Synthesis of Vitamin-B_{12} Derivatives with an Electropolymerizable Side Chain

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Three new derivatives of vitamin B_{12} with a pyrrole head group attached to the corrin ring have been prepared. Ligand-exchange reactions and reduction provided reactive Co^{III} and Co^{II} complexes. Their electrochemical properties and their potential for fixation at the surface of electrodes by electropolymerization were studied.

Introduction. – Model systems for enzyme-catalysed transformations play an important role for understanding the mechanism of such reactions. This is particularly important for reactions where cofactors are involved and become a *conditio sine qua non* for the coenzyme-B_{12}-dependent transformations [1]. Detailed investigations in several laboratories have unravelled important features of the vitamin-B_{12}-dependent reactions [2], and many attempts have been undertaken to incorporate these results into model systems. Although many structural features have been reproduced in this way, further attempts are necessary for a more comprehensive modelling of the *in vivo* reactions. For example, the enantioselectivity in the methylmalonyl-succinyl rearrangement is rather low and the enantiomeric excesses (ee) of the product do not exceed 20% in reactions of racemic methylmalonyl substrates [3]. Our experiments with a homochiral methylmalonyl substrate has recently led to similar observations [4][1]). Other aspects like stereospecific recognition of substrates by an appropriately modified vitamin-B_{12} catalyst deserve further attention. Whereas the mechanistic features of the *in vivo* methylmalonyl-succinyl rearrangement and similar rearrangements are emerging [6], corresponding investigations in model systems have hitherto remained inconclusive [4].

Our model systems, which incorporate features of molecular recognition between substrates and vitamin-B_{12}-derived catalysts both endowed with anchoring groups in the periphery, are driven by an electrochemical-photolytic cycle and lead to an enhanced rearrangement [7]. For further investigation of chiral recognition, transfer of chirality in the methylmalonyl-succinyl rearrangement, and other vitamin-B_{12}-dependent reactions, and for a detailed investigation of the electronic features of these transformations, it is

[1]) The cloning of *Pseudomonas denitrificans* genes involved in the vitamin-B_{12} biosynthesis allowed the preparation of a multitude of precorrins (and cobyrinic-acid intermediates) from which homochiral catalysts might be obtained by incorporation of a variety of transition-metal ions [5].

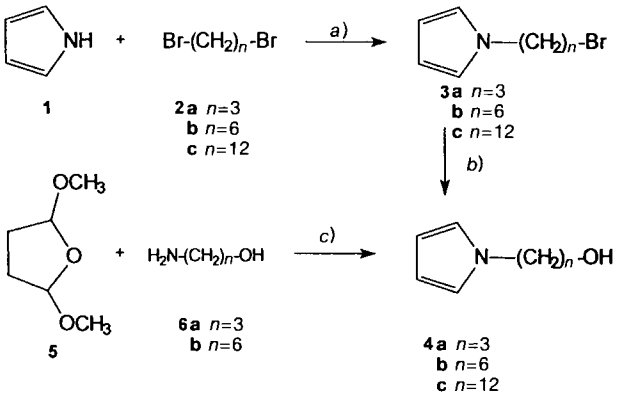
desirable to study these reactions in the microenvironment of appropriately modified electrodes. This would allow the use of the electrochemical methodology and provide at the same time a chiral environment for selective recognition and transformation of substrates. Polymer-coated electrodes had first been prepared by *Walder* and *Scheffold* and used by *Murakami* and *Hisaeda* for investigation of vitamin B_{12} related rearrangements [8][9]. We envisaged the formation of conductive films on Pt-electrodes by anodic oxidation of pyrrole. For this purpose, derivatives of vitamin B_{12} with a pyrrole head group have been prepared. Pyrrole-containing molecules are exceptionally convenient for the coating of electrode surfaces with polymer films, and this methodology has been extensively used for the immobilization of porphyrin derivatives [10–12].

Here we report the synthesis of vitamin-B_{12} derivatives with a pyrrole side chain and results of their electropolymerization.

Synthesis and Properties. – The synthesis of 1*H*-pyrrole (**1**) derivatives is well-developed, and *N*-alkylation is readily achieved *via* the 1*H*-pyrrole potassium salt, formed under a variety of conditions [13–15]. Thus the 1-(ω-bromoalkyl)-1*H*-pyrroles **3a–c** could be obtained by alkylation with the dibromoalkanes **2a–c** in yields of 61–68% (*Scheme*).

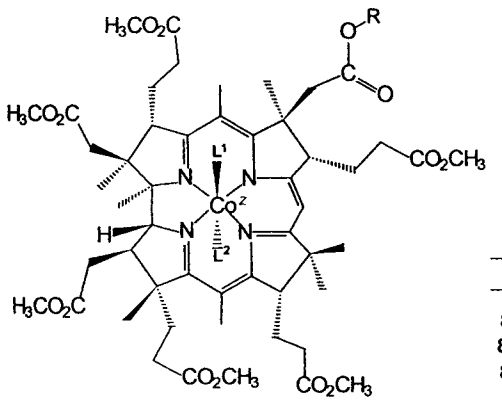
Hydrolysis of these bromides in aqueous hexamethylphosphoric triamide (HMPA) gave the 1*H*-pyrrol-1-alkanols **4a–c** in 76–78% [16]. Alternatively these compounds can be prepared from **1** and bromo alcohols or from **5** and amino alcohols like **6a, b** [17].

Esterification of *Coα,Coβ*-dicyanocob(III)yrinic acid *a,b,d,e,f,g*-hexamethyl ester (**7**) [18][19] with the 1*H*-pyrrol-1-alkanols **4a–c** using the carbodiimide method [20][21] afforded the cob(III)yrinates **8a–10a** in yields of 68–70%. Subsequent ligand exchange with CF_3COOH in CH_2Cl_2 led to the aqua-cyano complexes **8b–10b** in yields of 88% and a ligand isomer ratio of 1:1.8 for which the *Coα/Coβ* configuration was not assigned [22]. The cob(II)yrinates **8c–10c** were obtained by reduction with $NaBH_4$ and treatment with $HClO_4$. The UV and ^{1}H- and ^{13}C-NMR spectra as well as the FAB and ESI mass spectra supported these structures.



a) K, THF. *b*) HMPTA - H_2O, 100°. *c*) **5** + **6a**, reflux, 1h, ACOH.

Scheme



7 R = H, L^1=L^2=CN

8a -10c R = $-(CH_2)_n-N$

n			Co^z	L^1	L^2
3	6	12			
8a	**9a**	**10a**	$Co^{(III)}$	CN	CN
8b	**9b**	**10b**	$Co^{(III)}$	CN	H_2O, ClO_4
8c	**9c**	**10c**	$Co^{(II)}$	ClO_4	-

The electrochemical properties of the vitamin-B_{12} derivatives **8a–c**, **9a–c**, and **10a–c** were analysed by cyclic voltammetry (*cf. Exper. Part*). Independently of the length of the alkane chain, these complexes show the same type of redox behaviour in the range of −1.2 to + 1.0 V. The current peaks observed correspond to those assigned and discussed by *Lexa* and *Savéant*, *Scheffold* and coworkers, and *Murakami* and coworkers [8][23][24] (*cf.* also [25][26]). Under oxidative scanning, an additional peak is observed beyond + 1.0 V, which has been assigned to the oxidation of the pyrrole ring [10][27].

Electropolymerization. – It is known that the redox behaviour of vitamin-B_{12} derivatives is dependent on the selected solvent, electrolyte, and working electrode [23][25]. Hence, the conditions for the CV analysis and the electropolymerization of the monomers described above had to be chosen carefully. Cyclic voltammograms obtained for **8a** at a glassy carbon electrode are illustrated in *Fig. 1,a*. Upon reductive scanning from 0.0 V, a wave at −0.9 V is observed for the Co^{III}/Co^{II} reduction. At lower potentials, the current increases due to further conversion to Co^{I}. On the reverse potential scan, a peak at 0.13 V followed by a shoulder and a broad wave at 1.55 V can be observed. These features are absent in the direct oxidative scan starting from 0.0 V (*Fig. 1,b*). The current increase at a potential $E > 1.55$ V is likely due to pyrrole oxidation[2]). In this oxidation step, the interface is modified since, in the subsequent reverse scan, the current assigned to the Co^{III}/Co^{II} conversion decreases. However, continuous potential cycling within the same wide range of potential has shown that the new phase on the electrode surface is poorly conductive and hinders the thickening of a polymer film [28]. As previously reported, the high positive limit of the potential scan induces overoxidation of the polypyrrolic chains [29]. This leads to the loss of electronic conductivity of the polypyrrole backbone. Consequently, the classical electrochemical response of the electrogenerated polypyrrole backbone in the potential range of 0–0.7 V does not appear.

[2]) The large potential differences observed for the oxidation wave, which has been attributed to pyrrole head group oxidation, may result from electrode-surface poisoning and/or lack of electrolyte stability.

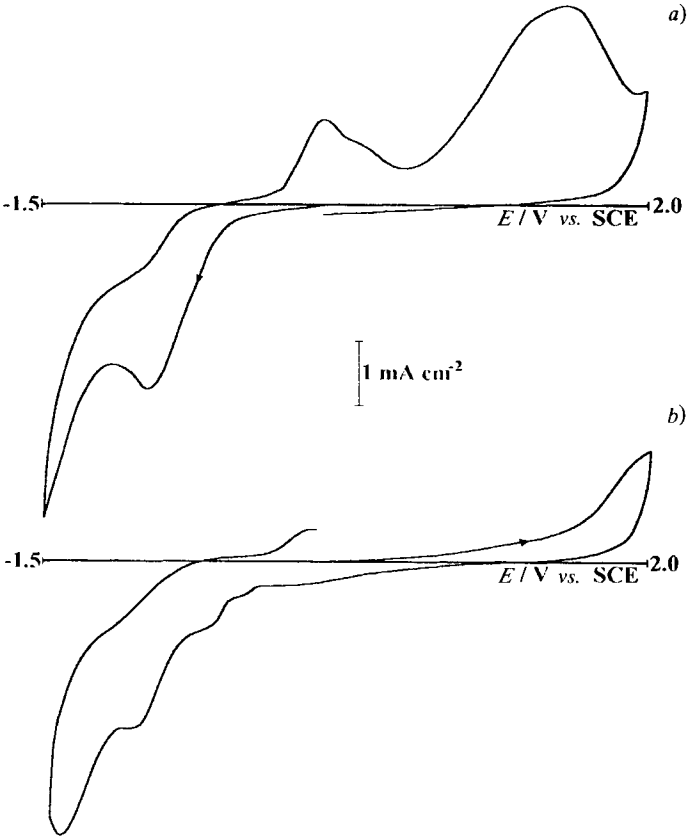


Fig. 1. *Cyclic voltammograms of derivative* **8a** *starting the potential scan* a) *cathodically and* b) *anodically*

The redox behaviour of **9a** (*Fig. 2*) should be compared with that of **8a** (*Fig. 1, a*). A close relation between the incomplete reduction of Co-centres and the anodic counterpart at *ca.* 0.1 V can be derived. The oxidation processes occur, and the pyrrole is oxidized as in the case of **8a** at a rather high potential. The significant anodic current still flowing after reversing the potential at + 2.0 V suggests that the pyrrole group in the adsorbed, oxidized Co^{III} form undergoes oxidation allowing the polymerization onset. Continuous potential cycling experiments reveal still structured cyclic voltammograms.

The cyclic voltammogram of **9c** (*Fig. 3*) shows that the overall process is quite complex, but some interesting features deserve mention: The shoulder and the wave observed in the conversion of Co^{II} to Co^{I} are probably due to the reduction of adsorbed and solution species. In the anodic region, the waves beyond the Co^{I}/Co^{II} and Co^{II}/Co^{III} oxidation are likely due to the oxidation of the pyrrole ring adsorbed at the electrode, followed by oxidation of the species in solution. In this anodic process, a polymer film is formed on the electrode. During the subsequent cycles, the current increases at *ca.* −0.35 V and gives rise to a broad peak which reflects polymer-film reduction. The new phase is conductive since an increase in the Co^{II}/Co^{I} cathodic wave and in the corresponding anodic counterparts are also observed. It should be noted that this con-

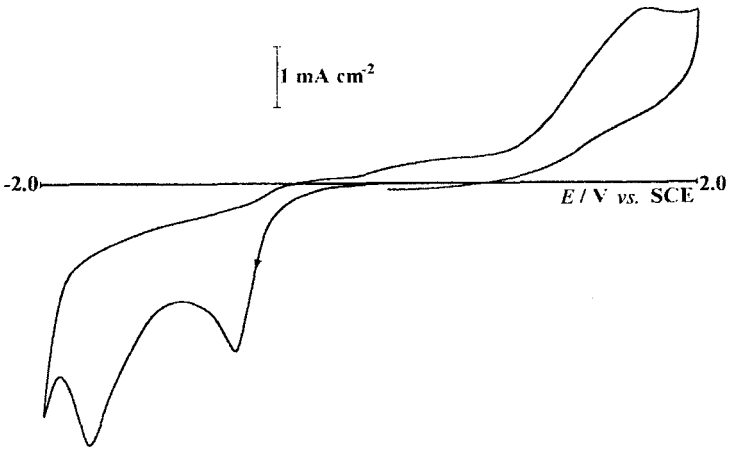


Fig. 2. *Redox behaviour of derivative* **9a**

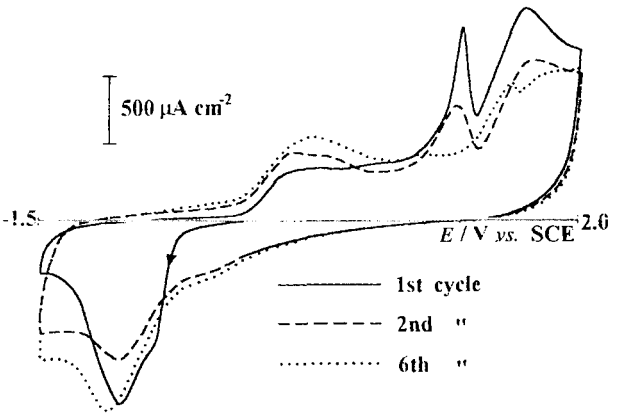


Fig. 3. *Repetitive cyclic voltammetry of derivative* **9c**

ductivity results from electron transport through the polymer by an electron-hopping mechanism between oxidized and reduced redox sites.

Thus, polymerization takes place *via* adsorbed Co^{III} species and requires a high anodic potential [28].

Conclusion. – Derivatives of vitamin B_{12} with a pyrrole head group attached to the *c*-carboxylic group at the B ring of the corrin by esterification with 1*H*-pyrrol-1-alkanols of different chain length were prepared. Ligand-exchange reactions with subsequent reduction gave the corresponding Co^{II} complexes in good yields. The preliminary electropolymerization results show that adsorption of the vitamin-B_{12} derivatives on the electrode and high potentials for the oxidation of adsorbed and solution species allow the preparation of polymer films from **9a** and **9c**. The properties of the films depend on the alkyl chain length introduced into the vitamin-B_{12} derivatives.

This work has been generously supported by the *Swiss National Science Foundation* under the *European COST Program D-5* (project No. 2128-44 420.95). The authors thank Dr. *M. Pfammatter* and Dr. *J. Schaller* for their advice with ESI-MS measurements.

Experimental Part

General. Reagents were purchased from *Fluka Chemie AG*. Solvents for chemical reactions and chromatography were distilled prior to use. TLC: reactions were monitored on *Alugram® Sil G/UV$_{254}$* or *Polygram® Alox N/UV$_{254}$* from *Macherey-Nagel*, detection with a *Camag-53000* UV lamp (λ 254 nm) or an aq. $KMnO_4$ soln. Column and flash (CC and FC, resp.) and TLC: silica gel for EX and TLC from *J.T. Baker* (30–60 μm) and neutral Al_2O_3 from *Camag*. Bulb-to-bulb distillation: *Büchi-KR-3* apparatus. UV/VIS: *Hewlett-Packard-8451-A* diode-array spectrophotometer in CH_2Cl_2; λ_{max} (log ε) in nm. IR: *Perkin-Elmer 1600 FTIR*; KBr discs or NaCl plates; $\tilde{\nu}$ in cm^{-1}. NMR: *Bruker AM 300* (^1H, 300 MHz; ^{13}C, 75 MHz, broadband 1*H*-decoupled); in $CDCl_3$; chemical shifts δ in ppm rel. to Me_4Si as internal standard, J in Hz; the ^{13}C measurements were generally supplemented by DEPT experiments. Mass spectra: EI: *Varian MAT CH7A*, acceleration voltage 70 eV; FAB (at 6 kV): *Fisions Instruments VG AutoSpec*, 1,3-dithiothreitol (DTT) and 1,3-dithioerythrol (DTE) as matrix, Ar (8 kV, 1 mA); ESI: *Fisions Instruments VG Platform II*, positive-ion measurements (3.5 kV); *m/z* (rel. int. (%)).

Cyclic Voltammetry. Potentiostat *AMEL 553*; software CACYCO 2.0 and 3.0 [30]; mess cell *Metrohm 6.14114.010* and *6.1415.110*; reference electrode *Metrohm 6.0724.000* (SCE), electrolyte bridge *Metrohm 6.1231.000* and *6.1227.000*; working electrode *Metrohm 6.0804.010* (glassy C-electrode pretreated by mechanical polishing with Al_2O_3 *Metrohm 6.2802.000*); auxiliary electrode was a Pt-wire; scan rates 100 mVs^{-1}; E in V; $LiClO_4$ and $(Bu_4N)ClO_4$ were used as electrolytes in MeCN. All solns. were deoxygenated by passing a stream of Ar (purified over a *BASF* BTS catalyst) through the soln.

Electropolymerization. Solns. of the vitamin-B_{12} derivatives (0.2 mmol/l) were prepared from MeCN (*Merck, Uvasol* spectroscopy grade; distilled under Ar) and $LiClO_4$ (*Riedel-de Haën*; 0.1 mol/l), dried in an oven at 110° for at least 24 h prior to use. They were thoroughly deoxygenated directly in the cell with Ar (purity > 99.9997%) before the measurements. Cyclic voltammetry, at a glassy C-electrode, in a conventional three-electrode cell, was performed at a sweep rate of 150 mVs^{-1}. The electrode potentials were controlled with respect to a saturated calomel electrode (SCE) by an *EG&G-PAR-273* potentiostat. A Pt-foil was used as counter electrode. Prior the experiments, the working electrode was mechanically polished to a mirror finishing with successively finer grades of alumina (down to 0.05 μm), rinsed with doubly distilled H_2O and with distilled MeCN.

1-(3-Bromopropyl)-1H-pyrrole (**3a**). Modification of the published procedure [14]: To a suspension of 1*H*-pyrrole potassium salt, prepared from 1*H*-pyrrole (**1**; 1.68 g, 1.74 ml, 25.00 mmol) and K (0.78 g, 20.00 mmol) in THF (10 ml) by reflux for 3–4 h, THF (10 ml) and 1,3-dibromopropane (20.19 g, 10.20 ml, 100.00 mmol) in THF (10 ml) were added at 0°. After stirring under reflux overnight, the mixture was diluted with H_2O and extracted with CH_2Cl_2. The org. phase was dried ($MgSO_4$) and evaporated and the residue purified by FC (hexane) to give 1,3-dibromopropane (14.15 g, R_f 0.63) and **3a** (1.27 g, 61%). Colourless oil. R_f 0.11 (hexane). B.p. 60°/12 Torr. ^1H-NMR: 2.23 (*q*, 2 H); 3.29 (*t*, 2 H); 4.05 (*t*, 2 H); 6.15 (*m*, 2 H); 6.66 (*m*, 2 H).

1-(6-Bromohexyl)-1H-pyrrole (**3b**) [15]. As described for **3a**, using K (1.17 g, 30.00 mmol) in THF (15 ml), **1** (2.52 g; 2.61 ml, 37.50 mmol), and 1,6-dibromohexane (**2b**; 39.59 g, 22.50 ml, 150.00 mmol; R_f 0.77) in THF (15 ml): **3b** (4.27 g, 62%). Colourless oil. R_f 0.18 (hexane). B.p. 110°/15 Torr. ^1H-NMR: 1.29 (*m*, 2 H); 1.44 (*m*, 2 H); 1.76 (*m*, 2 H); 1.82 (*m*, 2 H); 3.36 (*t*, 2 H); 3.85 (*t*, 2 H); 6.12 (*m*, 2 H); 6.62 (*m*, 2 H).

1-(12-Bromododecyl)-1H-pyrrole (**3c**). As described for **3a**, using K (0.64 g, 16.40 mmol) in THF (8 ml), **1** (1.38 g, 1.43 ml, 20.50 mmol) and 1,12-dibromododecane (**2c**; 26.91 g, 82.00 mmol; R_f 0.75) in THF (15 ml): **3c** (3.51 g, 68%). Colourless oil. R_f 0.18 (hexane). B.p. 130°/12 Torr. IR (film): 3100*m*, 2926*m*, 2854*m*, 1540*m*, 1464*m*, 1370*m*, 1280*m*, 1008*m*, 1088*m*, 1064*m*, 968*m*, 720*s*, 648*m*, 618*m*, 562*m*. ^1H-NMR: 1.25 (*m*, 14 H); 1.39 (*m*, 2 H); 1.71 (*m*, 2 H); 1.81 (*m*, 2 H); 3.38 (*t*, CH_2Br); 3.80 (*t*, 2 H); 6.08 (*m*, 2 H); 6.91 (*m*, 2 H). ^{13}C-NMR: 26.5 (*t*); 27.9 (*t*); 28.5 (*t*); 29.0 (*t*); 29.2 (*t*); 31.3 (*t*); 33.6 (*t*); 49.3 (*t*); 107.5 (*d*); 120.1 (*d*). EI-MS: 314 (58, M^+), 235 (39, $[M - Br]^+$), 206 (12), 192 (10), 64 (19), 150 (26), 136 (41), 122 (50), 108 (26), 94 (46), 68 (26), 55 (28).

1H-Pyrrole-1-propanol (**4a**) [17a]. The soln. of **3a** (0.61 g, 3.24 mmol) in HMPA (13 ml) and H_2O (2.2 ml) was heated for 7 h to 100°, cooled to r.t., diluted with H_2O, and extracted exhaustively with Et_2O. The org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated. Purification by FC (silica gel, hexane/AcOEt 2:1) yielded **4a** (0.31 g, 76%). Colourless oil.

Alternatively, **3a** was prepared from **5** and **6a** by the procedure [17b]. R_f 0.23 (hexane/AcOEt 2:1). ^1H-NMR: 1.93 (*m*, 2 H); 3.05 (br. *s*, 1 H); 3.53 (*t*, 2 H); 3.96 (*t*, 2 H); 6.13 (*t*, 2 H); 6.64 (*t*, 2 H).

1H-Pyrrole-1-hexanol (**4b**) [14]. As described for **4a**, with **3b** (2.00 g, 12.99 mmol): **4b** (1.65 g, 76%). Colourless oil. R_f 0.29 (hexane/AcOEt 2:1). ^{1}H-NMR: 1.33 (*m*, 4 H); 1.53 (*m*, 2 H); 1.76 (*m*, 3 H); 3.58 (*t*, 2 H); 3.86 (*t*, 2 H); 6.13 (*m*, 2 H); 6.64 (*m*, 2 H).

1H-Pyrrole-1-dodecanol (**4c**). As described for **4a**, with **3c** (2.60 g, 8.27 mmol): **4c** (1.61 g, 78%). Colourless oil which solidified in the refrigerator (*ca.* 5°). R_f 0.45 (hexane/AcOEt 2:1). ^{1}H-NMR: 1.27 (*m*, 16 H); 1.54 (*m*, 2 H); 1.74 (*m*, 2 H); 1.87 (br. *s*, 1 H); 3.59 (*t*, 2 H); 3.84 (*t*, 2 H); 6.12 (*m*, 2 H); 6.63 (*m*, 2 H). ^{13}C-NMR: 25.67 (*t*); 26.70 (*t*); 29.13 (*t*); 29.35 (*t*); 29.40 (*t*); 29.46 (2*t*); 29.50 (*t*); 31.50 (*t*); 32.72 (*t*); 49.56 (*t*); 62.94 (*t*); 107.67 (*d*), 120.37 (*d*). EI-MS: 251 (100, M^+), 250 (26), 164 (12), 150 (12), 136 (24), 122 (27), 94 (15), 81 (48), 80 (27). HR-MS: 251.224180 ($C_{16}H_{29}NO^+$; calc. 251.224915).

a,b,d,e,f,g-*Hexamethyl* c-*[3-(1H-Pyrrol-1-yl)propyl]* Coα,Coβ-*Di(cyano-κC)cob(III)yrinate* (**8a**). To the mixture of **7** [19] (0.40 g; 0.372 mmol), **4a** (70 mg, 0.558 mmol) and 4-(dimethylamino)pyridine (DMAP; 60 mg, 0.496 mmol) in dry CH_2Cl_2, (12 ml), cooled under Ar to 0°, *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodimide hydrochloride (178 mg, 0.930 mmol) was added. After stirring at r.t. for 3 h, the mixture was extracted with 5% aq. AcOH soln. (1 ×), sat. aq. $NaHCO_3$ soln. (1 ×), and 1M aq. KCN (1 ×). The org. phase was dried (Na_2SO_4) and evaporated and the residue purified by FC (hexane/CH_2Cl_2/i-PrOH/MeOH (0.1% HCN) 8:2:1:1): violet **8a** (300 mg, 68%) which was precipitated from benzene/hexane. R_f (hexane/CH_2Cl_2/i-PrOH/MeOH (0.1% HCN) 8:2:1:1) 0.28. UV ($c = 7.6 \cdot 10^{-5}$ M): 280 (4.02), 316 (3.95), 372 (4.42), 424 (3.58), 517 (3.70), 550 (3.93), 590 (4.04). IR (KBr): 2958*m*, 2124*w*, 1736*s*, 1587*m*, 1505*m*, 1438*m*, 1372*m*, 1158*m*, 1013*m*. ^{1}H-NMR: 1.20, 1.27, 1.35, 1.37, 1.51, 1.57 (6*s*, 18 H); 1.74 (*m*, 2 H); 1.77 (*m*, 2 H); 2.08 (*m*, 6 H); 2.19 (*s*, 3 H); 2.23 (*s*, 3 H); 2.28–2.78 (*m*, 14 H); 2.82 (*m*, 1 H); 3.03 (*t*, 1 H); 3.46 (*dd*, 1 H); 3.63, 3.66, 3.68, 3.70, 3.72, 3.76 (6*s*, 18 H); 3.80 (*m*, 1 H); 3.82 (*m*, 1 H); 3.97 (*t*, 2 H); 4.07 (*m*, 2 H); 5.58 (*s*, 1 H); 6.14 (*t*, 2 H); 6.64 (*t*, 2 H). ^{13}C-NMR: 15.3 (*q*); 16.0 (*q*); 17.0 (*q*); 18.5 (*q*); 19.2 (*q*); 19.8 (*q*); 22.0 (*q*); 25.0 (*t*); 25.7 (*t*); 26.5 (*t*); 29.7 (*t*); 30.6 (*t*); 30.7 (*t*); 31.1 (*q*); 31.2 (*t*); 31.8 (*t*); 32.6 (*t*); 33.7 (*t*); 39.3 (*d*); 41.2 (*t*); 42.2 (*t*); 45.7 (*s*); 46.2 (*s*); 47.0 (*t*); 48.7 (*s*); 51.61 (*q*); 51.63 (*q*); 51.80 (*q*); 51.84 (2*q*); 52.4 (*q*); 53.6 (*d*); 54.1 (*d*); 58.4 (*s*); 56.6 (*d*); 74.8 (*d*); 61.8 (*t*); 82.6 (*s*); 91.2 (*d*); 102.3 (*s*); 103.6 (*s*); 108.4 (*s*); 120.5 (*s*); 163.48 (*s*); 163.55 (*s*); 171.4 (*s*); 170.5 (*s*); 175.3 (*s*); 171.8 (*s*); 172.0 (*s*); 172.8 (*s*); 173.0 (*s*); 173.5 (*s*); 173.9 (*s*); 175.7 (*s*); 176.3 (*s*). FAB-MS: 1182 (5, M^+), 1156 (46, $[M - CN]^+$), 1130 (100, $[M - 2\,CN]^+$). Anal. calc. for $C_{60}H_{80}CoN_7O_{14}$ (1182.27): C 60.96, H 6.82, N 8.29; found: C 59.28, H 6.76, N 7.99. CV: red.: −0.67, −1.17; ox.: −0.72, −0.37, 1.01, 1.27.

a,b,d,e,f,g-*Hexamethyl* c-*[6-(1H-Pyrrol-1-yl)hexyl]* Coα,Coβ-*Di(cyano-κC)cob(III)yrinate* (**9a**). As described for **8a**, with **7** (400 mg, 0.372 mmol) and **4b** (93 mg, 0.558 mmol): 320 mg (70%) of violet **9a**. R_f (hexane/CH_2Cl_2/i-PrOH/MeOH (0.1% HCN) 8:2:1:1) 0.31. UV ($c = 1.06 \cdot 10^{-4}$ M): 280 (4.11), 316 (4.03), 372 (4.41), 424 (3.51), 517 (3.78), 550 (4.00), 590 (4.11). IR (KBr): 2958*m*, 2124*w*, 1736*s*, 1587*m*, 1505*m*, 1438*m*, 1372*m*, 1158*m*, 1013*m*, 732. ^{1}H-NMR: 1.20, 1.27, 1.35, 1.37, 1.51, 1.56 (6*s*, 18 H); 1.37 (*m*, 4 H); 1.61 (*m*, 2 H); 1.77 (*m*, 4 H); 2.08 (*m*, 6 H); 2.18 (*s*, 3 H); 2.23 (*s*, 3 H); 2.28–2.72 (*m*, 14 H); 2.81 (*m*, 1 H); 3.03 (*t*, 1 H); 3.47 (*dd*, 1 H); 3.63, 3.66, 3.68, 3.70, 3.72, 3.76 (6*s*, 18 H); 3.80 (*m*, 1 H); 3.82 (*m*, 1 H); 3.87 (*t*, 2 H); 4.06 (*m*, 2 H); 5.58 (*s*, 1 H); 6.13 (*t*, 2 H); 6.64 (*t*, 2 H). ^{13}C-NMR: 15.3 (*q*); 16.0 (*q*); 16.9 (*q*); 18.5 (*q*); 19.1 (*q*); 19.8 (*q*); 22.0 (*q*); 25.0 (*t*); 25.6 (*t*); 25.7 (*t*); 26.4 (*t*); 26.5 (*t*); 28.5 (*t*); 29.7 (*t*); 30.7 (*t*); 31.06 (*q*); 31.13 (*t*); 31.4 (*t*); 31.8 (*t*); 32.6 (*t*); 33.7 (*t*); 39.3 (*d*); 41.1 (*t*); 42.3 (*t*); 45.6 (*s*); 47.0 (*s*); 48.6 (*s*); 53.6 (*d*); 49.5 (*t*); 51.58 (*q*); 51.60 (*q*); 51.78 (*q*); 51.82 (*q*); 51.83 (*q*); 52.4 (*q*); 54.1 (*d*); 56.6 (*d*); 58.3 (*s*); 64.6 (*t*); 74.8 (*d*); 82.6 (*s*); 9.2 (*d*); 102.2 (*s*); 103.6 (*s*); 107.8 (*s*); 120.4 (*s*); 163.4 (*s*); 163.7 (*s*); 171.5 (*s*); 170.6 (*s*); 171.8 (*s*); 172.9 (*s*); 172.8 (*s*); 172.9 (*s*); 173.5 (*s*); 173.9 (*s*); 175.3 (*s*); 175.6 (*s*); 176.2 (*s*). FAB-MS: 1223 (7, $[M - H]^+$), 1197 (100, $[M - CN]^+$), 1171 (93, $[M - 2\,CN]^+$). Anal. calc. for $C_{63}H_{86}CoN_7O_{14}$ (1224.35): C 61.80, H 7.08, N 8.01; found: C 61.05, H 7.19, N 7.75. CV: red.: −0.69, −1.17; ox.: −0.72, −0.34, 1.03, 1.29.

a,b,d,e,f,g-*Hexamethyl* c-*[12-(1H-Pyrrol-1-yl)dodecyl]* Coα,Coβ-*Di(cyano-κC)cob(III)yrinate* (**10a**). As described for **8a**, with **7** (500 mg, 0.372 mmol) and **4c** (175 mg, 0.558 mmol): 420 mg (69%) of **10a**. Violet solid. R_f (hexane/CH_2Cl_2/i-PrOH/MeOH (0.1% HCN) 8:2:1:1) 0.34. UV ($c = 4.967 \cdot 10^{-5}$ M): 280 (4.10), 316 (4.00), 372 (4.48), 424 (3.49), 517 (3.74), 550 (3.97), 590 (4.09). IR (KBr): 2958*m* (CH), 2124*w*, 1736*s*, 1587*m*, 1505*m*, 1438*m*, 1372*m*, 1158*m*, 1013*m*, 732. ^{1}H-NMR: 1.20, 1.35, 1.37, 1.51, 1.56 (5*s*, 15 H); 1.26 (br. *s* + *s*, 19 H); 1.59 (*m*, 2 H); 1.76 (*m*, 6 H); 2.08 (*m*, 4 H); 2.18 (*s*, 3 H); 2.23 (*s*, 3 H); 2.25–2.72 (*m*, 14 H); 2.82 (*m*, 1 H); 3.03 (*t*, 1 H); 3.48 (*dd*, 1 H); 3.63, 3.66, 3.68, 3.70, 3.72, 3.76 (6*s*, 18 H); 3.80 (*m*, 1 H); 3.82 (*m*, 1 H); 3.86 (*t*, 2 H); 4.07 (*m*, 2 H); 5.58 (*s*, 1 H); 6.12 (*t*, 2 H); 6.64 (*t*, 2 H). ^{13}C-NMR: 15.3 (*q*); 16.0 (*q*); 17.0 (*q*); 18.5 (*q*); 19.1 (*q*); 19.8 (*q*); 22.1 (*q*); 25.0 (*t*); 25.7 (*t*); 26.0 (*t*); 26.6 (*t*); 26.8 (*t*); 28.6 (*t*); 29.20 (*t*); 29.24 (*t*); 29.4 (*t*); 29.51 (*t*); 29.54 (*t*); 29.7 (*t*); 30.7 (*t*); 31.1 (*t*); 31.2 (*q*); 31.6 (*t*); 31.8 (*t*); 32.6 (*t*); 33.7 (*t*); 39.3 (*d*); 41.1 (*t*); 42.3 (*t*); 45.6 (*s*); 47.0 (*s*); 48.7 (*s*); 49.6 (*t*); 51.6 (2*q*); 51.78 (*q*); 51.88 (*q*); 51.84 (*q*); 52.4 (*q*); 53.6 (*d*); 54.1 (*d*); 56.6 (*d*); 58.3 (*s*); 64.9 (*t*); 74.8 (*d*); 82.6 (*s*); 91.2 (*d*); 102.1 (*s*); 103.6 (*s*); 107.7 (*d*); 120.4 (*d*); 163.5 (*s*); 163.8 (*s*); 171.5 (*s*); 170.7 (*s*); 171.8 (*s*); 172.0 (*s*); 172.8 (*s*); 173.0 (*s*); 173.5 (*s*); 173.9 (*s*); 175.3 (*s*); 175.6 (*s*); 176.2 (*s*). FAB-MS: 1307 (3, $[M - H]^+$),

1281 (44, $[M - CN]^+$), 1255 (100, $[M - 2\ CN]^+$). Anal. calc. for $C_{69}H_{98}CoN_7O_{14}$ (1308.51): C 63.34, H 7.55, N 7.49; found: C 62.45, H 7.53. N 7.28. CV: red.: −0.69, −1.08; ox.: −0.73, −0.39, 1.02, 1.29.

a,b,d,e,f,g-*Hexamethyl* c-*[3-(1*H*-Pyrrol-1-yl)propyl]* Co-*Aqua*-Co*(cyano-*κC*)cob(III)yrinate Perchlorate* (**8b**). The soln. of **8a** (85 mg, 0.072 mmol) and CF_3CO_2H (15 ml) in CH_2Cl_2 (8 ml) was stirred at r.t. for 7 min. The HCN formed and 3/4 of the solvent were evaporated. CH_2Cl_2 (6 ml) was added, and after stirring for 10 min, 3/4 of the solvent was removed again. After dilution with CH_2Cl_2 and extraction with 1M aq. phosphate buffer (pH 7) under addition of $NaClO_4$, the org. phase was filtered and evaporated. Precipitation from benzene/hexane (2×) yielded **8b** (80 mg, 88%). Orange-red solid. UV ($c = 8.6 \cdot 10^{-5}$ M): 272 (4.10), 326 (4.15), 356 (4.26), 390 (3.85), 406 (3.85), 486 (3.90), 517 (sh, 4.09). IR (KBr): 3434*m* (H_2O), 2954*m* (CH), 2138*w* (CN), 1734*s* (CO), 1578*m*, 1500*m*, 1438*m*, 1364*m*, 1202*m*, 1164*m*, 1106*m* (ClO_4), 1027*m*, 732 (arom. H), 624*m* (ClO_4). ^{1}H-NMR: 1.18, 1.31, 1.40, 1.44, 1.45, 1.46, 1.55, 1.68, 1.76 (9*s*, 36 H); 1.82–2.43 (*m*, 26 H); 2.33, 2.36, 2.39 (3*s*, 12 H); 2.44–2.82 (*m*, 18 H); 3.08 (*m*, 2 H); 3.34, 3.40 (2*t*, 2 H); 3.61, 3.63, 3.66, 3.67, 3.69, 3.71, 3.74, 3.72, 3.79, 3.80 (10*s*, 36 H); 3.80 (stack, 2 H); 3.96 (*t*, 4 H); 4.09 (*m*, 5 H); 4.34 (*d*, 1 H); 6.14 (*m*, 4 H); 6.41, 6.45 (2*s*, 1 H); 6.64 (*m*, 4 H). FAB-MS (calc. for $C_{59}H_{82}ClCoN_6O_{19}$: 1273.72): 1156 (8, $[M - ClO_4 - H_2O]^+$), 1130 (100, $[M - ClO_4, -H_2O - CN]^+$). CV: red.: −0.49, −0.76, 1.20; ox.: −0.66, −0.35, 0.58, 1.05, 1.28.

a,b,d,e,f,g-*Hexamethyl* c-*[6-(1*H*-Pyrrol-1-yl)hexyl]* Co-*Aqua-Co-(cyano-*κC*)cob(III)yrinate* (**9b**). As described for **8b**: 88% yield. UV ($c = 6.08 \cdot 10^{-5}$ M): 272 (4.14), 326 (4.16), 356 (4.27), 390 (3.86), 406 (3.87), 484 (3.91), 517 (3.75). IR (KBr): 3455*m*, 2952*m*, 2138*w*, 1734*s*, 1580*m*, 1500*m*, 1438*m*, 1364*m*, 1202*m*, 1166*m*, 1106*m*, 102*m*, 732, 624*m*. ^{1}H-NMR: 1.17, 1.32, 1.46, 1.55, 1.67, 1.76 (6*s*, 36 H); 1.32 (stack, 8 H); 1.62 (stack, 4 H); 1.76 (stack, 4 H); 1.85–2.44 (*m*, 26 H); 2.33, 2.36, 2.39 (3*s*, 12 H); 2.45–2.85 (*m*, 18 H); 3.08 (*m*, 2 H); 3.33, 3.40 (2*m*, 2 H); 3.61, 3.63, 3.66, 3.67, 3.69, 3.71, 3.72, 3.74, 3.79, 3.80 (10*s*, 36 H); 3.80 (stack, 2 H); 3.86 (*t*, 4 H); 4.15 (*m*, 5 H); 4.34 (*d*, 1 H); 6.14 (*m*, 4 H); 6.41, 6.45 (*s*, 1 H); 6.64 (*m*, 4 H). FAB-MS (calc. for $C_{62}H_{88}ClCoN_6O_{19}$: 1315.80): 1198 (36, $[M - ClO_4 - H_2O]^+$), 1172 (100, $[M - ClO_4 - H_2O - CN]^+$). CV: red.: −0.51, −0.75, −1.16; ox.: −0.67, −0.37, 0.58, 0.95, 1.26.

a,b,d,e,f,g-*Hexamethyl* c-*[12-(1*H*-Pyrrol-1-yl)dodecyl]* Co-*Aqua*-Co-*(cyano-*κC*)cob(III)yrinate* (**10b**). As described for **8b**: 88% yield. UV ($c = 6.43 \cdot 10^{-5}$ M): 272 (4.14), 326 (4.16), 356 (4.25), 392 (3.87), 408 (3.86), 484 (3.90), 517 (3.73). IR (KBr): 3437*m*, 2930*m*, 2138*w*, 1734*s*, 1578*m*, 1500*m*, 1438*m*, 1369*m*, 1202*m*, 1164*m*, 1106*m*, 1027*m*, 732, 624*m*. ^{1}H-NMR: 1.18, 1.32, 1.45, 1.56, 1.61, 1.77 (7*s*, 36 H); 1.26 (stack, 32 H); 1.64 (stack, 4 H); 1.74 (stack, 4 H); 1.82–2.46 (*m*, 2 H); 2.33, 2.36, 2.39 (3*s*, 12 H); 2.47–2.82 (*m*); 3.06 (*m*, 2 H); 3.33, 3.40 (2*m*, 2 H); 3.61, 3.63, 3.66, 3.67, 3.69, 3.71, 3.72, 3.74, 3.79, 3.80 (10*s*, 36 H); 3.80 (stack, 2 H); 3.86 (*t*, 4 H); 4.08 (*m*, 5 H); 4.33 (*d*, 1 H); 6.12 (*m*, 4 H); 6.41, 6.45 (*s*, 1 H); 6.64 (*m*, 4 H). FAB-MS (calc. for $C_{68}H_{100}ClCoN_6O_{19}$): 1281 (40, $[M - ClO_4 - H_2O]^+$), 1255 (100, $[M - ClO_4 - H_2O - CN]^+$). CV: red.: −0.49, −0.78, −1.17; ox.: −0.70, −0.37, 0.50, 0.98, 1.24.

a,b,d,e,f,g-*Hexamethyl* c-*[3-(1*H*-Pyrrol-1-yl)propyl]* Co*β-(Perchlorato)cob(II)yrinate* (**8c**). To a soln. of $NaBH_4$ (150 mg, 4.00 mmol) in a deoxygenated mixture of H_2O (50 ml) and MeOH (50 ml) under Ar, a soln. of **8b** (50 mg, 0.039 mmol) in deoxygenated MeOH (5 ml) was slowly added at r.t. Stirring for 5–10 min gave a green soln. from which the Co^I complex partly precipitated. After addition of 30% aq. $HClO_4$ soln. (8 ml), the colour turned immediately to orange. The mixture was diluted with CH_2Cl_2, neutralized with 1M aq. phosphate buffer (pH 7), and extracted with CH_2Cl_2 (2×). The combined org. extract was dried (Na_2SO_4) and evaporated and the residue precipitated from benzene/hexane (2×): **8c** (40 mg, 85%). Brown solid. UV ($c = 4.0 \cdot 10^{-5}$ M): 266 (4.23), 316 (316), 406 (3.79), 468 (4.03). IR (KBr): 2954*m* (CH), 1734*s*, 1570*m*, 1492*m*, 1438*m*, 1356*m*, 1202*m*, 1164*m*, 1106*m*, 730*m*, 622*m*. ESI-MS (calc. for $C_{58}H_{80}ClCoN_5O_{18}$: 1229.68): 1130 (100, $[M + H, -ClO_4]^+$). FAB-MS: 1129 (100, $[M - ClO_4]^+$). CV: red.: −0.76; ox.: −0.65, 0.6, 1.15, 1.35.

a,b,d,e,f,g-*Hexamethyl* c-*[6-(1*H*-Pyrrol-1-yl)hexyl]* Co*β-(Perchlorato)cob(II)yrinate* (**9c**). As described for **8c**: 82% yield. UV (CH_2Cl_2): 266 (4.26), 3.16 (4.34), 404 (3.81), 470 (4.07). IR (KBr): 2952*m*, 1732*s*, 1570*m*, 1490*m*, 1436*m*, 1354*m*, 1202*m*, 1164*m*, 1106*m*, 728*m*, 624*m*. ESI-MS (calc. for $C_{61}H_{86}ClCoN_5O_{18}$: 1271.76): 1171.38 (100, $[M + H - ClO_4]^+$). FAB-MS: 1171 (100, $[M^+ - ClO_4]^+$). CV: red.: −0.74; ox.: −0.67, 0.64, 1.27, 1.42.

a,b,d,e,f,g-*Hexamethyl* c-*[12-(1*H*-Pyrrol-1-yl)dodecyl]* Co*β-(Perchlorato)cob(II)yrinate* (**10c**). As described for **8c**: 86% yield. UV ($c = 3.68 \cdot 10^{-5}$ M): 266 (4.26), 314 (4.34), 4.04 (3.81), 470 (4.07). IR (KBr): 2926*m*, 1734*s*, 1570*m*, 1490*m*, 1436*m*, 1354*m*, 1202*m*, 1164*m*, 1104*m*, 724*m*, 622*m*. ESI-MS (calc. for $C_{67}H_{98}ClCoN_5O_{18}$: 1355.92): 1256 (100, $[M - ClO_4]^+$). FAB-MS: 1255 (100, $[M - ClO_4 - H]^+$). CV: red.: −0.75; ox.: −0.66, 0.58, 1.25.

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Received February 25, 1998