136. Electronic and Steric Influence of Axial and Equatorial Ligands in Vitamin B_{12} Model Complexes Derived from Cobaloxime: Electrochemical and ^{59}Co-NMR Studies[1])

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In four series of strictly related organocobalt complexes, derived from cobaloximes by replacement of the $O \cdots H \cdots O$ with $O \cdots BF_2 \cdots O$ and/or $(CH_2)_3$ groups, the trends of ^{59}Co-NMR shielding and electrochemical data are discussed. A largely parallel behaviour of the plots of $E_{1/2}$(I) values for the first Co(III)/Co(II) electron transfer *vs.* the ^{59}Co chemical shifts reflects the similar sensitivity of the two parameters to a change in electron affinity of the central metal ion due to a variation of the organic group R. $E_{1/2}$(II) values for the second Co(II)/CO(I) electron transfer are less sensitive to the change of R, but the trend of the plot *vs.* $\delta(^{59}\text{Co})$ is still parallel in the four series. Consistent deviations from a roughly linear dependence of $E_{1/2}$(I) on pK_a of the hydrocarbon acid corresponding to R, on *Taft* constant σ^* and on ^{59}Co shielding are noticed for the isopropyl derivatives and attributed to a steric effect. This was confirmed in a series of R–Co(DMG)pyridine complexes in which ^{59}Co shielding decreases steadily with increasing steric parameter E_s *(Taft)* of the alkyl group. There is experimental evidence from X-ray data that $\delta(^{59}\text{Co})$ decreases with an increase of the Co–C bond length, illustrating steric hindrance in alkyl coordination to be responsible for the decreased shielding of the ^{59}Co nucleus. The relative displacements of the graphic displays for the different series reflect the effect of changes in electron affinity of the redox center, due to the equatorial ligand, which, in turn, is caused by variations in the electron-withdrawing power due to the introduction of the BF_2 group and by the change from −2 to −1 valence of the $(CH_2)_3$-capped ligands.

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1. Introduction. – The unique features of coenzyme B_{12} as a naturally occurring organometallic compound containing a Co–C σ-bond have attracted the interest of chemists over three decades and stimulated numerous structure and reactivity studies on the coenzyme, the vitamin, and several model systems containing the four-nitrogen equatorial template and the axial Co–C and Co–L bonds in an octahedral ligand sphere of the Co(III) ion [2–4]. In this context, a correlation of different features of the solution chemistry of vitamin-B_{12} model compounds constitutes a main entry to the evaluation of the factors influencing the chemistry of the coenzyme. Of special relevance is a knowledge of the effects caused by the structure of the equatorial ligand and by substitution of the axial ligands R and L which may relate with the essential Co–C bond homolysis step in vitamin-B_{12}-dependent, enzyme-catalyzed reactions. Thus, relationships between structure, kinetics of axial ligand exchange, and redox properties were examined by many research groups and reviewed [5].

Surprisingly, there is only limited information on the above question based upon NMR studies, although several attempts were made to correlate ^{1}H- [6] [7], ^{13}C- [6] [8], and

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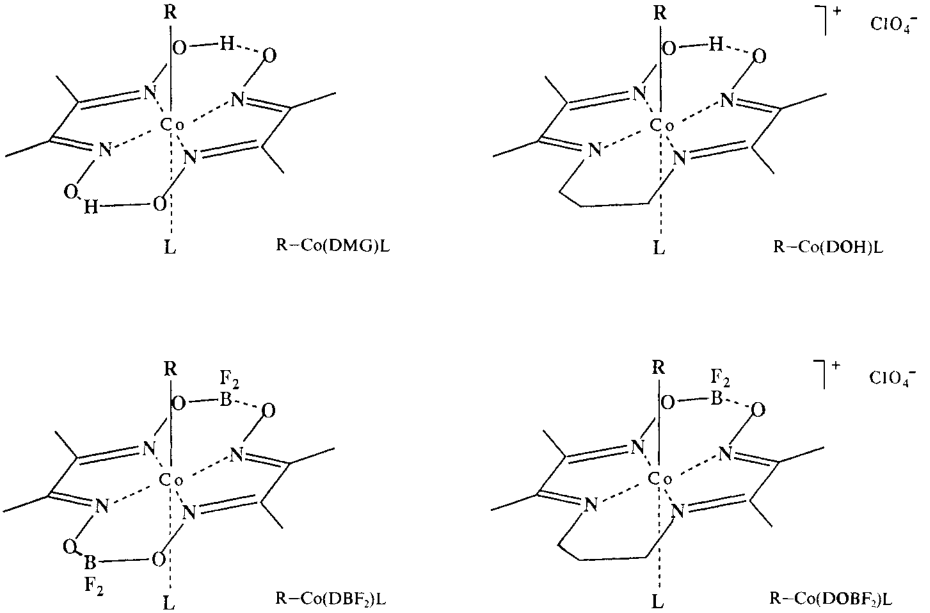
[1]) Transition-Metal NMR Spectroscopy, Part XIV; Part XIII: [1]. Presented in part at the 'XIII International Conference on Organometallic Chemistry', Torino, September 4–9, 1988.

^{31}P-NMR [4c] [6] [9] with structural features in this class of compounds. A series of correlations were presented in a review article by *Marzilli et al.* [10]. For example, ^{1}H-NMR shielding of the axial Me group in the CH_3–Co(DMG)L (DMG = dimethylglyoxime) series appears to be sensitive to the electronic influence of the axial donor ligand atom (L = O, N, P) but does not show a clear correlation with the Co–C bond length [5b]. On the other hand, in the (i-C_3H_7)–Co(DMG)L series the δ(^{1}H) values of the Me groups are sensitive to the *steric* but not to the *electronic* influence of L.

Very few NMR studies have been conducted on the nucleus of the central atom ^{59}Co, which is a sensitive isotope of 100% abundance but, in non-symmetric environments, gives rise to broad NMR signals because of a large electric quadrupole moment. As a consequence, early attempts to detect the ^{59}Co resonance in vitamin B_{12} failed [11], and the spectra of cyanocobalamin and methylcobalamin were first reported in 1986 [12]. ^{59}Co-NMR chemical shifts of model complexes, mainly cobaloximes, were reported by several research groups [11] [13] [14]. They have illustrated the influence of the atoms of the equatorial coordination sphere (N, O) and of the ligand L on the δ(^{59}Co). It was also pointed out that in a series of CH_3–Co(DMG)L complexes (L = O-, N-, P-donor ligands) δ(H) increases with the Co–C bond length, which, in turn, increases in the order P > N > O [5b].

In the present study, ^{59}Co-NMR chemical-shift determinations are extended to a large series of alkyl-substituted cobaloximes and three related model series in which the O···H···O bridge in the equatorial dioxime ligand is substituted by $(CH_2)_3$ or O···BF_2···O groups *(Scheme)*. A correlation of axial and equatorial ligand effects on

Scheme. *Structures of Alkyl-cobalamine Model Complexes with the Equatorial Ligands Dimethylglyoxime* (DMG) *and 2,3,9,10-Tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olato* (DOH). The BF_2-capped versions of the ligands are designated as DBF_2 and $DOBF_2$, respectively.



$\delta(^{59}Co)$ with the redox potentials of the organometallic complexes is attempted and the data are analyzed for electronic and steric effects of the axial ligands L and R.

2. Results and Discussion. – 2.1. *Electrochemistry.* The complexes of the four series bearing H_2O as axial ligand L *trans* to the organic group undergo two successive one electron transfers which are attributed to the Co(III)/(Co(II) and Co(II)/Co(I) steps [15]. The half wave potential $E_{1/2}$(I) of the first electron transfer occurs in the range −0.50 to −1.36 V *vs.* Saturated Calomel Electrode (SCE) at the Dropping Mercury Electrode (DME) in DMF and 0.1M Et_4NClO_4. From the polarographic and cyclic voltammetric behaviour, it was concluded that the electrode process is not a purely diffusion-controlled electron transfer, but it was shown to be quasi reversible. In fact, the kinetics of the process is ruled by the rate of the chemical reaction leading to the cleavage of the Co–C bond, which is coupled with the electron transfer [15b] [15c].

The $E_{1/2}$(I) values are strongly dependent on the nature of the organic group *(Tables 1–4, Figs. 1* and *2)* and also on that of the *trans*-axial ligand L *(Table 5, Fig. 4)*. For a given substituent R $E_{1/2}$(I) is remarkably shifted towards less negative values (increasing electron affinity), when the O···H···O bridge is replaced by the $(CH_2)_3$ moiety, and, thus, the charge of the equatorial ligand changes from −2 for the DMG and DBF_2 ligands to −1 for the DOH and $DOBF_2$ ligands. Moreover, substitution of the O···H···O bridge by the strongly electron-withdrawing BF_2 group causes further shifts of $E_{1/2}$(I) towards less negative values.

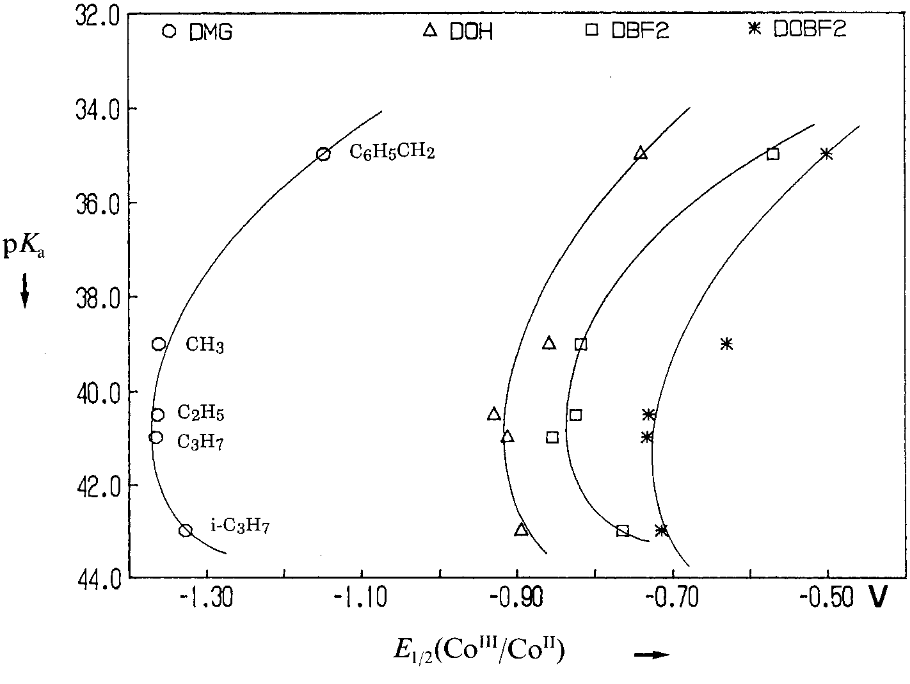


Fig. 1. $E_{1/2}$*(I) Values for the Co(III)/Co(II) reduction step of the four alkyl-cobalamin model series* (see the *Scheme*) vs. pK_a *values of the hydrocarbon acids RH.* Curves were not calculated but drawn to illustrate the trend.

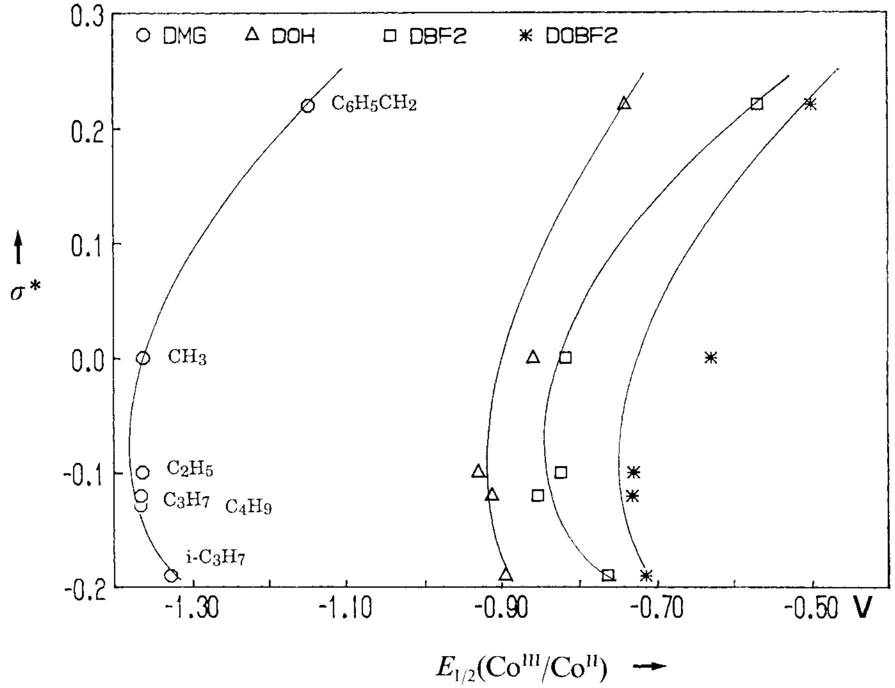


Fig. 2. $E_{1/2}$*(I) Values for the Co(III)/Co(II) reduction step of the four alkyl-cobalamin model series* (see the *Scheme*) vs. Taft σ* *values of the respective alkyl groups*

There is a parallel trend in the four series with respect to the influence of the alkyl group R on $E_{1/2}$(I) which shows increasing negative values in the sequence

$$PhCH_2 > CH_3 > C_2H_5 \approx C_3H_7$$

which is the order of increasing pK_a of the hydrocarbon acid corresponding to the alkyl group R *(Fig. 1)* and also the order of decreasing σ* (*Taft*) constant, an inductive (polar) substituent parameter *(Fig. 2)*. It is noteworthy that in the four series, $E_{1/2}$(I) of the i-Pr derivative is less negative than expected both from the pK_a value of the C_3H_8 acid and from the *Taft* σ* constant. This anomaly can be attributed to a steric effect of the bulky alkyl group.

The second electron transfer, assigned to the Co(II)/Co(I) redox process, takes place, for the aquo complexes, in the range from –0.75 to –1.65 V *vs.* SCE at the DME, as shown by the $E_{1/2}$(II) values of the reversible polarographic wave *(Tables 1–4)*. In this case, the plot of $E_{1/2}$(II) *vs.* pK_a *(Fig. 3)* shows only a slight influence of the axial substituent R on $E_{1/2}$(II) in both the DMG and DOH series. $E_{1/2}$(II) is apparently much less sensitive to changes of the axial alkyl substitution than $E_{1/2}$(I). In the DBF_2 and $DOBF_2$ series, however, the equatorial ligands and axial alkyl groups exert a stronger influence which parallels the $E_{1/2}$(I) data, including the i-Pr derivative whose $E_{1/2}$(II) value is again much less negative than expected from the pK_a and σ* data.

Table 1. *Electrochemical, ^{59}Co-NMR, and Other Relevant Physical Data of Alkyl-cobaloximes* $R-Co(DMG)H_2O$

	R =					
	Me	Et	Pr	Bu	i-Pr	$PhCH_2$
$E_{1/2}$(I)/V	– 1.362	1.364	– 1.366	– 1.366	– 1.328	– 1.15
$E_{1/2}$(II)/V	– 1.60	– 1.63	– 1.64	– 1.64	– 1.65	– 1.55
δ/ppm	4156	4180	4185	4195	4410	4565
$\Delta\nu_{1/2}$/kHz	2.4	7.0	8.5	8.0	7.0	12.5
σ^*(R)	0	– 0.10	– 0.12	– 0.13	– 0.19	+ 0.22
pK_a(RH)	39	40.5	41	–	43	35

Table 2. *Electrochemical, ^{59}Co-NMR, and Other Relevant Physical Data of* $R-Co(DOH)H_2O$ *Complexes*

	R =					
	Me	Et	Pr	Bu	i-Pr	$PhCH_2$
$E_{1/2}$(I)/V	– 0.861	– 0.932	– 0.914	–	– 0.897	– 0.741
$E_{1/2}$(II)/V	– 1.08	– 1.05	– 1.15	–	– 1.10	– 1.06
δ/ppm	4630	4660	4670	–	4905	5090
$\Delta\nu_{1/2}$/kHz	2.0	2.5	2.0	–	6.8	3.5
r(Co–C)/Å	1.990	2.020	–	–	2.073	2.052

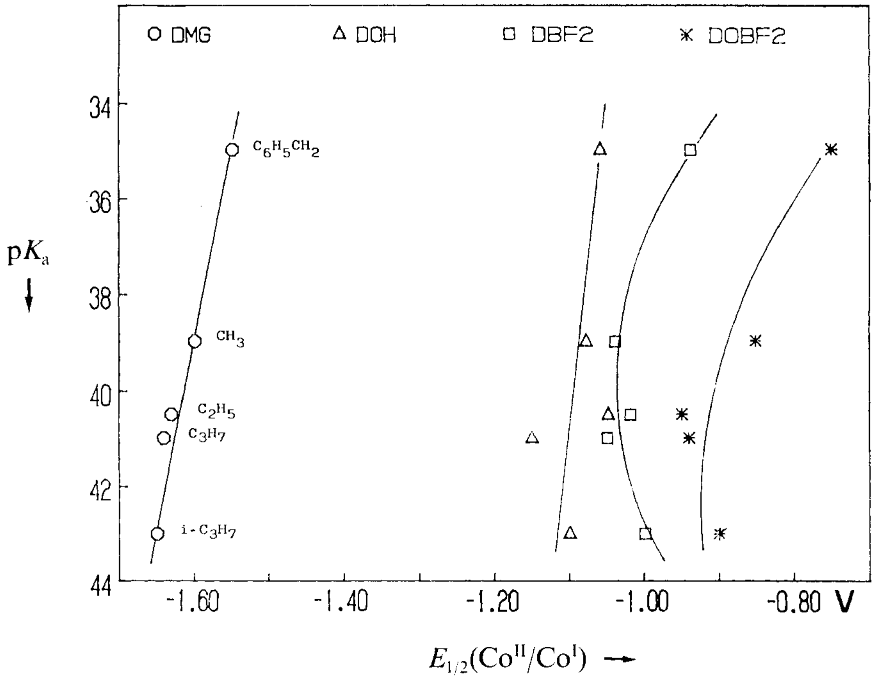


Fig. 3. $E_{1/2}$*(II) Values for the Co(II)/Co(I) reduction step of the four alkyl-cobalamin model series* (see the *Scheme*) vs. pK_a *values of the hydrocarbon acids RH*

Table 3. *Electrochemical and ^{59}Co-NMR Data of R–Co(DBF$_2$)H$_2$O Complexes*

	R =					
	Me	Et	Pr	Bu	i-Pr	PhCH$_2$
$E_{1/2}$(I)/V	– 0.819	– 0.825	– 0.855	–	– 0.765	– 0.570
$E_{1/2}$(II)/V	– 1.04	– 1.02	– 1.05	–	– 1.00	– 0.94
δ/ppm	3888	3898	3912	3915	4094	4264
$\Delta\nu_{1/2}$/kHz	1.7	2.4	3.9	2.4	4.8	3.0

Table 4. *Electrochemical and ^{59}Co-NMR Data of R–Co(DOBF$_2$)H$_2$O Complexes*

	R =					
	Me	Et	Pr	Bu	i-Pr	PhCH$_2$
$E_{1/2}$(I)/V	– 0.631	– 0.731	– 0.732	–	– 0.715	– 0.501
$E_{1/2}$(II)/V	– 0.85	– 0.95	– 0.94	–	– 0.90	– 0.75
δ/ppm	4588	4612	4678	–	–	5021
$\Delta\nu_{1/2}$/kHz	2.2	2.5	3.0	–	–	2.8

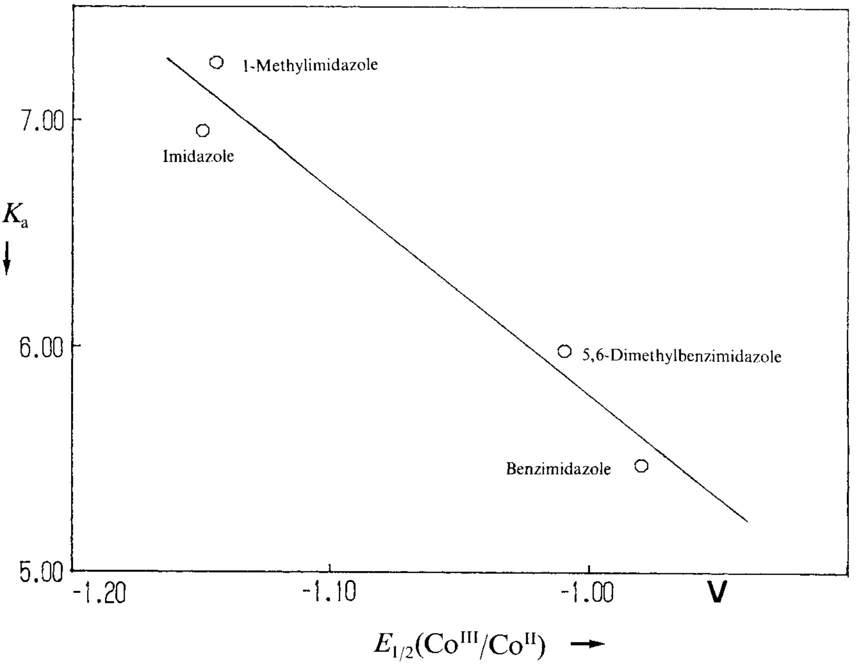


Fig. 4. $E_{1/2}$*(I) Values of Et–Co(DOH)L complexes* (L = imidazole, 1-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole) vs. *p*K$_a$ *values of the complexes*

Stronger electron donors than H_2O as axial ligands L, *e.g.* heterocyclic nitrogen bases, shift the $E_{1/2}$(I) values to more negative values in accord with the decreasing electron affinity of the coordinated Co ion. Again, the effect is related to the pK_a values of the different nitrogen donors *(Fig. 4)*, *i.e.* the strongest base in the C_2H_5–Co(DOH)L series,

Table 5. *Electrochemical, ^{59}Co-NMR, and pK_a Data of Et–Co(DOH)L Complexes*

	L =					
	H_2O	Benzimidazole	5,6-Dimethylbenzimidazole	Imidazole	1-Methylimidazole	Pyridine
$E_{1/2}$(I)/V	– 0.932	– 0.98	– 1.01	– 1.15	– 1.145	– 1.014
$E_{1/2}$(II)/V	– 1.05	– 1.20	–	–	–	– 1.17
δ/ppm	4660	4270	4250	4140	4130	4140
$\Delta\nu_{1/2}$/kHz	2.5	3.5	4.5	6.0	2.0	3.5
pK_a	7.00	5.48	5.98	6.95	7.25	5.17

1-methylimidazole as axial ligand, causes the most negative $E_{1/2}$(I) value (lowest electron affinity). On the other hand, the influence of the basicity of the axial nitrogen donor ligand on $E_{1/2}$(II) appears to be much less than on $E_{1/2}$(I) and as a consequence, the separation of the two half-wave reduction potentials decreases with an increase of donor strength of the axial ligand (*Table 5*). The decreased sensitivity of $E_{1/2}$(II) to the nature of the axial ligand is to be attributed to the decrease of the strength of the Co-axial ligand bond in the octahedral complexes in the Co(II) oxidation states relative to the octahedral Co(III) complexes.

2.2. *^{59}Co-NMR Measurements.* The ^{59}Co chemical shifts of the R–Co(DMG)L, R–Co(DOH)L, R–Co(DOBF$_2$)L, and R–Co(DBF$_2$)L complexes were determined at

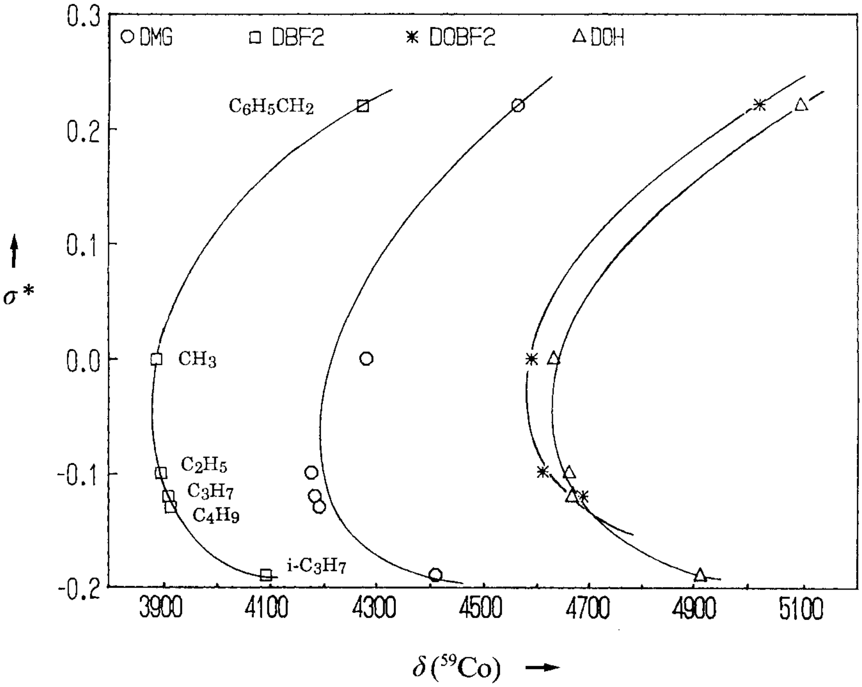


Fig. 5. *δ(^{59}Co) Values of the four alkyl-cobalamin model series* (see the *Scheme*) vs. Taft σ* *values of the respective alkyl groups*

94.6 MHz in acetone solution at ambient temperature and are contained in *Tables 1–5*, together with the line widths $\Delta\nu_{1/2}$. For details of the measurements, see *Exper. Part.*

The chemical shifts of the aquo complexes of the four series lie in a range of *ca.* 1200 ppm (3888–5090 ppm), and the observed line widths vary between 1.7 and 12.5 kHz. In evaluating shielding differences, it must be kept in mind that the accuracy of the chemical-shift determination decreases with increasing line width and is typically ±5 ppm. The chemical-shift range for the ^{59}Co nucleus in the monocations $[R{-}Co(DOH)H_2O]^+$ and $[R{-}Co(DOBF_2)H_2O]^+$ is clearly separated from the two neutral series which exhibit higher shielding values (smaller $\delta(^{59}Co)$). Thus, as expected from earlier ^{59}Co-NMR studies on cobaloximes and complexes with related equatorial ligands [13], the major chemical-shift effects originate from variations in the four-nitrogen equatorial template structure. However, the influence of the organic substituent R is quite pronounced and causes some overlap between the ^{59}Co chemical-shift ranges of the four series *(Fig. 5)*. The shape of the $\delta(^{59}Co)$ *vs.* $\sigma^*(R)$ curves closely resembles the observed trends in the $E_{1/2}(I)$ *vs.* $\sigma^*(R)$ plots *(Fig. 2)*, an indication that metal shielding and electrochemical reduction potential exhibit a parallel sensitivity to the electron affinity of the axial alkyl group R. It should be noted that the consistently lower shielding of the ^{59}Co nucleus in the $(i\text{-}C_3H_7)Co$ complexes is not in agreement with the σ^* value of the i-Pr substituent, which again points towards a steric effect. This is also noticeable, to a lesser extent, in the CH_3–, C_2H_5–, C_3H_7–, and C_4H_9–Co complexes.

Table 6. *$\delta(^{59}Co)$ Values* [ppm] *of Alkyl–Co(DMG)pyridine Complexes and σ^* and E_s Values of the Respective Alkyl Groups*[a])

R	$\delta(^{59}Co)$	σ^*	E_s	R	$\delta(^{59}Co)$	σ^*	E_s
Me	3640	0.00	0.00	Cyclopentyl	3746	– 0.20	– 0.51
Et	3654	– 0.10	– 0.07	i-Pr	3819	– 0.19	– 0.47
Pr	3673	– 0.12	– 0.36	Cyclohexyl	3842	– 0.15	– 0.79
Bu	3679	– 0.13	– 0.39	i-Bu	3887	– 0.21	– 1.19
Cyclobutyl	3700	– 0.15[b])	– 0.06	Neopentyl	3948	– 0.165	– 1.74

[a]) σ^* and E_s values from [17a].
[b]) From [17b].

Replacement of H_2O by stronger axial donor ligands L, such as benzimidazole, imidazole, or pyridine, results in increased shielding of the ^{59}Co nucleus *(Table 5)*, parallel to the increasing negative $E_{1/2}(I)$ values of the Co(III)/Co(II) redox process. The effect of the axial alkyl group R was also investigated in the R–Co(DMG)pyridine series *(Table 6)*. Structural variation of the carbon ligand causes chemical shift changes of up to 500 ppm. Not unexpectedly, the two latter effects are mutually dependent, *i.e.*, the shielding increments $\Delta\delta$ upon changing of L depend on the type of alkyl group R, thus, illustrating a '*trans*-effect' through the metal center [16].

2.3. *Correlation between Electrochemical and ^{59}Co-NMR Data.* A plot of $E_{1/2}(I)$ in the aquo complexes of the four series against the $\delta(^{59}Co)$ values *(Fig. 6)* illustrates a largely parallel behaviour, and the fact that both parameters are sensitive to the electron affinity of the organic group R. In contrast, the $E_{1/2}(II)$ values for the Co(II)/Co(I) reduction step

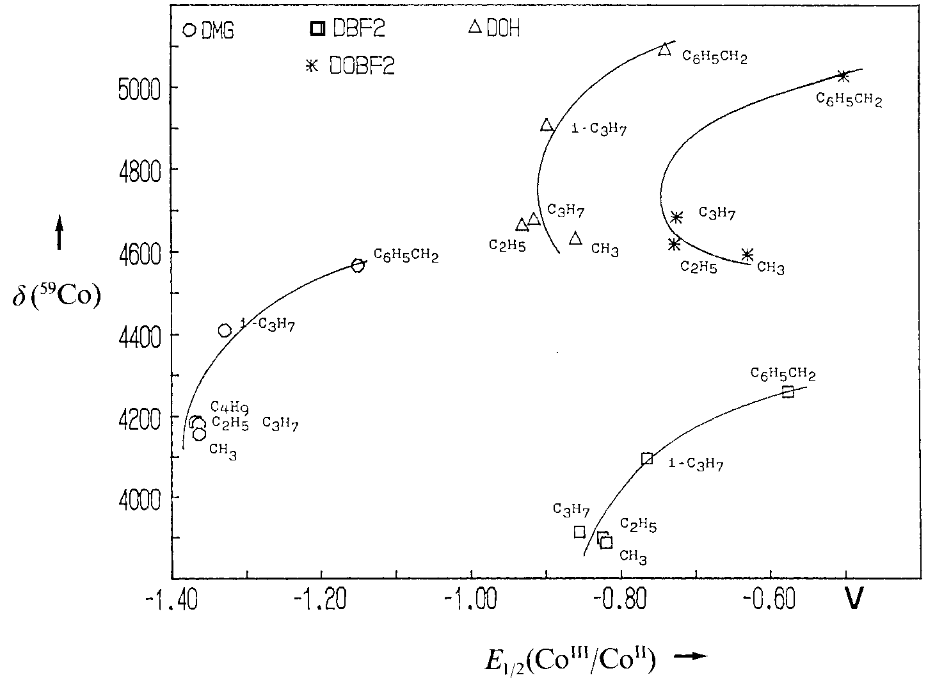


Fig. 6. $E_{1/2}$*(I) Values of the four alkyl-cobalamin model series* (see the *Scheme*) vs. δ*(^{59}Co) values*

are only slightly dependent on R when compared with the δ(^{59}Co) values *(Fig. 7)*, particularly in the R–Co(DMG)H_2O and R–Co(DOH)H_2O series.

The quite similar distribution of the curves for the two reduction steps in the four series are a strong indication that the analogous shape of the δ(Co) *vs.* $E_{1/2}$(I) plots mainly reflects the effect of the axial alkyl group R. A close inspection reveals, however, that the i-Pr complexes exhibit ^{59}Co data which are not in accord with the observed redox potentials. The consistent deshielding by *ca.* 200–250 ppm is tentatively assigned to a steric effect, as already observed in the correlations of $E_{1/2}$(I) *vs.* pK_a and σ^* (*Figs. 1* and *2*). This remarkable effect was, therefore, studied in greater detail by an investigation of the ^{59}Co chemical shifts of an extended series of alkyl–Co(DMG)pyridine complexes *(Table 6)*. Also listed are σ^* and E_s values according to *Taft* [17] describing the σ-inductive and steric properties, respectively, of the alkyl groups. Whereas the trend in the δ(^{59}Co) values does not correspond to the σ^* values (see also *Fig. 5*), a clear correlation with the steric substituent constant E_s is observed and presented in graphical form *(Fig. 8)*. Apparently, increased bulkiness of the alkyl group leads to substantial deshielding of the Co nucleus without an increase in the polarity of the Co–C bond. It may, thus, be expected that the deshielding effect is associated with a lengthening of the Co–C bond, and three data pairs in R–Co(DOH)H_2O series confirm the expected trend:

R = CH_3	δ(Co) = 4630 ppm	r(Co–C) = 1.990 Å	[18]
C_2H_5	4660 ppm	2.020 Å	[19]
i-C_3H_7	4905 ppm	2.073 Å	[19]

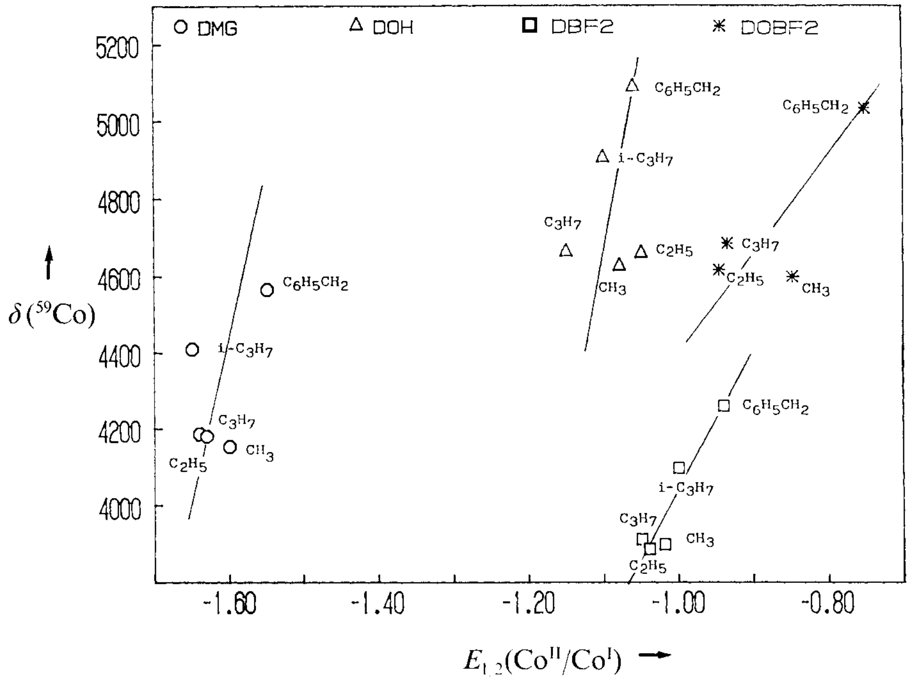


Fig. 7. $E_{1/2}$*(II) Values of the four alkyl-cobalamin model series* (see the *Scheme*) vs. $\delta(^{59}Co)$ *values*

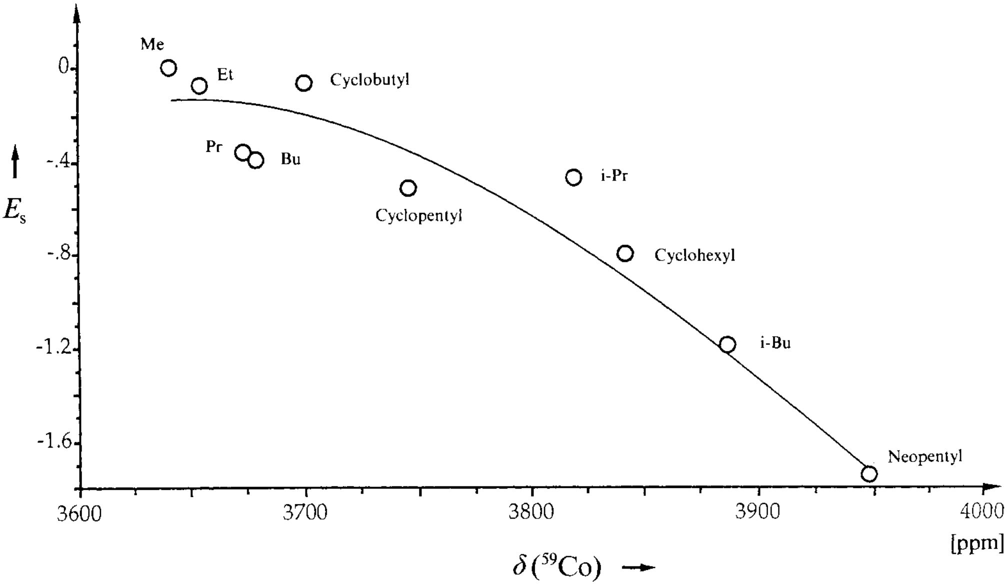


Fig. 8. $\delta(^{59}Co)$ *Values for R–Co(DOH)pyridine complexes* vs. Taft E_s *values of the alkyl groups*

Deshielding effects in transition metal resonances due to steric hindrance in π-coordination have already been observed in [CoCp(diene)] [12], [RhCp(diene)] [12] [20], and [$Fe(CO)_3$(diene)] complexes [21]. Transition-metal NMR spectroscopy appears to be a sensitive method for the detection of steric effects in metal coordination.

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Experimental Part

Caution. The perchlorates used in this investigation must be handled with great care and in small quantities, since they may explode violently when dry.

Chemicals. N,N-dimethylformamide (DMF; *Carlo Erba*) was dried over activated 4-Å molecular sieves and stored under N_2 in dark bottles. Et_4NClO_4 (*Fluka*) was recrystallized from hot H_2O and vacuum-dried for two days at 20°. Hg was filtered through perforated filter papers, treated with acidified $HgNO_3$ soln. by agitating it under dil. HNO_3 and distilled three times under vacuum [22]. The Co complexes were synthetized as reported in [15a] [23–28].

Electrochemical Apparatus and Equipment. All the electrochemical measurements were performed on freshly prepared solns. (*ca.* 1 mM) in a three-electrode cell with thermostated jacket at 0°. The reference electrode was an NaCl-saturated calomel electrode (SCE) separated from the soln. by a glass bridge with sintered glass bottom that was located 2 or 3 mm from the working electrode and filled with 0.1M soln. of TEAP in DMF. The counter electrode was a Pt ring or wire. The working electrode was a *Smoler*'s DME with a flow rate $m = 0.350$ mg/s, when the height of the Hg column was 55 cm and with drop time controlled at 3 s by a knocker. The electronic instrumentation included an *Amel 552* potentiostat with positive feed-back compensation, an *Amel 568* function generator, and an *Amel 863 X/Y* recorder. A stream of prepurified N_2 was bubbled through the soln. before the measurements and over the soln. during the experiment.

Evaluation of Polarographic $E_{1/2}$ *Values.* The number of electrons involved in the electron transfer and the $E_{1/2}$ values with reproducibility of ±3 mV were determined by the log[(*il-i*)/(*i*)] *vs. E* plot.

NMR Measurements. ^{59}Co-NMR spectroscopy was performed at (94.6 ± 0.5) MHz ($B_0 = 9.4$ T) on a *Bruker AM-400* spectrometer with 10- and 5-mm broad-band probeheads. The spectra were obtained with 0.05 ± 0.1M acetone or (D_6)acetone solns. of the substrates at (298 ± 1) K, whereby the deuterated instead of undeuterated solvent caused no observable effects. A concentration dependence was also not observed. $\delta(^{59}Co)$ values are relative to a 1.0M aq. soln. of $[Co(CN)_6]K_3$ as an external reference and are reported with an accuracy of ±5 ppm due to large line widths and a large temp. dependence of the chemical shift of *ca.* 1.5 to 2 ppm/K. All spectra were recorded without field frequency lock, but the reference sample was locked on the D_2O resonance. The line widths at half height ($\Delta\nu_{1/2}$) are reported in kHz. Acquisition times and pulse repetition delays were set in the range of 1 to 5 ms, depending on the rate of the free induction decay (FID) and resulting in a maximum number of 512 data points at a spectral width of 166.66 kHz or a dwell-time of 3 μs. The data were 'zero filled' up to 8192 data points prior to *Fourier* transformation. In some cases, *i.e.*, when rapid relaxation was observed, a pre-acquisition delay of 18–22 μs was applied in order to avoid strong baseline distortions due to pulse break-through. The same effect can be obtained by removing the first few data points of the FID.

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