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Synthetic Studies on Quinquedentate Macrocyclic Ligands. The Crystal and Molecular Structures of {Dibenzo[*b,o*][1,5,9,13,17]-pentaazacycloeicosa[4,13]diene}copper(II) Diperchlorate and of {7-(2-Pyridyl)-dibenzo[*b,k*][1,5,9,13]tetraaza-cyclopentadeca[4,9]-diene(2-)}copper(II)

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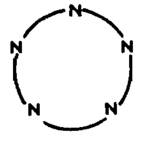
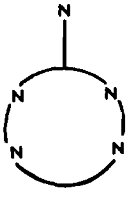
The synthesis of dibenzo[b,o] *[1,5,9,13,17]pentaazacycloeicosa[4,13]diene from bis(2-aminoethyl)amine and 4,8-diaza-2,3:9,10-dibenzoundecane-1,11-dione is described together with the crystal structure of the corresponding copper(II) diperchlorate; monoclinic,* $P2_1/c$ *with* $a = 9.170(4)$, $b = 17.059(6)$, $c = 19.026(4)$ Å, $\beta = 111.91(5)^\circ$, $R = 0.095$ *for 1546 data with* $I > 3\sigma(I)$. *The potentially quinquedentate ligand, 7-(2-pyridyl)-dibenzo*[b,k] *[1,5,9,13]tetraazacyclopenta[4,9]diene was prepared as the neutral copper(II) complex from the reaction of 2-(2-pyridyl)-1,3-propanediamine with 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione and the crystal structure of this compound was undertaken; monoclinic,* $P2_1/c$ *with* $a = 10.582(3)$, $b = 25.951(5)$, $c = 7.736(3)$ Å, $\beta = 106.37(5)^\circ$, $R = 0.077$ *for 1054 data with* $I > 3\sigma(I)$. *The macrocyclic '*N_5*' copper(II) complex was shown to contain five coordinate Cu(II) while the '*N_4*–N' bifurcated copper(II) complex consists of four coordinate Cu(II) molecules in the solid state.*

Introduction

Synthetic cyclic quinquedentate ligands capable of providing an equatorial 'N_4' donor set and an axial ligand to afford square-pyramidal coordination complexes are of interest [1, 2] and can be of two types. The macrocyclic ligands of Type *A* and the bifurcated ligand Type *B*, both offer possible models to porphyrin/imidazole type complexes.



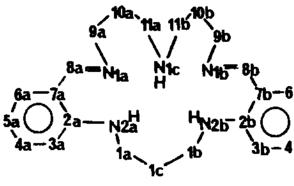
A



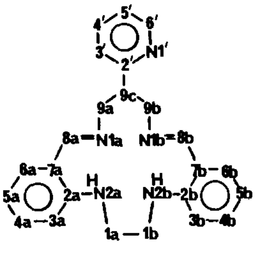
B

In their metal complexes the Type *A* ligands usually present an approximately planar 'N_5' equatorial donor set to the metal ion [3–6] for 15- and 16-membered analogues with the 17-membered macrocycle allowing a more three dimensional arrangement of the coordination sphere [7]. Ligands of Type *B* have been used previously to define 5-coordination sites at an octahedral metal ion [8]. Open chain analogues of Type *A* and Type *B* ligands have been reported, for example the cobalt(III) complex of N,N'-bis(salicylidene)dipropylene triamine [9] and α,α'{2-(2'-pyridyl)ethyl}ethylenebis(salicylideneiminato)cobalt(II) [10].

We report here the synthesis and crystal structures of copper(II) complexes of the ligands (I) and (II) [shown below with the crystallographic numbering scheme used.]. A preliminary report on part of this work has been published [11].



I

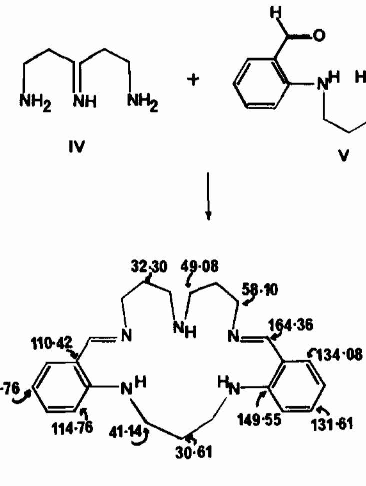


II

Results and Discussion

{*Dibenzo*[b,o] *[1,5,9,13,17]pentaazacycloeicosa[4,13]diene*}*copper(II) Diperchlorate (III)*

The compound (I) was prepared by a modification of the established template formation of Shiff's bases using the reaction of diamines with dialdehydes to give macrocyclic tetraaza ligand systems [12]. Reaction of bis(2-aminoethyl)amine (IV) with 4,8-diaza-2,3:9,10-dibenzoundecane-1,11-dione (V) in ethanol solution in the presence of zinc acetate gave (I) in 30% yield. The presence of the imine group in (I) was established by n.m.r. [N=C–*H*, 8.39 δ, *cf.* O=C–*H* 9.86 δ in (V); N=*C*–H, 164.36 ppm] and i.r. spectroscopy [$\nu_{C=N}$ 1634 cm^{-1}, *cf.* $\nu_{C=O}$ 1650 cm^{-1} in (V)]. The ^{13}C n.m.r. spectrum [C_5D_5N, 22.63 MHz, ppm TMS] was assigned on the basis of published shift values and is shown in Scheme 1.



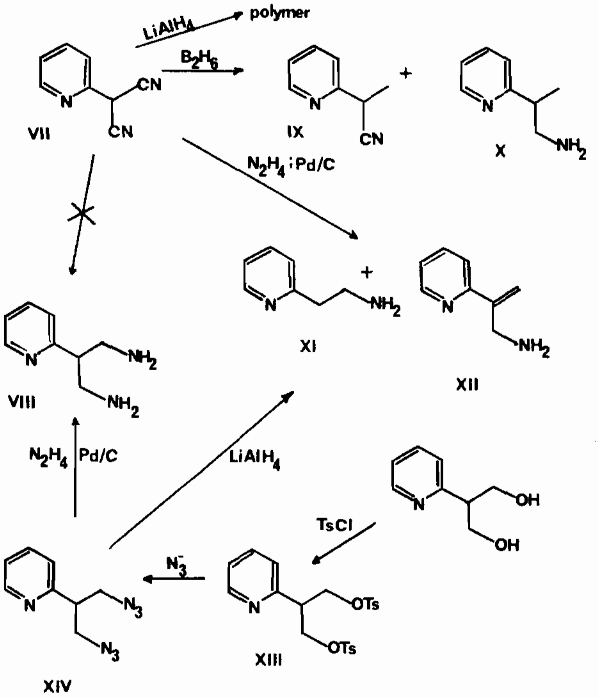
I

The penta-aza (I) was difficult to obtain pure and spectral data on the product obtained directly from the condensation reaction indicated the presence of a quantity of an amide fraction (~5%). A singlet at 2.16δ in the ^{1}H n.m.r. spectrum and an i.r. band at 1675 cm^{-1} both indicate an N-acyl group. The mass spectrum showed a small peak at *m/e* 419 ($RNCOCH_3$) together with the expected $M^{+\cdot}$ ion at *m/e* 377 for (I). The 419 ion could not be used as a measure of purity due to the ready loss of ketene (42 amu) from the spectra of N-acyl compounds, however, the impurity could be monitored by signals at *m/e* 143, 160, 190, and 201 which can be assigned to the acylated species and are not observed in the spectrum of pure (I). The acyl derivative may be produced *via* reaction of (I) with acetic anhydride formed by decomposition of the zinc acetate during prolonged refluxing (40 h).

A tetrahydrofuran (thf) solution of (I) was mixed with hydrated copper(II) perchlorate in thf and subsequent crystallisation of the precipitate from acetone gave (III) as blue-purple prisms. The i.r. spectrum of this complex showed sharp bands at 3590, 3260 cm^{-1} (ν_{N-H}), 1635 cm^{-1} ($\nu_{C=N}$) and a broad band at 1100 cm^{-1} (ClO_4^-). The ligand was relatively easy to displace from the Cu(II) ion by treatment with coordinating solvents such as dimethylformamide (dmf) and dimethylsulphoxide. The instability of (III), due in part to the flexibility of such a wrap-round 20-membered macrocycle, led us to develop a synthesis of a type *B* ligand which was expected to bind first row transition metal ions more strongly to give complexes of square pyramidal geometry.

{7-(2-pyridyl)-dibenzo[b,k] *[1,5,9,13] tetraazacyclopentadeca[4,9] diene(2-)}copper(II) (VI)*

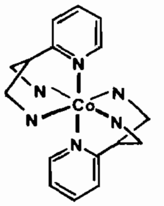
A survey of available methods for the preparation of pyridine derivatives suitable for condensation in Shiff's base reactions suggested that reduction of 2-pyridylmalonodinitrile(VII) offered a simple two step synthesis of 2-(2-pyridyl)-1,3-propanediamine-(VIII). The dicyano derivative (VII) is readily available from the treatment of 2-picoline with phenyl lithium followed by reaction with N-methyl-N-phenylcyanamide [13]. All attempts at reduction of (VII) to give the diamine (VIII) were however unsuccessful. Lithium aluminium hydride/thf gave polymer material; diborane/thf gave 1-cyano-1-(2-pyridyl)ethane (IX) and 2-(2-pyridyl)propylamine (X); hydrazine hydrate/palladium on carbon/EtOH gave a mixture of 2-(2-pyridyl)ethylamine (XI) and 2-(2-pyridyl)prop-2-enylamine (XII); [(IX)-(XII) were identified by ^{1}H n.m.r. and mass spectrometry] (Scheme 2).



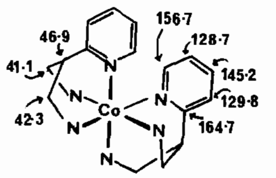
The $LiAlH_4$ reduction of azide intermediates using the scheme, ROH → $ROSO_2Ar$ → RN_3 → RNH_2 [14], for the conversion of aliphatic alcohols to their corresponding amines was tried as a multistep synthesis of (VIII). The bis(*p*-toluenesulfonate) of 2-(2-pyridyl)-1,3-propanediol (XIII) was prepared by the published procedure [15] and smoothly converted to the bisazide (XIV) by reaction with sodium azide (dmf). Reduction of (XIV) with $LiAlH_4$/thf gave a mixture of (XI) and (XII). The hydrazine-hydrate reduction ($H_2N–NH_2$, Pd/C, EtOH, 60 °C, 20 min) of (XIV) gave ~30:70 mixture of the required diamine (VIII) and the amine (XII) (Scheme 2). The amines (VIII) and (XII) could not be separated by distillation and the proportion of (VIII) in the mixture was considerably reduced upon distillation, apparently by elimination of NH_3. [The mass spectra of the reaction products exhibited an intense signal at *m/e* 134, $M^{+\bullet}$ for (XII), irrespective of the relative amounts of (VIII) and (XII), monitored by integration of the ^{1}H n.m.r. vinyl signals of (XII) to the pyridyl H(6) resonance for (VIII) and (XII).]

The tridentate (VIII), bidentate (XII) mixture could be separated by complex formation. Reaction of the crude product with nickel(II) perchlorate gave pink crystals of the bis{2-(2-pyridyl)-1,3-propanediamine} complex, i.r. 3365, 3310 cm^{-1} ν_{N-H}. Small quantities of pure (VIII) were obtained as the bis-(hydrochloride) salt by separation of the nickel(II) nitrate salt and decomposition of this product with HCl.

The diamagnetic cobalt(III) nitrate complex with (VIII) was prepared to further characterise the diamine by ^{13}C n.m.r. spectroscopy. The spectrum of the yellow bis{2-(2-pyridyl)-1,3-propane diamine} cobalt(III) trinitrate (XV), assigned below [22.63 MHz, D_2O, ppm TSP] not only demonstrated that the tridentate (VIII) was present in the product from the reduction of (XIV) but also allowed assignment of the stereochemistry to (XV). Previous ^{13}C n.m.r. studies on Co(III) tri-dentate amino isomers have shown that *μ-fac*-isomers contain multiple signals due to asymmetry compared to the *s-fac*-isomers [16]. The *s-fac-* (XV) isomer would be expected to show only one methylene resonance while the *μ-fac*-(XV) isomer would show two such signals due to the loss of the mirror plane. The sample (XV) showed two signals at 41.1 and 42.3 ppm, assigned to the CH_2 carbon atoms and is consequently the *μ-fac*-isomer [the *mer*-isomer was discounted due to steric considerations].

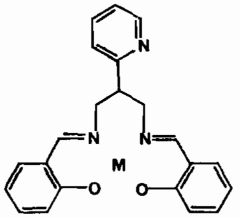


s-fac-XV



μ-fac-XV

The crude mixture (VIII)/(XII) was used for the preparation of the pentadentate derivatives described below and in the discussion the mixture is referred to as (VIIIa). The potential for the diamine (VIIIa) to give quinquedentate ligands was investigated by the preparation of the salicylaldehyde derivative (XVIa) which was isolated as yellow crystals [*m/e* 443 ($M^{+\bullet}$), i.r. 1625 ($\nu_{C=N}$), 1282 (ν_{C-O-H}) cm^{-1}, ^{1}H n.m.r. 8.26δ (N=C–*H*)]. The free ligand (XVIa) reacted with copper(II) acetate to give olive green needles of the neutral Cu(II) complex (XVIb), [*m/e* 420, 422 ($M^{+\bullet}$), i.r. 1625 ($\nu_{C=N}$) cm^{-1}]. Bands assignable to the O–H stretching vibrational mode were absent from the i.r. spectrum of this material. Bissalicylaldehyde copper(II) complexes have been shown to be bronze coloured when four coordinate and on complexation with a molecule of water the bright green five coordinate complexes were isolated [17].



XVIa M = 2H
b M = Cu(II)
c M = Fe(III)OAc

Similarly the Shiff's base copper(II) complex, {N,N'-bissalicylidenepropane-1,2-diamine}copper(II) has been reported [18] to be five-coordinate; green, in pyridine and four coordinate, violet, in $CHCl_3$ or CH_3OH solution. The complex (XVIb) gives a green colour in dry $CHCl_3$ and is presumably five coordinate. The possibility that the ligand (XVIa) is acting as a tetradentate with the pyridine nitrogen atom bridging to a second 'CuN_4' set cannot be ruled out as the X-ray structural analysis of the copper(II) complex of N,N'-bissalicylidene-1,5-diimino-3-azapentane, has shown that five coordination is achieved by dimerisation [19]. Reaction of the ligand (XVIa) with basic ferric acetate [20] in dmf/CH_3OH, gave black crystals of the Fe(III)–(OAc) complex (XVIc) [*m/e* 411, 413 ($M^{+\bullet}$), i.r. 1662 ($\nu_{C=O}$), 1621 ($\nu_{C=N}$) cm^{-1}]. Octahedral geometry is proposed for this complex.

Macrocyclic quinquedentate 'N_5' ligands were prepared from the diamine (VIIIa) by condensation with dialdehydes. Reaction of the C_3-dialdehyde (V) in the presence of Ni(II)$(ClO_4)_2$/dmf gave yellow crystals of the neutral Ni(II) complex (XVII) [*m/e* 453, 455 ($M^{+\bullet}$), i.r. 1620 ($\nu_{C=N}$) cm^{-1}]. Similar reaction of (VIIIa) with the C_2-dialdehyde, 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (XVIII) in the presence of Cu(II)$(OAc)_2$/dmf gave red-black crystals (from $CHCl_3$) of the neutral Cu(II) complex (VI), [*m/e* 444, 446 ($M^{+\bullet}$), i.r. 1620 ($\nu_{C=N}$) cm^{-1}].

TABLE I. Molecular Dimensions in the Coordination Groups of Compounds (III) and (VI) with E.s.d.s in Parentheses.

(a) Distances, A			
(III)		(VI)	
Cu–N(1a)	1.960(16)	Cu–N(1a)	1.989(12)
Cu–N(1b)	1.961(17)	Cu–N(1b)	1.976(12)
Cu–N(1c)	2.057(22)		
Cu–N(2a)	2.220(13)	Cu–N(2a)	1.953(12)
Cu–N(2b)	2.069(15)	Cu–N(2b)	1.955(12)
(b) Angles, deg.			
N(1a)–Cu–N(2a)	91.0(6)	N(1a)–Cu–N(2a)	90.3(5)
N(1a)–Cu–N(1b)	164.5(7)	N(1a)–Cu–N(1b)	97.5(5)
N(1a)–Cu–N(2b)	87.9(7)	N(1a)–Cu–N(2b)	166.9(5)
N(1a)–Cu–N(1c)	87.9(8)		
N(2a)–Cu–N(1b)	104.2(6)	N(2a)–Cu–N(1b)	164.0(5)
N(2a)–Cu–N(2b)	98.6(5)	N(2a)–Cu–N(2b)	85.8(5)
N(2a)–Cu–N(1c)	109.7(7)		
N(1b)–Cu–N(2b)	87.0(7)	N(1b)–Cu–N(2b)	89.4(5)
N(1b)–Cu–N(1c)	89.6(7)		
N(2b)–Cu–N(1c)	151.5(7)		
(c) Polyhedral edge lengths, A			
N(1a)···N(1c)	2.79	N(1a)···N(1b)	2.98
N(1c)···N(1b)	2.84	N(1b)···N(2b)	2.76
N(1b)···N(2b)	2.79	N(2b)···N(2a)	2.66
N(2b)···N(1a)	2.80	N(2a)···N(1a)	2.79
N(2a)···N(1a)	2.99		
N(2a)···N(1c)	3.51		
N(2a)···N(1b)	3.30		
N(2a)···N(2b)	3.26		

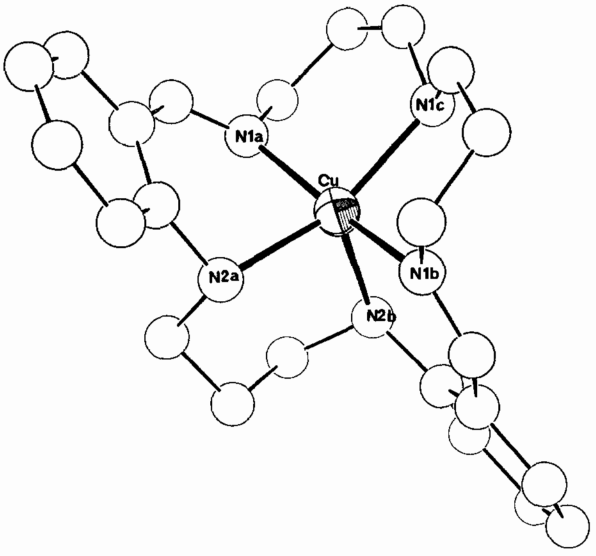
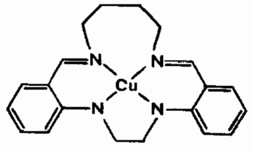


Fig. 1. The macrocyclic dication in the structure of (III). The conformation with the higher site occupation factor for the disordered chelate rings between N(1a)–N(1c) and N(1c)–N(1b) is shown.

The high solubility of the complex (VI) in solvents such as $CHCl_3$ indicated this complex to be five coordinate, the analogous 'N_4' neutral Cu(II) complexes such as (XIX) are relatively insoluble [21], although the red-black colour suggested four coordination.



XIX

Crystal Structures of the Copper(II) complexes (III) and (VI)

The molecular structures of (III) and (VI) are shown in Fig. 1 and 2 respectively. The bond lengths and angles in the coordination sphere for (III) and (VI) are listed in Table I.

Compound (III) consists of a dicationic five-coordinate copper(II) complex of the macrocycle which is well separated from the perchlorate ions.

TABLE II. Equation of Least-squares Planes in the Form PX + QY + RZ = S, where X = a x sinβ + cz cosβ, Y = by, Z = cz sinβ, for Compounds (III) and (VI). Atomic deviations (Å) are in square brackets.

(a) Compound (III)

Plane (i) N(1a), N(1b), N(1c), N(2b)
P = −0.6284, Q = 0.6868, R = −0.3652, S = −0.3709
[N(1a) 0.12; N(1b) 0.12; N(1c) −0.12; N(2b) −0.12; Cu 0.38; N(2a) 2.58]

Plane (ii) N(1c), N(2a), N(2b), Cu
P = 0.2736, Q = 0.7258, R = 0.6312, S = 4.3009
[N(1c) −0.017; N(2a) −0.007; N(2b) −0.016; Cu 0.039]

Plane (iii) Cu, N(1a), N(2a), C(2a)–C(8a)
P = −0.6851, Q = −0.2699, R = 0.6766, S = 2.1256
[Cu −0.06; N(1a) 0.14; N(2a) 0.14; C(2a) 0.11; C(3a) −0.03; C(4a) −0.13; C(5a) −0.07; C(6a) 0.05; C(7a) 0.12; C(8a) 0.01]

Plane (iv) Cu, N(1b), N(2b), C(2b)–C(8b)
P = −0.7069, Q = 0.3946, R = 0.5870, S = 3.9781
[Cu −0.73; N(1b) 0.54; N(2b) −0.01; C(2b) 0.26; C(3b) 0.04; C(4b) −0.25; C(5b) −0.25; C(6b) −0.01; C(7b) 0.19; C(8b) 0.24]

Angle (°) between the planes (iii)/(iv) = 39

(b) Compound (VI)

Plane (i) Cu, N(1a), N(1b), N(2a), N(2b)
P = −0.3289, Q = −0.6058, R = −0.7244, S = −4.0590
[Cu −0.018; N(1a) −0.208; N(1b) 0.219; N(2a) 0.244; N(2b) −0.238]

Plane (ii) Cu, N(1a) N(2a), C(2a)–C(8a)
P = −0.5514, Q = −0.5771, R = −0.6024, S = 3.6990
[Cu 0.075; N(1a) 0.012; N(2a) −0.146; C(2a) 0.021; C(3a) 0.049; C(4a) 0.036; C(5a) −0.005; C(6a) −0.034; C(7a) −0.021; C(8a) 0.012]

Plane (iii) Cu, N(1b), N(2b), C(2b)–C(8b)
P = −0.0709, Q = −0.6562, R = −0.7512, S = 4.2760
[Cu 0.048; N(1b) −0.126; N(2b) 0.141; C(2b) −0.058; C(3b) −0.105; C(4b) −0.052; C(5b) 0.048; C(6b) 0.095; C(7b) 0.043; C(8b) −0.033]

Plane (iv) N(1′), C(2′)–C(6′)
P = 0.2924, Q = 0.7921, R = −0.5358, S = −0.0840
[N(1′) 0.023; C(2′) −0.022; C(3′) 0.006; C(4′) −0.004; C(5′) −0.009; C(6′) 0.007]

Angles (°) between least-squares planes, (ii)/(iii) 29; (i)/(iv) −79.

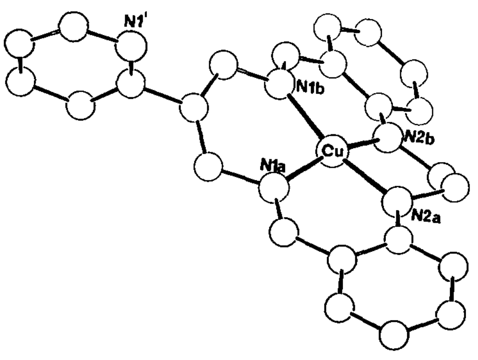


Fig. 2. The neutral 'N_4–N' copper(II) complex (VI).

The coordination polyhedron defined by the five nitrogen atoms is irregular. The atoms N(1a), N(1b), N(1c), N(2b) form the base of a distorted square pyramid with deviations from this 'N_4' plane of ±0.12 Å with the N(2a) atom occupying the apex. (Table II). The Cu atom lies 0.38 Å above the 'N_4' plane. The apical nitrogen N(2a) is only weakly bonded to the Cu atom (Cu–N 2.22 Å, *cf.* 2.01 Å mean for the basal Cu–N bond lengths). The macrocycle adopts an unusual conformation whereby the imino-N atoms are *trans* to each other. The imino-nitrogen to copper distances (1.96 Å) are significantly shorter than the secondary amine to copper distances 2.06 to 2.22 Å). The coordinate bonds for the anilino-nitrogen atoms are significantly longer than those

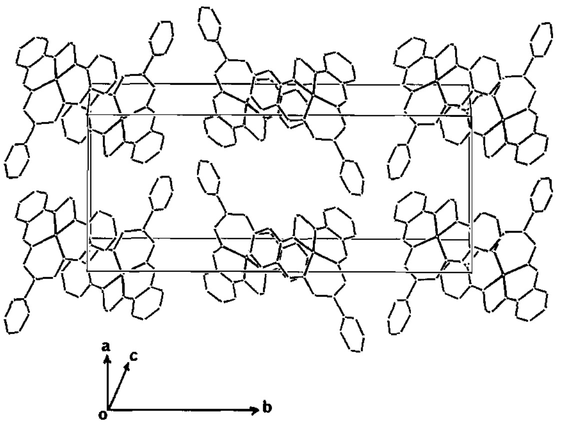


Fig. 3. The packing arrangement in the crystal structure of (VI).

(1.93(1) and 1.94(1)°) found [21] for the copper complex of a comparable deprotonated quadridentate macrocycle. The variations in Cu–N lengths in (III) may be partially attributed to steric restrictions associated with the wrapping of the ligand about the five vertices of the coordination polyhedron. Such strain effects may also partially account for the observation that the macrocycle can be relatively easily displaced from the copper ion on treatment with coordinating solvents such as dmf.

Compound (VI) in the solid state has a four-coordinate slightly tetrahedrally distorted square planar geometry. The pyridyl ring adopts an equatorial conformation *exo* to the macrocycle and is well removed from the Cu atom. There is no interaction between the pyridyl nitrogen atom of one molecule with the copper atoms of adjacent molecules as can be seen in the partial packing diagram presented in Fig. 3.

The closest non-bonded contact to the Cu atom is at 3.21 Å from H(6b)^{i} related by a center of symmetry. The closest contact to the pyridyl nitrogen atom is H(5b)^{ii} 2.78 Å. The 'N_4' plane in this case shows maximum deviations from planarity of ±0.22 Å with the copper atom lying in the least squares plane (0.02 Å deviation). The pyridine substituent lies at an angle of 79° to the 'N_4' plane.

The deprotonated amine bonds to the copper in complex (VI) (1.93, 1.95(1) Å) are shorter than the imino-nitrogen copper bond distances (1.98, 1.99(1) Å). All four donor nitrogen atoms in the structure of (VI) appear to be sp^2 hybridised with Σ angles at the N atoms of 360° in each case.

Experimental

^{13}C n.m.r. were obtained at 22.63 MHz on a Bruker HX90E spectrometer and ^{1}H n.m.r. spectra were obtained in lock mode on a Perkin-Elmer R12B spectrometer and at 220 MHz on a Varian HR-220 spectrometer. All spectra were run in deuteriochloroform solutions unless otherwise indicated, with tetramethylsilane as internal standard. Microanalysis data were determined on a Perkin-Elmer Elemental Analyser 240 within this Department. Mass spectra were recorded using a Kratos MS-50 spectrometer at 70 ev.

Reaction of Bis(2-aminoethyl)amine (IV) with 4,8-Diaza-2,3:9,10-dibenzoundecane-1,11-dione (V)

Zinc acetate (0.62 g, 5 mmol) was added to an EtOH solution (25 cm^3) of the dialdehyde (V) (0.70 g, 5 mmol) and the mixture was kept at 70 °C for 1 h. The triamine (IV) (0.65 g, 5 mmol) was added and the reaction mixture left for 40 h at 70 °C. The white precipitate was collected by filtration and crystallised (propyl alcohol, X4) to give white needles of (I) (0.51 g, 30%), m.p. 104 °C (Found C, 73.1; H, 8.1; N, 18.1; $C_{23}H_{31}N_5$ requires C, 73.2; H, 8.2; N, 18.6%). ^{1}H n.m.r. (220 MHz, C_5D_5N): δ 1.94 (4H, m, H(10)), 2.18 (2H, m, H(1c)), 3.10 (4H, t, J = 6.4 Hz, H(11)), 3.25 (4H, m, H(1a,b)), 3.60 (4H, t, J = 6.4 Hz, H(9)), 6.70–6.85 (4H, m, H(4,6)), 7.30–7.50 (4H, m, H(3,5)), 8.39 (2H, s, H(8)), 9.51 (3H, m, H(N1)). Mass spec: *m/e* 377 (6%, $M^{+\cdot}$).

{Dibenzo[b,o] *[1,5,9,13,17]pentaazacycloeicosa[4, 13]diene}copper(II) Diperchlorate (III)*

With copper(II) perchlorate in thf and (I) in EtOH blue-pruple prisms were obtained from acetone, m.p. > 300 °C (76%). (Found: C, 42.8; H, 4.6; N, 10.6. $C_{23}H_{31}Cl_2CuN_5O_8$ requires C, 43.2; H, 4.8; N, 10.9%). I.r. (NaCl): 3590, 3260 (N–H); 1635 (C=N); 1605, 1585, 1310, 1240, 1230, 1210, 1100 (ClO_4^-); 785, 775, 760, 630 cm^{-1}.

2-Pyridylmalonodinitrile (VII)

N-methyl-N-phenylcyanamide was prepared from N,N-dimethylaniline by reaction with cyanogen bromide and then reacted with 2-picoline lithium by the method of Lettré [13] to give the dicyano compound (VII) as fawn crystals (propyl alcohol, 42%). ^{1}H n.m.r.: δ 4.63 (1H, s, $CH(CN_2)$), 7.0–7.80 (3H, m, H(3,4,5)), 8.52 (1H, brd, H(6)). Mass spec: *m/e* 143 (11%, $M^{+\cdot}$).

Reduction of (VII)

$LiAlH_4$

Following the usual procedure for $LiAlH_4$ reductions in thf gave after aqueous work-up and extraction of the product into $CHCl_3$, an oil, for which pyridyl signals were absent from the ^{1}H n.m.r. spectrum.

Diborane

Reduction of (VII) in thf gave on work-up an oil which was fractionally distilled under reduced pressure. *Fraction (i),* a colourless liquid, b.p. 70–75°/ 1 mm (18%), ^{1}H n.m.r.: δ 1.60 (3H, d, J = 8.4 Hz, *C*H_3), 3.92 (1H, q, J = 8.4 Hz, *CH*(CN)), 7.0–7.8 (3H, m, H(3,4,5)), 8.45 (1H, brd, H(6)). Mass spec: *m/e* 132 (15%, $M^{+\bullet}$) for 1-cyano-1-(2-pyridyl)ethane (IX). *Fraction (ii),* a pale yellow oil, b.p. 110–118°/ 1 mm (38%), ^{1}H n.m.r.: δ 1.52 (3H, d, *C*H_3), 2.86 (2H, s, N–*H*), 3.10 (2H, brd, *C*H_2), 4.06 (1H, m, *CH*), 7.1–7.8 (3H, m, H(3,4,5)), 8.53 (1H, brd, H(6)), Mass spec: *m/e* 136 (8%, $M^{+\bullet}$) for 2-(2-pyridyl)-propylamine (X).

NH_2–NH_2·H_2O/Pd/C

To a solution of (VII) (1.4 g, 0.01 mol) in dmf (125 cm^3) at 60 °C was added Pd/C (0.1 g) followed by $NH_2NH_2 \cdot H_2O$ (0.9 g, 0.03 mol) in EtOH (25 cm^3) and the mixture kept at 60 °C for 1 h. The cooled mixture was filtered through a celite bed and the bed washed with hot EtOH.

A yellow oil remained after removal of the solvent and fractional distillation gave two significant fractions, the spectral details of which were consistent with 2-(2-pyridyl)ethylamine (XI) and 2-(2-pyridyl)-prop-2-enylamine (XII). *Fraction (i),* (XI), ^{1}H n.m.r. δ 3.10 (2H, t, J = 6.4 Hz, *C*H_2–NH_2), 4.10 (2H, t, J = 6.4 Hz, *C*H_2–CH_2–NH_2), 6.09 (2H, br s, N*H*$_2$), 6.91–7.75 (3H, m, H(3,4,5)), 8.45 (1H, br d, H(6)), mass spec: *m/e* 122 (12%, $M^{+\bullet}$). *Fraction (ii),* (XII), ^{1}H n.m.r. δ 3.26 (2H, br s, N–*H*$_2$), 4.60 (2H, br s, *C*H_2–NH_2), 5.55, 5.80 (2H, s = *C*H_2), 7.1–7.7 (3H, m, H (3,4,5)), 8.62 (1H, br s, H(6)), mass spec: m/e 134 (23% $M^{+\bullet}$).

2-(2-Pyridyl)-1,3-propanebis(p-toluenesulfonate) (XIII)

This material was prepared by the method of Mariella and Brown [15] and crystallised from isopropanol, m.p. 106 °C.

2-(2-Pyridyl)-1,3-propanediamine (VIII)

Treatment of the ditosylate (XIII) with sodium azide (3 mol equ.) in dmf at 60 °C by the method of Fleischer *et al.* [14] for 1 h gave on removal of the solvent a heavy oil of the diazido derivative (XIV). $LiAlH_4$ reduction of this oil in thf in the usual way gave a mixture of (XI) and (XII). Reduction of (XIV) using NH_2NH_2/Pd/C in EtOH by the procedure described above gave on work-up a yellow oil. The ^{1}H n.m.r. spectrum of this material showed signals which could be assigned to compound (XII) and one other product (~1:1). The second product had signals at, δ 3.08 (4H, br m, *C*H_2), 3.40 (1H, m, *CH*), ~7.4–7.6 (~3H, m, H(3,4,5)), 8.41 (1H, br d, H(6)). Mass spectra of the mixture, *m/e* 151 (3%, $M^{+\bullet}$), $C_8H_{13}N_3$, *m/e* 134 (100%, $M^{+\bullet}$, $C_8H_{11}N_2$; $M^{+\bullet}$–NH_3 for $C_8H_{13}N_3$). The components of the mixture could not be separated on distillation and the ratio of (XII) to (VIII) changed to ~2:1 after distillation.

Bis{2-pyridyl)-1,3-propane diamine}nickel(II) Perchlorate

With Ni(II)(ClO_4)$_2$ in EtOH and the mixture (VIIIa) in EtOH pink crystals were obtained, m.p. 297–300 °C (36%). (Found: C, 34.1; H, 4.2; N, 14.4. $C_{16}H_{26}Cl_2N_6NiO_8$ requires C, 34.3; H, 4.7; N, 15.0%), i.r. 3365, 3310, 1590, 1580, 1490, 1305, 1260, 1210, 800, 770, 625 cm^{-1}. Prepared similarly was the dinitrate salt, m.p. 276–280 °C (23%) (Found: C, 39.2; H, 5.0; N, 22.7. $C_{16}H_{26}N_8NiO_6$ requires C, 39.6; H, 5:4; N, 23.1%). A solution of the dinitrate in EtOH was treated with dry HCl and produced a white precipitate which was collected by filtration and dried. Crystallisation from EtOH–Et_2O gave the bishydrochloride of (VIII) as white needles (Found: C, 42.0; H, 6.5; N, 17.9. $C_8H_{15}Cl_2N_3$ requires C, 42.8; H, 6.7; N, 18.8%).

Bis{2-(2-pyridyl)-1,3-propane diamine}cobalt(III) Nitrate (XV)

A solution of the mixture (VIIIa) (~1:1) (5 g) in MeOH (15 cm^3) was added to a solution of Co(II)-(NO_3)$_2$·6H_2O (1 g), KNO_3 (1 g) in MeOH (15 cm^3) and the reaction mixture was left at 20 °C for 3 days with vigourous stirring. A small quantity of yellow crystals formed and Et_2O (5 cm^3) was added to the red-brown solution to produce a yellow powder which was crystallised from H_2O to give (XV) as yellow prisms (30%) (Found: C, 34.3; H, 5.0; N, 22.7; Co, 9.3. $C_{16}H_{26}CoN_9O_9$ requires C, 35.1; H, 4.8; N, 23.0; Co 10.8%), i.r. 1380–1350, 835 cm^{-1} (NO_3). ^{1}H n.m.r. (D_2O) δ 3.00 (8H, br d, *C*H_2) 4.10 (2H, m, *CH*), 7.40–8.60 (6H, m, pyridyl).

N,N'-Bissalicylidene-2-(2-pyridyl)propane-1,3-diamine (XVIa)

To a solution of the mixture (VIIIa) (300 mg, 1 mmol) and hydrated nickel(II) acetate (290 mg, 1 mmol) in EtOH (15 cm^3) was added salicylaldehyde (240 mg, 2 mmol) in EtOH (10 cm^3). The solution developed a deep yellow colour after several min. and on removal of most of the solvent *in vacuo* yielded a solid which was crystallised from the minimum quantity of isopropanol to give yellow needles of (XVIa), m.p. 180–181 °C (22%), (Found: C, 73.1; H, 5.1; N, 11.2. $C_{22}H_{21}N_3O_2$ requires C, 73.5; H, 5.8; N, 11.7%), ^{1}H n.m.r. δ 3.62 (1H, q, J = 7.2 Hz, *CH*-pyridyl), 4.04 (4H, br d, *C*H_2), 6.63–7.80 (11H, m, aromatics), 8.26 (2H, δ, N=C–*H*), 8.60 (1H, br d, H (6)), Mass spec: *m/e* 359 (11%, $M^{+\bullet}$), i.r. (KBr) 3035, 2940, 2920, 1625, 1580, 1330, 1320, 1282 cm^{-1}.

Reactions of the Disalicylidene (XVIa)

Hydrated copper(II) acetate in EtOH gave olive green needles of the neutral Cu(II) complex (XVIb) from $CHCl_3$ (Found: C, 62.4; H, 4.1; N, 9.7. $C_{22}H_{19}CuN_3O_2$ requires C, 62.8; H, 4.5; N, 9.9%), mass spec: *m/e* 420, 422 (16%, $M^{+\bullet}$), 286, 287 (26%, $M^{+\bullet}-C_6H_4(OH)(CH{=}NH)$), 224 (100%, $C_{14}H_{12}N_2O$), i.r. (KBr) 1625, 1615, 1595 cm^{-1}.

Basic ferric acetate [20] in dmf–MeOH similarly gave black crystals (XVIc) from $CHCl_3$ (Found: C, 60.6; H, 4.7; N, 8.1. $C_{24}H_{22}FeN_3O_4$ requires C, 61.1; H, 4.7; N 8.9%), mass spec: *m/e* 411, 413 (100%, $M^{+\bullet}$), 279, 281 (23%, $M^{+\bullet}-C_6H_4(OH)(CH{=}NH)$, $-OAc$), i.r. 1662, 1600, 1580, 1550, 1320, 1255, 1220, 780, 750, 670 cm^{-1}.

Reactions of the Pyridyldiamine (VIIIa) with Dialdehydes

A solution of the *C_3-dialdehyde* (V) (280 mg, 1 mmol) and hydrated nickel perchlorate (366 mg, 1 mmol) in dmf (15 cm^3) was added to a solution of the mixture (VIIIa) in dmf (5 cm^3) and the solution held at reflux for 8 h. Pale yellow crystals were deposited during this time and collected by filtration to give the neutral nickel(II) complex (XVIII) (21%) (Found: C, 65.2; H, 5.3; N, 14.9. $C_{25}H_{25}N_5Ni$ requires C, 66.1; H, 5.5; N, 15.4%), mass spec: *m/e* 453, 455 (71%, $M^{+\bullet}$), 395 (100%, $M^{+\bullet}-Ni$), i.r. 1620, 1585 cm^{-1}.

Prepared similarly was the copper(II) complex (VI) by the reaction of copper(II) acetate, (VIIIa) and the *C_2-dialdehyde* (XVIII) in dmf/EtOH solutions. Crystallisation of the product from $CHCl_3$ gave (VI) as red-black prisms (Found: C, 64.1; H, 4.7; N, 15.3. $C_{24}H_{23}CuN_5$ requires C, 64.8; H, 5.2; N, 15.7%), mass spec: *m/4* 444, 446 ($M^{+\bullet}$, 100%) i.r. (KBr) 1620, 1595, 1540, 1420, 1220, 765, 755, 740 cm^{-1}.

Crystal Data

For (III)

$C_{23}H_{31}Cl_2CuN_5O_8$, M = 639.5, monoclinic, a = 9.170(4), b = 17.059(6), c = 19.026(4) Å, β = 111.91(5)°, U = 2763.6 Å^3, Z = 4, F(000) = 1324, D_{cal} = 1.536 g cm^{-3}, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 9.87 cm^{-1}. The space group $P2_{1/c}$ was unambiguously determined from systematic absences in the $h0l$ = $2n$ + 1; $0k0$, K = $2n$ + 1. The data were collected in the space group $P2_{1/n}$, c = 17.774(4) Å and β = 96.30(5)°.

For (VI)

$C_{24}H_{23}CuN_5$, M = 444.5, monoclinic, a = 10.582(3), b = 25.951(5), c = 7.736(3) Å, β = 106.37(5)°, U = 2038.4 Å^3, Z = 4, F(000) = 924, D_{cal} = 1.448 g cm^{-3}, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 10.53 cm^{-1}. The space group $P2_1/c$ was determined from systematic absences in the data.

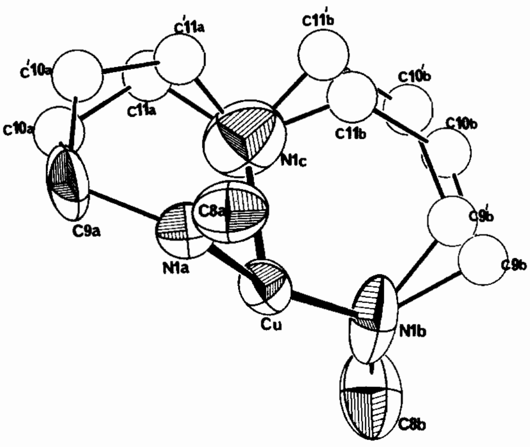


Fig. 4. The disorder in the trimethylene chelate rings in the structure of (III).

TABLE III. Fractional Atomic Co-ordinates (×10^4) for (III) with Standard Deviations in Parentheses.[a]

Atom	*x*	*y*	*z*
Cu	644(2)	1372(1)	2337(1)
N(1a)	−31(23)	511(9)	1655(10)
N(2a)	−1219(14)	2117(8)	1864(8)
N(1b)	1672(16)	2013(9)	3143(11)
N(2b)	−366(16)	814(8)	3174(8)
N(1c)	2381(24)	1513(12)	1709(10)
C(1a)	−2022(22)	2342(12)	2506(12)
C(1b)	−1453(21)	1291(14)	3523(10)
C(1c)	−2589(21)	1643(13)	2913(11)
C(2a)	−3324(25)	799(14)	390(12)
C(2b)	789(20)	506(11)	3752(10)
C(3a)	−4236(25)	1381(15)	50(13)
C(3b)	675(23)	−303(12)	3964(12)
C(4a)	−4211(22)	2103(13)	239(11)
C(4b)	1794(27)	−571(15)	4488(13)
C(5a)	−3169(22)	2357(12)	866(11)
C(5b)	2824(26)	−131(13)	4807(13)
C(6a)	−2208(20)	1823(11)	1226(10)
C(6b)	2938(27)	671(13)	4614(13)
C(7a)	−2259(23)	1073(13)	991(12)
C(7b)	1921(21)	983(13)	4049(11)
C(8a)	−1258(30)	480(13)	1169(12)
C(8b)	2189(22)	1757(13)	3795(13)
C(9a1)	878(48)	−265(19)	1784(26)
C(9a2)	1335(39)	−42(26)	1643(34)
C(9b)	2171(23)	2854(10)	2928(15)
C(10a1)	2177(53)	−3(22)	1393(22)
C(10a2)	2754(47)	296(33)	1422(25)
C(10b1)	3407(58)	2788(33)	2436(33)
C(10b2)	2539(58)	2889(26)	2122(18)
C(11a1)	2984(59)	735(18)	1672(35)
C(11a2)	3586(47)	970(28)	1817(34)
C(11b1)	3531(52)	2031(30)	2014(43)
C(11b2)	3185(56)	2235(21)	1704(31)

(continued on facing page)

TABLE III. *(continued)*

Atom	x	y	z
Cl(1)	3973(8)	594(4)	7056(4)
Cl(2)	1117(6)	2040(3)	−331(3)
O(111)	4519	1264	6685
O(112)	3917	1007	7851
O(121)	4462	627	6740
O(122)	5043	942	6947
O(131)	4512	−110	6349
O(132)	4339	−218	7611
O(141)	2397	596	6952
O(142)	2538	646	7310
O(211)	372	2014	−1085
O(112)	202	2504	−867
O(221)	1459	1257	−73
O(222)	1968	2548	192
O(231)	2449	2483	−332
O(232)	2084	1567	−724
O(241)	188	2408	166
O(242)	214	1542	76

[a] The atomic coordinates are given in the non-standard space group $P2_1/n$.

Intensity Measurements

For (III) and (VI) were made on a Philips PW1100 four-circle diffractometer using a θ–2θ scan and Mo-K_α radiation from a graphite crystal monochromator. For (III) a crystal of *ca.* 0.11 × 0.08 × 0.06 mm was used with a constant scan speed of 0.05 s^{-1} and a scan width of 0.7°, to examine reflections in the range θ 3–25°. For (VI) the scan speed was 0.04° s^{-1} and the scan width 1.0°, with a range in θ of 3–20°, using a crystal of *ca.* 0.09 × 0.08 × 0.05 mm. Three standard reflections were measured at intervals of 2 h during data collection for (III) and (VI) and showed no significant variation in intensity. The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer, I and $\sigma(I)$ were corrected for Lp factors but not absorption, and 1546 reflections for (III) and 1054 reflections for (VI) having $I > 3\sigma(I)$ were used.

TABLE IV. Fractional Atomic Co-ordinates (×10^4) for (VI) with Standard Deviations in Parentheses.

Atom	x	y	z
Cu	1229(2)	875(1)	4879(2)
N(1a)	281(11)	1515(5)	3836(17)
N(1b)	−43(12)	632(5)	6139(17)
N(2a)	2356(11)	934(5)	3276(16)
N(2b)	2486(10)	357(5)	6163(18)
C(1a)	3379(15)	532(6)	3671(21)
C(1b)	3705(17)	404(7)	5581(23)
C(2a)	2191(10)	1221(4)	1745(12)
C(2b)	2456(9)	37(4)	7536(14)
C(3a)	2986(10)	1140(4)	607(12)
C(3b)	3545(9)	−261(4)	8410(14)
C(4a)	2929(10)	1481(4)	−809(12)
C(4b)	3412(9)	−655(4)	9571(14)
C(5a)	2076(10)	1902(4)	−1087(12)
C(5b)	2190(9)	−752(4)	9858(14)
C(6a)	1280(10)	1983(4)	51(12)
C(6b)	1101(9)	−454(4)	8983(14)
C(7a)	1338(10)	1642(4)	1468(12)
C(7b)	1234(9)	−59(4)	7823(14)
C(8a)	422(14)	1755(6)	1489(20)
C(8b)	82(16)	244(6)	7171(22)
C(9a)	−809(17)	1732(7)	4530(26)
C(9b)	−1375(17)	897(8)	5761(27)
C(9c)	−1477(21)	1416(9)	5453(26)
N(1′)	−2427(16)	1953(6)	7207(23)
C(2′)	−2711(18)	1660(7)	5808(26)
C(3′)	−3901(19)	1582(8)	4601(27)
C(4′)	−4978(20)	1830(7)	4984(26)
C(5′)	−4770(19)	2113(7)	6408(25)
C(6′)	−3533(22)	2182(8)	7556(31)

Structure Solution and Refinement

The copper atom in (III) was located from a Patterson synthesis. The other non-hydrogen atom positions were obtained from a series of difference-Fourier syntheses. Two areas of disorder were apparent, the alkyl chains C(9a)–C(10a)–C(11a)–C(11b)–C(10b) and the perchlorate anions. Two positions for each of the carbon atoms were resolved and labelled as C(9a1), C(9a2) *etc.*, and for refinement equivalent bond lengths between disordered sites were refined to be equal. Two independent ClO_4^- groups were found and refined about each central chlorine atom. Site occupation factors of 0.69(3) and 0.31(3) for one perchlorate and 0.65(1), 0.35(1) for the other were obtained from the refinement of the ClO_4^- ions as rigid tetrahedral (O–Cl–O 109.5(5)°) pivoting on their central Cl atoms, with all the Cl–O bonds refined as one variable to a value of 1.436(8) Å. The two conformations of the trimethylene bridges were shown to have approximately equal population and are illustrated in Fig. 4. Full-matrix refinement of the positional and thermal parameters with the reflection weighted as $1/\sigma^2(F_o)$ gave a final R 0.095 and $R' = \Sigma w^{1/2} \| F_o | - | F_c \| / \Sigma w^{1/2} | F_o | = 0.101$. The copper and nitrogen atoms were assigned anisotropic temperature factors together with the neighbouring carbon atoms to the disordered bridges. For (VI) the copper atom was located from a Patterson synthesis. The non-hydrogen atoms were located from a difference-Fourier synthesis. Full-matrix refinement of 102 positional and thermal parameters (Cu, anisotropic) gave R 0.077 and $R' = 0.081$. Due to the poor quality of the data the phenyl rings were refined as rigid groups (C–C

TABLE V. Bond Distances (A) and Angles (°) in the Macrocyclic Skeleton for (III) with Standard Deviations in Parentheses.

(a) Distances			
C(1a)–C(1c)	1.52(3)	C(1b)–C(1c)	1.54(2)
C(1a)–N(2a)	1.47(2)	C(1b)–N(2b)	1.47(2)
C(2a)–N(2a)	1.46(2)	C(2b)–N(2b)	1.48(2)
C(2a)–C(3a)	1.39(3)	C(2b)–C(3b)	1.43(2)
C(3a)–C(4a)	1.27(3)	C(3b)–C(4b)	1.38(3)
C(4a)–C(5a)	1.45(2)	C(4b)–C(5b)	1.29(3)
C(5a)–C(6a)	1.37(2)	C(5b)–C(6b)	1.42(3)
C(6a)–C(7a)	1.35(2)	C(6b)–C(7b)	1.40(2)
C2a)–C(7a)	1.44(2)	C(2b)–C(7b)	1.38(2)
C(7a)–C(8a)	1.41(3)	C(7b)–C(8b)	1.43(3)
C(8a)–N(1a)	1.34(3)	C(8b)–N(1b)	1.28(2)
N(1a)–C(9a1), C(9a2)	1.57(4)	N(1b)–C(9b)	1.56(2)
C(9a1), C(9a2)–C(10a1), C(10a2)	1.51(6)	C(9b)–C(10b1), C(10b2)	1.50(6)
C(10a1), C(10a2)–C(11a1), C(11a2)	1.51(7)		
C(10b1), C(10b2)–C(11b1), C(11b2)	1.49(7)		
C(11a1), C(11a2)–N(1c)	1.44(4)	C(11b1), C(11b2)–N(1c)	1.44(5)
(b) Angles			
Cu–N(1a)–C(8a)	129(2)	Cu–N(1b)–C(8b)	125(1)
Cu–N(1a)–C(9a1)	114(2)	Cu–N(1b)–C(9b)	117(1)
Cu–N(1a)–C(9a2)	105(2)		
Cu–N(2a)–C(1a)	106(1)	Cu–N(2b)–C(1b)	115(1)
Cu–N(2a)–C(2a)	119(1)	Cu–N(2b)–C(2b)	108(1)
N(2a)–C(1a)–C(1c)	113(2)	N(2b)–C(1b)–C(1c)	111(1)
C(1a)–N(2a)–C(2a)	112(1)	C(1b)–N(2b)–C(2b)	111(1)
N(2a)–C(2a)–C(3a)	116(2)	N(2b)–C(2b)–C(3b)	117(2)
N(2a)–C(2a)–C(7a)	123(2)	N(2b)–C(2b)–C(7b)	120(2)
C(3a)–C(2a)–C(7a)	115(2)	C(3b)–C(2b)–C(7b)	123(2)
C(2a)–C(3a)–C(4a)	125(2)	C(2b)–C(3b)–C(4b)	115(2)
C(3a)–C(4a)–C(5a)	119(2)	C(3b)–C(4b)–C(5b)	124(2)
C(4a)–C(5a)–C(6a)	120(2)	C(4a)–C(5b)–C(6b)	122(2)
C(5a)–C(6a)–C(7a)	119(2)	C(5b)–C(6b)–C(7b)	119(2)
C(2a)–C(7a)–C(6a)	122(2)	C(2b)–C(7b)–C(6b)	118(2)
C(2a)–C(7a)–C(8a)	107(2)	C(2b)–C(7b)–C(8b)	125(2)
C(6a)–C(7a)–C(8a)	130(2)	C(6b)–C(7b)–C(8b)	117(2)
N(1a)–C(8a)–C(7a)	125(2)	N(1b)–C(8b)–C(7b)	123(2)
C(8a)–N(1a)–C(9a1)	116(2)	C(8b)–N(1b)–C(9b)	116(2)
C(8a)–N(1a)–C(9a2)	124(2)		
N(1a)–C(9a1)–C(10a1)	97(3)	N(1b)–C(9b)–C(10b1)	109(3)
N(1a)–C(9a2)–C(10a2)	119(4)	N(1b)–C(9b)–C(10b2)	112(2)
C(9a1)–C(10a1)–C(11a1)	118(4)	C(9b)–C(10b1)–C(11b1)	117(4)
C(9a2)–C(10a2)–C(11a2)	125(4)	C(9b)–C(10b2)–C(11b2)	126(4)
C(10a1)–C(11a1)–N(1c)	127(4)	C(10b1)–C(11b1)–N(1c)	129(4)
C(10a2)–C(11a2)–N(1c)	95(3)	C(10b2)–C(11b2)–N(1c)	114(4)
C(11a1)–N(1c)–C(11b1)	108(3)	C(11a2)–N(1c)–C(11b2)	100(3)
Cu–N(1c)–C(11a1)	104(2)	Cu–N(1c)–C(11b1)	116(3)
Cu–N(1c)–C(11a2)	118(3)	Cu–N(1c)–C(11b2)	122(3)
C(1a)–C(1c)–C(1b)	114(2)		

1.395 Å). The scattering factors used for all atoms in (III) and (VI) were those of Cromer and Mann. Computer programs were those of the SHELX 76 crystallographic system. The final atomic co-ordinates for (III) and (VI) are given in Tables III and IV respectively. The intramolecular bond lengths and angles for the macrocyclic skeleton for (III) and (VI) are listed in Tables V and VI respectively. Tables of isotropic and anisotropic thermal parameters for (III) and (VI), intermolecular contacts of less than 3.5 Å for (III) and (VI), and the observed and calculated structure factors for (III) and (VI), are available from the authors.

TABLE VI. Bond Distances (A) and Angles (°) in the Macrocyclic Skeleton for (VI) with Standard Deviations in Parentheses.

(a) Distances			
C(1a)–C(1b)	1.458(20)		
C(1a)–N(2a)	1.472(17)	C(1b)–N(2b)	1.487(19)
C(2a)–N(2a)	1.368(14)	C(2b)–N(2b)	1.354(16)
C(7a)–C(8a)	1.443(17)	C(7b)–C(8b)	1.418(17)
C(8a)–N(1a)	1.257(16)	C(8b)–N(1b)	1.270(17)
N(1a)–C(9a)	1.512(19)	N(1b)–C(9b)	1.520(19)
C(9a)–C(9c)	1.402(23)	C(9b)–C(9c)	1.368(24)
C(9c)–C(2′)	1.544(24)	N(1′)–C(2′)	1.287(21)
C(2′)–C(3′)	1.355(22)	C(3′)–C(4′)	1.410(23)
C(4′)–C(5′)	1.291(22)	C(5′)–C(6′)	1.371(25)
C(6′)–N(1′)	1.404(23)		
(b) Angles			
Cu–N(1a)–C(8a)	126(1)	Cu–N(1b)–C(8b)	127(1)
Cu–N(1a)–C(9a)	121(1)	Cu–N(1b)–C(9b)	119(1)
Cu–N(2a)–C(1a)	111(1)	Cu–N(2b)–C(1b)	108(1)
Cu–N(2a)–C(2a)	130(1)	Cu–N(2b)–C(2b)	131(1)
N(2a)–C(1a)–C(1b)	109(1)	N(2b)–C(1b)–C(1a)	110(1)
N(2a)–C(2a)–C(3a)	121(1)	N(2b)–C(2b)–C(3b)	117(1)
N(2a)–C(2a)–C(7a)	119(1)	N(2b)–C(2b)–C(7b)	121(1)
C(1a)–N(2a)–C(2a)	118(1)	C(1b)–N(2b)–C(2b)	120(1)
C(2a)–C(7a)–C(8a)	125(1)	C(2b)–N(7b)–C(8b)	114(1)
C(6a)–C(7a)–C(8a)	114(1)	C(6b)–C(7b)–C(8b)	126(1)
C(7a)–C(8a)–N(1a)	127(1)	C(7b)–C(8b)–N(1b)	126(1)
C(8a)–N(1a)–C(9a)	113(1)	C(8b)–N(1b)–C(9b)	114(1)
N(1a)–C(9a)–C(9c)	121(1)	N(1b)–C(9b)–C(9c)	120(1)
C(9a)–C(9c)–C(9b)	130(2)	C(9a)–C(9c)–C(2′)	115(2)
C(9b)–C(9c)–C(2′)	114(2)	C(9c)–C(2′)–C(3′)	119(2)
C(9c)–C(2′)–N(1′)	112(2)	C(3′)–C(2′)–N(1′)	128(2)
C(2′)–C(3′)–C(4′)	116(2)	C(3′)–C(4′)–C(5′)	119(2)
C(4)′)–C(5′)–C(6′)	121(2)	C(5′)–C(6′)–N(1′)	121(2)
C(6′)–N(1′)–C(2′)	114(2)		

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