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Adenosyl-176-norcobinamide – A likely biosynthetic precursor to natural 176-norvitamin B_{12} derivatives

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Abstract

The "complete" corrinoid 176-norpseudovitamin B_{12} was recently isolated as the cyano-Co(III)-form of the corrinoid cofactor of tetrachlorethene reductive dehalogenase of the anaerobe *Sulfurospirillum* (formerly *Dehalospirillum) multivorans*. 176-Norpseudovitamin B_{12} represents the first example of (the cyano-Co(III)-form of) a naturally occurring "complete" B_{12} cofactor lacking a characteristic peripheral methyl group of the cobamide ligand. Its discovery has generated interest in 176-nor-B_{12} derivatives, "complete" corrinoids lacking the methyl group attached to carbon 176. Here, we report the preparation of Co_{β}-5′-adenosyl-176-norcobinamide by *in situ* alkylation of Co(I)-176-norcobinamide, obtained from electrochemical reduction of Co_{α},Co_{β}-dicyano-176-norcobinamide. Since Co_{β}-5′-adenosylcobinamide is a biosynthetic intermediate of the complete cobamides, Co_{β}-5′-adenosyl-176-norcobinamide is a "rational" biosynthetic precursor for natural 176-nor-B_{12} derivatives. The spectroscopic data for adenosyl-176-norcobinamide establish the suggested structure of the title compound and give further evidence for the extensive flexibility and conformational dynamics of the organometallic 5′-deoxy-5′-adenosyl ligand.

Keywords: Bioorganometallic Chemistry; Biosynthesis; Coenzyme B_{12}; Dehalogenase; Electrochemistry; Vitamin B_{12}

1. Introduction

The corrinoid cofactor of tetrachlorethene reductive dehalogenase from the anaerobe *Sulfurospirillum* (formerly *Dehalospirillum) multivorans* was recently identified in its cyano-Co(III)-form as norpseudovitamin B_{12} (**1**, Co_{β}-cyano-7″-adeninyl-176-norcobinamide or 176-norpseudovitamin B_{12}) [1]. Tetrachloroethene reductive dehalogenase uses the cofactor form of norpseudo-B_{12} to catalyze the reductive dehalogenation of tetrachloroethene and trichloroethene to (*Z*)-1,2-dichloroethene with high specific activities and is also able to dechlorinate chlorinated propenes [2,3].

The "complete" corrinoid **1** is a homologue of pseudovitamin B_{12} (**2**), with the notable difference being the lack of the methyl group attached to carbon 176 (Fig. 1) [1]. In "complete" B_{12}-derivatives the constitution of the "nucleotide base" can vary and the known classes of nucleotide functionalities found are purines, such as adenine and 2-methyladenine found in pseudovitamin B_{12} (**2**) and factor A (**3**) respectively, benzimidazoles, such as the 5,6-dimethylbenzimidazole (DMB) of vitamin B_{12} (**4**), and phenols, such as *p*-cresol found in *p*-cresolylcobamides [4,5].

Natural B_{12} derivatives can occur either as "complete" corrinoids, where a nucleotide function extends from the *f*-propionic acid substituent (attached at C17 of the corrin ligand), or as "incomplete" corrinoids, i.e. cobyrinic acid derivatives which lack the nucleotide function. The latter generally represent biosynthetic intermediates on the way to the "complete" corrinoids [6,7]. However, **1** is the first naturally occurring "complete" B_{12} cofactor known to lack the characteristic peripheral methyl group at carbon 176 of the cobamide ligand. Recently, related 176-nor-derivatives

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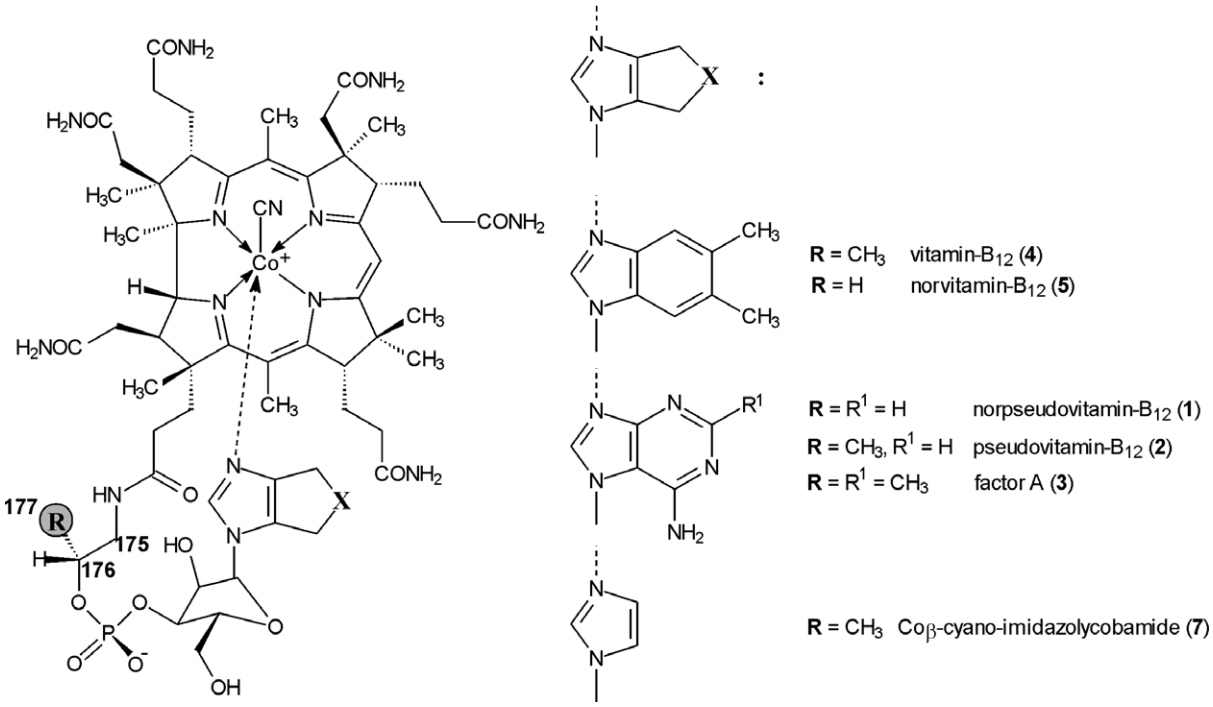


Fig. 1. Structural formulae of Co_β-cyano forms of vitamin B_{12} derivatives.

of vitamin B_{12} (**4**) have been synthesized, 176-norvitamin B_{12} (**5**, Co_β-cyano-176-norcobalamin) and Co_β-methyl-176-norcobalamin [8].

By comparing methylcobalamin and Co_β-methyl-176-norcobalamin it was shown that the methyl group of carbon 176 influences the coordination equilibrium of the nucleotide base, which can be cobalt-coordinated (i.e. "base-on") or de-coordinated (i.e. "base-off") [8]. The methyl group at carbon 176 (in the "complete" corrinoids) has specifically been suggested to be an element in control of the relevant conformations of the "base-off"-form, i.e. in which the nucleotide base is not coordinated to the corrin-bound Co centre. Thus, by assisting in the pre-formation of a "quasi-cyclic" conformation [9], as needed to achieve unstrained Co coordination of the nucleotide base, a remarkable long-distance effect of the methyl group, some eleven atoms away, arises at the Co centre [8]. To further investigate the effect of this methyl group on the organometallic reactivity of B_{12}-cofactors, preparative access to 176-norcobamides is of interest.

A possible way to produce 176-norpseudovitamin-B_{12} (**1**) or 176-norvitamin B_{12} (**5**) could rely on "guided" biosynthesis [10] using Co_β-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**) (Fig. 2). Due to the fact that the nucleotide portion of B_{12}-derivatives is attached in the later phases of the biosynthesis of "complete" cobamides [6,11], and in a variety of anaerobes the nucleotide moiety of "complete" corrinoids is subject to rapid biosynthetic exchange, (therefore, allowing exogenous heterocycles to be incorporated) "guided" biosynthesis indeed appears as a possible, rational way to the nor-cobamides [5]. Previous work in this field has involved, e.g. the biosynthesis of Co_β-cyano-imidazolylcobamide (**7**) from supplementing a *Propionibacterium shermanii* cell culture with imidazole and cobinamide [10] and the partial biosynthesis of **2** from supplementing *Propionibacterium* spp. with cobinamide and adenine [12]. By supplementing an appropriate cell culture with **6** (which has the advantage of being an analogue of an intermediate in the biosynthesis of coenzyme B_{12} and would be expected to be readily taken up by cells) and adenine or 5,6-dimethyl-benzimidazole, 176-norpseudovitamin-B_{12} (**1**) or 176-norvitamin-B_{12} (**5**) could be produced.

The required starting material for the work reported here, Co_α,Co_β-dicyano-176-norcobinamide (**8**) and its mono-cyano derivative **8a** have become available recently [13]. This paper now reports the electro-synthesis of Co_β-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**) from **8**, together with the spectroscopic characterization (by NMR spectroscopy in particular) of the solution structure of this "incomplete" organometallic B_{12}-derivative.

2. Experimental

2.1. General

Materials. Co-cyano,Co-aquo-176-norcobinamide (**8a**) was prepared, as published [13]; water purified using *Epure, Barnstead Co.*; acetone, CH_2Cl_2, CH_3OH, Hg, $(Bu_4N)PF_6$, CH_3COOH, KCN, CH_3CN, ethanolamine, triethylamine, all *Fluka puriss. p.a.*, or *Fluka MicroSelect*; DMF *Fluka, puriss., absolute, over molecular sieves* ($H_2O \leqslant 0.01\%$); benzoic acid *Fluka purum*. O_2-sensitive reactions were done in a glove box (*Mecaplex GB-80*, <10 ppm O_2). The electrochemical syntheses were carried out in an electrolysis cell

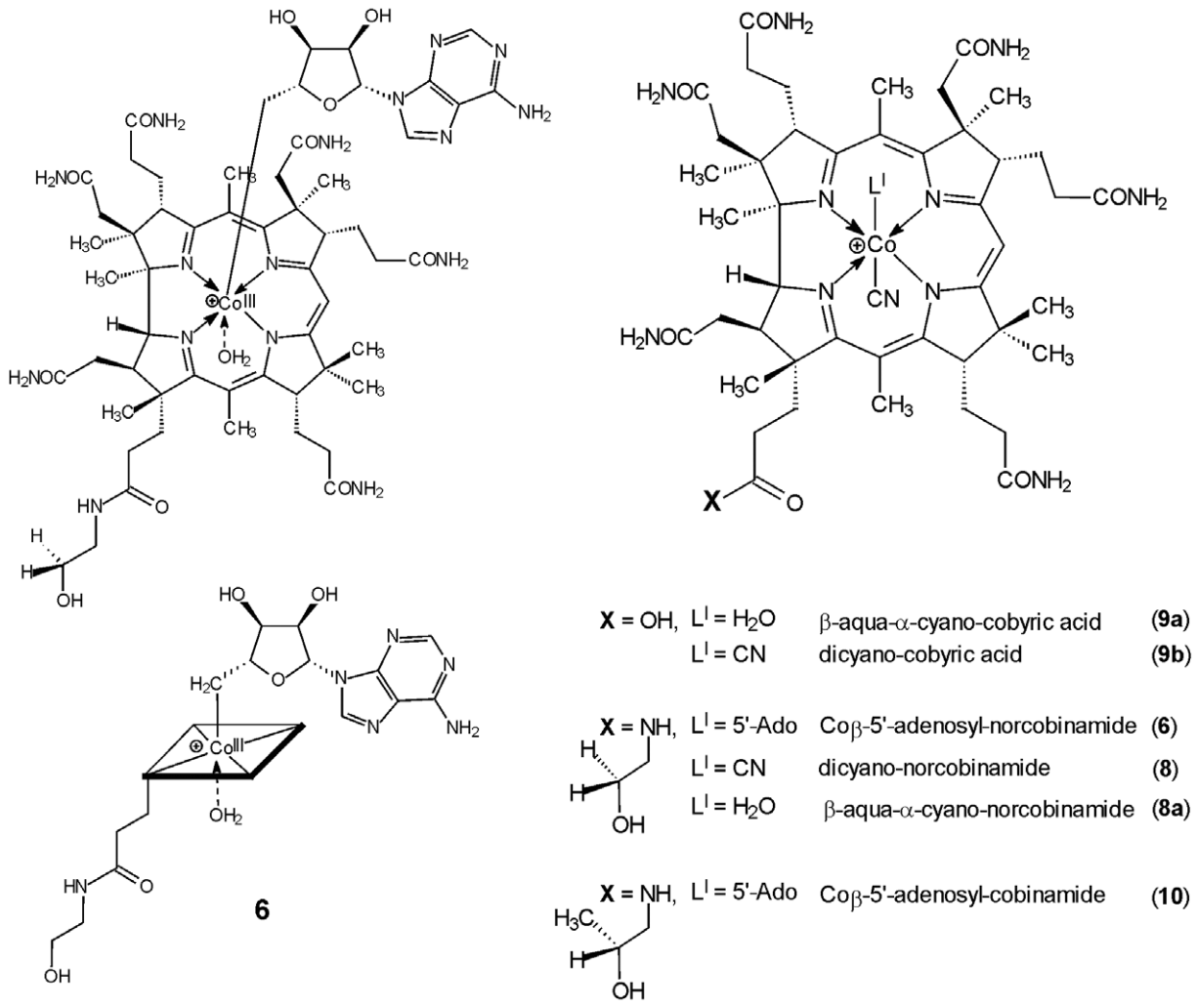


Fig. 2. Left: Structural and symbolic formulae of Co_β-5′-deoxy-5′-adenosyl-(176-) norcobinamide (**6**, prepared as chloride salt). Right: Structural formula of Co_α,Co_β-dicyano-(176-)norcobinamide (**8**), Co_β-5′-deoxyadenosyl-(176-)norcobinamide (**6**) and of other cobyric acid derivatives.

with two compartments, separated by a medium porosity glass frit; Hg pool working electrode; Pt-wire counter electrode; 0.1 N calomel electrode (0.1 N CE) as reference electrode; potentiostat *Amel 550*. pH values were measured with a *WTW SenTix 41* electrode connected to a *WTW inoLab digital pH meter*. TLC: *RP18 F254s* TLC plates 0.25 mm (*Merck* No. 115389). UV/Vis Spectra: *Hitachi-U3000*; $\lambda_{max}(\log\varepsilon)$ in nm. CD Spectra: *Jasco J715*; λ_{max} or λ_{min} ($\Delta\varepsilon$) in nm. ^{1}H and ^{13}C NMR spectra: *Varian Unity 500plus*; δ(H) in ppm referenced to δ(HDO) = 4.76 ppm and $\delta(^{13}C)$ in ppm referenced to external TSP, coupling constants J in Hz, spectra were recorded at 26 °C. FAB-MS: *Finnigan MAT 95S*, positive-ion mode; glycerin; Cs gun.

2.2. Synthesis of Co_β-5′-deoxy-5′-adenosine-176-norcobinamide chloride (*6*)

In the glove box, aqua-cyano norcobinamide (**8a**) (29 mg, 28.4 μmol) was dissolved in 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) in methanol in the cathode chamber of the electrolysis cell followed by benzoic acid (8 mg, 65.5 μmol). The norcobinamide was then reduced at a Hg-pool electrode and with magnetic stirring at −1.1 V *vs.* 0.1 N CE to nor-cob(I)inamide (under control; by UV/Vis spectroscopy). The mixture was protected from light, the tension reduced to −1.0 V *vs.* 0.1 N CE and a suspension of 5′-chloro-5′-deoxyadenosine (17 mg, 59.5 μmol) in 0.1 M TBAHFP in methanol was added. After 2 h, a UV-spectrum showed complete conversion to the product. The mixture was then transferred into a dark room, taken up in H_2O (10 ml) and extracted with dichloromethane (3 × 20 ml). The deep orange aqueous phase was evaporated, then dissolved in a minimum amount of water and precipitated by addition of acetone to give the product (24 mg, 68%). A second precipitation from the mother liquor gave further material (8 mg, 23%). Total yield = 32 mg (91%) after drying.

UV/Vis (c = 1.2 mmol L^{-1}, H_2O): 457(3.88), 378(3.93), 303(4.26). **CD** (c = 1.2 mmol L^{-1}, H_2O): 566(15.64),

503.5(−16.42), 469(−1.96), 433(−20.52), 401.5(7.04), 378.5(−5.89), 331(80.81). **FAB-MS**: 1227.5(39), 1226.4(78), 1225.4($C_{57}H_{82}N_{16}O_{11}Co$, 100, $[M–H_2O–Cl]^+$).

^{1}H NMR and **^{13}C NMR**: for list of signals and their assignments [14], see Table 1; Inter-ligand ^{1}H NOE contacts of H-atoms at the corrin ligand and at the deoxyadenosyl group of Co_β-5′-deoxyadenosyl-176-norcobinamide (**8**) (weak NOEs are listed in brackets, the signal for H(C3RL) overlaps that of H(C8), for atom numbering see Fig. 3):

H-atoms at corrin	H-atoms at deoxyadenosyl group
C21	C1RL, C5RL(*S*)
C71	C5RL(*R*) and C5RL(*S*)
C12B	C2L, C8L, C1RL, C4RL
C151	C2L, C1RL, (C4RL)
C17B	C2L, C8L, C1RL, C4RL,
C181	(C1RL)
C19	C4RL, C5RL(*S*), (C5RL (*R*))

3. Results and discussion

3.1. Synthesis of Co_β-5′-deoxy-5′-adenosyl-176-norcobinamide (6)

An electrochemical procedure [15] was used (Scheme 1) to reduce **8a** [13] to its Co(I) form, by setting a Hg-electrode to a potential of −1.1 V *vs.* a 0.1 N calomel electrode (CE) in a two-compartment electrolysis cell at room temperature and under N_2. (A small amount of benzoic acid was added in order to protonate the cyanide ion liberated by the reduction of **8a**.) The tension was then reduced to −1.0 V *vs.* a 0.1 N CE and 5′-chloro-5′-deoxyadenosine was added for the alkylation step. (If left at a more negative potential organo-cob(III)inamides were found to be prone reductive cleavage, involving either reduced cob(I)inamide or direct electrochemical reduction.) After 2 h, the reaction vessel was taken into a dark room where, after work-up, pure Co_β-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**) was obtained as an orange/red precipitate in 91% yield.

3.2. Spectroscopic properties

The UV/Vis- and CD-spectra for Co_β-5′-deoxy-5′-adenosyl-norcobinamide (**6**) were similar to that of Co_β-5′-deoxy-5′-adenosyl cobinamide (**10**) [16] and were typical of a base-off organometallic B_{12} derivative, or one lacking the nucleotide base. This type of spectrum has been previously also seen with the protonated form of coenzyme B_{12} [17] and of pseudo-coenzyme B_{12} [18,19].

The FAB-MS of a sample of Co_β-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**) showed a major signal at 1226.43 corresponding to $[M + H–H_2O]^+$. The ^{1}H and ^{13}C NMR spectra of **6** could be compared directly to those for Co_β-5′-deoxy-5′-adenosyl-cobinamide (**10**), which were published by Pagano et al. [16]. The only significant changes of chemical shifts of H-atoms between the two compounds occurred due to the lack of a methyl group on the *f*-chain, and reflecting the expected local substituent effects. The other signals of the H-atoms bound to the corrin ligand of **6** showed very little shift differences compared with those obtained for **10**. Even the signals of the deoxyadenosyl ligand showed very minor variations only: in the spectrum of **6** the signals of the two diastereotopic H-atoms of the directly cobalt-bound methylene group C5RL, occurred at 0.34 ppm and 0.59 ppm and could be assigned to H_{proR} and H_{proS}, respectively, based on the strong NOEs of C5RL-H_{proR} and the H-atom at C8L and of C5RL-H_{proS} and the H-atom at C19.

An interesting difference in the results obtained for **6**, when compared to the data of adenosyl-cobinamide (**10**) from Pagano et al. [16] is in the derived orientation of the adenosyl moiety. From the initial pioneering work of the solution structure of coenzyme B_{12} (adenosyl-cobalamin) two relevant orientations of the 5′-deoxy-5′-adenosyl ligand were detected [20,21], however for adenosyl-cobinamide only evidence for one major conformation was presented, as the NOE contact between C4RL and C12B was lacking [16]. Such NOE-contacts were used as support for an equilibrium between two conformations of the adenosyl moiety in both base-on and protonated, base-off coenzyme B_{12} [21]. In the spectra of **6** an NOE contact between C4RL and C12B could clearly be seen, indicating a more dynamic distribution of the Co-bound organometallic group. Such major orientations of the adenosyl group of **6** are also supported by the higher field shifts of the signals of CH_3(12B), CH_3(17B) and the values of CH_2(71) and CH_2(181), when compared to those of dicyano-norcobinamide (**8**), as the chemical shift of protons attached at the upper face of the corrin ring system are known to be sensitive to the (time averaged) positions of the 5′-deoxy-5′-adenosyl ligand [22]. Significant high-field shifts of several methyl or methylene protons of the corrin moiety in adenosyl-cobamides, when compared to cyano- and methyl-cobamides, have been previously observed, such as in pseudo-coenzyme B_{12} [19] and in neo-coenzyme B_{12} (the C13 epimer of coenzyme B_{12}) [22], where the existence of several relevant orientations of the organometallic ligand relative to the corrin ring was established by NMR-spectroscopy.

4. Conclusions and outlook

The organometallic norcobinamide, Co_β-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**), has been synthesized in a yield of >90% from the electrochemical reduction of aquacyano-norcobinamide (**8a**) and alkylation of the

Table 1
^{1}H and ^{13}C NMR data[a] for adenosyl-norcobinamide (**8**) and comparison with data [16] for adenosyl-cobinamide (**10**)

Assignment[a]	^{1}H-signals for adenosyl-norcobinamide (**8**)	^{1}H-signals[a] for adenosyl-cobinamide (**10**)	^{13}C-signals for adenosyl-norcobinamide (**8**)	^{13}C-signals for adenosyl-cobinamide (**10**)
C1			89.6	89.8
C1A	0.81	0.91	26.6	26.7
C2			48.4	48.5
C2A	1.43	1.52	19.1	19.2
C21	2.30, 2.67	2.42, 2.78	45.5	45.7
C3	4.21	4.32	57.9	58.0
C31	1.92, 2.07	2.03, 2.18	28.5	27.9
C32	2.50	2.62	37.7	37.8
C4			178.8	179.1
C5			110.9	111.0
C51	2.38	2.46	18.0	18.2
C6			166.1	166.2
C7			52.7	53.0
C7A	1.80	1.87	21.4	22.0
C71	1.73, 2.30	1.79, 2.32	45.5	45.7
C8	3.76	3.87	58.0	58.1
C81	1.83, 2.24	1.92, 2.54	28.9	29.1
C82	2.30, 2.40	2.33, 2.43	34.8	34.0
C9			174.4	174.7
C10	6.96	7.06	100.6	100.2
C11			178.8	178.9
C12			49.0	49.1
C12A	1.59	1.66	21.8	22.3
C12B	0.84	0.92	34.0	34.1
C13	3.41	3.50	54.9	55.1
C131	1.98, 2.26	2.07, 2.42	27.7	28.7
C132	1.73, 2.16	1.82, 2.26	34.0	34.0
C14			165.3	165.7
C15			109.8	110.1
C151	2.38	2.46	18.0	18.2
C16			178.7	178.8
C17			61.6	61.7
C17B	1.14	1.24	20.5	20.6
C171	1.81, 2.45	1.84, 2.37	34.1	34.3
C172	1.95, 2.35	2.06, 2.54	34.0	35.0
C175	3.30	3.30, 3.28	44.2	34.3
C176	3.61	3.98	62.7	69.1
C177		1.21		22.3
C18	2.81	2.92	41.8	42.0
C181	2.51, 2.66	2.63, 2.73	35.0	35.2
C19	4.67	4.77	77.5	77.6
C1RL	5.61	5.71	90.1	90.2
C2RL	4.40	4.50	75.1	75.4
C3RL	3.76	3.87	74.7	74.9
C4RL	1.96	2.05	88.4	88.6
C5RL	0.34 (*R*) 0.59 (*S*)	0.43 (*R*) 0.74 (*S*)	21.0	21.6
C2L	8.22	8.31	Not detected	155.4
C4L			151.5	151.6
C5L			121.4	121.5
C6L			158.3	158.1
C8L	8.01	8.13	Not detected	143.2

[a] Signal assignments from NOE-, ^{1}H,^{13}C HSQC-, and ^{1}H,^{13}C HMBC-spectra [23]; the ^{1}H-signals for **10** were referenced against internal TSP [16].

resulting Co(I)-form with 5′-deoxy-5′-adenosyl chloride. The comparison of the ^{1}H and ^{13}C NMR data of **6** and of adenosyl-cobinamide (**10**) showed only the expected differences due to the local substituent effects from the presence or absence of CH_3(177). However, the conformation of the 5′-deoxy-5′-adenosyl ligand in **6** was shown to be more dynamic than was reported earlier for Co_{β}-5′-deoxy-5′-adenosyl-cobinamide (**10**).

Our synthetic work has made available 176-norcobinamides, such as dicyano-176-norcobinamide (**8**) [13] and Co_{β}-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**). This latter organometallic norcobinamide is a homologue of the cobinamide **10**, which is a biosynthesis intermediate [6,7]. The organometallic norcobinamide **6** gives the opportunity to study the use of norcobinamides as biosynthetic precursors of 176-norpseudovitamin-B_{12} (**1**), 176-norvitamin-B_{12}

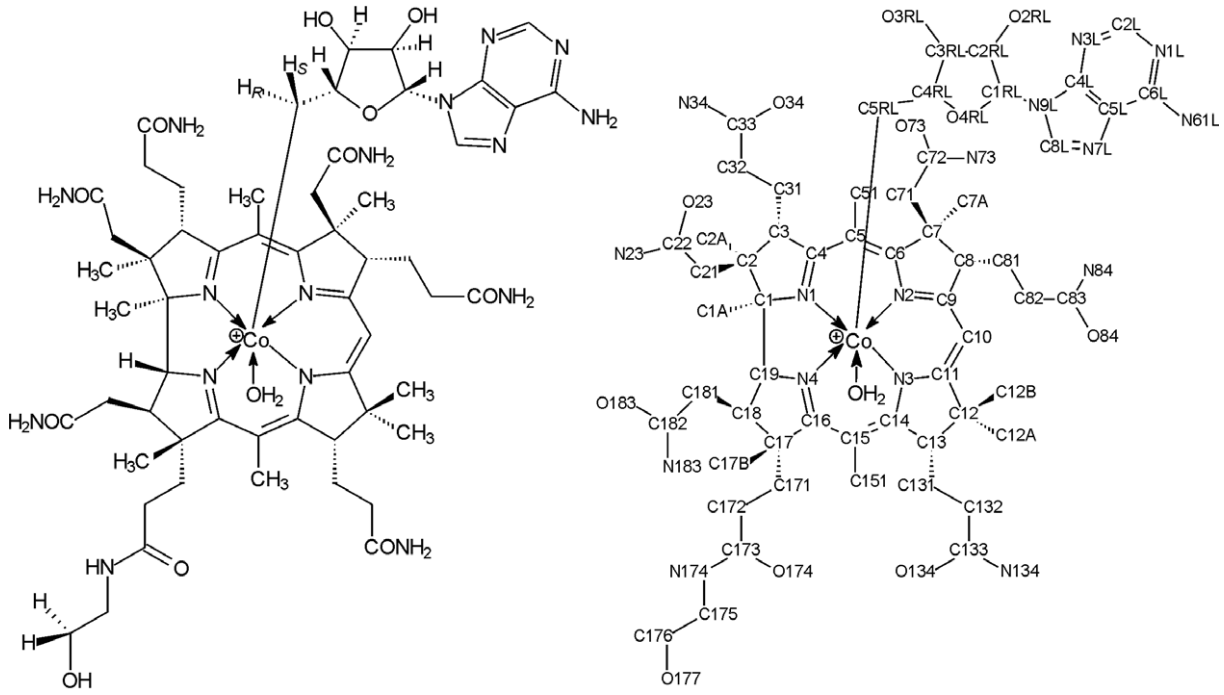
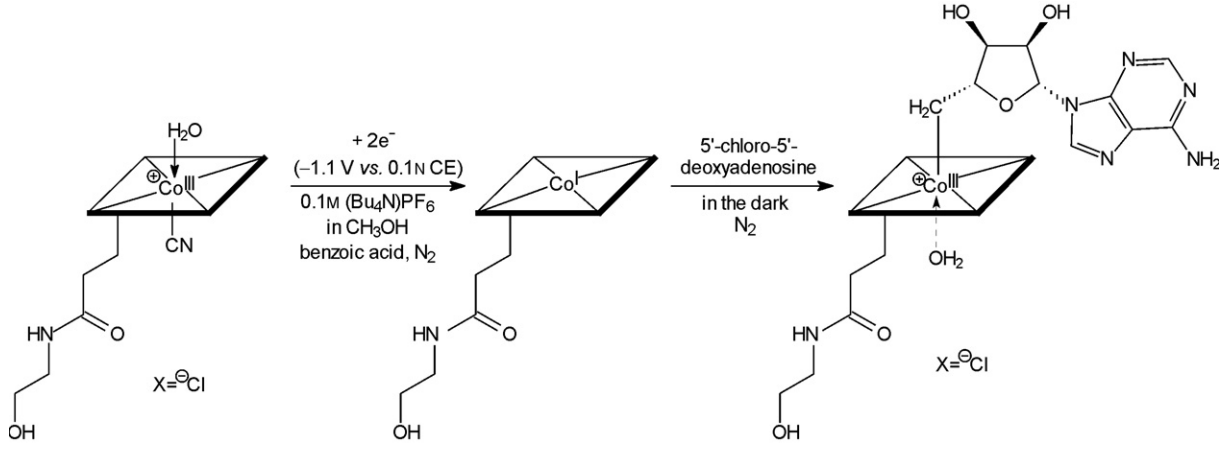


Fig. 3. Structural formula of Co_{β}-5′-deoxy-5′-adenosyl-(176-)norcobinamide (**6**) and atom numbering used here [14].



Scheme 1. Electrochemical synthesis of Co_{β}-5′-deoxy-5′-adenosyl-176-norcobinamide (**6**, chloride salt).

(**5**) and other 176-nor-B_{12} derivatives in suitable enzyme preparations or whole organisms.

Acknowledgements

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