2CH(CN)Cl$ [2] with the mean value of 1.792(2) in 1 and 1.782(2) Å in 2. The latter values are close to those reported for CCl_4 (1.771 Å) and CH_3Cl (1.781(2) Å), while the former is close to that of 1.828(5) Å

TABLE III. Co–C and Co–N Bond Lengths (Å) in $LCo(DH)_2R$ Complexes with L = py and Me_3Bzm and R = Electron-withdrawing Groups

	py		Me_3Bzm	
	Co–C	Co–N	Co–C	Co–N
$CHCl_2$	1.995(2)	2.045(2)[a]	1.983(2)	2.043(2)[a]
Me	1.998(5)	2.068(3)[b]	1.989(2)	2.060(2)[c]
CH_2CH_2CN	2.002(7)	2.050(5)[d]		
CH_2NO_2	2.002(3)	2.028(3)[b]	1.988(5)	2.013(3)[c]
CH(CN)Cl	2.015(3)	2.017(2)[d]	2.000(5)	2.010(3)[e]
CH_2CN	2.024(6)	2.014(4)[f]		
$CH(CN)CH_2CN$			2.061(3)	2.031(3)[c]
CH_2SiMe_3	2.031(6)	2.091(5)[b]		
i-Pr	2.085(3)	2.099(2)[g]	2.076(2)	2.097(2)[c]

For comparison, the corresponding values for cobaloximes containing the Me group, the good donor and bulky alkyl group i-Pr as well as the good donor and a relatively less bulky CH_2SiMe_3 group are also reported. [a]Present work. [b]Ref. 1. [c]Ref. 4. [d]Ref. 2. [e]Ref. 7. [f]Ref. 13. [g]Ref. 3.

TABLE IV. First Order Rate Constants, k_1 (s^{-1}), for the Dissociation of L from $LCo(DH)_2CHX_2$ (X = H, Cl, Br), Listed in Decreasing Order of Rate Constant[a]

	X = H	X = Cl		X = Br	
	k_1	k'_1	k'_1/k_1 (×100)	k''_1	k''_1/k_1 (×100)
2-NH_2py	$3.5 \pm 0.1 \times 10^{0}$ [b]	$2.42 \pm 0.05 \times 10^{-1}$	6.9		
NH_2Ph	$1.51 \pm 0.04 \times 10^{0}$ [c]	$1.87 \pm 0.02 \times 10^{-2}$	1.24	$7.92 \pm 0.05 \times 10^{-3}$	0.52
Anis	$4.7 \pm 0.1 \times 10^{-1}$ [c]	$4.36 \pm 0.06 \times 10^{-3}$	0.93		
PPh_3	$8.32 \pm 0.01 \times 10^{-2}$ [d]	$3.74 \pm 0.02 \times 10^{-3}$	4.50	$1.07 \pm 0.01 \times 10^{-3}$	1.29
$PPhChx_2$	$5.0 \pm 0.5 \times 10^{-2}$ [c]	$1.00 \pm 0.01 \times 10^{-3}$	2.0		
4-CNpy	$4.1 \pm 0.3 \times 10^{-2}$ [e]	$8.3 \pm 0.1 \times 10^{-4}$	2.0	$4.98 \pm 0.02 \times 10^{-4}$	1.2
py	$8.0 \pm 0.8 \times 10^{-3}$ [e]	$4.57 \pm 0.04 \times 10^{-5}$	0.57	$1.70 \pm 0.08 \times 10^{-5}$	0.21
DEA	$5.4 \pm 0.2 \times 10^{-3}$ [c]	$4.0 \pm 0.1 \times 10^{-5}$	0.74		
Me_3Bzm	$4.19 \pm 0.04 \times 10^{-3}$ [c]	$3.18 \pm 0.05 \times 10^{-5}$	0.76		
$P(OMe)_3$	$4.1 \pm 0.2 \times 10^{-3}$ [e]	$1.99 \pm 0.05 \times 10^{-5}$	0.48		

[a] Mean values ± standard deviations for at least three runs. [b] Ref. 5. [c] Ref. 10. [d] Ref. 12. [e] Ref. 1.

reported for $(CH_3)_3CCl$ [8]. The difference in these chloroalkanes has been attributed to steric effects [8]. However, at present it is unclear how we can allow for possible Co–C bond shortening due to electron-withdrawing substituents.

As expected, the Co–N bond length trend reflects the σ-donor power of the R group and the values for py and Me_3Bzm analogs are very similar. This latter point has been interpreted in terms of the geometry and the bulk of the neutral ligands [7].

Kinetics

The results of the rate constant measurements for $CHCl_2$ and $CHBr_2$ derivatives, obtained as described in 'Experimental', are summarized in Table IV and compared with the corresponding values for the methyl analogs.

Substitution of H with Cl or Br at the α-C provokes a significant decrease of k. The effect is greater in the Br derivatives. For Cl derivatives of the py and Me_3Bzm series this follows the shortening of the Co–N axial distance. However, the decrease in k depends upon the kind of neutral ligand, as shown by the k'_1/k_1 and k''_1/k_1 ratios given in Table IV. The electronic and steric properties of L influence the k values nearly to the same extent in all three series.

Thus the noticeably increased bulk of 2-NH_2py with respect to py is mainly responsible for the difference of about two orders of magnitude in the corresponding k values [5]. Analogously, the same difference between NH_2Ph and py dissociation rates can be mainly attributed to the weaker Co–NH_2Ph bond with respect to the Co–py bond of 2.129(1) and 2.068(3) Å in the respective $LCo(DH)_2Me$ compounds [9, 10]. Similar values of k for py and Me_3Bzm are in agreement with structural features of the corresponding compounds [7]. Finally, the trend in P ligands may be justified on the grounds of their bulk.

We have shown [9] that in cobaloximes, for a given L ligand, the trend of the Co–L bond length and of log k mainly reflects the σ-donor power of the influencing ligand. However, the steric effect of a group on the *trans* ligand through the equatorial one (steric *trans*-influence) has also been detected both in the solid state [11] and in solution [9]. Although structural data are not available for $CHBr_2$ derivatives, it is likely to assume a similar bulk for the $CHBr_2$ and $CHCl_2$ groups. Therefore, the kinetic results agree with our previous findings that the $CHBr_2$ donating ability is smaller than that of $CHCl_2$ [2].

Supplementary Material

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

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