Tetrahedron Vol. 39, No 11, pp 1865 to 1874, 1983
Printed in Great Britain

0040 4020/83/111865-10$03.00/0
Pergamon Press Ltd

LINEAR TETRAPYRROLES AS LIGANDS

SYNTHESES AND X-RAY ANALYSES OF BORON AND NICKEL COMPLEXES OF OCTAETHYL-21*H*,24*H*-BILIN-1,19-DIONE

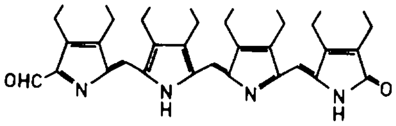
Joseph V. Bonfiglio, Raymond Bonnett,* Dennis G. Buckley,
Dariush Hamzetash, Michael B. Hursthouse, K. M. Abdul Malik,
Antony F. McDonagh and Jill Trotter
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

(*Received in U.K.* 28 *May* 1982)

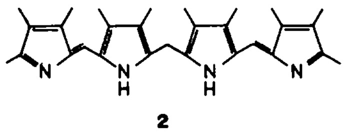
Abstract—The preparation of the difluoroboron(III) complex (**4**) of octaethyl-21*H*,24*H*-bilin-1,19-dione is described. X-ray crystal structures are presented for this complex, and for the corresponding nickel complex (**5**). Both compounds are 1 : 1 complexes, and have the *Z* configuration at all meso bridges. However, complex **4** is *anti,syn,anti* and thus has an open conformation, whereas **5** is *syn,syn,syn*, and thus has a helical conformation. Structural features are discussed and related to electronic structure and paramagnetism.

Compared with the metalloporphyrins, and with respect both to chemistry and crystal structure, the metal complexes of linear tetrapyrroles have been little studied.[1] They are more difficult to make, and generally much less robust. Yet they are important intermediates in some synthetic approaches to metal complexes of macrocyclic tetrapyrroles (e.g. metalloporphyrins,[2] metallocorrins[3]), and may well have a role in some metabolic processes. For example, an iron biliverdin complex might reasonably be expected to arise during the latter stages of haem catabolism.[4]

A number of metal complexes of *seco*-corrinoids and related compounds obtained during Eschenmoser's synthetic approaches to vitamin B_{12} have been subjected to X-ray analysis. Co,[5] Ni,[6,7] Pd,[7] Cd[7] and Pt[7] complexes have been examined: this comprises by far the largest group of structures, and they are, of course, all heavily reduced systems which are chemically related to the vitamin B_{12} chromophore rather than to the bile pigments. As for substances resembling natural linear tetrapyrroles, very few crystal structures have been elucidated. The Zn complex of the formylbilinone derivative (**1**) was obtained in two crystalline forms.[8] The first, obtained as brown crystals from neutral solvents, was shown to be a monomer, with the ligand wrapped around the aquozinc ion in a helical fashion. The Zn ion was thus pentacoordinate, the coordination sphere approximating to an irregular trigonal bipyramid. Acid treatment removed the water ligand to give green crystals possessing a dimeric structure in which each of two Zn ions had a distorted tetrahedral coordination sphere involving bonding to N-21 and N-22 of one tetrapyrrole unit and to N-23 and N-24 of the other to give an arrangement of intertwined irregular helices of opposite handedness, as shown schematically in Fig. 1.



I



2

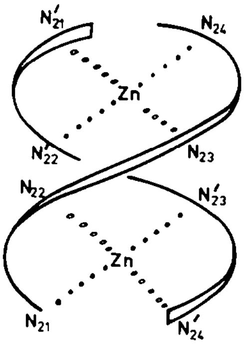


Fig. 1. Schematic representation of the structure of the dimeric zinc complex of the formylbilinone derivative (**1**).[8]

The Zn complex of the decamethyl-10,23-dihydrobilin (**2**) possesses a related dimeric structure.[9] Since C-10 is reduced, the dimeric arrangement is more like two interpenetrating ridge tiles: the interplanar angle between the two *syn,Z* pyrromethene systems in each tetrapyrrole is only 88.8°, which is significantly less than is observed in a metal-free dihydro system such as bilirubin (98°).[10]

Prior to the work presently described,[11] there were no examples of crystal structures of metal complexes of bile pigment derivatives (bilin-1,19-diones). We describe here the preparation from octaethyl-21*H*,24*H*-bilin-1,19-dione (**3**) of the difluoroboron (**4**) and nickel (**5**) complexes and report the crystal structures of these two metal complexes.

RESULTS AND DISCUSSION

Treatment of octaethyl-21*H*,24*H*-bilin-1,19-dione (**3**) with boron trifluoride etherate and triethylamine produced a mixture of products, amongst which an olive green compound, a blue green compound, and a

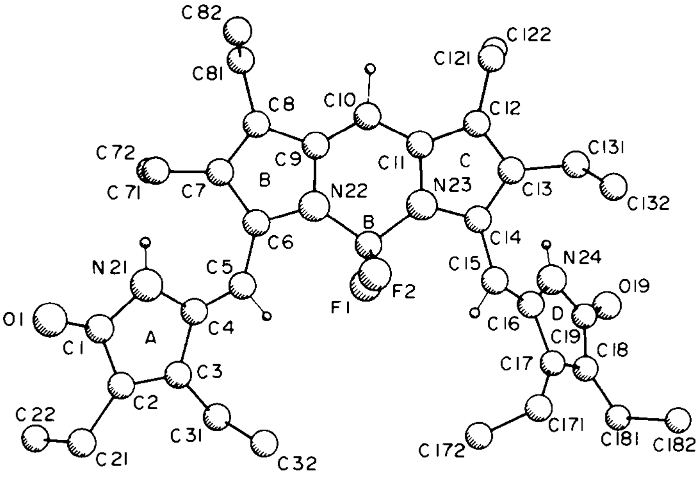
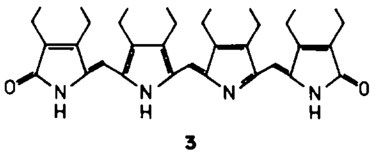


Fig. 2. View of the molecule of the difluoroboron complex (4) showing the atom numbering scheme: hydrogen atoms have the number of the carbon or nitrogen atom to which they are bonded. Ethyl hydrogen atoms have been omitted from the diagram for clarity.



3

blue compound were the major products. Further treatment of the first two compounds with boron trifluoride etherate gave more of the blue compound. The blue complex was obtained from chloroform-hexane solution as dark green prisms possessing a golden lustre. Elemental analysis and spectroscopic examination showed that the crystalline complex, solutions of which emitted an intense red fluorescence in ultraviolet light (366 nm), was the difluoroboron complex. Although difluoroboron complexes of pyrromethenes are known,[12] this appears to be the first such complex of a linear tetrapyrrole to be described.

Crystals of the difluoroboron complex (**4**) and the nickel complex (**5**)[13] of octaethyl-21*H*,24*H*-bilin-1,19-dione (**3**) were subjected to X-ray structure analysis. Data on molecular geometry is assembled in Table 1, and on least squares planes in Table 2. Both structures are monomeric and all bridge double bonds have the *Z* configuration: in other respects the two structures

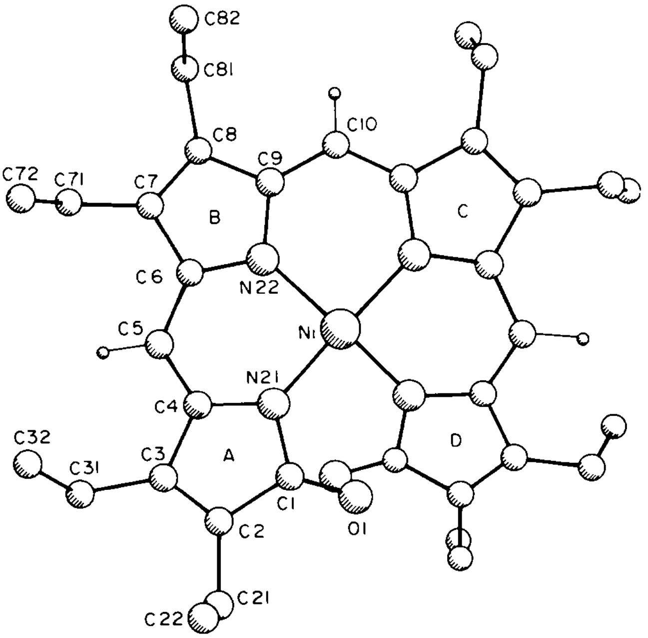


Fig. 3. View of the molecule of the nickel complex (5) showing the atom numbering scheme: the molecule possesses a crystallographic two-fold axis through Ni and C-10. Hydrogen atoms have the number of the carbon atom to which they are bonded; ethyl hydrogen atoms have been omitted from the diagram for clarity.

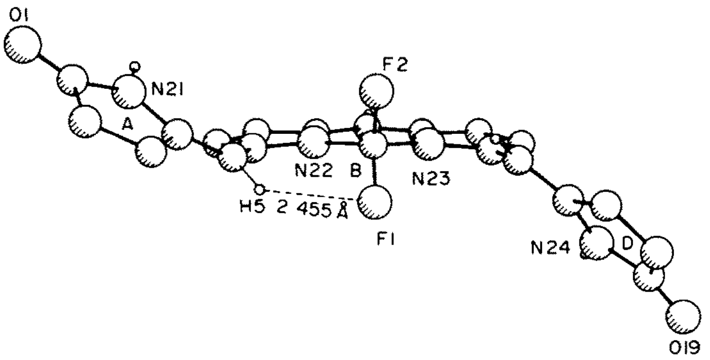


Fig. 4. Twisting of pyrrole rings A and D relative to the pyrromethene plane in the BF_2 complex (**4**). Ethyl groups have been omitted from the diagram.

are very different from one another. Thus, in the difluoroboron complex (**4**) the B atom is tetrahedrally coordinated by two pyrrole N atoms and two F atoms (Fig. 2), and the bilindione ligand adopts a twisted *anti,syn,anti* conformation. In the Ni complex (**5**) the metal is coordinated by the four pyrrole N atoms in a severely distorted square-planar arrangement (Fig. 3) and the bilindione ligand has a helical conformation (*syn,syn,syn*).

In **4** the pyrromethene portion (that is, rings B and C) of the molecule is planar (Table 2) and shows considerable π-electron delocalisation; the C–C bonds

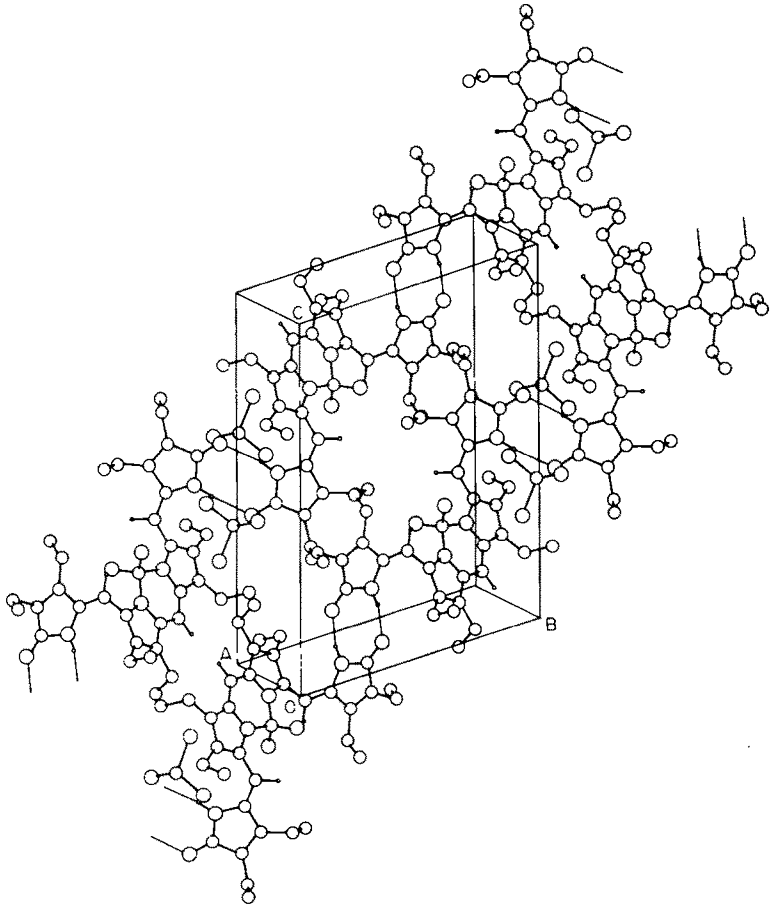


Fig. 5. Molecular packing and intermolecular hydrogen bonding in BF_2 complex (**4**). For clarity only one disordered chloroform solvent molecule is illustrated. The hydrogen bonding geometry is as follows:

$N(21)^{i} \ldots O(1)^{ii}$ 2.94Å; $H(21)^{i} \ldots O(1)^{ii}$ 1.95Å; $\angle N(21)\text{-}H(21)^{i} \ldots O(1)^{ii}$ 164.4°
$N(24)^{i} \ldots O(19)^{iii}$ 3.06Å; $H(24)^{i} \ldots O(19)^{iii}$ 2.10Å; $\angle N(24)\text{-}H(24)^{i} \ldots O(19)^{iii}$ 173.0°.

symmetry code i = x, y, z; ii = 2 − x, 1 − y, − z; iii = − x, 2 − y, 1 − z.

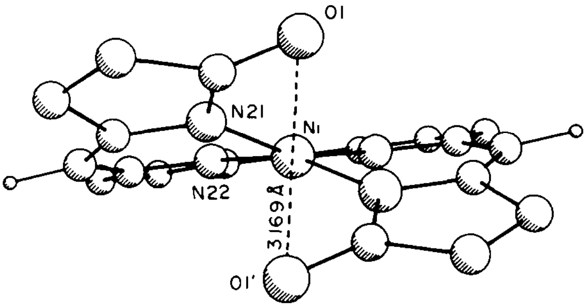


Fig. 6. Helical conformation of the bilindione ligand in the nickel complex (**5**). Ethyl groups have been omitted from the diagram.

at the C-10 methine bridge are of equal length whereas those at the C-5 and C-15 bridges show fairly distinct single and double bond character (Table 1). Comparison of the geometries of pyrrole rings A and D with those of rings B and C also illustrates the π-delocalisation in the pyrromethene. The B atom is displaced by 0.16Å from the pyrromethene plane. Inspection of the molecular geometry (Table 1) shows there to be no significant differences between chemically equivalent bond lengths and angles in the two halves of the ligand.

Pyrrole rings A and D of **4** are twisted out of the pyrromethene plane (Fig. 4). The torsion angles indicate that the twisting occurs essentially by rotation about the single bonds, C(5)-C(6) and C(14)-C(15) of the methine bridges; *viz* C(4)-C(5)-C(6)-N(22) 145.5°, N(21)-C(4)-C(5)-C(6) −3.8°, C(16)-C(15)-C(14)-N(23) 142.0°, N(24)-C(16)-C(15)-C(14) −8.7°. Both pyrrole rings twist in a clockwise sense when viewed in a direction looking along the single bond of the methine bridge towards the pyrromethene. The pyrrole-pyrromethene interplanar angles at C-5 and C-15 are respectively 33.0° and 48.3° (Table 2). The difference in the twist angles of the two pyrrole rings may be partially attributed to the optimisation of intermolecular H-bonding (see below): in addition the twisting of ring A is restricted by interaction between the methine bridge H and one of the F atoms [H(5)... F(1) 2.455Å]. The molecules of **4** are linked together in the crystal by weak intermolecular N-H ... O-C H-bonds between symmetry-related A and D rings (Fig. 5).

The molecule of **5** has a crystallographic two-fold axis through Ni, C-10 and H-10. The four pyrrole N atoms are tetrahedrally displaced above and below the mean plane of the NiN_4 system (Table 2), the distortion from square-planar coordination arising because of the repulsive interactions between the terminal O atoms of the bilindione helix [O(1)...O(1′) 3.169Å] (Fig. 6). The average Ni-N distance is 1.886(7)Å compared to a normal value of ~1.85Å for square-planar complexes.[14] The longer bond lengths observed here probably arise because the repulsive O(1)... O(1′) interaction prevents the ligand wrapping more tightly around the metal. The Ni-N distances are shorter than those in nickel octaethylporphyrin[15] [triclinic form 1.958(2)Å, tetragonal form 1.929(3)Å]; in these metalloporphyrins the NiN_4 moiety is planar but the porphyrinato core must contract, reducing the "hole" radius from its undistorted value of 2.01Å,[16] in order to meet the requirements of the metal ion.

The bonds at the C-10 methine bridge in **5** are constrained by crystallographic symmetry to be equal; the bonds at the C-5 methine bridge do not show the distinct single and double bond character observed in **4** and the geometries of pyrrole rings A and B do not differ significantly from each other. Thus in **5** there is considerable π-electron delocalisation over the bilindione ligand even though the four pyrrole rings are slanted with respect to each other with interplanar angles at the C-5 and C-10 methine bridges of 17.7° and 8.9° respectively (Table 2).

No intermolecular distances shorter than the normal van der Waals contacts are observed; the molecular packing in the crystal structure is illustrated in Fig. 7.

Comparison of the structural features of these two complexes of octaethyl-21*H*,24*H*-bilin-1,19-dione illustrates the flexible nature of the linear tetrapyrrole ligand. The different ligand conformations in the difluoroboron and nickel complexes arise because of the different steric requirements of the coordinated species. Although tetrahedral coordination of B by the four N atoms of the tetrapyrrole could be achieved by wrapping the ligand around the central atom in a

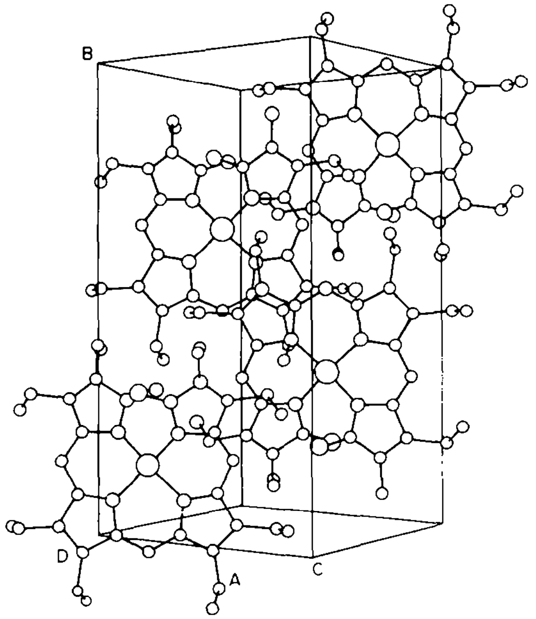


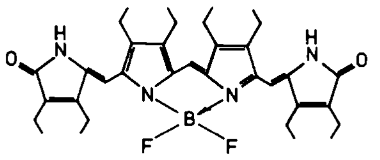
Fig. 7. Molecular packing in the crystal structure of the nickel complex (**5**).

helical fashion, this would be likely to cause some strain. In the nickel complex the ligand forms a fairly flat helix and the terminal O atoms are in close proximity to each other. Tetrahedral coordination would require a helix with a greater pitch, resulting in the terminal portions of the tetrapyrrole ligand being further apart, but the smaller size of B compared to Ni (B-pyrrole N, 1.545Å; Ni-pyrrole N, 1.886Å) would require the ligand to wrap very tightly around the coordinated atom reducing the radius of the helix and resulting in short intramolecular N ... N contacts.

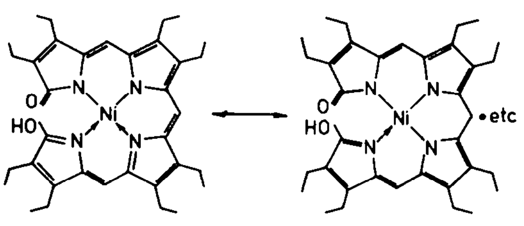
Inspection of Table 2 shows that there are large differences in the tilt angles at the methine bridges in the two structures which result in differences in the geometrical arrangement of the ligand donor atoms, as illustrated by the N ... N intramolecular distances. The distance N(22) ... N(23) in **4** is 2.50Å compared to 2.75Å in **5**; this increase in the Ni complex results from the tilting of pyrrole rings B and C relative to each other rather than from any significant increase in the angle at C-10 (Table 1).

In (**5**) the distances N(21) ... N(22), N(22) ... N(22′), and N(21) ... N(21′) are 2.66Å, 2.76Å, and 2.72Å respectively giving a mean N ... N intramolecular distance of 2.71Å in this complex. The corresponding distances in the tetragonal and triclinic forms of nickel(II)octaethylporphyrin[15] are respectively 2.73Å and 2.77Å. Consideration of the methine bridge geometries in both complexes (Table 1) suggests that appreciable conjugation occurs between adjacent pyrrole rings in the ligand provided that the steric requirements of the coordinated species do not result in a severely twisted conformation, in which case only very limited π-electron delocalisation is possible.

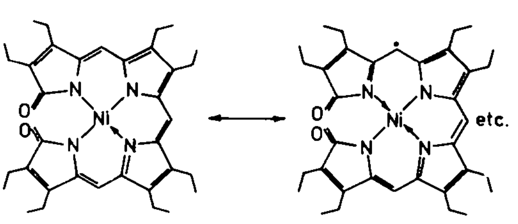
A striking difference between complexes (**4** and **5**) deserves comment. Whereas the NMR spectrum of **4** was as expected, that of **5** was not, being broad and shifted, evidently due to unpaired spin. This may be associated with the tetrahedral distortion suffered by the nickel ion. However, ESR studies on the Ni complexes of biliverdin (**L4**) and mesobiliverdin (**L5**) in organic solvents at room temperature showed single line signals which are attributable to ligand radical character.[17] This might arise by electron delocalisation (metal/ligand), or by oxidation ($-H^+$, $-e$) of the ligand during the preparation of the complex. We can write a definitive structure (**4**) for the difluoroboron complex. For the Ni complex, however, we are forced to consider a more delocalised system, as indicated by the bond length measurements already discussed. The electron transfer representation (**5a**, **5b**) requires a H_{44} formulation: the oxidised ligand representation (**5c**, **5d**) requires a H_{43} formulation. Elemental analysis does not distinguish these, and the X-ray analysis is not sufficiently precise to answer the question of the presence or absence of a hydrogen atom on O-1 (O-19) beyond all reasonable doubt. The observed two-fold symmetry is not to be taken as proof of a symmetrical structure since an unsymmetrical one (*i.e.* with one C=O and one C–OH) could simulate symmetry by packing disorder. This particular point of structure therefore remains to be settled, but in either case the metal acquires some Ni(III) character as represented here.



4



5a **5b**



5c **5d**

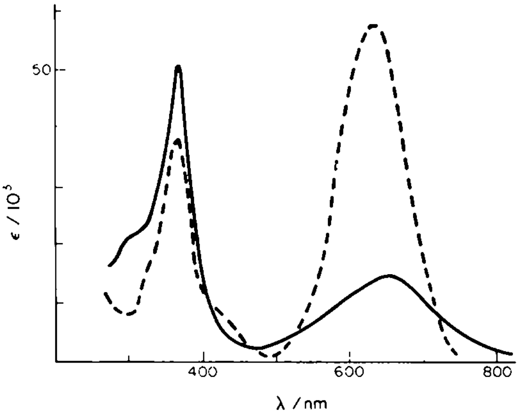


Fig. 8. Electronic spectra in $CHCl_3$:
—— octaethylbilindione (**3**);
----- its difluoroboron(III) complex (**4**).

Finally, a comment on the electronic spectrum of the difluoroboron complex (**4**). Like that of the parent ligand (**3**) this shows bands in the 370 nm and 650 nm regions, but the relative intensities of the two bands are reversed (Fig. 8, $\varepsilon_{vis}/\varepsilon_{uv}$ = *ca* 0.2 for **3** and *ca* 1.5 for **4**). On theoretical grounds it has been predicted that a low $\varepsilon_{vis}/\varepsilon_{uv}$ ratio is expected to be shown by a bilindione in a macrocyclic conformation, whereas a high ratio is expected for a more open conformation.[18] Evidently compound **3** has a macrocyclic conformation (as does the dimethyl ester of mesobiliverdin (**L5**) in the crystal[19]): compound **4** has now been demonstrated to have an open one, thus providing definitive structural support for the earlier theoretical approach to the electronic spectroscopy of linear tetrapyrroles.

Table 1. Molecular geometry

		Bond lengths Å		
	BF$_2$ complex (**4**)	Ni complex (**5**)		BF$_2$ complex (**4**)
C(1)-O(1)	1.200(10)	1.248(9)	C(19)-O(19)	1.242(9)
C(1)-C(2)	1.480(12)	1.454(11)	C(18)-C(19)	1.468(9)
C(1)-N(21)	1.396(9)	1.418(10)	C(19)-N(24)	1.373(10)
C(2)-C(3)	1.348(9)	1.311(10)	C(17)-C(18)	1.350(10)
C(3)-C(4)	1.475(10)	1.481(11)	C(16)-C(17)	1.466(9)
C(4)-C(5)	1.337(9)	1.363(10)	C(15)-C(16)	1.346(10)
C(4)-N(21)	1.406(10)	1.364(10)	C(16)-N(24)	1.390(8)
C(5)-C(6)	1.452(10)	1.396(11)	C(14)-C(15)	1.449(9)
C(6)-C(7)	1.424(9)	1.460(11)	C(13)-C(14)	1.402(9)
C(6)-N(22)	1.367(8)	1.368(10)	C(14)-N(23)	1.374(8)
C(7)-C(8)	1.373(10)	1.334(10)	C(12)-C(13)	1.387(11)
C(8)-C(9)	1.426(10)	1.441(10)	C(11)-C(12)	1.421(10)
C(9)-N(22)	1.393(9)	1.399(10)	C(11)-N(23)	1.390(9)
C(9)-C(10)	1.369(10)	1.367(9)	C(10)-C(11)	1.374(10)
C(2)-C(21)	1.509(10)	1.491(12)	C(18)-C(181)	1.503(11)
C(21)-C(22)	1.511(13)	1.506(13)	C(181)-C(182)	1.480(15)
C(3)-C(31)	1.510(11)	1.494(11)	C(17)-C(171)	1.489(8)
C(31)-C(32)	1.529(12)	1.516(12)	C(171)-C(172)	1.535(11)
C(7)-C(71)	1.509(11)	1.514(11)	C(13)-C(131)	1.511(10)
C(71)-C(72)	1.468(23)	1.518(12)	C(131)-C(132)	1.480(15)
C(8)-C(81)	1.50(12)	1.516(11)	C(12)-C(121)	1.536(12)
C(81)-C(82)	1.568(21)	1.513(12)	C(121)-C(122)	1.471(15)
B-N(21)	1.537(9)	—	B-N(23)	1.553(9)
B-F(1)	1.386(12)	—	B-F(2)	1.374(9)
Ni-N(21)	—	1.875(7)		
Ni-N(22)	—	1.897(7)		
		Bond angles (°)		
N(21)-C(1)-O(1)	125.3(8)	123.7(8)	N(24)-C(19)-O(19)	123.8(6)
O(1)-C(1)-C(2)	128.9(6)	126.4(8)	O(19)-C(19)-C(18)	128.7(7)
N(21)-C(1)-C(2)	105.8(6)	109.8(7)	N(24)-C(19)-C(18)	107.5(6)
C(1)-C(2)-C(3)	109.0(6)	108.3(8)	C(19)-C(18)-C(17)	107.8(6)
C(1)-C(2)-C(21)	121.8(6)	121.4(8)	C(19)-C(18)-C(181)	123.4(7)
C(21)-C(2)-C(3)	129.2(7)	130.2(9)	C(181)-C(18)-C(17)	128.8(6)
C(2)-C(3)-C(4)	108.7(6)	106.7(8)	C(18)-C(17)-C(16)	108.2(5)
C(2)-C(3)-C(31)	127.8(6)	130.5(9)	C(18)-C(17)-C(171)	128.4(6)
C(31)-C(3)-C(4)	123.5(6)	122.6(8)	C(171)-C(17)-C(16)	123.4(6)
C(3)-C(4)-C(5)	125.6(7)	125.0(8)	C(17)-C(16)-C(15)	126.5(6)
C(3)-C(4)-N(21)	105.9(5)	111.1(7)	C(17)-C(16)-N(24)	106.9(6)
N(21)-C(4)-C(4)	128.5(7)	123.6(9)	N(24)-C(16)-C(15)	126.6(6)
C(4)-C(5)-C(6)	127.5(7)	122.6(8)	C(16)-C(15)-C(14)	126.7(6)
C(4)-C(5)-H(5)	110(3)	118.7(5)	C(16)-C(15)-H(15)	112(4)
H(5)-C(5)-C(6)	123(3)	118.7(5)	H(15)-C(15)-C(14)	121(4)
C(5)-C(6)-C(7)	131.7(6)	126.3(8)	C(15)-C(14)-C(13)	129.8(6)
C(5)-C(6)-N(22)	119.1(6)	123.6(8)	C(15)-C(14)-N(23)	119.5(5)
N(22)-C(6)-C(7)	109.3(6)	109.8(7)	N(23)-C(14)-C(13)	110.6(6)
C(6)-C(7)-C(8)	107.1(6)	106.8(7)	C(14)-C(13)-C(12)	106.5(6)
C(6)-C(7)-C(71)	126.7(7)	123.0(8)	C(14)-C(13)-C(131)	129.9(6)
C(71)-C(7)-C(8)	125.3(6)	129.8(8)	C(131)-C(13)-C(12)	122.8(7)
C(7)-C(8)-C(9)	107.8(7)	108.4(8)	C(13)-C(12)-C(11)	107.7(6)
C(7)-C(8)-C(81)	128.5(7)	128.2(8)	C(13)-C(12)-C(121)	128.3(6)
C(81)-C(8)-C(9)	123.6(7)	123.4(8)	C(121)-C(12)-C(11)	124.0(7)
C(8)-C(9)-C(10)	130.6(7)	127.6(9)	C(12)-C(11)-C(10)	131.5(7)
C(8)-C(9)-N(22)	107.9(6)	108.8(7)	C(12)-C(11)-N(23)	108.4(6)
N(22)-C(9)-C(10)	121.5(6)	123.5(9)	C(23)-C(11)-C(10)	120.0(6)
C(9)-C(10)-C(11)/C(9′)	122.3(7)	125.9(11)	—	
C(9)-C(10)-H(10)	123(3)	117.1(6)	C(11)-C(10)-H(10)	115(3)
C(2)-C(21)-C(22)	112.7(6)	112.6(9)	C(18)-C(181)-C(182)	114.7(9)
C(3)-C(31)-C(32)	110.7(8)	112.1(8)	C(17)-C(171)-C(172)	113.2(6)
C(7)-C(71)-C(72)	113.5(9)	110.7(8)	C(13)-C(131)-C(132)	113.8(8)
C(8)-C(81)-C(82)	109.0(8)	112.1(8)	C(12)-C(121)-C(122)	107.0(9)
C(9)-N(22)-B	123.4(5)	—	C(11)-N(23)-B	124.3(5)
C(9)-N(22)-Ni	—	126.8(6)		
C(6)-N(22)-B	128.8(5)	—	C(14)-N(23)-B	128.9(5)
C(6)-N(22)-Ni	—	126.7(6)		
N(22)-B-N(23)	107.8(5)			
N(22)-Ni-N(22′)		93.1(3)		

Table 1 (*continued*)

	BF_2 complex (4)	Ni complex (5)		BF_2 complex (4)
C(1)-N(21)-Ni		127.5(6)		
C(4)-N(21)-Ni		128.5(6)		
N(21)-Ni-N(22)		89.8(3)		
N(22)-B-F(1)	110.4(6)	—	N(23)-B-F(2)	109.7(6)
N(22)-B-F(2)	110.6(7)		N(23)-B-F(1)	109.1(6)
F(1)-B-F(2)	109.2(6)	—		
C(1)-N(21)-C(4)	110.6(6)	104.0(7)	C(19)-N(24)-C(16)	109.5(5)
C(1)-N(21)-H(21)	121(4)	—	C(19)-N(24)-H(24)	117(4)
H(21)-N(21)-C(4)	127(4)		H(24)-N(24)-C(16)	134(4)
C(6)-N(22)-C(9)	107.8(5)	106.2(7)	C(14)-N(23)-C(11)	106.7(5)
N(21)-Ni-N(21')	—	92.9(3)		
N(21)-Ni-N(22')		162.1(3)		

Table 2. Distances of atoms (Å) from least-squares planes

Atoms marked * are not included in plane calculation.

(a) BF_2 complex (4)

Plane 1: pyrromethene + C(5), C(10), B

$3.669x + 13.968y + 4.940z = 13.179$

[C(5) −0.031, C(6) 0.006, C(7) 0.103, C(8) 0.038, C(9) −0.029, C(10) −0.063, C(11) −0.053, C(12) −0.007, C(13) 0.086, C(14) 0.038, C(15) 0.003, N(22) −0.054, N(23) −0.038, *B −0.161, $\Delta = 0.051$]

Plane 2: pyrrole ring A + C(5)

$4.695x + 11.286y - 3.978z = 10.538$

[C(1) 0.003, C(2) 0.034, C(3) −0.034, C(4) −0.021, C(5) 0.030, N(21) −0.013, *O(1) −0.007, $\Delta = 0.024$]

Plane 3: pyrrole ring D + C(15)

$7.878x + 7.688y - 0.028z = 7.596$

[C(15) −0.002, C(16) 0.000, C(17) 0.008, C(18) −0.009, C(19) 0.005, N(24) −0.001, *O(19) 0.008, $\Delta = 0.005$]

Interplanar angles 1 ∧ 2 33.0°
1 ∧ 3 48.3°

(b) Ni complex (5)

Plane 1: NiN_4

$14.722x - 0.000y - 7.307z = -1.827$

[Ni 0.000, N(21) −0.296, N(22) 0.292, N(21') 0.296, N(22') −0.292, $\Delta = 0.263$]

Plane 2: pyrrole ring A + C(5)

$12.635x + 7.070y - 9.316z = -1.396$

[N(21) 0.037, C(1) −0.037, C(2) −0.022, C(3) 0.029, C(4) 0.045, C(5) −0.052, $\Delta = 0.009$]

Plane 3: pyrrole ring B + C(5), C(10)

$-13.601x - 1.447y + 10.032z = 2.522$

[N(22) −0.033, C(5) 0.055, C(6) −0.046, C(7) −0.025, C(8) 0.030, C(9) 0.003, C(10) 0.017, $\Delta = 0.034$]

Plane 4: pyrrole ring C + C(10), C(5')

$-13.601x + 1.447y + 10.032z = 2.494$

[N(22') 0.033, C(5') −0.055, C(6') 0.046, C(7') 0.025, C(8) −0.030, C(9') −0.003, C(10) −0.017, $\Delta = 0.034$]

Interplanar angles 2 ∧ 3 17.7°
3 ∧ 4 8.9°

EXPERIMENTAL

General experimental directions have been given in a recent paper from this laboratory.[20]

Difluoroboron(III) 2,3,7,8,12,13,17,18-*octaethyl*-21*H*,24*H*-*bilin*-1,19-*dione*-N^{22},N^{23} (4). Octaethylbilindione[13] (55.5 mg) in $CHCl_3$ (150 ml) was treated with a large excess of Et_3N (7 ml): freshly distilled BF_3-etherate (25 ml) was added during a 10 min period (colour change blue → olive green). The soln was stirred (2 hr, RT), washed with water (4 × 400 ml), dried (Na_2SO_4) and taken to dryness. The residue was

Table 3. Crystal data

	BF_2 complex (4)	Ni complex (5)
formula	$C_{35}H_{45}BF_2N_4O_2 \cdot CHCl_3$	$C_{35}H_{43}N_4NiO_2$
MW	722.0	610.5
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$†
a (Å)	8.546(2)	14.812(2)
b (Å)	14.159(2)	18.743(3)
c (Å)	17.386(3)	12.956(2)
α (°)	74.82(1)	90.0
β (°)	79.56(2)	118.02(2)
γ (°)	73.99(2)	90.0
u (Å^3)	1938.1	3175.3
z	2	4
D_x (g cm^{-3})	1.24	1.28
D_m (g cm^{-3})	—	1.29
$F(000)$	760	1292
X-ray radiation	Ni-filtered Cu-$K\alpha$ $\lambda = 1.54178$Å	Zr-monochromated Mo-$K\alpha$ $\lambda = 0.71069$Å
μ (cm^{-1})	24.0	6.5
Crystal dimensions (mm^3)	$0.38 \times 0.13 \times 0.05$	$0.40 \times 0.10 \times 0.10$
θ range	3.0–60.0°	1.5–20.0°
No. of reflexions measured	5940	1486
No. of independent reflexions with $F \geqslant 3\sigma(F)$ used in structure refinement	2463	686
R $(= \Sigma\Delta/\Sigma F_0)$	0.082	0.053
R_w $(= \Sigma w^{1/2}\Delta/\Sigma w^{1/2} F_0)$	0.087	0.040
w‡	$1/(\sigma^2(F_0) + 0.0015F_0{}^2)$	$1/\sigma^2(F_0)$
No. of least-squares parameters	432	102

† Systematic absences: hkl $h+k = 2n+1$, $h0l$ $l = 2n+1$.

‡ Chosen to give flat analyses of variance with $\sin\theta$ and $(F_0/F_{max})^{1/2}$.

subjected to preparative TLC (8 plates, $20 \times 20 \times 0.2$ cm Merck Kieselgel HF, acetone : light petroleum = 7 : 13). Three major components were removed—olive green (R_f 0.52), blue green (R_f 0.4), and blue (R_f 0.3). The olive green and blue green components were combined, dissolved in $CHCl_3$ (10 ml) and treated again with BF_3-etherate (2 ml) for 30 min and worked up as before. Preparative TLC (2 plates, as before) gave the blue component (R_f 0.3) as the main product. The main and subsidiary samples of this component were combined and crystallised from $CHCl_3$-hexane to give golden green prisms (25.3 mg, 42%) of difluoroboron(III) octaethyl-21*H*,24*H*-bilin-1,19-dione-N^{22},N^{23}, m.p. 226–228° (d.) (Found: C, 69.7; H, 7.5; N, 9.3; B, 1.4%. $C_{35}H_{45}BF_2N_4O_2$ requires: C, 69.75; H,, 7.55; N, 9.30; B, 1.8%). λ_{max} ($CHCl_3$)(ε) 330 (i, 17,500), 364 (38,000), 430 (i, 7000) and 629 nm (57,500). Strong red fluorescence, λ_{max} 660 nm with excitation at 430 nm. IR (KBr) ν_{max} 3160, 1680, 1630, 1557, 1507, 1458, 1395, 1274, 1258, 1212, 1176, 1140, 1110, 1034, 867, 748, 682, 663 and 594 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 7.06 (s, H at C-10), 6.40 (s, H at C-5 and C-15), 2.55 (m, $8 \times CH_2$) and 1.17 (m, $8 \times CH_3$). MS (EI, 226°) *m/e* 602 (M, 6), 564 (6), 563 (25), 562 (M-2HF, 64. Found: 562.349. $C_{35}H_{43}BN_4O_2$ requires 562.348), 561 (16), 547 (3), 281 (22), 280 (5), 259 (5), 252 (7), 244 (5), and 202 (10).

Crystals suitable for X-ray analysis were grown as small greenish plates with a metallic lustre from chloroform—pentane using the isothermal distillation method.

Nickel complex of 2,3,7,8,12,13,17,18-*octaethyl*-21*H*,24*H*-*bilin*-1,19-*dione* (**5**). The preparation of the Ni complex of octaethyl-21*H*,24*H*-bilin-1,19-dione has been described.[13] From $CHCl_3$-hexane it gave small brown green needles, m.p. >330° (loss of crystallinity at 230–234°). λ_{max} ($CHCl_3$)(ε) 300 (21,000), 361 (25,600), 435 (22,100), 600 (4800, plateau 570–620 nm) and 773 nm (7700). IR(CsI) ν_{max} 3500, 1678, 1670, 1660, 1593, 1553, 1520, 1472, 1463, 1450, 1373, 1364, 1294, 1108, 1090, 1065, 1053, 1020, 1012, 991, 947, 905, 861, and 718 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 2.55 (br.), 1.5 (br.), 1.28, 0.93 (br.). MS (EI, 281°) *m/e* 610 ($C_{35}H_{44}N_4{}^{58}NiO_2$, 10), 609 ($C_{35}H_{43}N_4{}^{58}NiO_2$, 8) 608 (23), 606 (5), 596 (5), 595 (9), 594 (16), 593 (21), 592 (21), 591 (9), 590 (16), 580 (6), 579 (15), 578 (17), 577 (25), 565 (7), 563 (11), and 549 (6).

The sample for X-ray analysis was crystallised as long dark green needles from $CHCl_3$-MeOH.

X-ray analyses. Crystallographic data and details of intensity data collection are given in Table 3. In both cases the crystal system, possible space groups, and preliminary unit cell dimensions were determined photographically. Accurate cell parameters were obtained by least squares refinement from the diffractometer setting angles of 25 high angle reflections. Single crystal X-ray diffraction data were collected using a Nonius CAD4 diffractometer as described previously.[21] Structure solution and refinement were carried out using the SHELX or SHELX76 programs,[22] and the diagrams were drawn using the program PLUTO.[23]

The structure of 4 was solved by direct methods. *E*-maps were calculated using 484 reflexions with $E \geqslant 1.6$ and 16 multisolution reflexions in the starting set: the *E*-map with the highest reliability index (2.196 compared to 1.051 for the next best map) gave the positions of 23/48 atoms in the asymmetric unit. The remaining atoms were located on subsequent difference maps. The structure was refined using blocked full-matrix least-squares techniques. Owing to the shortage of data isotropic thermal parameters were refined for the boron and pyrromethene group (rings B and C); anisotropic thermal parameters were refined for the remaining heavy atoms which were expected to show more thermal vibration. The $CHCl_3$ solvent molecule was refined using a disordered model with two sets of fractional chlorine atom positions (site-occupation factors Cla 0.56, Clb 0.44). Ethyl H atoms were included in calculated positions and refined using a riding model (C-H 1.08Å, H-C-H 109.5°). The positions of the methine bridge H atoms and the two N-H protons were revealed clearly on a difference map; these H atoms were allowed to refine freely but with C-H bonds constrained to 1.080(5)Å and N-H bonds to 1.00(5)Å. Group isotropic temperature factors for

Table 4. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$). Values of U in square brackets are U_{Eqn} values, calculated as $[U_{11} \times U_{22} \times U_{33}]^{1/3}$

(a) BF complex (**4**)

	x	y	z	U
O(1)	11972(6)	4481(4)	370(3)	[83(2)]
C(1)	11346(9)	4932(6)	887(5)	[60(2)]
C(2)	12019(8)	4936(5)	1613(4)	[54(2)]
C(3)	10867(8)	5509(5)	2051(4)	[48(2)]
C(4)	9422(9)	5966(5)	1609(4)	[55(2)]
C(5)	8091(9)	6642(5)	1827(4)	54(2)
C(6)	6722(8)	7189(5)	1372(4)	43(2)
C(7)	6644(9)	7576(5)	534(4)	61(2)
C(8)	5021(10)	7992(6)	431(5)	69(2)
C(9)	4099(9)	7912(6)	1206(4)	63(2)
C(10)	2455(10)	8241(6)	1427(5)	65(2)
C(11)	1792(9)	8143(5)	2217(4)	59(2)
C(12)	167(9)	8467(6)	2576(5)	68(2)
C(13)	195(9)	8243(5)	3400(4)	59(2)
C(14)	1812(8)	7736(5)	3537(4)	46(2)
C(15)	2502(8)	6264(5)	4287(4)	50(2)
C(16)	2154(8)	7626(5)	4958(4)	[49(2)]
C(17)	2688(8)	7092(5)	5746(4)	[48(2)]
C(18)	2065(9)	7710(5)	6259(4)	[58(2)]
C(19)	1145(9)	8670(5)	5808(4)	[54(2)]
O(19)	396(7)	9442(4)	6015(3)	[68(2)]
N(21)	9783(8)	5577(5)	914(3)	[62(2)]
N(22)	5183(6)	7408(4)	1774(3)	50(1)
N(23)	2793(6)	7676(4)	2824(3)	48(1)
N(24)	1224(7)	8578(4)	5034(3)	[51(2)]
B	4640(10)	7153(7)	2681(5)	52(2)
F(1)	5525(5)	7511(4)	3088(2)	[74(2)]
F(2)	4868(5)	6129(3)	2963(2)	[67(2)]
C(21)	13749(9)	4375(6)	1773(5)	[69(2)]
C(22)	15007(11)	4938(8)	1296(6)	[94(2)]
C(31)	10960(9)	5677(6)	2862(4)	[66(2)]
C(32)	10143(13)	4965(7)	3531(5)	[92(2)]
C(71)	8068(12)	7693(7)	−108(5)	[79(2)]
C(72)	8504(25)	8662(13)	−243(9)	[225(2)]
C(81)	4259(12)	8427(8)	−339(5)	[81(2)]
C(82)	3702(18)	7583(10)	−573(7)	[161(2)]
C(121)	−1305(11)	9001(7)	2100(5)	[63(2)]
C(122)	−1640(14)	10085(8)	2072(6)	[114(2)]
C(131)	−1342(9)	8382(7)	3987(5)	[73(2)]
C(132)	−1702(14)	7423(9)	4475(8)	[137(2)]
C(171)	3723(9)	6043(5)	5911(4)	[59(2)]
C(172)	5552(10)	5978(6)	5633(6)	[80(2)]
C(181)	2219(11)	7505(6)	7138(4)	[76(2)]
C(182)	877(15)	7113(11)	7677(6)	[123(2)]
C(100)	3173(17)	10716(12)	3336(11)	[161(2)]
Cl(1a)	4346(16)	9901(15)	3997(14)	[299(2)]
Cl(2a)	3379(23)	11812(10)	3195(14)	[295(2)]
Cl(3a)	3553(17)	10242(12)	2423(9)	[271(2)]
Cl(1b)	4043(17)	9675(10)	3264(16)	[190(2)]
Cl(2b)	4295(38)	10849(24)	4122(17)	[447(2)]
Cl(3b)	3608(22)	11710(15)	2571(13)	[262(2)]

(b) Ni complex (**5**)

	x	y	z	U
O(1)	−929(4)	3087(3)	2786(5)	51(2)
C(1)	−95(7)	2905(5)	3621(8)	44(3)
C(2)	493(6)	3302(5)	4996(7)	39(3)
C(3)	1272(6)	2909(5)	5400(8)	42(3)
C(4)	1201(7)	2233(5)	4774(8)	41(3)
C(5)	1805(6)	1650(5)	5254(7)	38(3)
C(6)	1563(6)	978(5)	4729(8)	38(3)
C(7)	2028(6)	301(5)	5282(8)	38(3)
C(8)	1490(6)	−214(5)	4533(7)	38(3)
C(9)	706(6)	114(5)	3491(7)	38(3)
C(10)	0	−218(7)	2500	39(4)
N(21)	385(5)	2240(4)	3681(6)	36(2)
N(22)	765(5)	855(4)	3642(6)	36(2)
Ni	0	1551(1)	2500	33(2)

Table 4 (*continued*)

C(21)	146(8)	4013(5)	4892(9)	58(3)
C(22)	−588(9)	3954(7)	5390(12)	107(5)
C(31)	2066(7)	3034(5)	6636(8)	54(3)
C(32)	1792(9)	2679(6)	7504(9)	78(4)
C(71)	2884(7)	248(5)	6524(7)	48(3)
C(72)	2462(8)	256(6)	7389(9)	71(3)
C(81)	1627(7)	−1014(5)	4700(8)	54(3)
C(82)	826(8)	−1350(6)	4960(10)	87(4)

methyl and non-Me hydrogens refined to 0.183(10)Å^2 and 0.095(5)Å^2 respectively.

The structure of **5** was solved by the heavy atom method and refined using full-matrix least-squares techniques. Anisotropic thermal parameters were refined for Ni, but owing to the shortage of data the remaining atoms were refined isotropically and all hydrogen atoms were included in calculated positions and refined using a riding model (see above). A common isotropic hydrogen temp factor refined to 0.085(7)Å^2.

The final *R*-factors for both structures are given in Table 3. The fractional atom coordinates and isotropic temperature factors are listed in Table 4. Tables of H atom coordinates, anisotropic thermal parameters, the geometry of the disordered $CHCl_3$ molecule (in structure **4**) and observed and calculated structure factors have been deposited in the Cambridge Crystallographic Data Centre.

Acknowledgement – The support of the S.E.R.C. and M.R.C. is gratefully acknowledged.

REFERENCES

[1] For review see J. Subramanian and J. H. Fuhrhop, *The Porphyrins* (Edited by D. Dolphin) Vol. II, p. 255. Academic Press, New York and London (1978).

[2] A. W. Johnson, *Quart. Rev. Chem. Soc.* **29**, 1 (1975).

[3] A. Eschenmoser, *Naturwiss.* **61**, 513 (1974); A. Eschenmoser and C. E. Wintner, *Science* **196**, 1410 (1977); R. V. Stevens, B_{12} (Edited by D. Dolphin) Vol. 1, p. 169. Wiley, New York (1982).

[4] R. Lemberg, *Rev. Pure Appl. Chem.* **6**, 1 (1956); T. Kondo, D. C. Nicholson, A. H. Jackson and G. W. Kenner, *Biochem. J.* **121**, 601 (1971); R. Schmid and A. F. McDonagh, *Ann. N.Y. Acad. Sci.* **244**, 533 (1975).

[5] B. Kamenar, C. K. Prout, T. N. Waters and J. M. Waters, *J. Chem. Soc. A* 2081 (1967).

[6] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta* **54**, 90 (1971).

[7] M. Currie and J. D. Dunitz, *Ibid.* **54**, 98 (1971).

[8] G. Struckmeier, U. Thewalt and J. H. Fuhrhop, *J. Am. Chem. Soc.* **98**, 278 (1976).

[9] W. S. Sheldrick and J. Engel, *Acta Crystallogr. B* **37**, 250 (1981).

[10] R. Bonnett, J. E. Davies, M. B. Hursthouse and G. M. Sheldrick, *Proc. R. Soc. London, Ser. B* **202**, 249 (1978).

[11] J. V. Bonfiglio, R. Bonnett, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc.*, Chem. Commun. 83 (1977).

[12] E. V. de Wael, J. A. Pardoen, J. A. Van Koeveringe and J. Lugtenburg, *J. Roy. Netherlands Chem. Soc.* **96**, 306 (1977).

[13] R. Bonnett, D. G. Buckley and D. Hamzetash, *J. Chem. Soc.*, Perkin Trans. **1**, 322 (1981).

[14] L. Sacconi, *Transition Metal Chem.* **4**, 199 (1968).

[15] D. L. Cullen and E. F. Meyer, *J. Am. Chem. Soc.* **96**, 2095 (1974); E. F. Meyer, *Acta Crystallogr. B* **28**, 2162 (1972).

[16] D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.* **92**, 3761 (1970).

[17] J. Subramanian, J. H. Fuhrhop, A. Salek and A. Gossauer, *J. Mag. Res.* **15**, 19 (1974).

[18] M. J. Burke, D. C. Pratt and A. Moscowitz, *Biochemistry* **11**, 4025 (1972); Q. Chae and P. S. Song, *J. Am. Chem. Soc.* **97**, 4176 (1975); G. Wagnière and G. Blauer, *Ibid.* **98**, 7806 (1976).

[19] W. Sheldrick, *J. Chem. Soc.*, Perkin Trans. **2**, 1457 (1976).

[20] J. V. Bonfiglio, R. Bonnett, D. G. Buckley, D. Hamzetash, M. B. Hursthouse, K. M. A. Malik, S. C. Naithani and J. Trotter, *Ibid.*, Perkin Trans. **1**, 1291 (1982).

[21] R. A. Jones, G. Wilkinson, M. B. Hursthouse and K. M. A. Malik, *Ibid.*, Perkin Trans. **1**, 117 (1980).

[22] G. M. Sheldrick, SHELX, SHELX-76, *Program for Crystal Structure Determination.* University of Cambridge (1976).

[23] W. Clegg, PLUTO, *Program for Plotting Molecular and Crystal Structures.* University of Göttingen (1978).