195. Crystallographic Studies of Synthetic Corrinoids IV. Molecular Structure of a Ni(II)Oxa-porphyrinoid from Electrochemical Oxidation of a Ni(II) Seco-Corrin

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(26. V. 76)

Summary. X-ray analysis of a crystalline product obtained by electrochemical oxidation of the Ni(II)-seco-corrinoid **1** has established the structure as that of a 1,19 oxygen-bridged porphyrinoid **2**. The crystals (perchlorate salt of **2**) are triclinic, space group $P\overline{1}$, with $a = 10.205$, $b = 11.616$, $c = 14.52$ Å, $\alpha = 115.30$, $\beta = 107.34$, $\gamma = 85.90°$, $Z = 2$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares analysis to a final R factor of 9.4%. Some features of the molecular structure are discussed.

Introduction. – Electrochemical oxidation of Ni(II) A/D-seco-corrinoids resulted in the isolation of a Ni-containing crystalline complex which showed spectral similarity to Ni(II) corrin complexes. In this paper we describe the results of an X-ray analysis which establishes the compound as the first representative of a new class of oxygen-containing porphyrinoid molecules with an ether link between rings A and D. The reactions leading to and from this compound turn out to have both mechanistic and synthetic interest; they are reported elsewhere [1].

Crystal Data. – $C_{27}H_{34}N_5O$ Ni·ClO_4, Mol.-Wt. 602.8, triclinic, $a = 10.205$, $b = 11.616$, $c = 14.52$ Å, $\alpha = 115.30$, $\beta = 107.34$, $\gamma = 115.30°$, $V = 1482$ Å^3, space group $P\overline{1}$, $Z = 2$, $D_x = 1.41$, $D_m = 1.48$. The discrepancy between D_x and D_m (measured by flotation in CCl_4/benzene mixture) is accounted for by the presence of about 1.2 molecules of included solvent (methyl acetate, confirmed by NMR. measurements).

Experimental. – Crystals suitable for X-ray studies were obtained by slow vapor-diffusion of methyl acetate into a concentrated methylene chloride solution of the compound in a partly evacuated dessicator. Specimens for X-ray analysis were mounted on glass fibers with araldite epoxy adhesive. Cell dimensions (see crystal data) were measured from 30° precession photographs (Cu*K*α) and refined by least-squares analysis of setting angles for 14 reflections in the range $\theta = 4$–16° (*Hilger-Watts* Y290 diffractometer) using Mo*K*α radiation ($\lambda = 0.71069$ Å) monochromatized by reflection from graphite.

The crystal chosen for data collection was a small parallelepiped of dimensions 0.4 × 0.3 × 0.3 mm, which gave ω-scan widths at half-height of 0.24 and 0.30° for the (030) and (200) reflections respectively. Intensity data were collected out to $\theta = 25°$ (θ–2θ scan mode, 80 steps at 0.01 intervals, each measured for 1 sec., 20 sec. stationary backgrounds at beginning and end of

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each scan). During data collection the intensity of the (030) reflection was monitored after every 25 measurements as a check on crystal and instrumental stability. Less than 2% fluctuation was observed throughout the data collection.

Intensities were corrected for *Lorentz* and polarization effects but not for absorption (μ = 5.8 cm^{-1}). Statistically significant F^2 values ($F^2 > 3\sigma(F^2)$) were obtained for 3066 independent reflections, all of which were used in the final refinement.

Structure Analysis and Refinement. – The structure was solved by routine application of the heavy-atom method. The Ni and Cl atoms were easily located from the three-dimensional *Patterson* function. After three cycles of isotropic least-squares analysis on the Ni and Cl positions, an (F_o-F_c)-synthesis showed a set of 33 peaks in a spatial arrangement that corresponded to a reasonable molecular model, containing a 16-membered inner ring surrounding the Ni atom. The remaining 17 peaks could be identified as those required to complete the four pyrrolidene rings with substituents at positions expected from the structure of the starting material. This results showed that the polarographic reaction had led not to a corrinoid product with rings A and D linked directly, but rather to a porphyrinoid one with a bridging atom between these two rings. The bridging atom was tentatively identified as oxygen (from its peak height), a choice that was confirmed by subsequent interpretation of NMR. spectral data and new chemical evidence.

The oxygen atoms of the perchlorate anion were identifiable in the (F_o-F_c)-synthesis as weak, diffuse, elongated peaks, suggesting that some sort of orientational disorder is present in this crystal, as in many other crystals containing this anion. Since the disorder problem was of secondary interest for our purposes, it was not analysed in any detail. Three cycles of full-matrix least-squares analysis with anisotropic vibration parameters for Ni and the atoms of the ClO_4^- anion, with other atoms isotropic, reduced the R-factor from 14% to 10%. The positional and vibrational parameters of the perchlorate anion were held fixed in all subsequent refinements.

For the final refinements, hydrogen atoms were included in the structure model at fixed positions (calculated by assuming the appropriate tetrahedral or trigonal geometry with C–H bond lengths of 1.0 Å) and with fixed temperature factor (B = 6 $Å^2$), the Ni atom was treated as anisotropic and all other non-hydrogen atoms were isotropic. The function minimized was $\Sigma(\omega|F_o| - |F_c|)^2$ with $\omega = 4\,F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors for neutral Ni, Cl, O, N, and C were taken from *Cromer & Mann* [2], those for neutral hydrogen from *Stewart, Davidson & Simpson* [3]. Corrections for anomalous dispersion effects of Ni and Cl were applied. The final R-factor was 0.094.

A final (F_o-F_c)-synthesis showed no peaks larger than 0.7 e/$Å^3$. Most of the residual density was spread around the inversion center at (1/2, 0, 1/2) and can probably be attributed to included molecules of methylacetate. The distribution and amount of included solvent was not further investigated.

Positional and thermal parameters from the final least-squares analysis are given in Table 1.

Description of Structure and Discussion. – The primary purpose of this work was to establish the nature of the product formed during electrochemical investiga-

Table 1. *Positional*[a]) *parameters*[b]) *with standard deviations*

Anisotropic	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.2308 (2)	−0.2044 (2)	−0.1350 (1)	0.0076 (2)	0.0047 (2)	0.0026 (1)	−0.002 (1)	−0.0009 (1)	0.0011 (1)
Cl	0.1254 (4)	−0.4589 (4)	0.2689 (3)	0.0169 (3)	0.0106 (5)	0.0071 (3)	0.0007 (4)	0.0036 (4)	0.0034 (3)
O(34)[c])	0.1023	0.4752	0.3211	0.0581	0.0215	0.0168	0.0050	0.0187	0.0123
O(35)[c])	0.0680	0.4282	0.1629	0.0371	0.0391	0.0116	−0.0139	−0.0012	0.0102
O(36)[c])	0.0920	−0.3378	0.3141	0.0739	0.0167	0.0335	0.0170	0.0315	0.0115
O(37)[c])	0.2550	−0.4631	0.2621	0.0199	0.0429	0.0281	0	0.0041	0.0185

Isotropic	X	Y	Z	B_{iso}		X	Y	Z	B_{iso}
C(1)	0.3113 (13)	−0.0135 (11)	0.0943 (9)	2.8 (2)	C(17)	0.2196 (15)	−0.3896 (14)	0.0527 (11)	4.2 (3)
C(2)	0.2788 (13)	0.1262 (12)	0.1568 (10)	3.1 (3)	C(18)	0.1278 (15)	−0.2843 (14)	−0.0870 (11)	4.2 (3)
C(3)	0.2703 (14)	0.1841 (12)	0.0785 (10)	3.4 (3)	C(19)	0.1536 (13)	−0.1893 (12)	0.1451 (10)	3.2 (3)
C(4)	0.2274 (12)	0.0694 (11)	−0.0276 (9)	2.5 (2)	N(20)	0.2457 (10)	−0.0380 (9)	−0.0199 (7)	2.4 (2)
C(5)	0.1806 (12)	0.0827 (11)	−0.1232 (9)	2.7 (2)	N(21)	0.2010 (10)	−0.1386 (9)	−0.2364 (8)	2.7 (2)
C(6)	0.1686 (12)	−0.0129 (11)	−0.2192 (10)	2.7 (2)	N(22)	0.2664 (10)	−0.3683 (9)	−0.2300 (8)	2.7 (2)
C(7)	0.1220 (13)	0.0022 (12)	−0.3257 (10)	3.1 (3)	N(23)	0.2123 (10)	−0.2709 (9)	−0.0437 (8)	2.8 (2)
C(8)	0.1646 (15)	−0.1235 (14)	−0.4018 (11)	4.3 (3)	C(24)	0.4650 (14)	−0.0342 (13)	0.1106 (11)	3.7 (3)
C(9)	0.1984 (13)	−0.2074 (12)	−0.3418 (10)	3.1 (3)	C(25)	0.3879 (16)	0.2009 (14)	0.2660 (12)	4.7 (3)
C(10)	0.2255 (13)	−0.3316 (12)	−0.3851 (10)	3.3 (3)	C(26)	0.1359 (15)	0.1295 (14)	0.1766 (11)	4.4 (3)
C(11)	0.2598 (12)	−0.4062 (11)	−0.3345 (9)	2.7 (2)	C(27)	0.0335 (16)	−0.0085 (15)	0.3586 (12)	5.0 (3)
C(12)	0.2970 (13)	0.4574 (12)	−0.3847 (10)	2.2 (3)	C(28)	0.1875 (17)	0.1222 (15)	−0.3170 (13)	5.3 (4)
C(13)	0.3592 (15)	0.4256 (14)	−0.2896 (11)	4.2 (3)	C(29)	0.1637 (17)	0.3717 (15)	−0.4595 (13)	5.4 (4)
C(14)	0.3093 (14)	−0.4661 (12)	−0.1987 (10)	3.2 (3)	C(30)	0.4012 (17)	0.4401 (15)	−0.4476 (13)	5.4 (4)
C(15)	0.3063 (12)	−0.4715 (11)	−0.1105 (9)	2.7 (2)	C(31)	0.3560 (14)	0.4240 (13)	−0.0893 (11)	3.7 (3)
C(16)	0.2481 (13)	−0.3774 (11)	−0.0363 (9)	2.7 (2)	N(32)	0.3968 (14)	0.3392 (13)	−0.0676 (10)	5.4 (3)
					O(33)	0.2608 (8)	−0.0980 (8)	0.1250 (7)	3.4 (2)

[a]) Fractional cell coordinates; atom numbering given in Fig. 1.

[b]) Thermal parameters expressed as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{33}kl)]$.

[c]) Held fixed in final least-squares refinements.

tion of racemic Ni(II)-1-methylidene-2,2,7,7,12,12-hexamethyl-15-cyano-seco-corrin perchlorate (**1**). Our work establishes that this product is not a corrinoid but an oxaporphyrinoid compound, **2**.

Several features of the molecule are apparent in Fig. 1 and 2, particularly the ether bridge between rings A and D and the *trans* relationship between C(24) and the H atom attached to C(19). The four nitrogen atoms are distinctly non-planar; they lie alternately 0.24 Å above and below their mean plane, in which the Ni atom lies

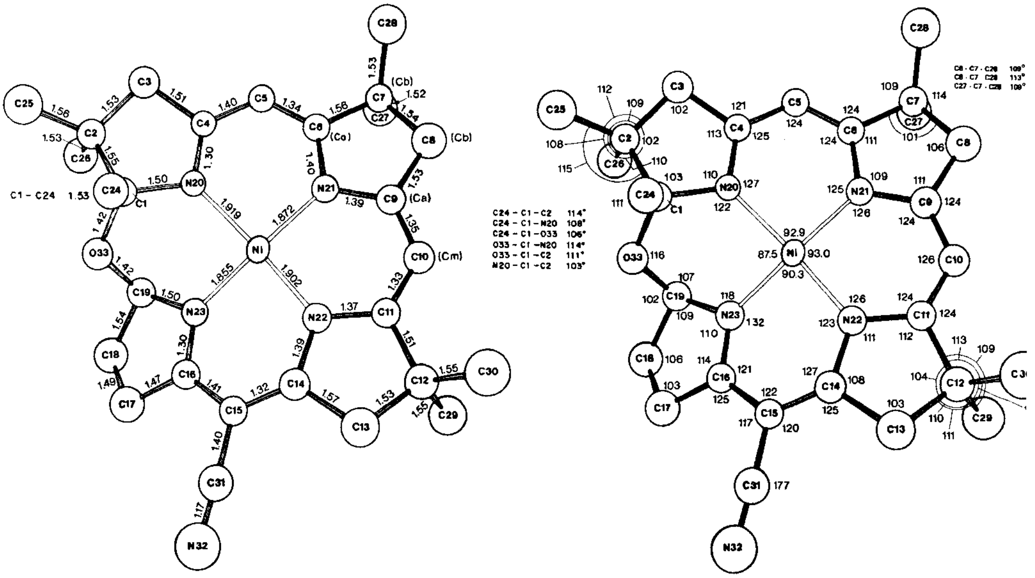


Fig. 1. *Bond distances and angles in **2**, view perpendicular to mean molecular plane*

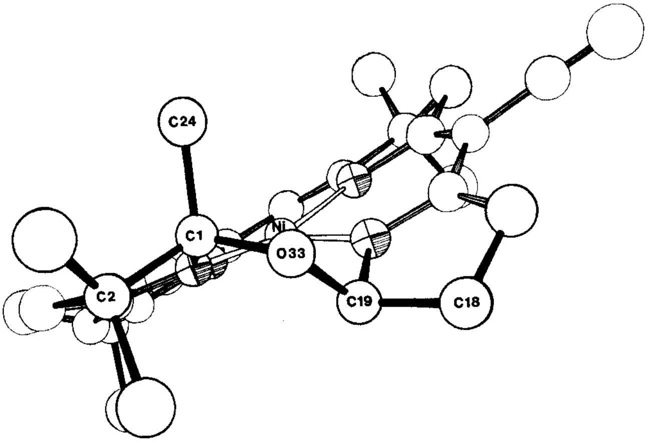


Fig. 2. *View of **2**, parallel to the molecular plane*

exactly, so that the tendency towards tetrahedral coordination is more pronounced than in the Ni(II)-corrin compound **3** (0.12 Å [4]), although less than in the *seco-corrinoid* **1** (0.32 Å [5]).

Table 2. *Average bond distances in Ni(II) porphyrin and oxa-porphyrinoid compound* **2**. The nomenclature is taken over from [6] – see also Fig. 1: C_a and C_b are the α- and β-C atoms of the five-membered rings; C_m is the methine (or oxygen) atom

Bond	**2**	Ni(II)porphyrin [6]
Ni–N	1.887 Å	1.960 Å
$N-C_a$	1.393	1.383
C_a-C_b	1.530	1.447
C_b-C_b	1.523	1.350
C_a-C_m	1.374	1.375

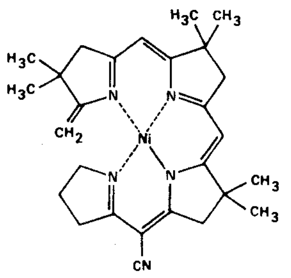
Bond distances and angles calculated from the positional parameters are shown in Fig. 1. Standard deviations estimated from the variance-covariance matrix are about 0.01 Å for the Ni–N distances and about 0.02 Å for those involving C, N, and O. Standard deviations of the bond angles are about 1°.

Table 2 compares averaged distances for the various types of bonds in Ni(II)-porphyrins and in **2**. The N-C(a) and C(a)-C(m) distances [6] are almost the same, and the C(a)–C(b) and C(b)–C(b) distances are, as expected, larger in **2** than in Ni(II)-porphyrin with its unsaturated pyrrole rings. However, the mean Ni–N distance in **2** is 0.07 Å shorter than in the porphyrin. It would be still shorter (by about 0.015 Å) if the N-atoms in **2** were coplanar.

Table 3. *Comparison of torsion angles and bond-angle sums in five-membered rings of* **2** *and the Ni(II)-corrin derivative* **3** [4]

Ring A	**2**	**3**	Ring B	**2**	**3**
N(20)–C(1)	–21°	–20°	N(21)–C(6)	– 8°	5°
C(1)–C(2)	29	29	C(6)–C(7)	13	–13
C(2)–C(3)	–27	–28	C(7)–C(8)	–12	14
C(3)–C(4)	16	18	C(8)–C(9)	9	–12
C(4)–N(20)	3	1	C(9)–N(21)	– 1	5
Sum of bond angles	530.9°	530.7°	Sum of bond angles	538.2°	537.5°
Ring C	**2**	**3**	Ring D	**2**	**3**
N(22)–C(11)	– 2°	– 3°	N(23)–C(16)	– 1°	– 1°
C(11)–C(12)	12	12	C(16)–C(17)	–13	17
C(12)–C(13)	–17	–15	C(17)–C(18)	21	–25
C(13)–C(14)	17	14	C(18)–C(19)	–22	25
C(14)–N(22)	–10	– 8	C(19)–N(23)	14	–16
Sum of bond angles	536.8°	537.6°	Sum of bond angles	535.0°	533.2°

The shortening of the Ni–N bonds in **2** seems to be due mainly to angle changes in the inner 16-membered ring. These changes are associated with replacements of two trigonal C-atoms by the tetrahedral atoms C(1) and C(19), and of a methine C-atom by the oxygen atom O(33). Replacements of the trigonal C_b-atoms of the porphyrin by tetrahedral atoms not only increases the C_b-C_b and C_a-C_b bond dis-



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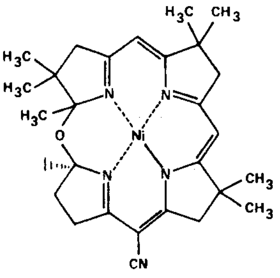

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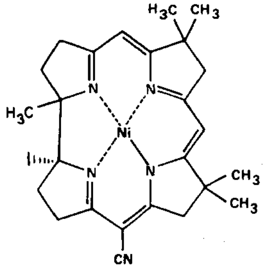

3

tances, it also reduces the mean bond angles at C_b and hence increases the bond angles at the N atoms, or leads to a greater puckering of the five-membered rings, or both. The correlations noted by *Hoard* [6] give some idea of how these bond length and bond angle changes might influence the Ni–N distances. The decrease in C_a–C_b–C_a (from 123.7° to 119.8°) and in C_a–C_m–C_a (from 123.9° to 122.0°) would appear to favor shortening, the increase in C_a–N–C_a (from 104.4° to 108°) to disfavor it. Detailed force-field calculations would be required to obtain more insight into the problem.

The mean Ni–N distance in **2** is about 0.02 Å longer than in the Ni(II)-corrin compound **3**.

The most striking feature of the torsion angles in the outer perimeter (Fig. 3) is the large deviation of C(19)–O(33)–C(1)–C(2) from a value round 180° to 114°.

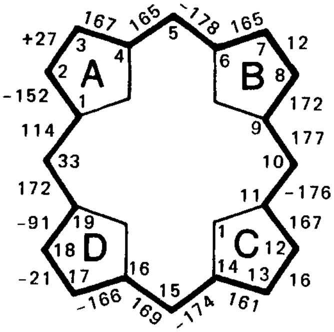

Fig. 3. *Torsion angles in outer ring of* **2**

This causes C(19) and the adjacent β-carbon to be displaced from the mean molecular plane, as is evident from Fig. 2. If both C–C–O–C bonds were antiplanar, there would be an unfavorable 'gauche' interaction [7] between C(1)–C(24) and C(19)–N(23).

Some details about the conformations of the five-membered rings are given in Table 3. The values of $\Sigma\omega_i^2$ and of $540°-\Sigma\theta_i$ are both measures of the non-planarity of the rings [8]. Ring A, which deviates most from planarity, is in the envelope conformation, with C(2) as flap, the same as in the Ni(II)-corrin compound **3**, various A/D-seco-corrinoid compounds, and others in the natural vitamin-B_{12} series. Rings B and C are much flatter and their conformations vary from compound to compound. Ring D adopts the envelope conformation with C(18) as flap, but the torsion angles show that the conformation occurring in **2** is enantiomorphic to that occurring in corrin compounds. Presumably it is the angular methyl group on C(1) that is responsible for the invariant conformation of ring A, but no force-field calculations have been carried out so far to test this suggestion.

One of us (*K.H.*) acknowledges the award of a *NATO*-Postdoctoral Fellowship for the academic year 1972–1973. This work was carried out with the financial support of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.*

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196. A Specific Synthesis of Ethyl (2Z)-2-Bromomethyl-2-butenoate and its Conversion into Mikanecic Ester[1]

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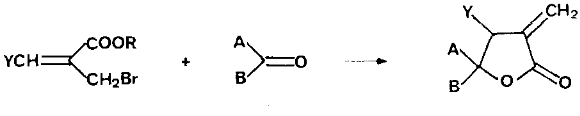
(28. IV. 76)

Eine spezifische Synthese von (2Z)-2-Brommethyl-2-butensäure-äthylester und seine Umwandlung in Mikanezester[1]). – *Zusammenfassung.* Das Lithiumsalz **12**, hergestellt aus 2-Bromorthopropensäure-triäthylester (**11**) und *n*-Butyl-lithium, wurde mit Acetaldehyd umgesetzt, wobei 2-Methyliden-3-hydroxy-orthobutansäure-triäthylester (**13**) und daraus, durch saure Hydrolyse, 2-Methyliden-3-hydroxybutansäure-äthylester (**14**) entstand. Behandlung von **14** mit *N*-Bromsuccinimid und Dimethylsulfid lieferte den gewünschten (2*Z*)-2-Brommethyl-2-butensäure-äthylester (**6**), der sich mit HBr zur entsprechenden Säure **4** hydrolysieren liess.

Die (2*Z*)-Konfiguration von **4** wurde aufgrund der *vicinalen* $^1H/^{13}C$ Kopplungen zwischen *H*–C(3) und *C*OOH bzw. *C*H$_2$Br im ^{13}C-NMR.-Spektrum bestätigt. Die ^1H-NMR.-Signale der beiden Methylidenprotonen in **9**, **11**, **13** und **14** liessen sich mit Hilfe von additiven Entschirmungsbeiträgen der Substituenten um die Doppelbindung zuordnen.

1,4-Eliminierung von HBr aus (2*Z*)-2-Brommethyl-2-butensäure-äthylester (**6**) mit Kalium-*t*-butylat ergab Mikanezsäure-diäthylester (**21**), der bei der Aufarbeitung teilweise zum Monoester **20** und zur Mikanezsäure[1]) (**19**) verseift wurde.

1. Introduction. – Some years ago it was discovered [1] that β-bromoesters of type **1** react readily with carbonyl compounds **2** under *Reformatsky* conditions to give α-methylidene-γ-butyrolactones (**3**). The reaction was found with methyl (2*Z*)-



1 **2** **3**

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[1] The systematic name for mikanecic acid (**19**) is 4-vinyl-1-cyclohexene-1,4-dicarboxylic acid.
[2] Postdoctoral Fellow, 1974–1976.