# A Crystalline Cobalt(II)corrinate derived from Vitamin $B_{12}$: Preparation and *X*-Ray Crystal Structure

**Bernhard Kräutler,*[a] Walter Keller,[b] Mark Hughes,[a] Christian Caderas,[a] and Christoph Kratky*[b]**

[a] *Laboratory of Organic Chemistry, Eidgenössische Technische Hochschule, Universitätstrasse 16, CH-8092 Zürich, Switzerland*

[b] *Institute of Physical Chemistry, University of Graz, Heinrichstrasse 28, A-8010 Graz, Austria*

The preparation and *X*-ray crystal structure of a monomeric cobalt(II)corrinate derived from vitamin $B_{12}$ is reported.

Detailed information on the structure of cobalt(II) corrinates is of interest, particularly in the context of studies on the coenzyme $B_{12}$ catalysed enzymatic reactions, where cob(II)-alamin (**1**) has been detected as a reaction intermediate.[1] Hitherto, however, only one specimen of that class of Co(II) complexes has been studied by *X*-ray analysis,[2] the unusual, diamagnetic, iodonium bridged, Co(II) corrin dimer (**2**), prepared by Werthemann in Eschenmoser's laboratory.[3] We report here the preparation and *X*-ray structural analysis of a related monomeric Co(II) corrinate derived from vitamin $B_{12}$.

Formic acid reduction[4] of a crystalline sample of the vitamin $B_{12}$ methanolysis product 'cobester' (**3**, dicyano-heptamethyl-Co(III)cobyrinate)[3] cleanly furnished 'Co(II)cobester' (**4**, heptamethyl-Co(II) cobyrinate perchlorate).†[5] Crystals of (**4**)

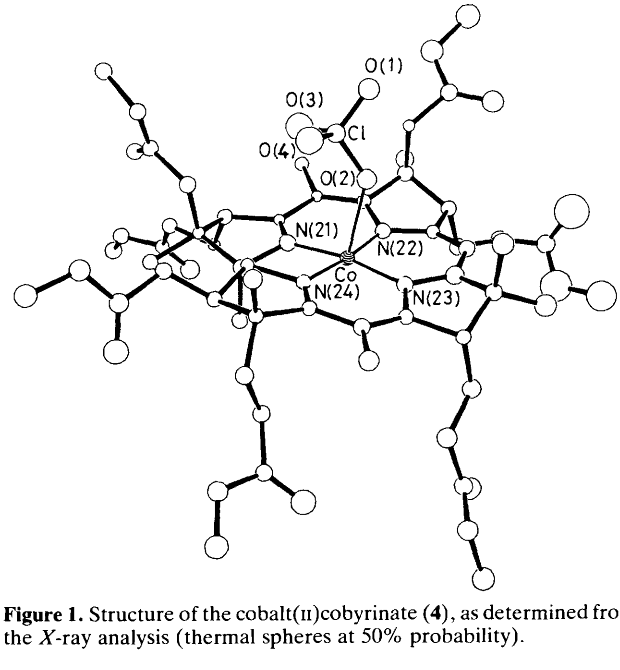
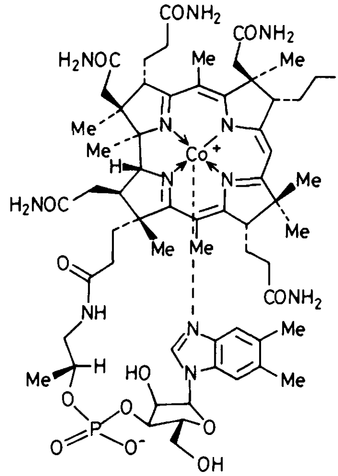


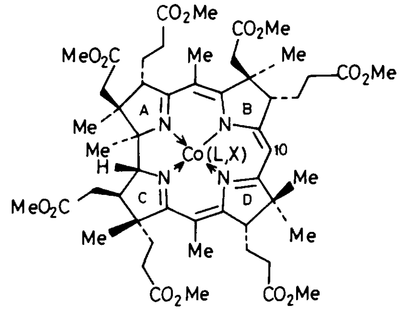
**Figure 1.** Structure of the cobalt(II)cobyrinate (**4**), as determined from the *X*-ray analysis (thermal spheres at 50% probability).

---

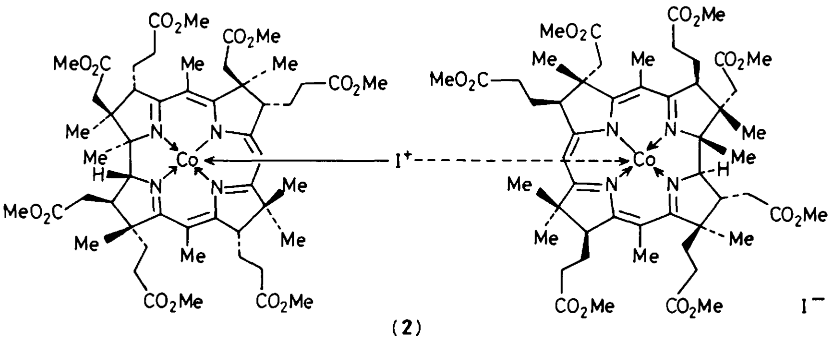
† The reaction mixture[4] was dried at room temperature, taken up in toluene and shaken with 0.1 M aq. $NaClO_4$ under $N_2$. The crude (**4**) was recrystallised from toluene (*ca.* 70% yield). U.v.-visible and c.d. spectra of crystallised (**4**) were similar to ones published previously;[5] the e.s.r. spectrum ($CHCl_3$ : benzene 2 : 1; 77 K) indicated two Co(II) species (*ca.* 9 : 1, possibly co-ordination isomers). In $CDCl_3$ solution (**4**) has $\mu$ = 2.6 B.M. (*ca.* 300K; Evans–Scheffold method[6]). The i.r. spectrum ($CHCl_3$) indicated $ClO_4$ co-ordination (bands at 1050 and 627 $cm^{-1}$).[7]



(1)



(3) Co(L,X) = $Co^{III}(CN)_2$
(4) Co(L,X) = $Co^{II}ClO_4$



(2)

suitable for *X*-ray analysis[‡] were obtained by recrystallising the crude Co(II) cobyrinate (**4**) twice from deaerated solutions in toluene.

In the Co(II) cobyrinate (**4**), the corrin ligand is identical in constitution and configuration with that in the parent cobalt(III) complex (**3**), and also shows a very similar geometry.[8] The cobalt–nitrogen bond lengths in (**4**) [Co–N(21) 1.89, Co–N(22) 1.93, Co–N(23) 1.91, Co–N(24) 1.87 Å (av. 1.90 Å)] are not significantly different from the ones in (**3**) (av. 1.91 Å)[8] [or in (**2**) (1.92), vitamin $B_{12}$ (1.90), or coenzyme $B_{12}$ (1.91 Å)[2]]. The structure of the corrin ligand in (**4**) differs [as does the one in (**3**)] from that of the Co(III) corrin vitamin $B_{12}$, particularly with respect to the 'upward folding' about the Co–C(10) axis (6° in (**4**), 18° in vitamin $B_{12}$)[2b] and in the peripheral torsion angles, *e.g.* of rings B and C (−30.4 and −30.0°, respectively in (**4**), −21 and −26°, respectively in vitamin $B_{12}$[2b]), affecting the orientation of the peripheral substituents.

A perchlorate ligand is directly bound *via* oxygen to a five-co-ordinate Co(II) centre[§] of the Co(II) cobyrinate (**4**) (see Figure 1). The axial Co–O(2) bond in (**4**) (2.31 Å) is considerably longer than the one in aquo-Co(III) corrins (2.06 Å in $Co_\beta$-aquo-$Co_\alpha$-cyanocobyrate[2b]). Co-ordination of the $ClO_4$ group is accompanied by only a 0.048 Å movement of the Co(II) centre out of the best plane through the corrin nitrogen atoms towards the apical ligand [nitrogen root mean square deviation from plane: 0.075 Å (tetrahedral distortion)]. This is less than the out of plane displacement of the five-co-ordinate cobalt centre in (**2**) (0.12 Å)[§][2] or in several Co(II)porphinoids (average displacement 0.14 Å).[9] The Co–O–Cl fragment lies close to the plane through Co and C(10) and vertical to the corrin ligand, but the Co–O bond is tilted from the normal by 9.8° towards C(10). The Co–O–Cl bond angle (133.5°) resembles that in other Co(II) perchlorate complexes.[7] In crystalline (**4**) the perchlorate ligand is bound to the β side of the Co(II) corrin, thus to the face opposite the one to which the nucleotide is presumably bound in cob(II)-alamin (**1**).

The structure of the Co(II) corrin (**4**) differs from that of Co(III) corrins[2b] mainly by a reduction of the co-ordination number at the cobalt centre (from 6 to 5)[§] and by an

---

[‡] *Crystal data* for (**4**): $C_{52}H_{73}N_4O_{18}ClCo$, *M* = 1136.5 space group $P2_12_12_1$, *a* = 13.215(13), *b* = 15.707(14), *c* = 25.484(23) Å, *V* = 5289.7(17) Å$^3$, *Z* = 4, $D_c$ = 1.427 g cm$^{-1}$, *F*(000) = 2404, 3914 unique reflections [2988 with $F > 4\sigma(F)$], *R* = 0.085 ($R_w$ = 0.081) for 608 parameters and 3061 observables; data were collected on a Stoe 4-circle diffractometer ($\lambda$(Mo $K_\alpha$) = 0.71069 Å) at 98 K for all independent reflections with $3° \leqslant 2\theta \leqslant 45°$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] The ester-O(49) of the symmetry equivalent molecule ($\frac{1}{2}$ + x, $\frac{1}{2}$ − y, −z) occupies the sixth co-ordination site with a Co–O distance of 3.56 Å (in crystalline (**2**)[2] an ester methyl group is found at Co–C = 4.12 Å).

elongation of the remaining axial bond. The geometries of the corrin ligand in (**4**) and of its binding of the cobalt centre differ but little, particularly when compared to that in (**3**). The transition from Co(III) to Co(II) corrin (and *vice versa*) thus appears to concern mainly the geometry of the axial ligation, but to have little effect on the residual cobalt–corrin portion. Such a conservation of the geometry of the cobalt–corrin fragment would presumably be a factor in support of particularly low activation barriers in radical bond forming and cleavage reactions at cobalt, relevant to the coenzyme $B_{12}$ biochemistry.[10] The long axial bond in (**4**) points to a structural feature of Co(II) cobyrinates that also might be taken into account when considering the modes of activation[10] in the $B_{12}$-catalysed enzymatic radical reactions.

We thank Prof. A. Eschenmoser for his support, Dr. A. Schweiger (ETH-Zürich) for the e.s.r. measurements, and the Swiss National Science Foundation and Austrian Science Foundation for financial support.

*Received, 18th May 1987; Com. 672*

## References

1 J. R. Pilbrow in '$B_{12}$', ed. D. Dolphin, Wiley, New York 1982, vol. I, p. 431.

2 (a) E. Edmond, D. C. Hodgkin, L. Werthemann, and A. Eschenmoser, unpublished results; (b) J. P. Glusker in '$B_{12}$', ed. D. Dolphin, Wiley, New York, 1982, vol. I, p. 23.

3 L. Werthemann, R. Keese, and A. Eschenmoser, in 'Investigations on Co(II)- and Co(III)-complexes of Cobyrinic acid heptamethylester', L. Werthemann, thesis ETH No. 4097, 1968.

4 B. Kräutler and C. Caderas, *Helv. Chim. Acta*, 1984, **67**, 1891.

5 Y. Murakami, Y. Hisaeda, and A. Kajihara, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3642.

6 (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (b) J. Löliger and R. Scheffold, *J. Chem. Educ.*, 1972, **49**, 646.

7 N. M. N. Gowda, S. B. Naikar, and G. K. N. Reddy, *Adv. Inorg. Chem. Radiochem.*, 1984, **28**, 255.

8 (a) A. Fischli and J. J. Daly, *Helv. Chim. Acta*, 1980, **63**, 1628; (b) K. Kamiya and O. Kennard, *J. Chem. Soc., Perkin Trans. I*, 1982, 2279.

9 W. R. Scheidt, in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, vol. III, p. 463.

10 (a) J. Halpern, *Science*, 1985, **227**, 869; (b) B. T. Golding in '$B_{12}$,' ed. D. Dolphin, Wiley, New York, 1982, vol. I, p. 543.