Copper(II) Complexes of Pyrrole-containing Schiff-base Macrocycles: Crystal and Molecular Structures of a Mononuclear Macrocyclic Complex, and of Pyrrole-2,5-dicarbaldehyde†

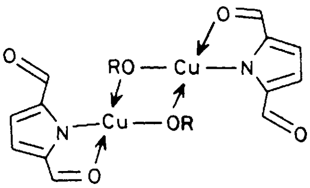
Harry Adams, Neil A. Bailey,* David E. Fenton,* Stephen Moss, and Cecilia O. Rodriguez de Barbarin
Department of Chemistry, The University, Sheffield S3 7HF
Geraint Jones
ICI plc, Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Cheshire SK10 4TG

Mono- and homodi-nuclear copper(II) complexes of macrocyclic Schiff-bases derived from the condensation of pyrrole-2,5-dicarbaldehyde and α,ω-alkanediamines are reported. The crystal structure of the mononuclear complex (3,7,14,18,23,24-hexa-azatricyclo[18.2.1.1^{9,12}]tetracosane-2,7,9,11,13,18,20,22-octaene-N^3,N^7,N^{23},N^{24})copper(II) has been determined. Crystals are orthorhombic, of space group *Pbcn* (D_{2h}^{14}, no. 60), with a = 11.701(9), b = 13.702(9), c = 10.600(6) Å, and Z = 4. 557 Independent reflections with $I/\sigma(I) > 3.0$ gave R = 0.0518. The copper(II) atom is sited at one end of the macrocycle where it is bonded to two pyrrole and two imino nitrogen atoms in a co-ordination geometry having a 30.3° tetrahedral distortion from square planar. The pyrrole-dicarbimine fragments adopt *cis–trans* conformations. The crystal structure of pyrrole-2,5-dicarbaldehyde has also been determined. Crystals are monoclinic, of space group *Pn* (a non-standard setting of *Pc*; C_s^2, no. 7), with a = 3.8166(6), b = 14.637(3), c = 20.755(5) Å, β = 91.665(16)°, and Z = 8. 1 876 Independent reflections with $|F|/\sigma(|F|) > 3.0$ gave R = 0.0449.

The synthesis of metal complexes of '2 + 2' tetraimine Schiff-base macrocycles derived from heterocyclic dicarbaldehydes such as pyridine-2,6-, furan-2,5-, and thiophen-2,5-dicarbaldehyde has claimed much recent attention,[1–3] particularly in view of their utility in investigations of substrate binding and activation at bimetallic centres. The publication[4] of a relatively facile route to pyrrole-2,5-dicarbaldehyde, which was previously accessible only through low yield, multi-step preparations involving lengthy separation procedures,[5–7] has given the opportunity to extend the above series of macrocycles by introducing the pyrrolyl moiety as a head unit therein.‡ In this paper we report the synthesis of mono- and homobi-nuclear copper(II) complexes of pyrrole-containing macrocycles, together with the *X*-ray crystal and molecular structures of the mononuclear copper(II) complex of the macrocycle derived from pyrrole-2,5-dicarbaldehyde and 1,3-diaminopropane, and of pyrrole-2,5-dicarbaldehyde itself.

Results and Discussion

μ-Alkoxy-bridged copper(II) complexes, (1), of pyrrole-2,5-dicarbaldehyde (Hpdc) were prepared by reaction of copper(II) acetate, an alcoholic solution of Hpdc, and a slight excess of KOH. The green complexes are assigned as (1) on the basis of analytical and spectroscopic data.



(1a, R = Me)
(1b, R = Et)

Methoxide anions show characteristic ν_{CH} frequencies in the region 2 800—2 850 cm^{-1} of the i.r.[8,9] The spectrum of (**1a**) has a sharp band at 2 820 cm^{-1}; a peak at 2 970 cm^{-1} in the spectrum of (**1b**) is probably due to the ν_{CH} of the ethoxide anion. The ν_{C-O} mode for a bridging methoxide is reported to occur below 1 040 cm^{-1} whilst that for a terminal methoxide lies above 1 060 cm^{-1}.[10,11] Compound (**1a**) exhibits two sharp absorptions at 1 025 and 1 040 cm^{-1} which may be due to bridging methoxide. This assignment is complicated by the presence of ligand bands in the same region. Two absorptions assignable to $\nu_{C=O}$ are found at 1 620 and 1 665 cm^{-1}; these may be compared with bands found at 1 640 cm^{-1} for Hpdc and at 1 665 cm^{-1} for K(pdc). The observation of two bands indicates that one aldehyde is co-ordinated to the metal whilst the second is remote.

The diffuse-reflectance spectra (d.r.s.) of the alkoxy compounds consist of single absorptions at *ca.* 16 000 cm^{-1}, indicative of square-planar geometry for the metal, and the room-temperature magnetic moments of 0.7 B.M. per copper(II) atom show substantial reductions from the spin-only value, further supporting the proposed alkoxy-bridged dimer.

There are several examples of dialkoxy-bridged copper(II) dimers in the literature; for example, di-μ-methoxy-bis(pentane-2,4-dionato)dicopper(II) is prepared from basic methanolic solutions of pentane-2,4-dione and copper(II) salts.[10] In this compound the copper atoms have square-planar geometry (d.r.s. at 16 000 cm^{-1}), and a reduced magnetic moment of 0.75 B.M. The structure of bis(pentane-2,4-dionato)-di-μ-phenylmethoxy-dicopper(II) has been solved and confirms the planarity of the molecule.[12]

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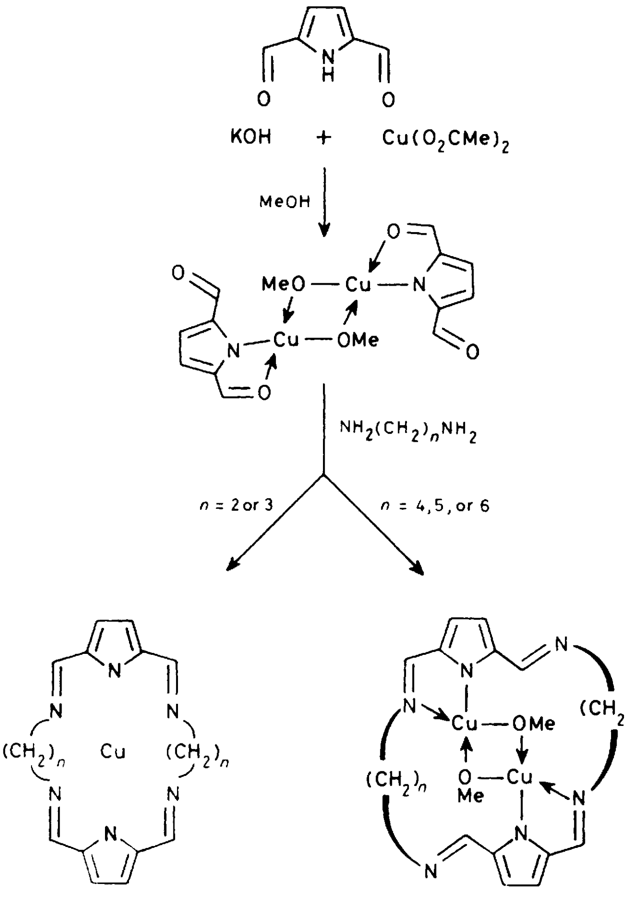
† *Supplementary data available* (No. SUP 56447, 8 pp.): thermal parameters, H-atom co-ordinates, planar fragments of (**2b**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. = 0.927 × 10^{-23} A m^2.

‡ The synthesis of a binucleating tetrapyrrole Schiff-base macrocycle derived from 2,2′-methylenedi(3-ethyl-4-methylpyrrole-5-carbaldehyde) and 1,3-diaminopropane as its dicopper(II) complex has recently been reported (F. X. Acholla and K. B. Mertes, *Tetrahedron Lett.*, 1984, **25**, 3269).



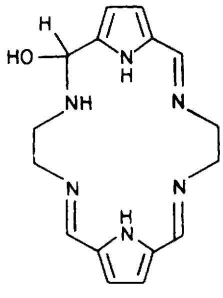
(2a) *n* = 2
(2b) *n* = 3

(3a) *n* = 4
(3b) *n* = 5
(3c) *n* = 6

Scheme.

The macrocyclic complexes are prepared by application of one of the following three approaches. In the first, (**1**) is reacted with an excess of the appropriate α,ω-diaminoalkane in boiling alcohol; the second method requires preformation of the potassium salt of Hpdc which is isolated as a solid and then reacted in methanol with copper(II) acetate and the α,ω-diaminoalkane. The third method is a 'template' approach in which the macrocyclic complex is prepared directly from the reaction in MeOH of Hpdc with the α,ω-diaminoalkane, copper(II) acetate, and KOH. In this last approach a ready precipitation of (**1a**) occurs first and prolonged reflux gives a clear solution from which the product is recovered. The products of these reactions are mononuclear complexes, (**2**), for α,ω-diaminoalkanes having a two- or three-atom chain length, and homobinuclear complexes, (**3**), for α,ω-diaminoalkanes having longer chain lengths (see Scheme).

If no metal is used in the reaction of Hpdc with the α,ω-diaminoalkanes then, with one exception, carbonyl-containing products were isolated, most of which were oligomeric in nature. The reaction of Hpdc with 1,2-diaminoethane gave a product, the i.r. of which shows a strong band at 1 640 cm^{-1} but no bands ascribable to free NH_2. The mass spectrum (m.s.) of the product showed a parent peak at m/e = 294 ascribable to the '2 + 2' macrocycle, however a further feature of the i.r. is a band at 3 460 cm^{-1} ascribable to an –OH frequency. This, together with the analytical data, suggests that the product could be the carbinolamine (**4**) in which either water has added back across the imine bond to relieve strain set up in the tetraimine molecule, or that an intermediate carbinolamine from the forward reaction has been recovered.



(**4**)

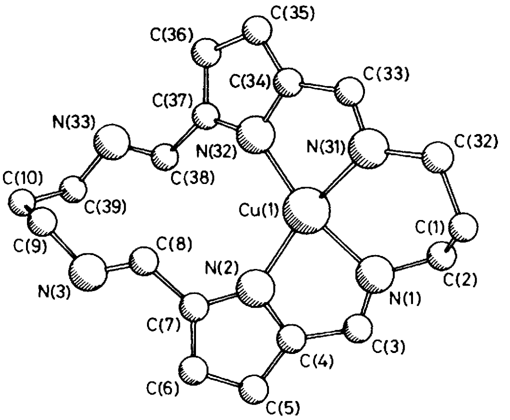


Figure 1. The molecular structure of one disorder component of (**2b**); the crystallographic C_2 axis about which disorder occurs is horizontal

The macrocyclic complexes (**2**) were assigned on the basis of analytical and spectroscopic data; this assignment has been confirmed by an *X*-ray structural determination of (**2b**). The i.r. exhibit two or three bands in the region 1 600—1 630 cm^{-1} which arise from imine $\nu_{C=N}$ and aromatic $\nu_{C=C}$ frequencies. Retrospectively it can be proposed that the bands at 1 605 and 1 635 cm^{-1} in the spectrum of (**2b**) are due to the co-ordinated and unco-ordinated imines. No bands are detected for free carbonyl or amine functions. The m.s. of (**2b**) gave a peak corresponding to the macrocyclic ligand (at m/e = 322); it is interesting to note that a highest molecular-weight peak of 446 is observed, in low intensity, corresponding to the homobinuclear complex ion $[Cu + (\mathbf{2b})]^+$. No peaks are found for $[(\mathbf{2b})]^+$. It is possible that the mononuclear complex disproportionates in the m.s. probe; the dinuclear complex has not been isolated from the reaction mixture.

The d.r.s. of (**2b**) shows a shoulder at 17 500 cm^{-1} which reflects the distorted square-planar geometry at the copper(II) atom: (**2a**) shows a similar reflectance pattern with a band centred on 16 800 cm^{-1}. The macrocyclic nature of (**2b**) is confirmed by the *X*-ray crystal structure.

The structure of (**2b**) is illustrated in Figure 1 with the atom labelling used in Table 1 which summarises the bond lengths and angles together with their estimated standard deviations.

The copper ion is accommodated at one end of the macrocycle where it is bonded to two pyrrole and two imino nitrogen atoms in a co-ordination geometry which has a 30.3° tetrahedral distortion from square planar. The complex has approximate C_2 symmetry and is disordered about the crystallographic C_2 axis. Both pyrrole-dicarbimine fragments adopt *cis–trans*

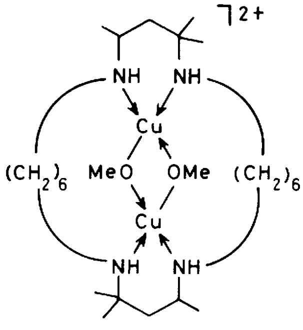
Table 1. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for (**2b**)

Cu(1)–N(1)	1.999(24)	Cu(1)–N(31)	2.002(24)
Cu(1)–N(2)	2.001(31)	Cu(1)–N(32)	2.002(30)
C(1)–C(2)	1.523(21)	C(1)–C(32)	1.535(26)
C(2)–N(1)	1.461(24)	C(32)–N(31)	1.471(22)
N(1)–C(3)	1.271(37)	N(31)–C(33)	1.280(38)
C(3)–C(4)	1.442(22)	C(33)–C(34)	1.437(23)
N(2)–C(4)	1.369(30)	N(32)–C(34)	1.377(31)
C(4)–C(5)	1.379(28)	C(34)–C(35)	1.384(28)
C(5)–C(6)	1.381(25)	C(35)–C(36)	1.379(24)
C(6)–C(7)	1.405(35)	C(36)–C(37)	1.394(36)
N(2)–C(7)	1.372(31)	N(32)–C(37)	1.369(31)
C(7)–C(8)	1.460(31)	C(37)–C(38)	1.457(32)
C(8)–N(3)	1.269(21)	C(38)–N(33)	1.265(24)
N(3)–C(9)	1.476(18)	N(33)–C(39)	1.474(24)
C(9)–C(10)	1.534(16)	C(39)–C(10)	1.526(21)
N(1)–Cu(1)–N(31)	90.7(9)	N(2)–Cu(1)–N(32)	112.3(10)
N(1)–Cu(1)–N(32)	159.0(16)	N(2)–Cu(1)–N(31)	155.6(15)
N(1)–Cu(1)–N(2)	79.6(11)	N(31)–Cu(1)–N(32)	84.3(11)
C(32)–C(1)–C(2)	114.6(12)		
C(1)–C(2)–N(1)	107.9(15)	C(1)–C(32)–N(31)	113.9(17)
Cu(1)–N(1)–C(2)	120.6(18)	Cu(1)–N(31)–C(32)	130.6(18)
Cu(1)–N(1)–C(3)	117.0(13)	Cu(1)–N(31)–C(33)	110.4(14)
C(2)–N(1)–C(3)	121.8(18)	C(32)–N(31)–C(33)	117.5(21)
N(1)–C(3)–C(4)	114.5(18)	N(31)–C(33)–C(34)	119.9(20)
N(2)–C(4)–C(3)	115.5(19)	N(32)–C(34)–C(33)	116.2(19)
N(2)–C(4)–C(5)	109.6(17)	N(32)–C(34)–C(35)	109.5(17)
C(3)–C(4)–C(5)	134.7(18)	C(33)–C(34)–C(35)	134.1(19)
C(4)–C(5)–C(6)	107.0(19)	C(34)–C(35)–C(36)	107.1(19)
C(5)–C(6)–C(7)	107.8(19)	C(35)–C(36)–C(37)	107.6(17)
Cu(1)–N(2)–C(4)	112.5(15)	Cu(1)–N(32)–C(34)	108.8(14)
Cu(1)–N(2)–C(7)	139.6(20)	Cu(1)–N(32)–C(37)	143.5(21)
C(4)–N(2)–C(7)	107.8(23)	C(34)–N(32)–C(37)	106.9(23)
N(2)–C(7)–C(6)	107.7(20)	N(32)–C(37)–C(36)	108.9(20)
N(2)–C(7)–C(8)	119.8(25)	N(32)–C(37)–C(38)	123.4(25)
C(6)–C(7)–C(8)	132.4(21)	C(36)–C(37)–C(38)	127.5(21)
C(7)–C(8)–N(3)	122.1(23)	C(37)–C(38)–N(33)	121.1(23)
C(8)–N(3)–C(9)	116.5(17)	C(38)–N(33)–C(39)	116.8(19)
N(3)–C(9)–C(10)	109.6(9)	N(33)–C(39)–C(10)	110.2(13)
		C(9)–C(10)–C(39)	114.7(9)

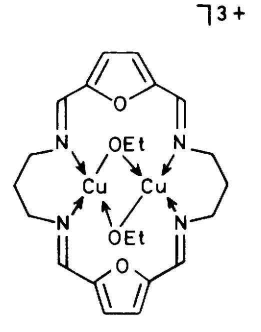
conformations of the carbimine fragments. The macrocycle is twisted with the major twist occurring in the region remote from the co-ordinated copper ion. The torsion angles around the 1,3-di-iminopropane fragments are N(1) ··· N(31) −125.1, −76.3, +41.8, and −162.5° and N(3) ··· N(33) +117.0, −51.9, −56.8, and +113.4°.

The use of longer chain diaminoalkanes led to the preparation of methoxy-bridged dicopper(II) complexes of the '2 + 2' macrocycles. Their i.r. show two imine bands, *ca.* 1 610 and 1 640 cm^{-1}, indicative of co-ordinated and unco-ordinated imine bonds. In addition there are bands *ca.* 2 800 cm^{-1} ascribed to the methoxide ν_{CH}. The absence of pyrrolic proton absorptions suggests that the heterocyclic nitrogen is deprotonated and binding to the copper(II). These data, together with the microanalyses, led to the formulation of (**3**) for these complexes: at present we have been unable to grow crystals suitable for an *X*-ray study.

There are literature precedents for the inclusion of a di-μ-alkoxy-dicopper(II) fragment within a macrocyclic cavity. In complex (**5**) the –Cu(OMe)$_2$Cu– unit is terminally co-ordinated by the tridentate head-units of the macrocycle;[13] and in (**6**) there is a lateral co-ordination of –Cu(OEt)$_2$Cu– reflecting the poor donor capability of the furanyl oxygen atom.[14] Molecular models indicate that the diagonalised arrangement of –Cu(OMe)$_2$Cu– shown in (**3**) and stemming from the bidentate interaction from a potentially tridentate head-unit is sterically favoured, and that with short carbon chains (less than four carbon atoms) the bridge is of insufficient length to generate a cavity of appropriate diameter to contain the binuclear unit. The cavity is in part constrained by the need for the *cis,trans* conformation of the head-unit: in previous structures of '2 + 2' tetraimine Schiff-base macrocyclic complexes only *cis,cis* conformers have been reported for the head-units.[3,9,14] As there was a paucity of information concerning the conformation of heterocyclic dicarbaldehydes in the solid state we have carried out the *X*-ray crystal structure determination of Hpdc.



(**5**)



(**6**)

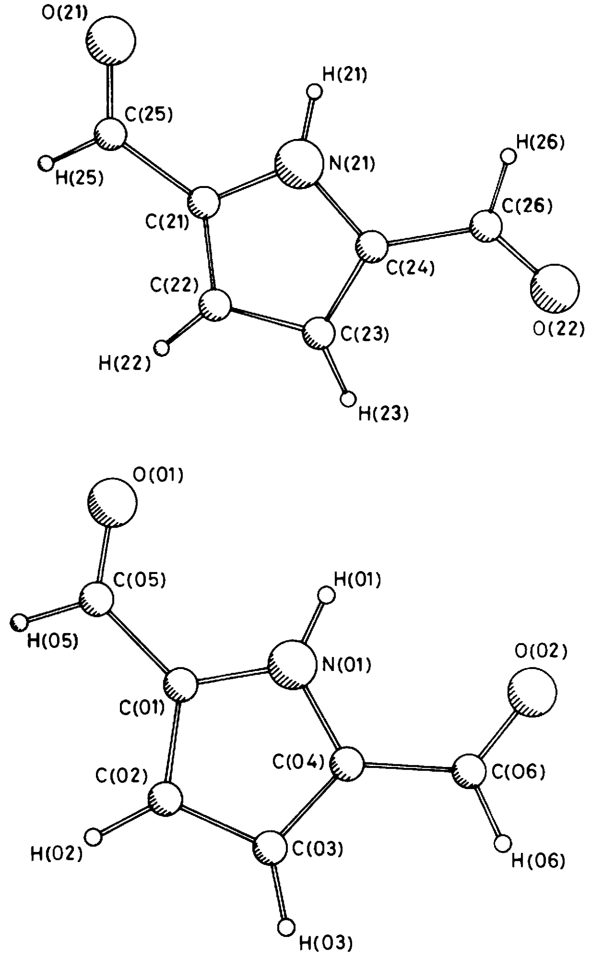


Figure 2. Molecule 2 and molecule 0 of pyrrole-2,5-dicarbaldehyde showing, respectively, the *cis–trans* and *cis–cis* conformations of the carbaldehyde substituents. Molecules 1 and 3 are similarly labelled

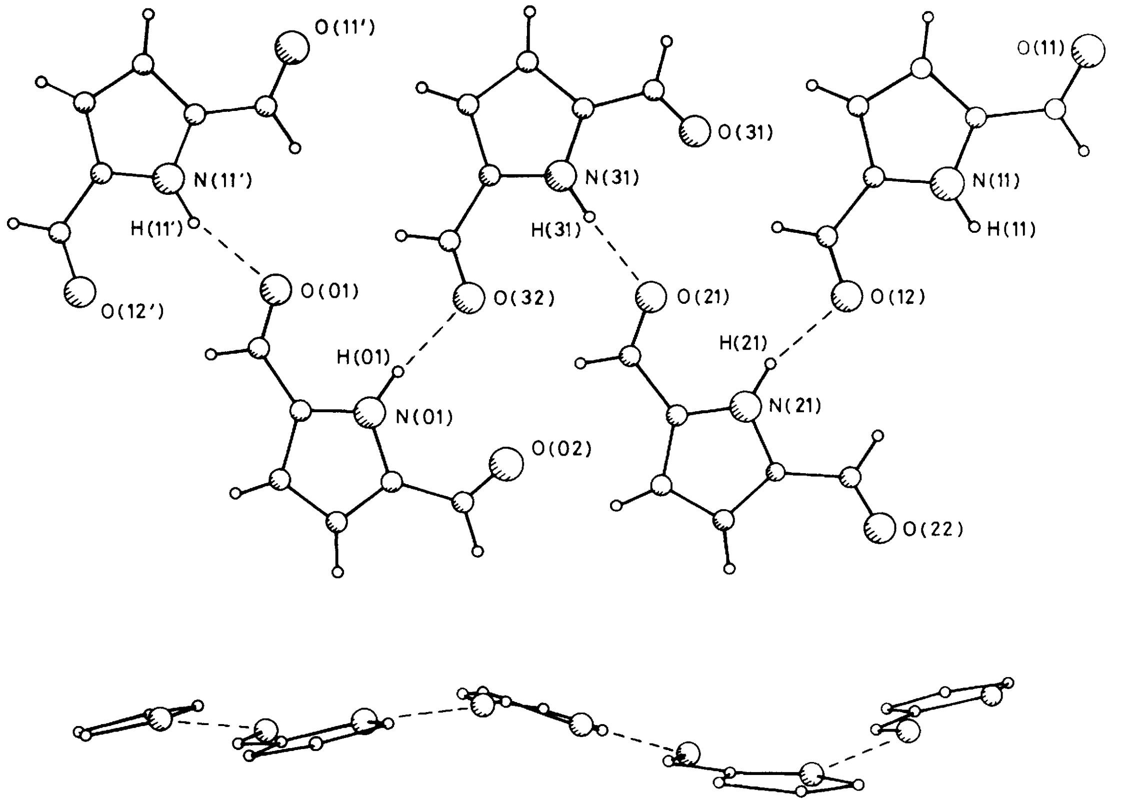


Figure 3. Two views showing the relative orientations of the four independent molecules of pyrrole-2,5-dicarbaldehyde and the hydrogen bonding between them. The lower view omits hydrogen atoms and the carbaldehyde residues not involved in the hydrogen bonding

The ^1H n.m.r. spectrum of Hpdc has been studied in detail[15] and shows that there is an 80:20 ratio of *cis,cis* to *cis,trans* conformers present at low temperature.

The crystal structure of Hpdc comprises four independent molecules which are hydrogen bonded (from pyrrole nitrogen to an aldehyde oxygen atom) to form a continuous chain parallel to the unit-cell *b* axis, with the mean plane of the four molecules lying closely parallel to the crystallographic (103) plane. Figure 2 shows the atom labelling of two of the molecules and Figure 3 shows the hydrogen-bonded interactions between all four molecules. Bond lengths and angles with estimated standard deviations are compared in Table 2 which also details the hydrogen-bonded contacts: details of planar fragments are given in Table 3. Two of the four independent molecules adopt *cis,trans* conformations of the carbaldehyde fragments (as in the copper complex above) whereas the other two adopt the more symmetric *cis–cis* conformation.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service; the recording of physical measurements is detailed in ref. 3. Pyrrole-2,5-dicarbaldehyde was prepared by the method of Miller and Olsson;[4] the diamines were used as supplied.

Copper(II) *Complexes of Pyrrole-*2,5-*dicarbaldehyde*.—Pyrrole-2,5-dicarbaldehyde (0.246 g) and potassium hydroxide (0.2 g, excess) were dissolved in warm ethanol (40 cm^3) and copper(II) acetate dihydrate (0.199 g) in ethanol (10 cm^3) was added. The green solution was warmed for 1 h; on cooling a dark green precipitate of $[Cu_2(pdc)_2(OEt)_2]$ (**1b**) was deposited

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for the four molecules of Hpdc

	Molecule 0	Molecule 1	Molecule 2	Molecule 3
N(1)–C(1)	1.361(4)	1.363(3)	1.358(4)	1.364(4)
N(1)–C(4)	1.365(4)	1.368(4)	1.372(4)	1.382(4)
C(1)–C(2)	1.388(4)	1.394(4)	1.387(4)	1.399(4)
C(2)–C(3)	1.383(4)	1.375(4)	1.383(4)	1.380(4)
C(3)–C(4)	1.379(4)	1.389(4)	1.363(4)	1.390(4)
C(1)–C(5)	1.425(4)	1.433(4)	1.456(4)	1.451(4)
C(5)–O(1)	1.216(4)	1.212(4)	1.200(4)	1.194(3)
C(4)–C(6)	1.457(4)	1.440(4)	1.455(4)	1.424(4)
C(6)–O(2)	1.210(3)	1.217(4)	1.207(4)	1.220(4)
C(1)–N(1)–C(4)	108.1(2)	109.8(2)	108.2(2)	108.5(2)
N(1)–C(1)–C(2)	108.1(2)	107.1(2)	107.9(2)	108.4(2)
N(1)–C(1)–C(5)	124.4(2)	121.5(3)	121.2(2)	123.0(2)
C(2)–C(1)–C(5)	127.4(3)	131.4(3)	130.9(3)	128.6(3)
C(1)–C(2)–C(3)	107.9(3)	108.0(3)	107.7(3)	107.3(3)
C(2)–C(3)–C(4)	106.7(3)	108.0(3)	107.3(3)	108.1(2)
C(3)–C(4)–C(6)	128.7(3)	130.2(3)	131.6(3)	128.2(3)
N(1)–C(4)–C(6)	122.0(2)	122.6(3)	119.4(3)	124.0(2)
C(3)–C(4)–N(1)	109.2(3)	107.2(2)	108.9(2)	107.8(2)
C(1)–C(5)–O(1)	127.1(3)	124.9(3)	123.7(3)	125.0(3)
C(4)–C(6)–O(2)	125.0(3)	124.1(3)	124.9(3)	126.1(3)

Hydrogen bonded contacts

O(01) ··· H(11')*	2.048
O(32) ··· H(01)	1.963
O(21) ··· H(31)	1.953
O(12) ··· H(21)	2.015

* Symmetry operation x, $1 + y$, z.

(yield *ca.* 50%). If the reaction was carried out in methanol then [$Cu_2(pdc)_2(OMe)_2$] (**1a**) was recovered. Analytical and spectroscopic details are given in Table 4.

Reactions of Pyrrole-2,5-*dicarbaldehyde with* α,ω-*Diamines in the Presence of Copper*(II) *Acetate.*—Several methods were attempted; the most reliable involved the prior isolation of the potassium salt of pyrrole-2,5-dicarbaldehyde by addition of an excess of KOH to a solution of pyrrole-2,5-dicarbaldehyde in methanol. The addition of diethyl ether precipitated the potassium salt as a yellow powder.

Table 3. Details of planar fragments of Hpdc. Equations of mean planes are of the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to orthogonal crystal axes a, b, c^*. Deviations (Å) of atoms from mean planes are given in parentheses; r.m.s. = root mean square

		p	q	r	d
Plane 0:	N(01), C(01)—C(04)			r.m.s. deviation 0.001 Å	
		−0.8809	0.1962	−0.4308	−1.2386
	[N(01) 0.001, C(01) −0.001, C(02) 0.001, C(03) −0.001, C(04) 0.000, C(05) 0.055, C(06) 0.067, O(01) 0.105, O(02) 0.262]				
Plane 1:	N(11), C(11)—C(14)			r.m.s. deviation 0.002 Å	
		−0.8797	0.1954	−0.4335	−3.5728
	[N(11) −0.002, C(11) 0.002, C(12) −0.002, C(13) 0.000, C(14) 0.001, C(15) 0.060, C(16) −0.007, O(11) 0.144, O(12) −0.028]				
Plane 2:	N(21), C(21)—C(24)			r.m.s. deviation 0.003 Å	
		−0.8883	−0.0694	−0.4540	−3.7707
	[N(21) −0.002, C(21) −0.001, C(22) 0.003, C(23) −0.005, C(24) 0.004, C(25) 0.001, C(26) −0.061, O(21) 0.013, O(22) −0.156]				
Plane 3:	N(31), C(31)—C(34)			r.m.s. deviation 0.004 Å	
		−0.8710	−0.3252	−0.3682	−3.9343
	[N(31) 0.006, C(31) −0.005, C(32) 0.002, C(33) 0.001, C(34) −0.005, C(35) −0.040, C(36) −0.072, O(31) −0.189, O(32) −0.150]				
Plane 1′:*	N(11′), C(11′)—C(14′)			r.m.s. deviation 0.002 Å	
		−0.8797	0.1954	−0.4335	−0.7132

Angles between planes (°):	
1—2	15.3
2—3	15.5
3—0	30.5
0—1′	0.2

* Symmetry operation x, $1 + y$, z.

The relevant diamine (0.001 mol) in methanol (10 cm^3) was added dropwise to a solution of the potassium salt (0.001 mol) and copper(II) acetate dihydrate (0.0005 mol) in methanol (20 cm^3). The green solution either produced a precipitate immediately, or after warming for 0.5 h. The solid was separated by filtration and dried *in vacuo* over silica gel (yields *ca.* 50%). Analytical and spectroscopic details are given in Table 4.

Reaction of [$Cu_2(pdc)_2(OEt)_2$] (**1b**) *with* 1,3-*Diaminopropane.*—[$Cu_2(pdc)_2(OEt)_2$] (0.0025 mol) was dissolved in hot ethanol (100 cm^3) and 1,3-diaminopropane (0.002 mol) in ethanol (5 cm^3) was added. The solution was dark green and after refluxing for 0.5 h was evaporated to 20 cm^3. Crystals of the macrocyclic complex (**2b**) were deposited on standing, from which a crystal was selected for an *X*-ray study.

Structural Determinations.—*Crystal data* for (**2b**). $C_{18}H_{20}CuN_6$, $M = 383.94$, crystallises from ethanol as red-brown needles, crystal dimensions 0.70 × 0.06 × 0.03 mm, orthorhombic, $a = 11.701(9)$, $b = 13.702(9)$, $c = 10.600(6)$ Å, $U = 1\,699.5(20)$ Å^3, $Z = 4$, $D_c = 1.501$ g cm^{-3}, space group *Pbcn* (D_{2h}^{14}, no. 60), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 12.99 cm^{-1}, $F(000) = 796$.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet *R3m* diffractometer by the ω-scan method. The 557 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was partially solved by Patterson and Fourier methods, however it was soon clear that the molecule, which apparently lay across the crystallographic C_2 axis at 0, y, 0.25 was extensively disordered. The central carbon atoms of each 1,3-di-iminopropane fragment were each clearly located displaced from this C_2 symmetry axis and, although the structure of one such fragment could be satisfactorily viewed as a 50% disorder of carbon atom C(1) between two sites, the carbon–carbon bond lengths to the other such atom, C(10), were very unequal, differing by up to 0.5 Å from an acceptable value. Clearly the two sides of each macrocycle were slightly different but, if the determined space group were proved to be correct, each macrocycle randomly adopted either configuration in all possible lattice sites. Accordingly, constraints were imposed on the geometry of the macrocycles in such a way that the values of chemically equivalent parameters (both bond lengths and angles) were obliged to be similar with maximum permitted deviations as follows: Cu–N 0.01, N–C and C–C 0.02 Å; all macrocycle angles 0.66° except 0.97° for exocyclic angles at C(4) and chemically equivalent atoms. The actual values of the geometric parameters were free to refine within these constraints; this also resulted in the disorder of the copper atom off the C_2 axis. The isotropic thermal parameters of some pairs of skeletal atoms which were closely related by the C_2 disorder symmetry were correlated together. Refinement was by

Table 4. Microanalytical and spectroscopic data[a]

	Found (%)			Calc. (%)			Selected i.r. bands (cm^{-1})		
Complex	C	H	N	C	H	N	$\nu_{C=N}$	ν_{CH}	D.r.s. bands (nm)
(**1a**)	38.7	3.0	6.5	38.8	3.3	6.5	1 610	2 820	16 200
(**1b**)	42.6	4.1	6.2	41.7	3.9	6.1	1 620	2 970	16 000
(**2a**)·0.5H_2O	53.6	5.6	23.1	53.3	5.6	23.2	1 605br		23 000, 16 800(sh)
(**2b**)	56.4	5.3	22.1	56.3	5.2	21.9	1 588, 1 605, 1 635		22 000, 17 500(sh)
(**3a**)	49.2	5.6	15.6	49.7	5.2	15.8	1 610br, 1 635br	2 820	23 200, 14 200, 12 600, 11 600(sh)
(**3c**)	54.5	6.2	13.6	54.6	6.8	14.0	1 615s, 1 645(sh)	2 820	23 200, 13 800, 11 600(sh)
(**3b**)[b]							1 610br, 1 640br	2 820	23 400, 13 600, 12 600(sh), 12 000(sh)

[a] s = Strong, br = broad, sh = shoulder. [b] Although the analytical results were of the correct order, inconsistent sets were obtained from several runs.

Table 5. Atom co-ordinates (× 10^4) for (**2b**)*

Atom	*x*	*y*	*z*
Cu(1)	21(13)	995(2)	2 518(17)
N(1)	−1 085(21)	2 043(11)	2 039(30)
N(2)	−998(22)	256(14)	1 340(31)
N(3)	−413(12)	−2 296(9)	887(17)
N(31)	1 189(21)	1 997(10)	2 993(31)
N(32)	945(23)	109(15)	3 621(31)
N(33)	384(14)	−2 450(12)	3 966(17)
C(1)	156(15)	3 450(13)	2 086(4)
C(2)	−971(10)	3 027(10)	2 557(18)
C(3)	−1 956(21)	1 786(10)	1 406(29)
C(4)	−1 928(15)	789(11)	968(19)
C(5)	−2 592(18)	240(12)	161(22)
C(6)	−2 068(18)	−658(13)	41(25)
C(7)	−1 078(21)	−649(14)	792(29)
C(8)	−229(21)	−1 396(11)	1 084(38)
C(9)	514(8)	−2 974(9)	1 239(14)
C(10)	95(5)	−3 662(1)	2 283(11)
C(32)	1 221(18)	3 055(12)	2 760(23)
C(33)	1 880(22)	1 652(13)	3 815(28)
C(34)	1 810(15)	642(10)	4 171(18)
C(35)	2 383(20)	64(13)	5 035(23)
C(36)	1 848(19)	−832(8)	5 044(24)
C(37)	965(21)	−798(13)	4 163(28)
C(38)	127(22)	−1 555(12)	3 886(36)
C(39)	−435(15)	−3 150(14)	3 420(17)

* The approximate C_2 symmetry relates atom-pairs C(2)/C(32) *etc.*

Table 6. Atom co-ordinates (× 10^4) for the four molecules of Hpdc*

Atom	*x*	*y*	*z*
N(01)	4 989(4)	4 928(2)	1 161(1)
C(01)	5 649(4)	5 840(2)	1 210(1)
C(02)	7 271(4)	6 118(2)	654(2)
C(03)	7 613(4)	5 362(2)	261(2)
C(04)	6 183(4)	4 634(2)	583(1)
C(05)	4 641(4)	6 396(2)	1 737(2)
C(06)	5 725(4)	3 694(2)	366(2)
O(01)	3 098(4)	6 154(2)	2 212(1)
O(02)	3 992(4)	3 122(2)	632(1)
N(11)	702(4)	−2 466(2)	3 112(1)
C(11)	−924(4)	−2 838(2)	3 626(1)
C(12)	−1 426(4)	−2 136(2)	4 067(1)
C(13)	−112(4)	−1 344(2)	3 811(2)
C(14)	1 218(4)	−1 551(2)	3 213(2)
C(15)	−1 920(4)	−3 782(2)	3 635(2)
C(16)	2 894(4)	−973(2)	2 753(2)
O(11)	−3 547(4)	−4 144(2)	4 058(1)
O(12)	4 011(4)	−1 241(2)	2 244(1)
N(21)	7 455(4)	43(2)	1 397(1)
C(21)	7 409(4)	962(2)	1 308(1)
C(22)	8 885(4)	1 145(2)	719(2)
C(23)	9 856(4)	320(2)	452(1)
C(24)	8 936(4)	−351(2)	870(1)
C(25)	5 966(4)	1 571(2)	1 787(2)
C(26)	9 456(4)	−1 336(2)	857(2)
O(21)	4 720(4)	1 313(2)	2 279(1)
O(22)	10 950(4)	−1 745(2)	441(1)
N(31)	1 388(4)	2 467(2)	3 223(1)
C(31)	529(4)	2 188(2)	3 826(1)
C(32)	−1 173(4)	2 908(2)	4 130(2)
C(33)	−1 298(4)	3 632(2)	3 705(2)
C(34)	309(4)	3 362(2)	3 143(1)
C(35)	1 388(4)	1 287(2)	4 077(2)
C(36)	947(4)	3 893(2)	2 584(2)
O(31)	3 178(4)	739(2)	3 816(1)
O(32)	2 546(4)	3 645(2)	2 114(1)

* Atoms N(01), C(01)–C(06), O(01), O(02) comprise molecule 0 *etc.*

blocked-cascade least-squares methods. Hydrogen atoms were inserted in calculated positions (C–H 0.95 Å) after many had been clearly evident in difference electron-density syntheses: some limited angular refinement was permitted, again with correlation for chemically equivalent atoms. Their isotropic thermal parameters were set at 10% greater than that of the carbon atom to which they were attached. Refinement converged at R 0.0518 with allowance for anisotropic thermal motion and for anomalous scattering of copper only.

The possibility was investigated that the space group was either of the orthorhombic sub-groups $Pbc2_1$ or $P2_1cn$ (the two monoclinic sub-groups $P2_1/n$ and $P2_1/b$ were not considered since there was no evidence for loss of orthorhombic symmetry), although no systematic absences exceeded the rejection criterion. Neither such ordered structure yielded a lower value of R (0.0518 and 0.0554 respectively) and both showed similar shortest non-bonded contacts giving strong support for the disorder model. Unit weights were used in the refinement. Table 5 lists the atomic positional parameters with estimated standard deviations.

Crystal data for Hpdc. $C_6H_5NO_2$, M = 123.11, crystallises from toluene as long, fine, yellow needles, monoclinic, a = 3.8166(6), b = 14.637(3), c = 20.755(5) Å, β = 91.665(16)°, U = 1 158.9(4) Å^3, D_m = 1.37, Z = 8, D_c = 1.412 g cm^{-3}, space group Pn (a non-standard setting of Pc; C_s^2, no. 7), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 1.0 cm^{-1}, $F(000)$ = 512.

The data were collected and processed [1 876 independent reflections with $|F|/\sigma(|F|) > 3.0$] as for the copper macrocycle above: a correction was made for 30% crystal decay during data collection based on the monitoring of two reflections. The structure was solved by tangent refinement with random starting phases (the RANT routine of SHELXTL[16]) and refined by blocked-cascade least-squares methods. Hydrogen atoms were refined with flexible interatomic bond-length constraints (X–H 0.96 Å, X = N or C; σ = 0.02 Å). The structure showed no disorder and refinement converged at R 0.0449 with allowance for thermal anisotropy for all non-hydrogen atoms and for isotropic thermal motion of hydrogen atoms. The weighting scheme was $w = [\sigma^2(F_o) + 0.000\,841(F_o)^2]^{-1}$. Table 6 lists atomic positions and estimated standard deviations.

Real and anomalous scattering factors were supplied internally by the computer program SHELXTL[16] which, along with those of the Sheffield X-ray system, were used in the analyses.

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