fact, observed with rings *A* and *B* making respective angles of 20·9 and 20·1°, whereas the C(4)—C(6)—C(8) angle of 121·5 (4)° is normal. The bond lengths and angles are similar in both thiophene systems lending the molecule an approximate C_2 symmetry. Both thiophene rings are planar [maximum deviation from their weighted least-squares planes = 0·02 Å at C(10)]. The disordered *B′* ring represents a 175·6° rotation of ring *B* about C(8)—C(6). The bond length distribution indicates that the contribution of the dipolar structures is limited. In octaethylxanthoporphinogen dihydrate (Sheldrick, 1976) bridging C—C distances of 1·440 (5) and 1·481 (5) Å were recorded, which indicated significant π-delocalization between the C=O bond and the first pyrrole ring. It is not possible to explain the short C(4)—C(5) and C(8)—C(7) distances in (I) in terms of any possible mesomeric contribution.

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5,6,7,8,15,16,17,18-Octahydrodibenzo[*e*,*o*][1,4,8,13]tetraazacyclohexadecene

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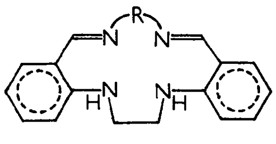
Abstract. $C_{20}H_{24}N_4$, $M_r = 320·4$, orthorhombic, *Fdd*2, $a = 40·778$ (26), $b = 34·990$ (24), $c = 4·928$ (1) Å, $V = 7031·4$ Å^3, $Z = 16$, $D_x = 1·21$ g cm^{-3}. The arrangement of N atoms is approximately planar but the geometry of the ligand shows considerable distortion from that observed in the corresponding Cu^{II} complex [Losman, D., Engelhardt, L. M. & Green, M. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 791–796].

Introduction. $C_{20}H_{24}N_4$ (I) was recrystallized from dichloromethane/methanol. Intensities were measured on a Philips PW1100 diffractometer using graphite-monochromated Mo *Kα* radiation and an ω–2θ scan. Unit-cell dimensions were obtained by least-squares analysis from the setting angles of 25 reflexions. Owing to poor crystal quality two octants of data were collected and equivalent reflexions were averaged. All independent reflexions *hkl* (all indices positive) were measured in the range $3·0 \leq \theta \leq 25·0°$. Reflexions $\bar{h}kl$ were measured for $3·0 \leq \theta \leq 28·0°$ but weak reflexions giving $I_t - 2\sqrt{I_t} < I_b$ on the first scan were omitted from the data set: I_t and I_b are respectively the count rates at the top of the reflexion profile and in the background. To increase the accuracy of measured reflexions a multiple-scan technique was employed; each reflexion was scanned repeatedly until 500 counts had been recorded or until a maximum of three scans had been made. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 0·40$ cm^{-1}); 932 unique reflexions with $F \geq 3\sigma(F)$ were used in the structure refinement. Space group *Fdd*2 is determined unambiguously by the systematic absences: *hkl*, $h + k$, $k + l$, $l + h \neq 2n$; $0kl$, $k + l \neq 4n$; $h0l$, $h + l \neq 4n$.



(I) R = $(CH_2)_4$

Conventional direct methods failed to give any encouraging molecular fragments so an attempt was

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U
N(1)	1779 (2)	1697 (2)	1938*	73 (3)
C(2)	1731 (2)	2115 (3)	1774 (38)	86 (4)
C(3)	1383 (2)	2217 (3)	2006 (32)	68 (3)
C(4)	1175 (2)	2120 (3)	−467 (34)	73 (3)
C(5)	826 (2)	2056 (3)	119 (33)	83 (4)
N(6)	785 (2)	1695 (2)	1785 (28)	70 (3)
C(7)	576 (3)	1456 (3)	908 (34)	72 (3)
C(8)	517 (2)	1089 (3)	2136 (31)	57 (3)
C(9)	707 (2)	921 (2)	4182 (30)	52 (3)
N(10)	963 (2)	1127 (2)	5333 (29)	62 (3)
C(11)	1214 (2)	962 (3)	7112 (30)	62 (3)
C(12)	1467 (2)	731 (3)	5567 (31)	60 (3)
N(13)	1647 (2)	982 (2)	3745 (28)	63 (3)
C(14)	1893 (2)	869 (3)	2069 (31)	60 (3)
C(15)	2044 (2)	1135 (3)	345 (32)	62 (3)
C(16)	1967 (2)	1541 (3)	282 (29)	71 (3)
C(17)	258 (2)	871 (3)	1109 (34)	73 (3)
C(18)	179 (3)	513 (3)	1998 (31)	79 (3)
C(19)	369 (3)	362 (3)	4064 (32)	75 (3)
C(20)	636 (2)	552 (2)	5155 (32)	61 (3)
C(21)	1995 (3)	475 (3)	1990 (34)	72 (3)
C(22)	2247 (3)	378 (3)	210 (34)	80 (4)
C(23)	2387 (3)	632 (3)	−1533 (35)	91 (4)
C(24)	2283 (3)	1008 (3)	−1464 (34)	80 (4)

* The z coordinate of N(1) was fixed for origin definition.

Table 2. *Molecular geometry*

(a) Bond lengths (Å) (all e.s.d.'s 0·01 Å)

N(1)–C(2)	1·48	C(14)–C(15)	1·40
C(2)–C(3)	1·47	C(15)–C(16)	1·46
C(3)–C(4)	1·52	C(16)–N(1)	1·25
C(4)–C(5)	1·47	C(8)–C(17)	1·40
C(5)–N(6)	1·52	C(17)–C(18)	1·36
N(6)–C(7)	1·27	C(18)–C(19)	1·39
C(7)–C(8)	1·44	C(19)–C(20)	1·39
C(8)–C(9)	1·40	C(20)–C(9)	1·41
C(9)–N(10)	1·39	C(14)–C(21)	1·44
N(10)–C(11)	1·47	C(21)–C(22)	1·39
C(11)–C(12)	1·52	C(22)–C(23)	1·36
C(12)–N(13)	1·46	C(23)–C(24)	1·38
N(13)–C(14)	1·36	C(24)–C(15)	1·39

(b) Selected bond angles (°) (e.s.d.'s 1·0° except where indicated)

C(16)–N(1)–C(2)	119	C(12)–N(13)–C(14)	125
N(1)–C(2)–C(3)	111	C(12)–N(13)–H(13)	110 (7)
C(2)–C(3)–C(4)	115	H(13)–N(13)–C(14)	124 (7)
C(3)–C(4)–C(5)	115	N(13)–C(14)–C(15)	120
C(4)–C(5)–N(6)	110	N(13)–C(14)–C(21)	121
C(5)–N(6)–C(7)	116	C(21)–C(14)–C(15)	119
N(6)–C(7)–C(8)	124	C(14)–C(15)–C(16)	124
C(7)–C(8)–C(9)	126	C(14)–C(15)–C(24)	119
C(7)–C(8)–C(17)	118	C(24)–C(15)–C(16)	117
C(17)–C(8)–C(9)	117	C(15)–C(16)–N(1)	123
C(8)–C(9)–N(10)	120	C(8)–C(17)–C(18)	124
C(8)–C(9)–C(20)	121	C(17)–C(18)–C(19)	117
C(20)–C(9)–N(10)	119	C(18)–C(19)–C(20)	123
C(9)–N(10)–C(11)	124	C(19)–C(20)–C(9)	118
C(9)–N(10)–H(10)	109 (7)	C(14)–C(21)–C(22)	118
H(10)–N(10)–C(11)	121 (6)	C(21)–C(22)–C(23)	123
N(10)–C(11)–C(12)	113	C(22)–C(23)–C(24)	118
C(11)–C(12)–N(13)	109	C(23)–C(24)–C(15)	122

made to construct a larger starting set. Two reflexions were assigned fixed phases on the basis of seminvariant indications derived by combining triple and quartet phase relations (Sheldrick, 1976). One reflexion with $l = 1$ was assigned $\varphi = 0°$ to fix the origin and 10 reflexions were assigned 'magic integer' phases of the form $\varphi = Mx$, where φ was taken modulo 360°, x ranged from 0 to 118° in steps of (360/4096)°, and M took the values 513, 769, 897, 961, 993, 1009, 1017, 1021, 1023 and 1024 (Main, 1977). (In retrospect it was noted that this does not give complete coverage of the phase space of one enantiomorph in *Fdd*2 which would require moving the origin to $\frac{1}{8},\frac{1}{8},0$ and then covering $x = 0$ to 180°.) The phase sets were expanded to 469 phases with $E > 1{\cdot}0$ by the tangent formula, figures of merit being calculated at the 250-phase stage. The E map calculated from the phase set with the lowest value of *NQEST* ($-0{\cdot}275$ compared with $-0{\cdot}201$ for the next; De Titta, Edmonds, Langs & Hauptman, 1975) and R_α (0·186 compared with 0·205; Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) gave a correct 18-atom fragment. One cycle of tangent expansion (Karle, 1968) for $E > 1{\cdot}0$, with fixed calculated phases for reflexions with $E > 1{\cdot}5$ and $E_{\text{calc}} > 0{\cdot}6E_{\text{obs}}$, gave the 24 non-hydrogen atoms of the molecule as the highest 24 peaks.

Isotropic least-squares refinement (to $R = 0{\cdot}14$) followed by a difference synthesis showed 17 of the 24 H atoms. H(10) and H(13) were inserted in positions deduced from the difference map and were refined with N–H distances constrained to be 1·00 (5) Å. The

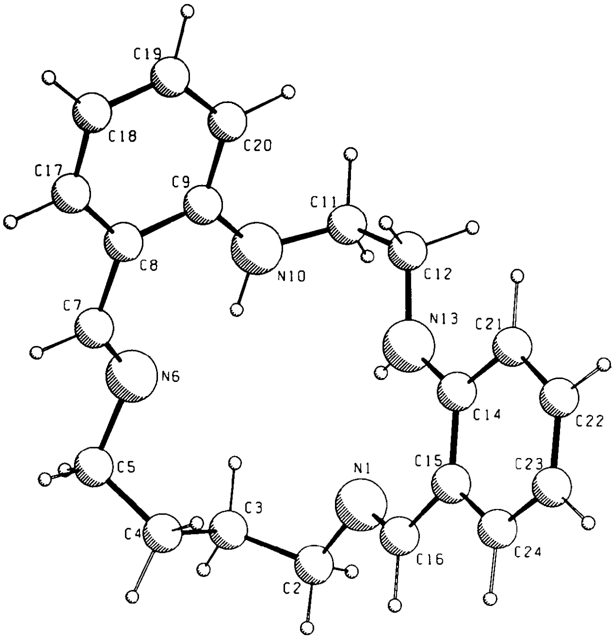

Fig. 1. A view of one molecule showing the atom-numbering scheme. H atoms are given the number of the C or N atom to which they are attached.

Table 3. *Least-squares planes and atom deviations* (Å)

The equations of the planes are expressed in direct space as $Px + Qy + Rz = S$. The atoms listed are those included in the plane calculation.

Ligand (I) $3{\cdot}996x + 17{\cdot}729y + 4{\cdot}221z = 4{\cdot}306$

N(1)	0·232	N(10)	0·328
N(6)	−0·233	N(13)	−0·326

r.m.s. deviation from plane = 0·284 Å.

Cu$^{\rm II}$ complex $1{\cdot}145x + 8{\cdot}460y + 3{\cdot}115z = 3{\cdot}589$

N(1)*	0·284	N(10)	0·327
N(6)	−0·289	N(13)	−0·323

r.m.s. deviation from plane = 0·307 Å.

Ligand (I) $-24{\cdot}309x + 14{\cdot}009y + 3{\cdot}430z = 0{\cdot}999$

N(6)	0·080	C(9)	0·007
C(7)	−0·048	N(10)	0·068
C(8)	0·003	H(10)	−0·109

Ligand (I) $29{\cdot}560x + 4{\cdot}394y + 3{\cdot}338z = 6{\cdot}633$

N(13)	−0·084	C(15)	0·023
H(13)	0·055	C(16)	−0·048
C(14)	0·035	N(1)	0·018

* Atoms renumbered to correspond to numbering scheme used for (I).

remaining H atoms were inserted in calculated positions (C—H 1·08 Å) and refined subject to the constraint that the C—H vectors were constant in magnitude and direction but not position (*i.e.* a riding model was employed for H attached to C). A common isotropic temperature factor for all H atoms was refined [0·12 (1) Å^2]. The refinement converged at $R = 0{\cdot}120$, $R' = 0{\cdot}090$ [$R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$] for 103 parameters; reflexions were weighted as $w = 1/\sigma^2(F_o)$. Final atomic coordinates and isotropic temperature factors are given in Table 1 and the molecular geometry in Table 2.* The molecule is illustrated in Fig. 1.

Discussion. The structure determination of the title compound was undertaken as part of a study of the conformational changes undergone by macrocyclic N ligands on complexation to transition-metal ions. The effects of variation of macrocyclic-ring size and levels of conjugation upon the metal–donor interactions have also been examined (Peters, Owston, Tasker & Trotter, 1978).

Table 4. *Non-bonded intramolecular* N···N *distances* (Å)

	Ligand	Cu$^{\rm II}$ complex
N(1)···N(6)	4·05	2·98
N(6)···N(10)	2·75	2·79
N(10)···N(13)	2·94	2·66
N(13)···N(1)	2·71	2·82

The molecular geometry of the present structure may be compared with that of the Cu$^{\rm II}$ complex of (I) (Losman, Engelhardt & Green, 1973). In both structures the arrangement of N atoms is approximately planar (Table 3) with N(1) and N(10) above the mean plane and N(6) and N(13) below. Comparison of the non-bonded N···N distances (Table 4) shows that the geometry of the N_4 system is considerably modified upon complexation: in particular the N(1)···N(6) distance is reduced by the geometrical requirements for the formation of Cu—N(imine) bonds.

The non-bonded N···H—N distances and angles [N(1)···H(13) 2·04 Å, N(1)···H(13)—N(13) 123°, N(6)···H(10) 1·92 Å, N(6)···H(10)—N(10) 139°] suggest that there may be intramolecular hydrogen bonding. The molecular fragments N(6), C(7), C(8), C(9), N(10), H(10) and N(13), H(13), C(14), C(15), C(16), N(1) are both planar (Table 3) and it is postulated that the distortion of the ligand from planarity arises because of the displacement of these two planar moieties relative to each other to minimize the interaction between the secondary amine H atoms [H(10)···H(13) 2·45 Å]. Both H(10) and H(13) are displaced to the same side of the N_4 plane resulting in a reduction of the angle between the benzene rings from 180° (planar structure) to 82·1°. No corresponding interplanar angle is given for the Cu$^{\rm II}$ complex but it appears from the diagram of the molecule that the distortion from planarity is less than in the free ligand.

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* Lists of structure factors and hydrogen atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33677 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.