8. Crystallographic Studies of Synthetic Corrinoids. II. Molecular Structure of a C/D-seco-corrinoid nickel(II) complex

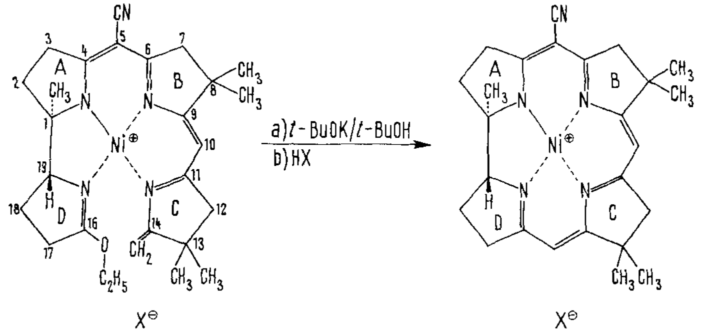
by **M. Dobler** and **J. D. Dunitz**

Laboratorium für organische Chemie der Eidg. Technischen Hochschule, 8006 Zürich

(19. XI. 70)

Summary. An X-ray crystal structure analysis of the perchlorate salt of the C/D-seco-corrinoid nickel(II) complex I is reported. The structural transformations that occur in the base-catalysed iminoester-enamine condensation of I leading to the corrin complex II are discussed.

The final step in the synthesis of corrin complexes is a cyclization, the success of which is believed to depend on the rôle of a metal atom within a pre-corrinoid complex in bringing about mutual proximity of the relevant condensation centres. In the synthesis of the nickel corrin complex II, whose structure is described in the preceeding paper [1], this final step is the base-catalysed iminoester-enamine condensation of the C/D-seco-corrinoid complex I [2]. The crystallinity of this complex offered the rare opportunity to study the detailed topographical relationship between its reacting centres, and thus, together with the results of the preceeding analysis, to delineate the structural transformations involved in the final synthetic step, presumed to occur under template control. The present paper describes the results of an X-ray analysis of the seco-corrinoid complex I ($X^- = ClO_4^-$). The work was carried out in 1965–66 and a preliminary account published at that time [3].



I II

Crystallographic Data[1]. – The seco-corrinoid complex I ($X^- = ClO_4^-$), $C_{27}H_{56}ClN_5O_5Ni$, molecular weight 605, yields several polymorphic crystal modifications, obtained under various conditions.

a) Crystallized from ethanol – ethyl acetate solution: monoclinic, $a = 12.93$, $b = 32.40$, $c = 6.94$ Å, $\beta = 95°7'$, $V = 2899$ Å^3, $D_x = 1.38$ (assuming $Z = 4$), $D_m = 1.44$; space group $P2_1/a$ (2nd setting). The crystals were usually twinned.

---

[1] Much of the data given in this section are based on preliminary examinations of the crystals carried out by Dr. *E.F. Meyer* and Mr. *B.G. Dürr*.

b) Crystallized from methanol – ethyl acetate solution: triclinic, $a = 14.47$, $b = 15.76$, $c = 6.57$ Å, $\alpha = 97°36'$, $\beta = 92°56'$, $\gamma = 95°07'$, $V = 1477$ Å^3, $D_x = 1.36$ (assuming $Z = 2$), $D_m = 1.39$; space group $P\bar{1}$ (assumed from racemic nature of synthetic product).

c) Crystallized from methanol – ethyl acetate solution: monoclinic, $a = 9.94$, $b = 21.12$, $c = 14.9$ Å, $\beta = 92°55'$, $V = 3039$ Å^3, $D_x = 1.32$ (assuming $Z = 4$), $D_m = 1.35$; space group $P2_1/n$ (2nd setting).

d) Crystallized from methanol – ethyl acetate solution: monoclinic, $a = 11.62$, $b = 24.40$, $c = 10.50$, $\gamma = 90°10'$, $V = 2960$ Å^3, $D_x = 1.35$ (assuming $Z = 4$), $D_m = 1.36$, space group $P2_1/b$ (1st setting).

The modification d), which occurs as well-formed crystals, was chosen for the more detailed analysis described below. Crystals of the other three modifications are inferior to those of d), and the discrepancies between D_x and D_m suggest that they probably contain solvent of crystallization.

Cell dimensions are based on measurements on 30°-precession photographs and should be accurate to within about 0.2%.

Intensity Measurements. – The layers $hk0$–$hk11$ were measured out to a limit of $\sin\theta = 0.42$ from a crystal of dimensions $0.2 \times 0.4 \times 0.56$ mm mounted on the *Arndt-Phillips* linear diffractometer [4] in its commercially available version with Mo$K\alpha$ radiation and Sr/Zr balanced filters. About 5400 independent reflexions were measured, but the subsequent analysis was based exclusively on the 1329 reflexions with net intensity greater than four times the standard deviation of the measurement. The intensities were corrected for *Lorentz*-polarization effects, but not for absorption, to give the relative F^2-values.

Structure Analysis and Refinement. – The structure was solved by the heavy-atom method in a fairly straightforward manner, except for certain complications connected with problems of disorder in the O atoms of the perchlorate anion and the terminal atom C(33) of the ethoxy group. The other non-hydrogen atoms were clearly recognizable in the first *Fourier* synthesis, calculated with the signs of Ni-contributions alone, and their positional and vibrational parameters could be refined to reasonable values without serious difficulties, first by improved *Fourier* syntheses and later by several cycles of full-matrix least-squares analysis. In contrast, the O atoms of the ClO_4^- anion and C(33) were represented in the *Fourier* syntheses by weak, diffuse electron-density peaks, and the isotropic vibrational parameters of these atoms, after three least-squares cycles, were far larger than those of the other non-hydrogen atoms ($B = 16$–26 Å^2, compared with $B = 4$–11 Å^2).

Fig. 1 shows the electron-density distribution over a spherical surface at 1.5 Å distance from the Cl atom. The *Fourier* synthesis from which this distribution was taken was based on a phasing model from which the perchlorate O atoms had been omitted, so that the distribution is not biased in favour of any particular orientation of the perchlorate anion. There are five diffuse maxima of height 1.5–2 e/Å^3, and it is obviously difficult to reconcile the observed distribution with any simple superposition of tetrahedra in different orientations. Since it was clear that some sort of orientational disorder of the perchlorate group is present, and since the exact nature of this disorder is in any case irrelevant to the main problem, the five maxima were included in the structural model as oxygen atoms, each with weight 0.8 and isotropic vibrational parameter $B = 15$ Å^2, and not further refined.

A tentative position for C(33) was found already from the first *Fourier* synthesis (based only on the Ni atom as phasing model) as a weak, ill-defined electron-density maximum of height approximately 1 e/Å^3. This maximum persisted in the subsequent syntheses, but without any substantial improvement in definition. Inclusion of the

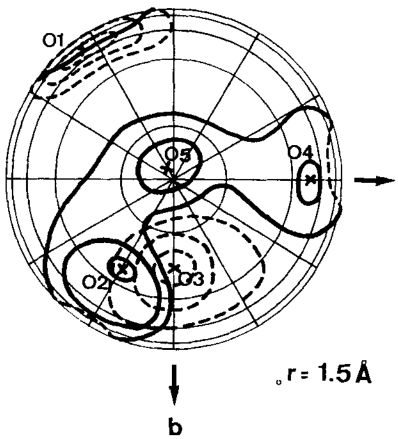


Fig. 1. *Perchlorate anion*

Electron density distribution over a spherical surface at 1.5 Å distance from the Cl atom. Contours are drawn at 0.5 e/Å^3 intervals, starting at 1 e/Å^3

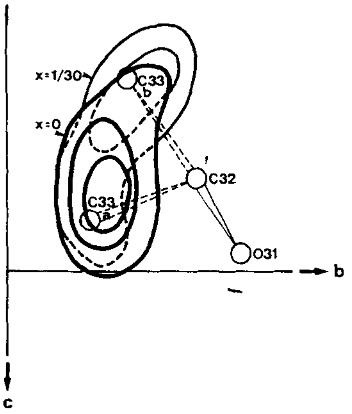


Fig. 2. *Ethoxy group at ring D, difference synthesis*

C(33)a and C(33)b show extreme positions of C(33) assumed for Fig. 4. Contours are drawn at 0.25 e/Å^3 intervals, starting at 0.5 e/Å^3

atom in the least-squares model led to an isotropic vibrational parameter B = 25–30 Å^2, and anisotropic refinement yielded B values along the principal axes of the vibrational ellipsoid of 4,8 and 98 Å^2, with the high value roughly parallel to the c-axis of the crystal. Fig. 2 shows the electron-density distribution around C(33) as seen in a difference synthesis based on a phasing model from which the atom was omitted. The atom is seen as a long, narrow, curved electron-density ridge extending over a distance of about 3 Å. The distribution is close to that expected from a model in which the bond C(32)–C(33) is allowed to rotate between two extreme positions approximately 120° apart about the axis O(31)–C(32), one position corresponding to an antiplanar, the other to a syn-clinal partial conformation [5] about the O(31)–C(32) bond. For simplicity, C(33) was included in the final model as one atom approximately in the centre of the electron-density distribution with a highly anisotropic temperature factor.

The final structure-factor calculation, based on anisotropic vibrational parameters for the Ni, Cl and C(33) atoms, isotropic vibrational parameters for all others, gave an R-factor of 0.104. This could doubtless be reduced in a number of ways, *e.g.* by inclusion of hydrogen atoms (there are 36 per molecule) in the structure model and by introducing anisotropic vibrational parameters for other atoms besides Ni and Cl. However, the marginal improvement in accuracy that could be achieved would hardly justify the additional labour and computation time involved.

Final parameters (and standard deviations, where applicable, as calculated by inversion of the least-squares normal equations matrix) are given in Tables 1, 2 and 3. Bond distances and angles are shown in Fig. 3. Typical standard deviations are 0.017 Å for Ni-N bonds, 0.025–0.035 Å for bonds within the ligand, 0.04 Å for bonds to methyl

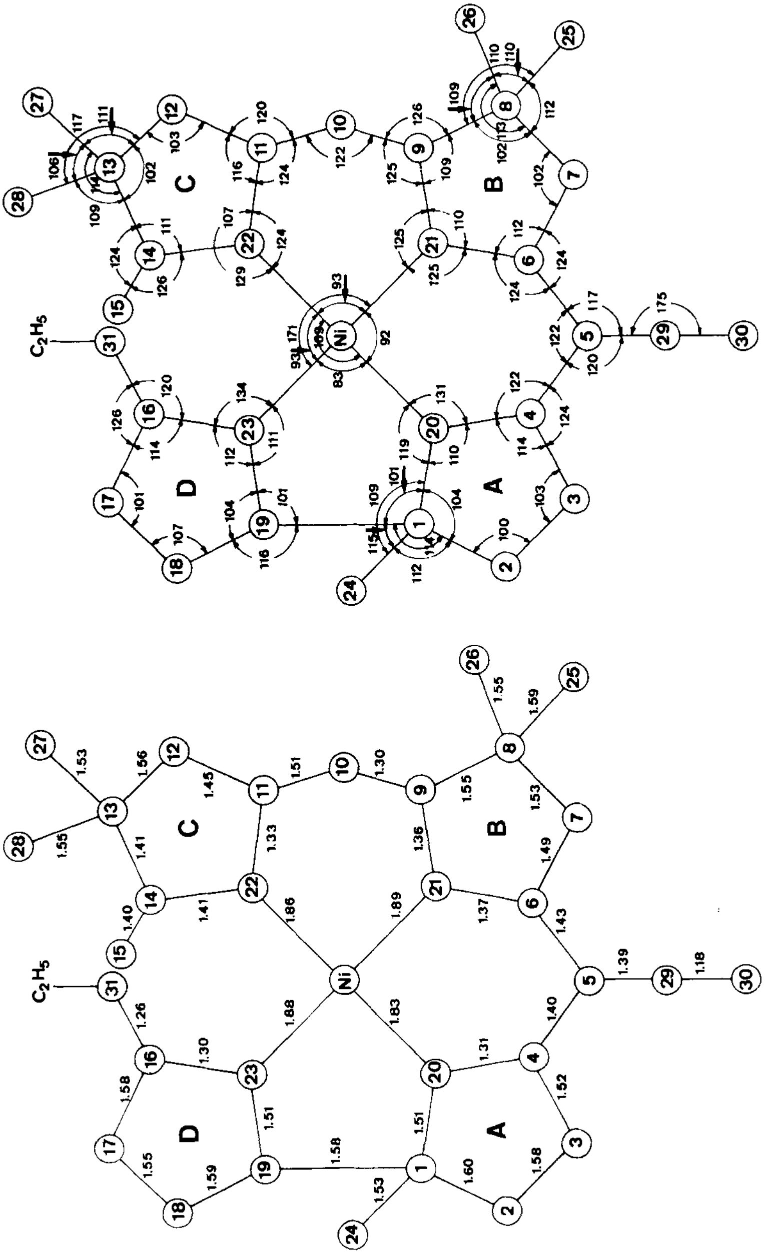


Fig. 3. Bond distances and angles

substituents, and 2–$2^{1}/_{2}$° for bond angles. The twelve C–C bonds between tetrahedral C atoms range from 1.53 Å to 1.60 Å, mean value 1.55 Å, r.m.s. deviation 0.03 Å. A list of observed and calculated F-values may be obtained on request from the authors.

Table 1. *Coordinates of atoms after refinement* ($\times 10^4$)
(estimated standard deviations $\times 10^4$)

	x	y	z	B (Å^2)
Ni	3707 (2)	1463 (1)	917 (3)	
Cl	2641 (7)	3795 (3)	1710 (9)	
C(1)	3991 (20)	2248 (10)	–1109 (23)	5.03
C(2)	4853 (26)	2760 (13)	–1278 (29)	8.04
C(3)	6042 (21)	2477 (10)	–994 (26)	5.90
C(4)	5695 (21)	2001 (10)	–138 (22)	4.71
C(5)	6470 (20)	1693 (10)	583 (20)	4.44
C(6)	6122 (18)	1220 (9)	1292 (19)	3.92
C(7)	6930 (22)	833 (11)	1914 (23)	5.71
C(8)	6165 (21)	328 (10)	2133 (22)	5.12
C(9)	4946 (18)	578 (9)	2104 (18)	3.21
C(10)	4020 (18)	354 (9)	2573 (20)	3.91
C(11)	2915 (17)	673 (8)	2700 (18)	3.08
C(12)	2005 (24)	477 (11)	3542 (26)	6.35
C(13)	1197 (20)	979 (10)	3661 (21)	4.46
C(14)	1806 (20)	1399 (10)	2788 (21)	4.35
C(15)	1487 (23)	1950 (11)	2703 (25)	6.13
C(16)	1546 (22)	1651 (11)	–461 (22)	4.92
C(17)	1011 (24)	2077 (12)	–1428 (26)	6.39
C(18)	1792 (25)	2587 (12)	–1198 (27)	6.89
C(19)	2849 (23)	2385 (11)	–358 (25)	5.91
N(20)	4589 (15)	1884 (7)	–161 (15)	3.76
N(21)	5001 (14)	1069 (7)	1498 (15)	3.45
N(22)	2751 (14)	1159 (7)	2167 (15)	3.50
N(23)	2487 (16)	1821 (7)	91 (17)	4.22
C(24)	3812 (22)	1932 (11)	–2360 (24)	5.66
C(25)	6400 (24)	48 (11)	3481 (27)	6.68
C(26)	6253 (24)	–103 (12)	1048 (28)	7.00
C(27)	–28 (31)	829 (14)	3227 (32)	9.37
C(28)	1070 (34)	1233 (17)	5010 (38)	10.98
C(29)	7643 (26)	1815 (11)	546 (25)	6.01
N(30)	8622 (24)	1950 (11)	594 (24)	8.55
O(31)	1160 (15)	1176 (7)	–244 (16)	5.99
C(32)	65 (28)	983 (15)	–973 (32)	8.49
C(33)	266	567	–1506	

Table 2. *Coordinations for O atoms in disordered ClO_4^- ion model used in structure-factor calculations* ($\times 10^3$)
(weight = 0.8; isotropic B = 15 Å^2)

	x	y	z
O(1)	201	331	196
O(2)	210	415	97
O(3)	269	415	294
O(4)	372	379	128
O(5)	267	372	14

Table 3. *Anisotropic temperature factors* ($\times 10^4$)
$T = \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	49	12	97	15	–6	8
Cl	162	23	273	7	81	39
C(33)	531	82	1504	312	–1398	–622

Discussion. – In view of the rather large uncertainties associated with some of the atomic positions (see Table 1) any detailed discussion of individual bond lengths and angles obtained in this analysis would be unwarranted. The most that can be said is that the Ni-N distances are quite similar to those observed in the cyclic complex [1] and that the overall distribution of long and short bonds in the seco-corrinoid ligand is in reasonable accord with expectations based on the formula I, allowing for some delocalization in the π-electron system.

It is more interesting to try to follow the structural transformations that occur in the cyclization step. Fig. 4 shows the structures of the seco-corrinoid educt I and of the corrinoid product II, as seen parallel and perpendicular to the mean plane through the 4 central N-atoms in each case. Fig. 4 shows that the cyclization has been effected with a minimum of structural reorganization. In particular, the condensation centres C(15) and C(16) are already in close proximity in the educt. However, there are also several structural differences connected with the change in the distance between C(15) and C(16), from a non-bonded distance of about 3.4 Å in the educt, to a bonded distance of about 1.4 Å in the product. It is cumbersome to describe all these changes in words, but most of them, including differences in the conformations and orientations of the 5-membered rings and their substituents, can be recognized in Fig. 4 and 5 and followed, if desired, with the help of a model.

In both educt and product, there is a marked distortion of the planar coordination of the 4 central N atoms about the Ni atom. In both cases the distortion is in the direction of tetrahedral coordination and has the same magnitude (Table 4). However the sense of chirality of the tetrahedron is reversed on passing from educt to product. In the educt the deviation of N(20) from the mean plane is in the opposite sense to the direction of the bond C(1)–C(24), whereas in the cyclic product the deviation is in the same sense. It is also worth noting that in the seco-corrinoid educt, ring D has to be turned strongly out of the mean molecular plane in order to prevent the atoms of the exocylic ethoxy substituent on C(16) from making intolerably close contacts with the methylidene substituent (C(15)) on ring C. As a result the Ni atom no longer lies even approximately in the plane defined by C(19), N(23), C(16)—it deviates from it by 0.50 Å, compared with the much smaller deviation of 0.06 Å in the corrinoid product. The deviation of the Ni atom from the plane defined by C(1), N(20), C(4) (Ring A) is also considerable—0.28 Å; it is much smaller (0.11–0.22 Å) for the corresponding planes of rings B and C.

The relationship between the two condensation centres C(15) and C(16) in the educt is shown in Fig. 6, where the arrows define the directions normal to the planes C(13)–C(14)–C(15) and N(23)–C(16)–C(17), *i.e.* the directions of extension of the *p*-orbitals formally attached to C(15) and C(16). It is seen that not only are these two

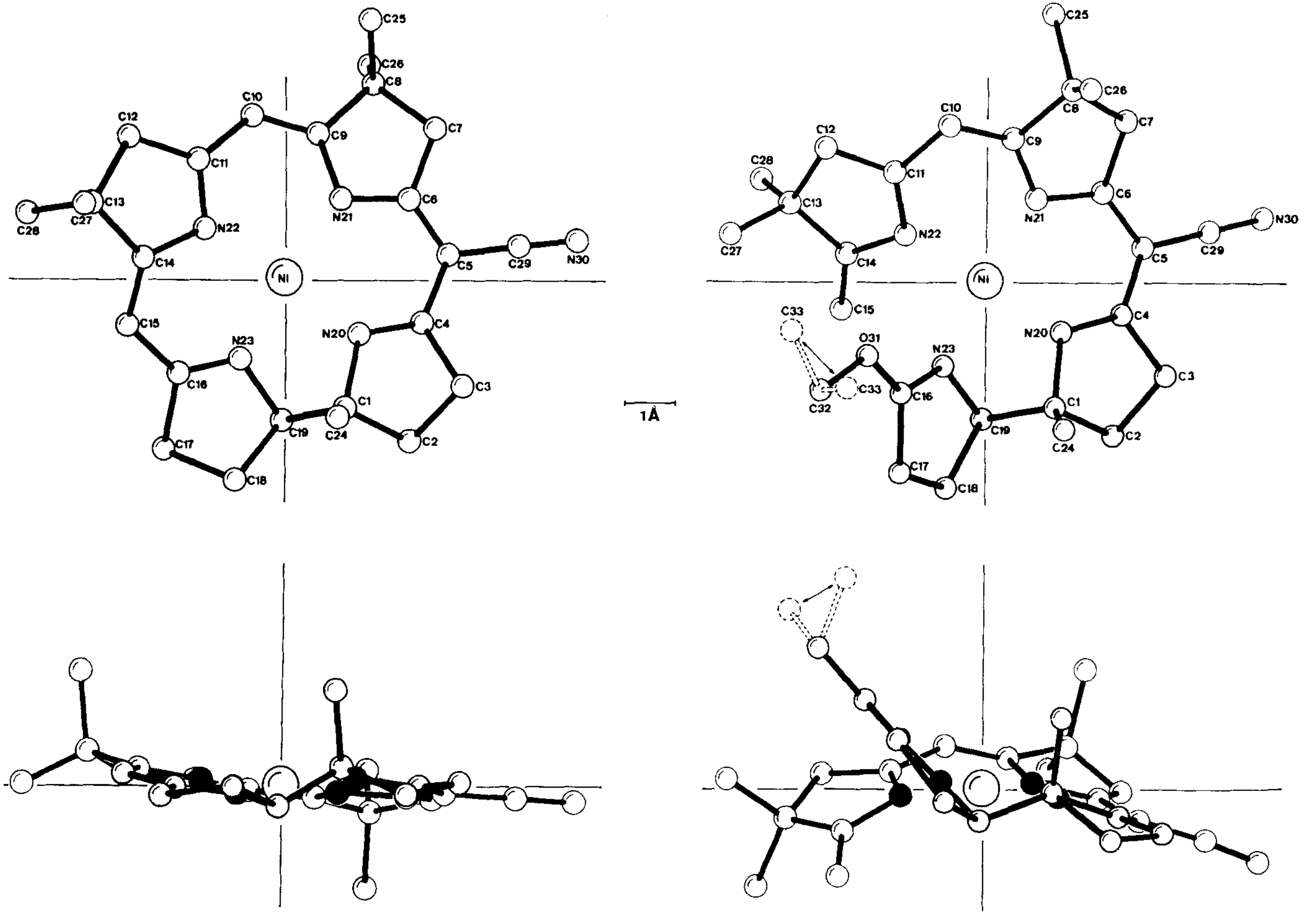


Fig. 4. *Structures of the seco-corrinoid educt (right) and the corrinoid product (left) as seen parallel and perpendicular to the mean plane through the 4 central N atoms*

atoms in contact (distance ~ 3.4 Å), but also that the geometric relationships are such that a good overlap of these two *p*-orbitals is achieved. The stereoelectronic requirements for cyclization would therefore seem to be almost ideal in the seco-

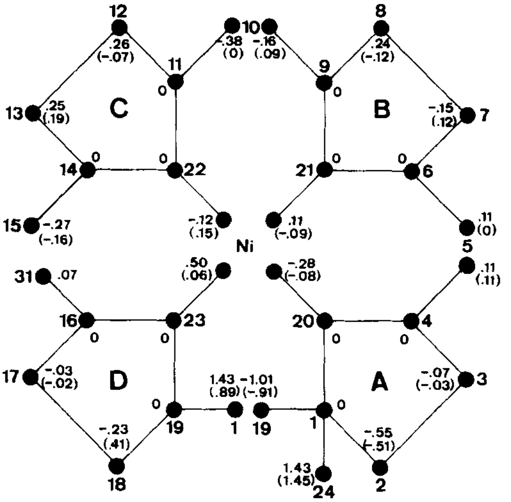


Fig. 5. *Conformation of five-membered rings. Deviations of atoms (in Å) from the plane through N and its two neighbouring C atoms*

Numbers in brackets are values in the corrinoid product

Table 4. *Deviations from mean plane of the 4 central N atoms; Ni...N distances*

	seco-corrinoid educt deviation in Å	Ni...N (Å)	corrinoid product deviation in Å	Ni...N (Å)
Ni	0.02		0.01	
N(20)	–0.14	1.83	0.14	1.85
N(21)	0.13	1.89	–0.12	1.91
N(22)	–0.13	1.86	0.12	1.88
N(23)	0.14	1.88	–0.14	1.85

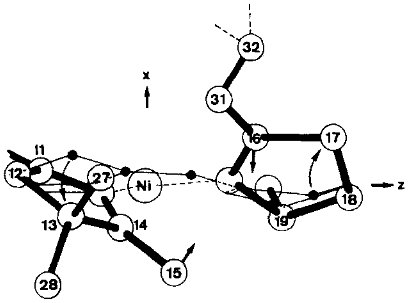


Fig. 6. *Relationship between the condensation centres C(15) and C(16)*

The positions of atoms C(13), C(14), C(15), C(16) and C(17) after cyclization are indicated by black circles. Arrows at C(15) and C(16) define the directions of extension of the *p*-orbitals associated with these atoms. Distance between C(15) and C(16) is 3.4 Å corrinoid educt. The observation–surprising at the time–that this complex is thermally stable, and the subsequent finding that cyclization requires prior base-induced deprotonation of a peripheral methylene group, can therefore not be ascribed to stereoelectric factors in the seco-corrinoid educt. The structural results would seem to provide strong support for the alternative hypothesis–that the main function of the base is to increase the nucleophilicity of the exocyclic methylidene carbon C(15).

BIBLIOGRAPHY

[1] *J.D.Dunitz & E.F.Meyer Jr.*, Helv. *54*, 77 (1971).
[2] *E.Bertele, H.Boos, J.D.Dunitz, F.Elsinger, A.Eschenmoser, I.Felner, H.P.Gribi, H.Gschwend, E.F.Meyer, M.Pesaro & R.Scheffold*, Angew. Chem. *76*, 393; Angew. Chem. Internat. Ed. *3*, 490 (1964).
[3] *M.Dobler & J.D.Dunitz*, Acta crystallogr. *21*, A 110 (1966).
[4] *U.W.Arndt & D.C.Phillips*, Acta crystallogr. *14*, 807 (1961).
[5] *W.Klyne & V.Prelog*, Experientia *16*, 581 (1960).

9. Crystallographic Studies of Synthetic Corrinoids.

III. Structural similarities and differences between A/D-seco-corrinoid complexes of divalent nickel, palladium and platinum

by **Murdoch Currie**[1]) and **J. D. Dunitz**

Laboratorium für organische Chemie der Eidg. Technischen Hochschule, 8006 Zürich

(19. XI. 70)

Summary. X-ray crystal structure investigations of the isomorphous perchlorate salts of complexes of an A/D-seco-corrinoid ligand (I) with divalent nickel, palladium and platinum are reported. The structures determined for the Pd- and Pt-complexes are virtually superposable, that of the Ni-complex, although similar to the other two, shows significant differences with respect to metal coordination and to the spatial relationship of the A and D rings and their substituents. These similarities and differences are discussed in relation to the photochemical A/D cyclization leading to corrin complexes (II).

The synthesis of corrin compounds (II) by A/D ring closure of seco-corrins (I) devised, accomplished and investigated by *Eschenmoser* and co-workers [1] has led to a number of unexpected results concerning the rôle of the central metal atom. Initially, this rôle was presumed to be limited to imposing the necessary geometric restrictions on the seco-corrinoid ligand. If the ligand could be made to form a coil in which one of the hydrogen atoms of the α-methylene group of ring D was exactly above or below the exocyclic double bond and in reasonable proximity to it, then the geometric conditions for an antarafacial 1,16-hydrogen shift would be approximately fulfilled. From orbital-symmetry considerations, such a shift should be forbidden

---

[1]) Present address: Chemistry Department, University of Glasgow, Glasgow W. 2, Scotland.