7. Crystallographic Studies of Synthetic Corrinoids. I. Nickel(II)-1, 8, 8, 13, 13-pentamethyl-5-cyano-*trans*-corrin chloride

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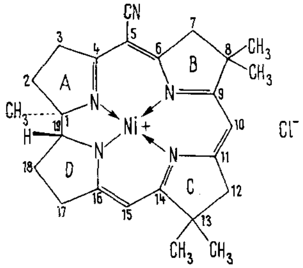
Summary. The crystal and molecular structure of nickel(II)-1,8,8,13,13-pentamethyl-5-cyano-*trans*-corrin chloride has been determined by X-ray analysis. The shape and dimensions of the corrin nucleus are discussed in some detail.

This series of papers describes the results of crystallographic studies on a number of synthetic corrinoid compounds prepared in Zurich during the last few years [1]. The first paper in the series deals with nickel(II)-1,8,8,13,13-pentamethyl-5-cyano-*trans*-corrin chloride (numbering system shown below), the first synthetic corrin complex, prepared in 1964 [2]. The X-ray analysis of this compound was carried out in 1964–65, and preliminary accounts have already appeared [2] [3].



The crystallographic study was carried out, in the first place, to confirm that the synthesis had indeed led to the desired product. But it was also clear that the availability of synthetic, racemic corrin compounds offered the opportunity to establish the topography of the corrin system with better accuracy than could be achieved with the optically active compounds of the naturally occurring series. For an optically active crystal, necessarily lacking crystallographic inversion centres, the phase angles associated with the measured structure amplitudes may have any values; for a centrosymmetric crystal, the phase angles are restricted to the values 0 or π, so that the correct values, and not merely approximately correct ones, can be assigned on the basis of an approximately correct trial structure. This leads to a substantial improvement in the accuracy with which the structural parameters can be measured, assuming the quality of the experimental data to be about the same in both cases, and hence to greater confidence in the conclusions that can be drawn concerning the molecular structure [4].

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Crystallographic data. – Well developed, triclinic prisms (Fig. 1) of the compound, obtained by slow cooling of aqueous methanol – methyl acetate solutions, were kindly supplied by Dr. *E. Bertele*. The air-dried crystals have cell dimensions: $a = 11.10$ Å, $b = 12.31$ Å, $c = 10.69$ Å, $\alpha = 103°53'$, $\beta = 95°59'$, $\gamma = 77°55'$, $V = 1383$ Å^3. Space group (assumed), $P\bar{1}$.

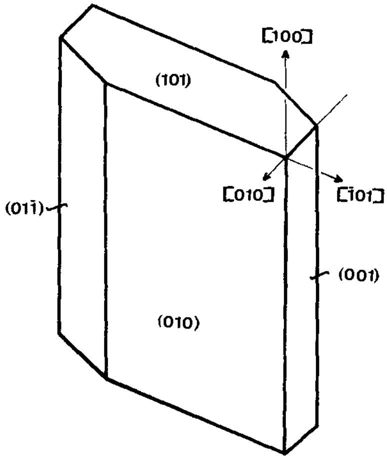


Fig. 1. *Typical habit of crystals investigated*

The observed density, measured by flotation in a benzene + carbon tetrachloride system, lay between 1.360 and 1.372 g cm^{-3} with a mean value of 1.364 g cm^{-3}, leading to a molecular weight of 1136 for the unit-cell contents. The difference of 147 between this value and that calculated for two molecules of $C_{25}H_{30}ClN_5Ni$ (M.W. = 494.7) suggests that the crystals are solvated. NMR. spectra of crystals dissolved in $CDCl_3$ indicated the presence of 1–2 mols of methanol (per $C_{25}H_{30}ClN_5Ni$ unit) and of a smaller, variable amount of water. It was only in the latter stages of the X-ray analysis that several maxima attributable to occluded solvent could be recognized in the electron-density distributions. The analysis showed that the solvent molecules must be disordered and that they are probably present in non-stoichiometric amounts. Nevertheless, the solvent-containing crystals appear to be quite stable and can be kept in an open atmosphere for several months without any appreciable change in their outer appearance or X-ray diffraction pattern.

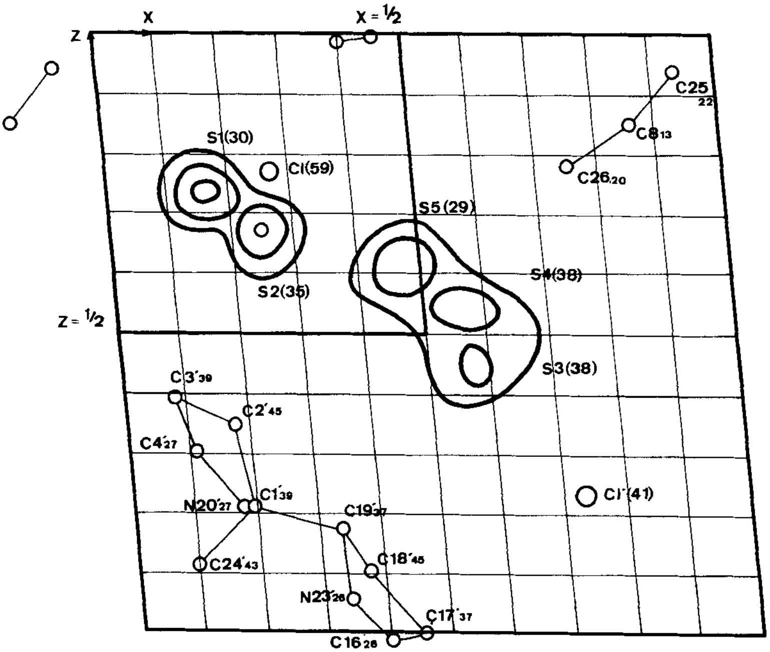
The cell dimensions were estimated from 30°-precession photographs (Cu$K\alpha$- and Mo$K\alpha$-radiation) and should be accurate to within about 0.02–0.03 Å in lengths and 10–15' in angles.

Intensity Measurements. – The layers $0kl$–$9kl$ were measured from a needle-shaped crystal elongated along the a-axis (dimensions $0.4 \times 0.11 \times 0.13$ mm^3) with the *Arndt-Phillips* linear diffractometer [5] in its commercially available version. With the use of Mo$K\alpha$ radiation with Sr/Zr balanced filters, intensities of about 2900 independent reflexions were measured with a scintillation counter. The analysis was based mainly on the 1956 reflexions with net intensity, after correction for background scattering, at least 4 times greater than the corresponding standard deviation. Absorption corrections were not applied.

Structure Analysis and Refinement. – The structure analysis, up to the establishment of the overall geometry of the *trans*-corrin nucleus with all its substituents, followed a fairly direct course [3]. The subsequent course of the refinement was not so straightforward, partly because it was dependent on the parallel development of the necessary computer programmes, and partly because of the problem of locating and identifying the atoms of the solvent molecules.

Our least-squares refinements were carried out with a version of the full-matrix programme of *Gantzel, Sparks & Trueblood* [6], modified by one of us (*E.F.M.*) for use on the CDC-1604 computer of the E.T.H. This version allowed simultaneous fitting of 180 parameters to 2000 observed F-values, permitting refinement of up to 44 atoms with isotropic thermal parameters, but only up to 19 atoms with anisotropic thermal parameters. For the anisotropic refinement it was therefore necessary to split the structure into groups of up to 19 atoms. The Ni and Cl atoms were included in each such group, since the non-diagonal matrix elements involving these atoms could be expected to be relatively large.

In 4 cycles of isotropic refinement (Ni + Cl + 5N + 25C) the R factor was reduced from 0.24 to 0.16. A subsequent difference synthesis showed maxima corresponding to possible positions for 2 atoms of the missing solvent, provisionally attributed to a methanol molecule. In the course of several further least-squares cycles (anisotropic B-values for Ni and Cl) the slight decrease in the R-factor (to 0.12) was accompanied by an increase in the isotropic B-values of the atoms of the assumed methanol molecule to unreasonably high values. A second difference synthesis then led to a modified model for the solvent atoms; electron-density maxima could also be found for most of the 30 hydrogen atoms, close to the positions expected on stereochemical grounds. With contributions from 30 hydrogen atoms and 5 'solvent' atoms included in the calculated F-values (but not refined), a series of further least-squares cycles led to a final R-factor of 0.088.



S1 — S2	1.6 Å
S2 — Cl	2.9
S4 — S3	1.3
S4 — S5	1.8
S3 — S5	2.6
S2 — S5	2.6
S3 — Cl'	3.1

Fig. 2. *Portion of final difference synthesis*

The maxima S(1)–S(5) correspond to a probably disordered arrangement of occluded solvent molecules. Numbers in brackets give the y-coordinates × 10^2 of the maxima. Contours at intervals of 0.4 $e/\text{Å}^3$, beginning at 0.4 $e/\text{Å}^3$. The positions of some of the neighbouring atoms are also indicated with their y-coordinates × 10^2 in small script

Table 1. *Positional parameters (and standard deviations), both* $\times 10^4$, *from final least-squares refinement*

Atom	x	y	z	Atom	x	y	z
Ni	7476 (1)	– 1511 (1)	– 0837 (1)	C(15)	5752 (14)	– 1760 (11)	1402 (13)
Cl	2646 (7)	– 4129 (5)	– 2346 (7)	C(16)	5990 (13)	– 2640 (12)	0262 (12)
C(1)	8024 (13)	– 3874 (10)	– 2120 (12)	C(17)	5484 (14)	– 3742 (11)	0010 (14)
C(2)	8266 (15)	– 4490 (11)	– 3529 (12)	C(18)	6316 (14)	– 4526 (11)	– 1086 (13)
C(3)	9188 (15)	– 3862 (10)	– 3915 (14)	C(19	6731 (12)	– 3661 (9)	– 1716 (10)
C(4)	8853 (13)	– 2708 (10)	– 3064 (12)	N(20)	8221 (10)	– 2688 (8)	– 2111 (9)
C(5)	9248 (14)	– 1705 (11)	– 3200 (13)	N(21)	8234 (9)	– 0443 (7)	– 1358 (8)
C(6)	8932 (12)	– 0667 (10)	– 2401 (12)	N(22)	6799 (9)	– 0485 (7)	0641 (8)
C(7)	9395 (16)	0358 (11)	– 2469 (14)	N(23)	6630 (10)	– 2598 (7)	– 0645 (9)
C(8)	8653 (11)	1337 (9)	– 1506 (11)	C(24)	9006 (14)	– 4339 (10)	– 1175 (14)
C(9)	8097 (11)	0682 (9)	– 0769 (10)	C(25)	9386 (17)	2172 (15)	– 0678 (18)
C(10)	7513 (12)	1176 (9)	0369 (13)	C(26)	7562 (14)	2001 (12)	– 2234 (14)
C(11)	6932 (13)	0626 (10)	1053 (12)	C(27)	7063 (14)	– 0164 (13)	3791 (13)
C(12)	6324 (15)	1196 (12)	2288 (13)	C(28)	4796 (14)	0427 (12)	3312 (12)
C(13)	6022 (13)	0192 (12)	2759 (12)	C(29)	9986 (16)	– 1788 (11)	– 4254 (16)
C(14)	6178 (14)	– 0778 (11)	1547 (14)	N(30)	10605 (19)	– 1875 (12)	– 5098 (16)

Table 2. *Anisotropic thermal parameters from final least-squares refinement*

The temperature factors are expressed in the form $T = \exp\left[-10^{-4}\left(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl\right)\right]$. The principal axes of the corresponding ellipsoids (B_{11}, B_{22} and B_{33}) and the mean isotropic paramter $\overline{B}$ are given in *Debye* units

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_{11}	B_{22}	B_{33}	$\overline{B}$
Ni	68	33	53	– 33	23	12	1.6 Å²	2.1 Å²	3.4 Å²	2.4 Å²
Cl	291	152	303	– 181	– 69	11	6.2	13.3	16.0	11.8
C(1)	116	51	96	– 50	43	38	2.3	3.9	5.7	4.0
C(2)	158	74	76	– 44	28	– 21	2.5	5.4	7.4	5.1
C(3)	142	48	144	– 3	154	9	2.4	3.9	9.4	5.2
C(4)	107	63	83	– 18	56	30	3.0	3.5	5.5	4.0
C(5)	126	56	113	12	165	9	1.6	3.7	8.7	4.7
C(6)	72	71	122	– 13	87	71	2.0	3.6	6.4	4.0
C(7)	163	77	145	– 50	198	45	2.0	4.3	10.8	5.7
C(8)	50	73	110	– 64	– 5	62	1.6	3.8	5.0	3.5
C(9)	64	58	61	– 26	– 9	50	2.1	3.0	3.5	2.9
C(10)	77	34	107	– 33	58	4	1.7	2.9	5.4	3.3
C(11)	104	54	114	– 84	24	44	1.7	4.8	5.5	4.0
C(12)	163	73	85	– 36	138	– 1	2.1	4.3	8.9	5.1
C(13)	77	80	86	– 18	54	39	2.5	4.3	4.8	3.9
C(14)	64	65	67	– 27	38	33	2.1	3.6	3.6	3.1
C(15)	110	88	86	– 87	37	53	2.5	4.3	6.1	4.3
C(16)	83	95	79	– 61	35	30	2.7	3.9	5.6	4.1
C(17)	126	89	136	– 160	43	4	1.6	5.4	8.7	5.2
C(18)	122	85	152	– 124	45	53	2.1	6.2	7.5	5.3
C(19)	128	48	64	– 58	31	– 10	2.0	3.4	6.1	3.8
N(20)	94	59	88	– 38	23	45	2.8	3.8	4.5	3.7
N(21)	86	36	70	– 19	30	17	2.0	2.9	4.2	3.0
N(22)	68	67	68	– 17	22	40	2.6	3.2	3.9	3.2
N(23)	118	64	72	– 44	– 17	37	3.0	3.4	5.7	4.0
C(24)	134	48	140	– 12	16	61	2.4	6.0	6.5	5.0
C(25)	172	144	206	– 182	– 106	153	4.2	6.4	12.6	7.7

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_{11}	B_{22}	B_{33}	$\overline{B}$
C(26)	114	107	153	–16	49	126	3.9	5.1	8.1	5.7
C(27)	111	130	91	–60	–48	27	3.1	6.1	7.6	5.6
C(28)	126	109	74	–8	89	3	2.2	6.3	7.1	5.2
C(29)	170	80	167	0	199	79	3.2	4.3	11.4	6.3
N(30)	296	135	237	–27	353	77	4.0	7.4	19.2	10.2

Typical standard deviations are 10–20 for $b_{ii} \times 10^4$ and 10–30 for $b_{ij} \times 10^4$, corresponding to about 0.5 Å^2 in B-values.

Table 3. *Positional parameters* $\times 10^3$ *for hydrogen and 'solvent' atoms*

Atom	x	y	z	Atom	x	y	z
C(2) H(1)	863	–543	–363	C(25) H(1)	881	288	–001
C(2) H(2)	740	–451	–418	C(25) H(2)	975	265	–122
C(3) H(1)	1015	–426	–378	C(25) H(3)	1014	176	–016
C(3) H(2)	908	–384	–495	C(26) H(1)	701	264	–157
C(7) H(1)	1043	028	–219	C(26) H(2)	795	241	–278
C(7) H(2)	936	054	–343	C(26) H(3)	706	135	–282
C(10) H	749	210	077	C(27) H(1)	684	–085	417
C(12) H(1)	693	168	299	C(27) H(2)	695	054	468
C(12) H(2)	550	182	216	C(27) H(3)	793	–032	343
C(15) H	526	–186	218	C(28) H(1)	458	–027	366
C(17) H(1)	558	–411	089	C(28) H(2)	468	112	417
C(17) H(2)	448	–362	–023	C(28) H(3)	406	067	257
C(18) H(1)	706	–512	–077	S(1)	156	300	733
C(18) H(2)	576	–509	–182	S(2)	250	350	670
C(19) H	615	–360	–262	S(3)	570	375	430
C(24) H(1)	991	–449	–146	S(4)	570	383	550
C(24) H(2)	883	–387	–016	S(5)	480	292	600
C(24) H(3)	885	–515	–117				

The nature and distribution of the solvent molecules in the crystal is still unsettled. Fig. 2 reproduces a portion of a difference synthesis, showing a group of five rather diffuse residual electron-density peaks of height 0.9 – 1.3 electrons/Å^3. These peaks are much stronger than the remaining peaks and troughs in the difference synthesis; they are much too strong for hydrogen atoms, much too weak for normal carbon or oxygen atoms, and they have to be ascribed to the atoms of the missing solvent molecules. Two peaks (S(1) and S(2)) may be identified as a methanol molecule, and the set of three smaller, poorly resolved peaks (S(3), S(4), S(5)) must correspond to some disordered arrangement of methanol and possibly also of water molecules. The space in question could be occupied by methanol molecules in two different orientations (one with OH... OH, the other with OH... Cl$^-$ hydrogen bonds) or by water molecules in two different positions. For the structure-factor calculations all 5 atoms were included simply as oxygen atoms, but with very large isotropic thermal parameters ($B = 25$ Å^2) in order to simulate to some extent the effect of disorder.

Results. – Positional parameters for the atoms of the Ni-complex and chloride ion are listed in Table 1. The corresponding standard deviations were calculated by inversion of the least-squares normal-equations matrix. Table 2 contains the anisotropic thermal parameters with their standard deviations. Positional parameters for the hydrogen atoms and for the 'solvent' atoms are listed in Table 3. These parameters were derived partly from difference syntheses, partly from stereochemical considerations; they were not refined but were included in the later least-squares cycles with isotropic thermal parameters ($B = 7\,Å^2$ for hydrogen, $B = 25\,Å^2$ for S(1) – S(5)) as constants of the structural model. A table of observed and calculated F-values is not given here but can be made available to anyone interested.

Discussion. – Interatomic distances and angles, calculated from the final positional parameters, are shown in Figs. 3 and 4. The standard deviations in the

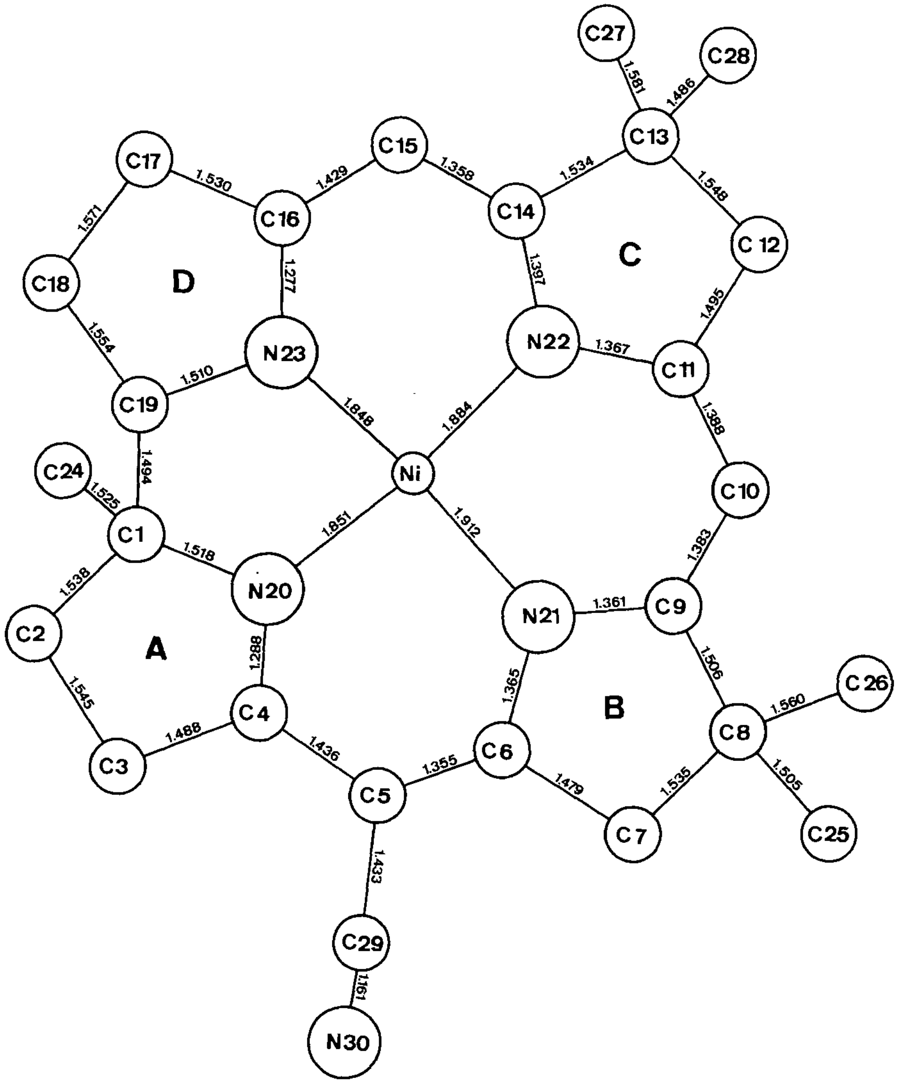


Fig. 3. *Bond lengths*

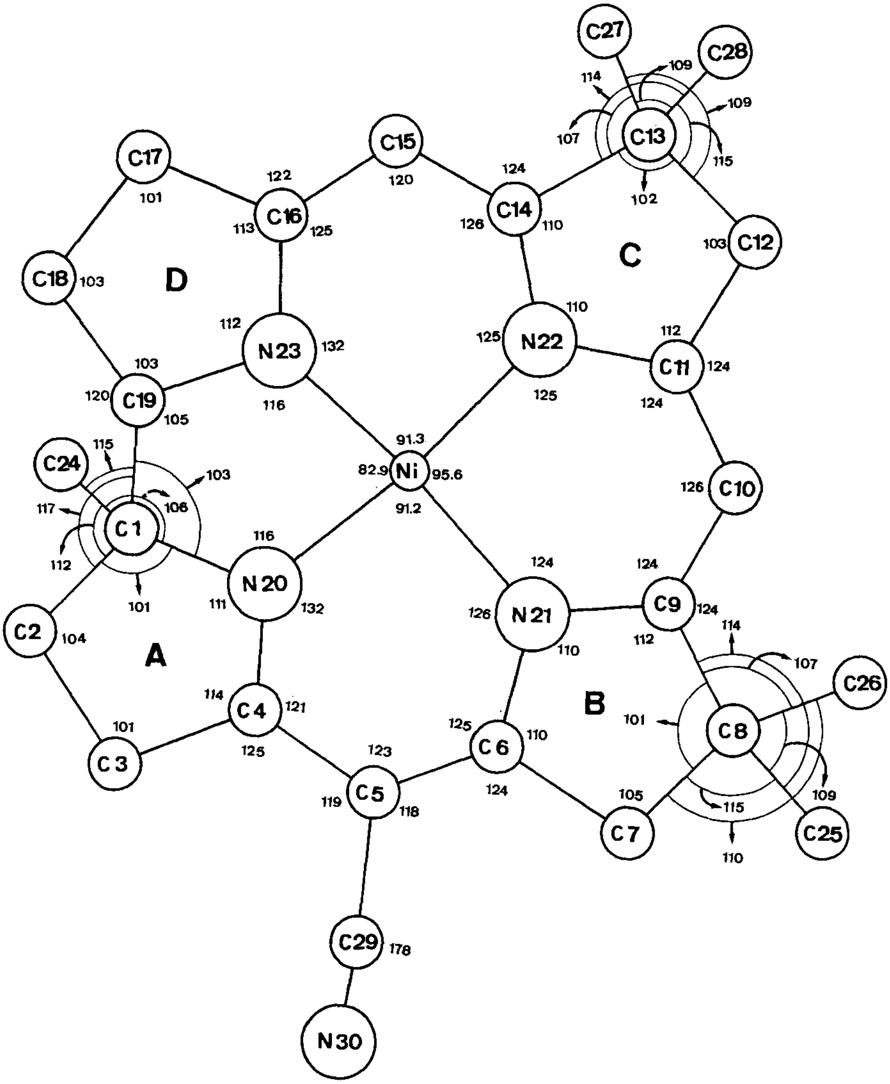


Fig. 4. *Bond angles*

positions of most of the atoms are approximately isotropic; taking the largest of the three values for each atom, one obtains values of less than 0.002 Å for Ni, about 0.008 Å for Cl and 0.011 Å for the four central N atoms. For the C atoms of the corrin nucleus the corresponding values lie in the range 0.012–0.017 Å, for those of the methyl substituents they are somewhat larger, 0.015–0.019 Å. The atoms of the cyano group have relatively large standard deviations of 0.018 Å (C(29)) and 0.021 Å (N(30)) with more pronounced anisotropy.

An independent estimate of the standard deviations in the positions of the C atoms can be made from stereochemical considerations. The 12 bonds between tetrahedral

C atoms have a range between 1.486 Å and 1.581 Å and a mean length of 1.527 Å, the standard deviation of a single observation from the mean being 0.028 Å, corresponding to a standard deviation of 0.020 Å in an atomic position, slightly larger than the least-squares values.

Within these error estimates, the observed bond lengths and angles are in keeping with expected values for the corrin nucleus. In particular, the pattern of bond distances in the conjugated part of the corrin ring has approximate mirror symmetry (in spite of the perturbation due to the cyano substituent at C(5)) and agrees as well as can be expected with the results of HMO calculations [7] for a conjugated system containing six double bonds as found in vitamin B12 [8]. The most significant apparent deviation from mirror symmetry is the difference of 0.028 Å between the observed distances Ni–N(21) (1.912 Å) and Ni–N(22) (1.884 Å), each with standard deviation 0.011 Å.

The most questionable feature of the observed molecular topography is probably the apparent difference of 0.09 Å between the bond lengths C(13)–C(27) and C(13)–C(28). In the course of the analysis, even in the later least-squares cycles, the positional parameters of the three atoms concerned showed a greater than normal tendency to oscillate, and termination of the analysis at a different point would have led to quite different values for the two bond lengths. For example, in the refinement cycle immediately preceeding introduction of the hydrogen atoms the apparent bond lengths were both 1.52 Å. The hydrogen atoms of these two methyl groups were scarcely recognizable in the difference syntheses. Their positions were estimated by assuming staggered arrangements about the two C–C bonds and it is quite possible that this assumption is incorrect. The unsatisfactory results in this region of the structure may then be connected with inadequacies in the least-squares model, or they may be due simply to experimental error.

Another striking feature is the apparent widening of some of the bond angles at C(1) and C(19), particularly C(18)–C(19)–C(1) (120°) and C(2)–C(1)–C(19) (117°). Other angles found around tetrahedral carbon atoms lie in the range 101° (intra-annular at C(1), C(3), C(8) and C(17)) and 115° (extra-annular at C(8), C(13) and C(1), the three atoms with methyl substituents). One might be tempted to ascribe the two extreme values to experimental error, were it not that values of approximately 120° have been found for the corresponding angle at C(19) in other analyses of corrinoid compounds [8] [9] [10] [11]. The widening of the angles C(18)–C(19)–C(1) and C(2)–C(1)–C(19) is probably a real effect related to the strain in this type of system.

Figure 5 shows that the partial conformation around the C(1)–C(19) bond deviates from the energetically favourable staggered arrangement. The perfectly staggered arrangement is obviously incompatible with the tendency for the trigonal nitrogen atoms N(20) and N(23) to be coplanar with the Ni atom and C(4), C(1), C(19), C(16); the observed torsion angles around C(1)–C(19) then represent a compromise between these two opposing tendencies. The atom groupings C(19), N(23), C(16), Ni and C(1), N(20), C(4), Ni are each almost exactly coplanar. For tetrahedral CCC angles, the observed torsion angle C(24)–C(1)–C(19)–C(18) of 41° would lead to a C(24)... C(18) distance of only 2.76 Å; the observed distance of 3.05 Å is achieved by widening the angles C(24)–C(1)–C(19) (to 115°) and C(1)–C(19)–C(18) (to 120°). The observed widening of some CCC angles is thus attributable to repulsion between non-bonded

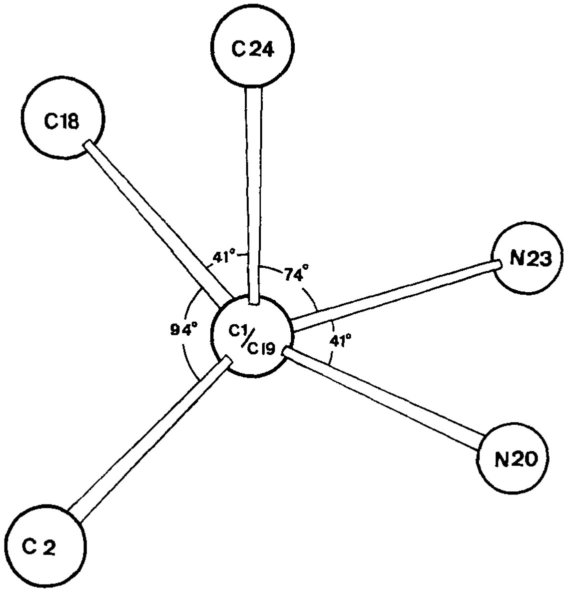


Fig. 5. *Partial conformation about the bond C(1)–C(19)*

atoms. In the heptamethylcorrin derivative studied by *Lenhert & Schaffner* [11], the overcrowding in this region of the molecule is still more severe and the observed widening of certain CCC angles (up to 123°) is correspondingly more extreme.

The difference of more than 12° between the angles N(23)–Ni–N(20) (82.9°) and N(22)–Ni–N(21) (95.6°) arises from the different geometric constraints in the 5- and 6-membered chelate rings. In the 5-membered ring the other 4 angles are 103° and 105° (at the tetrahedral C atoms), and 116° (at the two trigonal N atoms), all somewhat smaller than the corresponding 'natural' angles. If the strain in the markedly non-planar ring (angle sum 523°) is to be approximately evenly distributed over all 5 angles, then the angle at the Ni atom must also be smaller than its natural angle of 90°. Similar geometrical considerations also explain the shortness of the Ni–N bonds in the 5-membered chelate ring; elongation of these bonds would lead to a still smaller N–Ni–N angle (for constant N(20)... N(23) distance). In the opposite 6-membered ring the geometric constraints are not so severe as in the 5-membered ring, and the bond lengths and angles are closer to their natural values. In contrast to the 5-membered ring, the 6-membered rings are nearly planar (angle sum 718.5–719.5°). The widening of the angle N(22)–Ni–N(21) from 90° to 95.6° is a consequence of the contraction of the opposite angle N(23)–Ni–N(20). These geometric factors are valid in all metal-corrin complexes and lead to very similar bond-angles at the metal atom in the other complexes that have been studied [8] [9].

The four central N atoms do not lie in a plane, but are alternately 0.12 Å above and below their mean plane ($7.509x - 3.349y + 6.501z = 5.566$ Å). The Ni atom deviates by only 0.01 Å from this plane, so that there is a pronounced tendency away from planar coordination towards tetrahedral. The tendency towards tetrahedral coordination shows itself throughout the entire corrin ligand system. The deviations of the atoms in the central ring from the mean plane show a wavelike variation in which the five-membered rings are alternately above and below (Fig. 6). The deviation of the inner ring from planarity appears to be quite similar to that observed in other natural and synthetic corrin compounds [10] [11], whose structures are known with sufficient accuracy to permit a meaningful comparison. It has been suggested that the observed type of non-planarity is an intrinsic property of the corrin system, arising from the stereochemistry of the ring junction C(1)–C(19) [12].

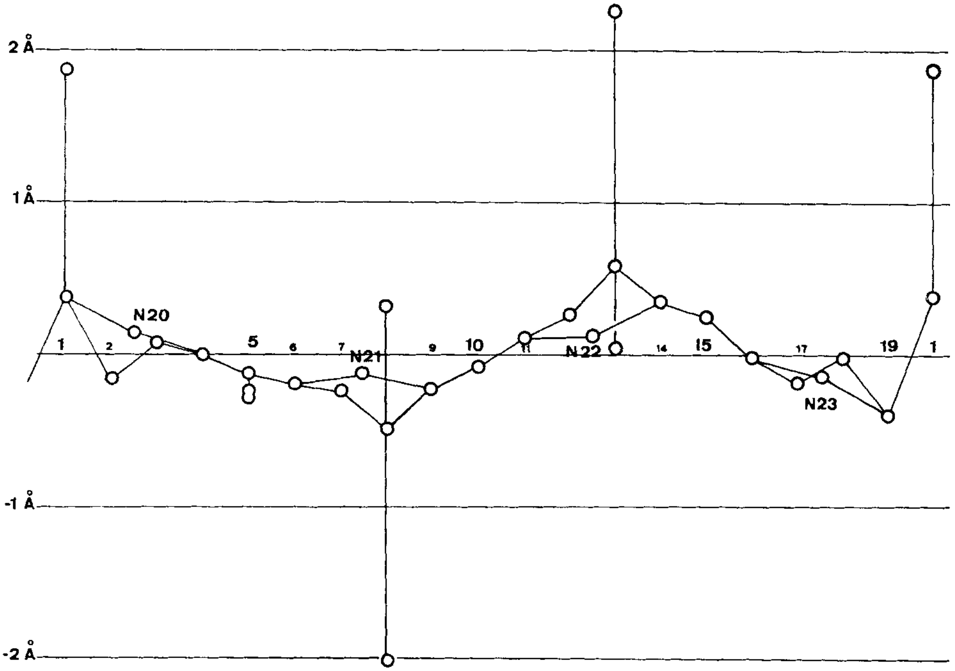


Fig. 6. *Deviations of the atoms from the mean plane through the 4 central nitrogen atoms*

The five-membered rings are not planar (Fig. 7). Rings A and D adopt the envelope conformation with one atom out of the plane of the other four (C(2) in ring A by 0.51 Å, C(18) in ring D by 0.41 Å). In ring B two atoms, C(7) and C(8), deviate by 0.12 Å in opposite directions from the plane of the other three atoms to give the ring-effective C_2 symmetry. Finally the conformation of ring C is intermediate between the envelope and C_2 forms in that the deviations of two atoms, C(12) and C(13), from the plane of the other three are in opposite directions but of unequal magnitudes (0.19 Å and –0.07 Å). Rings A and D, with only two trigonal ring-members, are markedly more puckered than rings B and C, with three trigonal ring-members, and just the same type of envelope conformations, with C(2) and C(18) out-of-plane, is observed in other corrin compounds [10] [11]. For rings B and C, the deviations from planarity are smaller and more irregular. In all four rings the CCC-angles at the β-methylene C atoms are significantly smaller (101°–105°) than those at the trigonal atoms (110°–114°), as was to be expected.

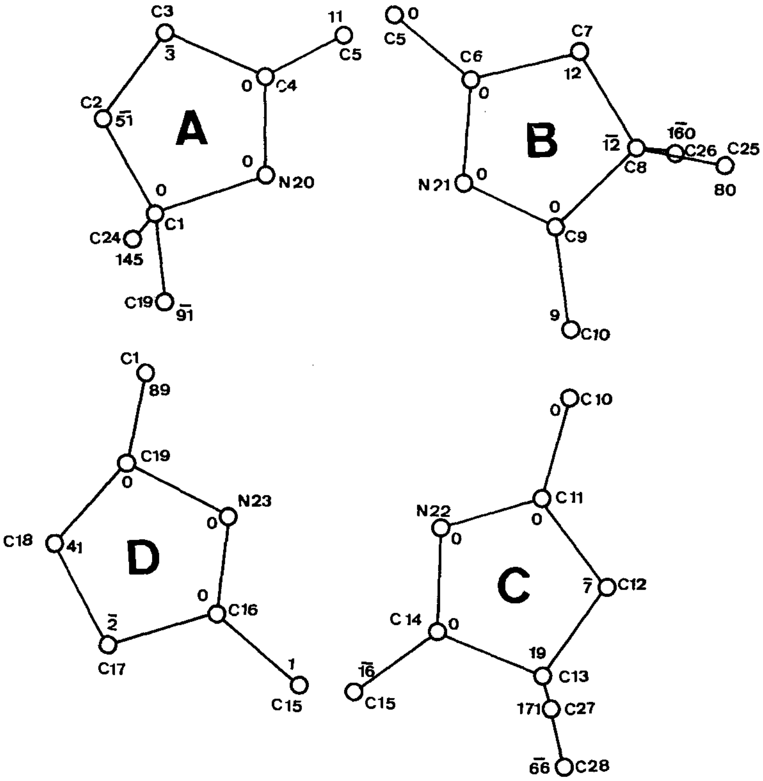


Fig. 7. *Conformations of the five-membered rings with substituents*

The numbers give the deviations (in Å × 10^2) from the plane defined by the N atom and its two bonded C atoms in each ring

The magnitudes of the principal axes of the thermal motion ellipsoids are given in *Debye*-B-units in Tab. 2, together with the mean isotropic values. The Ni atom and the 15 atoms of the inner ring have the smallest mean values, in the range $B = 2.3 - 4.7$ Å^2. For the 8 β-methylene C atoms the mean B values lie in the range $3.5 - 5.7$ Å^2, the lowest values being associated with the quaternary substituted atoms C(8) and C(13). The C atoms of the five methyl groups have higher mean B-values, in the range 5.0–7.7 Å^2, and the N atom of the cyano group has the still higher B-value of 10.2 Å^2 with pronounced anisotropy. The chloride ion has the highest B-value of all, 11.9 Å^2, also very anisotropic. The large thermal motion of this ion is probably a consequence of the disorder in the arrangement of the solvent molecules, which occupy the otherwise vacant cavities at $(x, y, z) = (1/2, 1/2, 1/2)$ between pairs of Cl ions, as indicated in Fig. 2. The maxima S(2) and S(3) are approximately 3 Å distant from Cl ions (corresponding to –OH ... Cl hydrogen bonds?). It is possible that the position of the Cl ion may vary somewhat from one unit cell to another, depending on the nature and numbers of solvent molecules occupying the solvent cavity.

As can be seen from Figs. 8 and 9 the corrin molecules are stacked into columns running in the [100] direction. The Cl ions and solvent molecules are accomodated in the rather irregular tunnels separating these columns and would appear to have considerable freedom of movement. As mentioned above, the very large thermal parameters of these atoms are indicative of a high degree of disorder in this part of the structure. It is also noteworthy that the chloride ions are insulated from the nickel atoms by the aliphatic peripheries of the corrin molecules. The nearest neighbours of the Ni atoms in the vacant 'octahedral' directions are H atoms belonging to

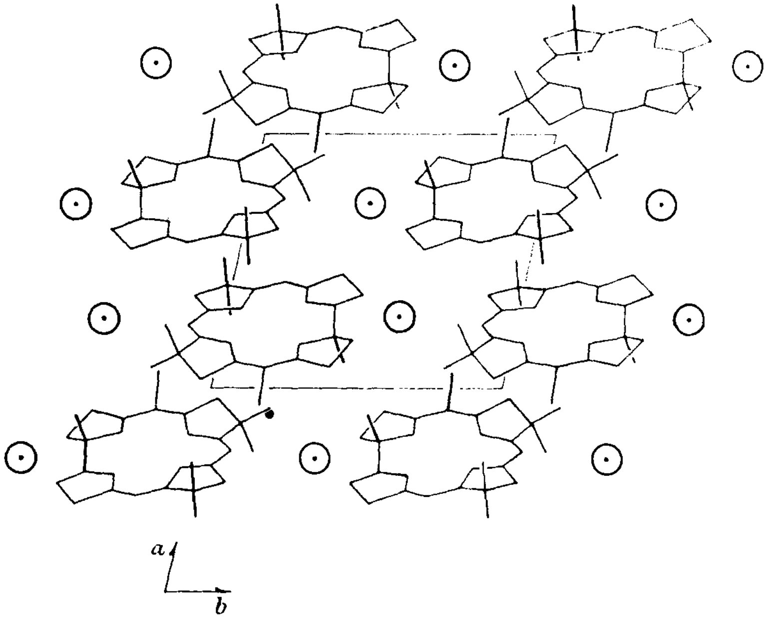


Fig. 8. *Crystal structure projected on (001) plane*

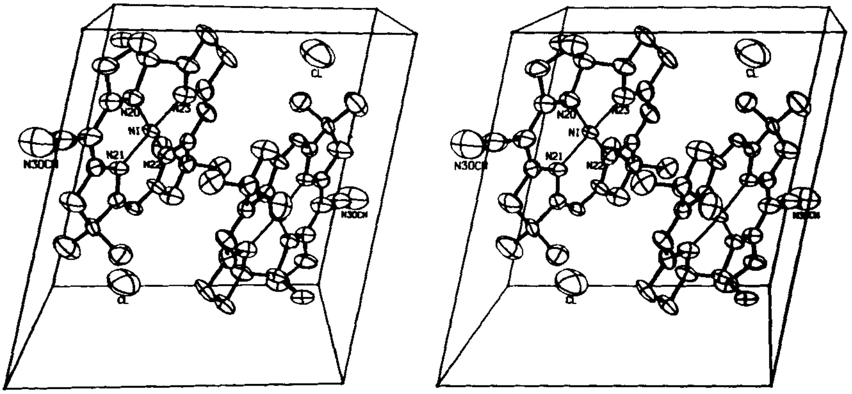


Fig. 9. *Stereoscopic view of crystal structure showing the thermal motion ellipsoids associated with the atoms*

The inversion centre (0, $^1/_2$, 0) is at the lower, left, rear corner, with *a* running horizontally to the right and *b* upwards the methyl groups C(25) and C(28) of other molecules (Ni... H, 2.6–2.7 Å; the corresponding Ni... C distances are about 3.6 Å). The nearest neighbours of the Cl ions are the poorly defined solvent atoms S(2) and S(3) at distances of 2.9 Å and 3.1 Å respectively, together with the H atom of the methine group C(10) (Cl... H, 2.65 Å; Cl... C(10), 3.72 Å). There are also some fairly short contacts between solvent atoms and H atoms of the corrin molecules, the shortest being S(2)... C(3)H(2), S(3)...C(19)H and S(5)–C(15)H, all about 2.5–2.6 Å. The solvent atoms S(1) and S(4) are at least 2.8 Å from any H atom of a corrin molecule, which suggests the tentative identification of S(2), S(3) and S(5) as oxygen atoms, S(1) and S(4) as methyl groups. Apart from three intermolecular N... H distances of about 2.8 Å, all other intermolecular distances shorter than 3 Å correspond to contacts between the peripheral H atoms of different corrin molecules. The shortest are about 2.4 Å, the *van der Waals* diameter of a H atom.

One might well wonder why such a structure is adopted by what is formally an ionic compound. The reason may lie in the constraints on the environment of a d^8 metal that are set by the geometry of the corrin ligand. Occupancy of the empty 'octahedral' sites by nucleophilic groups (chloride ions, O atoms of H_2O or CH_3OH molecules) would be associated with a displacement of electrons from the non-bonding $d(z^2)$ orbital to the empty anti-bonding orbital $d(x^2–y^2)$ of the nickel atom, leading to paramagnetism and, more pertinently, to an increase in the Ni-N bond distances that could not be accomodated within the nearly planar ligand ring system without serious buckling.

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