

Structure of a Tetratertiaryamino-Diphenolato Macrocyclic Ligand

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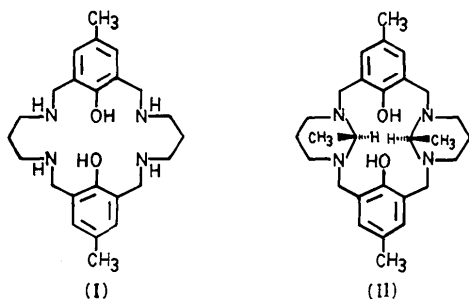
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Abstract. 11,23,26,28-Tetramethyl-3,7,15,19-tetraaza-pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane-1(25),9,11,13(27),21,23-hexaene-25,27-diol, C₂₈H₄₀N₄O₂, $M_r = 464.65$, monoclinic, $P2_1/n$, $a = 12.529(1)$, $b = 13.068(1)$, $c = 15.815(1)$ Å, $\beta = 93.58(1)^\circ$, $V = 2584.3(3)$ Å³, $Z = 4$, $D_x = 1.194$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71068$ Å, $\mu = 0.709$ cm⁻¹, $F(000) = 1008$, $T = 293(1)$ K, $R(F) = 0.052$, $wR(F) = 0.052$ for 2115 observed reflections with $I > 3\sigma(I)$. The macrocycle has an asymmetric configuration; the interplanar angle between the two phenyl rings is $54.6(1)^\circ$, and the mean planes of the two C—C—C—N—C—N rings are almost at a right angle, $88.93(15)^\circ$. The phenolic OH groups are intramolecularly hydrogen bonded to the nearest N atoms.

Introduction. The macrocyclic ligand (I) was introduced (Mandal & Nag, 1986) to investigate the mutual interactions between two metal centres held in close proximity. Ligand (I) forms binuclear complexes in which the two metal centres (M^{2+}) are bridged by two phenoxide O atoms with two secondary amine N donors completing the distorted



MN_2O_2 plane. The X-ray structures of the dicopper (II) and dinickel (II) complexes of (I) with axially elongated octahedral or square pyramidal geometries

have been determined and structure–property correlations involving redox, magnetic and spectroscopic properties have been found (Mandal, Thompson, Nag, Charland & Gabe, 1987*a,b*; Das & Nag, 1991; Nanda, Das, Newlands, Hynes, Gabe & Nag, 1992). In order to study the effect of squeezing the hole size of the macrocycle ring on metal binding we have synthesized a new series of macrocyclic ligands by reacting (I) with various aldehydes, $RCHO$ [$R = H, Me, Bu, Ph, o\text{-}p\text{-}C_6H_4OH, C_5H_4N$ or C_4H_3S (Nanda, Adhikary & Nag, 1992)]. In contrast to (I) these new ligands specifically bind Cu^{2+} ions, but not Ni^{2+} ions. The structure of (II) ($R = CH_3$) has been determined to see the effect of introducing additional N—C—N bridges on the overall configuration of the macrocycle.

Experimental. Ligand (II) was prepared by reacting (I) with acetaldehyde in methanol at room temperature. Colourless crystals of suitable size and shape were obtained from a solution in petroleum ether (313–333 K). X-ray diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated $Mo K\alpha$ radiation. Cell dimensions were determined by a least-squares fit of 25 arbitrarily chosen higher order reflections. Intensity data were collected in the 2θ range $2\text{--}47^\circ$ (h 0–14, k 0–14, l 17–17); $\theta/2\theta$ scan mode. 3824 reflections were measured of which 2115 with $I > 3\sigma(I)$ were considered observed. The orientation and decay of the crystal during data collection were checked periodically by monitoring two sets of three control reflections; the extent of crystal decay was found to be insignificant. The intensities were corrected for Lorentz–polarization, but absorption correction was not made owing to the small absorption coefficient ($\mu = 0.709$ cm⁻¹) of the crystal. The structure was solved by direct methods using the program *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H atoms

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were located from the difference Fourier map. Block-diagonal least-squares refinement with a unit-weighting scheme employing Dunitz–Seiler factors (Dunitz & Seiler, 1973) resulted in convergence at $R(F) = 0.052$ and $wR(F) = 0.052$; $(\Delta/\sigma)_{\max} = 0.03$ for 289 parameters. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final difference map showed ripples of about $0.22 \text{ e } \text{Å}^{-3}$ around some of the non-H atoms. All computations were carried out with the Enraf–Nonius (1988) *Structure Determination Package* available on the PDP-11/73 system.

Discussion. An ORTEPII (Johnson, 1976) diagram of (II) along with the atom-numbering scheme is shown in Fig. 1. The final positional and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1, and the selected bond distances, bond angles and torsion angles are listed in Table 2.*

The observed C—C and C—N distances in (II) are normal. The average of solid angles at the N centres is $337 (2)^\circ$, which indicates considerable pyramidal distortions of these atoms. In the six-membered rings, $\overline{N(1)C(9)C(10)C(11)N(2)C(13)}$ and $\overline{N(4)C(24)C(25)C(26)N(3)C(23)}$, the atoms are displaced above or below the mean planes by about $0.23 (4) \text{ Å}$, and these two mean planes are almost perpendicular to each other [$88.93 (15)^\circ$]. The two phenyl rings of the molecule do not lie in the same plane, the interplanar angle being $54.6 (1)^\circ$. A consideration of the C—N—C—C torsional angles

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54978 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0518]

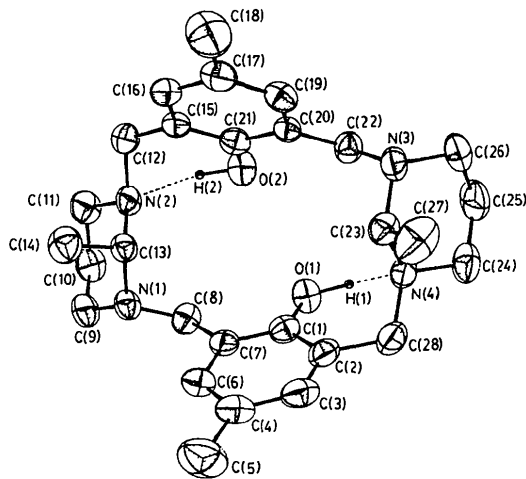


Fig. 1. ORTEPII (Johnson, 1976) diagram of (II) with atom-labelling scheme.

Table 1. Positional and equivalent isotropic thermal parameters (Å^2) of non-H atoms with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(1)	0.5736 (2)	0.1174 (2)	0.5213 (2)	4.12 (8)
O(2)	0.7270 (2)	0.1547 (2)	0.7013 (2)	3.97 (8)
N(1)	0.8147 (3)	0.3328 (3)	0.4994 (2)	3.31 (9)
N(2)	0.8709 (3)	0.2944 (3)	0.6460 (2)	3.30 (9)
N(3)	0.3999 (3)	0.1682 (3)	0.7308 (2)	3.73 (9)
N(4)	0.3719 (3)	0.1306 (3)	0.5807 (2)	3.50 (9)
C(1)	0.5500 (3)	0.2104 (3)	0.4846 (3)	3.4 (1)
C(2)	0.4429 (3)	0.2410 (4)	0.4700 (3)	3.6 (1)
C(3)	0.4203 (4)	0.3346 (4)	0.4316 (3)	4.2 (1)
C(4)	0.5011 (4)	0.3988 (4)	0.4071 (3)	4.2 (1)
C(5)	0.4765 (5)	0.5026 (5)	0.3665 (4)	6.6 (2)
C(6)	0.6065 (4)	0.3668 (4)	0.4221 (3)	3.8 (1)
C(7)	0.6325 (3)	0.2737 (3)	0.4611 (3)	3.2 (1)
C(8)	0.7490 (3)	0.2430 (4)	0.4773 (3)	3.6 (1)
C(9)	0.9252 (4)	0.3246 (4)	0.4759 (3)	4.1 (1)
C(10)	0.9913 (4)	0.2535 (4)	0.5340 (3)	4.9 (1)
C(11)	0.9849 (4)	0.2866 (4)	0.6258 (3)	4.5 (1)
C(12)	0.8653 (3)	0.3231 (4)	0.7361 (3)	3.9 (1)
C(13)	0.8070 (3)	0.3641 (3)	0.5868 (3)	3.1 (1)
C(14)	0.8340 (4)	0.4784 (4)	0.5965 (3)	4.6 (1)
C(15)	0.7515 (3)	0.3218 (3)	0.7623 (3)	3.0 (1)
C(16)	0.7100 (4)	0.4030 (4)	0.8064 (3)	3.5 (1)
C(17)	0.6063 (4)	0.4003 (4)	0.8314 (3)	3.7 (1)
C(18)	0.5611 (5)	0.4902 (4)	0.8788 (4)	5.9 (2)
C(19)	0.5422 (4)	0.3163 (3)	0.8100 (3)	3.4 (1)
C(20)	0.5811 (3)	0.2326 (3)	0.7658 (2)	2.8 (1)
C(21)	0.6869 (3)	0.2368 (3)	0.7433 (3)	3.1 (1)
C(22)	0.5119 (3)	0.1396 (4)	0.7452 (3)	3.5 (1)
C(23)	0.3772 (3)	0.2115 (4)	0.6472 (3)	3.5 (1)
C(24)	0.2932 (4)	0.0497 (4)	0.5960 (4)	5.0 (1)
C(25)	0.3190 (5)	0.0018 (4)	0.6817 (4)	5.9 (2)
C(26)	0.3254 (4)	0.0842 (5)	0.7498 (3)	5.6 (2)
C(27)	0.2777 (4)	0.2806 (5)	0.6461 (4)	6.1 (2)
C(28)	0.3549 (4)	0.1692 (4)	0.4931 (3)	4.3 (1)

Table 2. Selected bond lengths (Å), bond angles ($^\circ$) hydrogen-bond geometry ($\text{Å}, ^\circ$) and torsion angles ($^\circ$) with *e.s.d.*'s in parentheses

O(1)—C(1)	1.371 (5)	N(4)—C(23)	1.489 (6)
O(2)—C(21)	1.374 (5)	N(4)—C(24)	1.476 (6)
N(1)—C(8)	1.463 (6)	N(4)—C(28)	1.478 (6)
N(1)—C(9)	1.459 (6)	C(7)—C(8)	1.520 (6)
N(1)—C(13)	1.451 (5)	C(9)—C(10)	1.516 (7)
N(2)—C(11)	1.487 (6)	C(10)—C(11)	1.522 (7)
N(2)—C(12)	1.479 (6)	C(12)—C(15)	1.510 (6)
N(2)—C(13)	1.501 (5)	C(13)—C(14)	1.537 (7)
N(3)—C(22)	1.456 (5)	C(23)—C(27)	1.540 (8)
N(3)—C(23)	1.450 (6)	C(24)—C(25)	1.510 (8)
N(3)—C(26)	1.483 (7)	C(25)—C(26)	1.522 (9)
C(8)—N(1)—C(9)	114.2 (3)	C(9)—C(10)—C(11)	110.1 (4)
C(8)—N(1)—C(13)	112.6 (3)	N(2)—C(11)—C(10)	109.5 (4)
C(9)—N(1)—C(13)	112.6 (3)	N(2)—C(12)—C(15)	111.4 (3)
C(11)—N(2)—C(12)	109.1 (3)	N(1)—C(13)—N(2)	111.0 (3)
C(11)—N(2)—C(13)	113.0 (3)	N(1)—C(13)—C(14)	110.0 (4)
C(12)—N(2)—C(13)	113.1 (3)	N(2)—C(13)—C(14)	114.9 (3)
C(22)—N(3)—C(23)	112.0 (3)	N(3)—C(22)—C(20)	111.1 (4)
C(22)—N(3)—C(26)	113.0 (4)	N(3)—C(23)—N(4)	111.4 (4)
C(23)—N(3)—C(26)	112.5 (3)	N(3)—C(23)—C(27)	110.6 (4)
C(23)—N(4)—C(24)	113.2 (4)	N(4)—C(23)—C(27)	114.1 (4)
C(23)—N(4)—C(28)	114.6 (4)	N(4)—C(24)—C(25)	109.6 (5)
C(24)—N(4)—C(28)	109.9 (3)	C(24)—C(25)—C(26)	109.9 (5)
N(1)—C(8)—C(7)	110.4 (4)	N(3)—C(26)—C(25)	112.8 (4)
N(1)—C(9)—C(10)	112.5 (4)	N(4)—C(28)—C(2)	111.9 (3)
O(1)···N(4)	2.74	O(2)···N(2)	2.76
O(1)—H(1)	1.06	O(2)—H(2)	1.03
N(4)—H(1)	1.80	N(2)—H(2)	1.81
O(1)—H(1)···N(4)	147.5	O(2)—H(2)···N(2)	149.2
C(13)—N(1)—C(8)—C(7)	78.7 (4)	C(23)—N(3)—C(22)—C(20)	78.4 (4)
C(13)—N(1)—C(9)—C(10)	55.4 (5)	C(23)—N(3)—C(26)—C(25)	52.7 (5)
C(13)—N(2)—C(12)—C(15)	59.0 (5)	C(23)—N(4)—C(24)—C(25)	−57.2 (5)
C(13)—N(2)—C(11)—C(10)	−55.3 (5)	C(23)—N(4)—C(28)—C(2)	59.5 (5)

reveals puckering of the chains to different extents. Effectively, the molecule acquires an asymmetric configuration.

The protons of the two phenolic OH groups, which are *trans* axially directed, are involved in intramolecular hydrogen bonding with the nearest N atoms. The short O(1)—N(4) and O(2)—N(2) distances [2.75 (1) Å] and near linearity of the angles O(1)—H(1)···N(4) (147.5°) and O(2)—H(2)···N(2) (149.2°) indicate the fairly strong nature of these hydrogen bonds. No other intermolecular distances shorter than the sum of the van der Waals radii of two atoms could be located.

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Structure of 2,6-Dihydroxy-2,6-dimethylheptan-4-one

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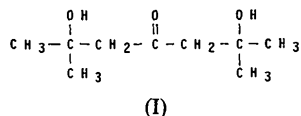
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Abstract. C₉H₁₈O₃, *M_r* = 174.2, monoclinic, *C2/c*, *a* = 10.496 (3), *b* = 17.305 (4), *c* = 7.500 (2) Å, β = 128.94 (2)°, *V* = 1059.6 (5) Å³, *Z* = 4, *D_x* = 1.092 Mg m⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 0.075 mm⁻¹, *F*(000) = 384, *T* = 298 K, *R* = 0.0449 and *wR* = 0.0507 for 88 variable parameters and 547 averaged reflections with *F* > 0σ(*F*). The asymmetric unit consists of one half of the molecule which possesses twofold (*C*₂) point-group symmetry and resides on a special position. There are no unusual intermolecular contacts in the lattice and no evidence of either inter- or intramolecular hydrogen-bonding interactions.

Introduction. A number of azoxy compounds are known to be converted into *ortho*-hydroxyazo compounds upon exposure to light. This rearrangement is formally similar to a Wallach rearrangement, except that the O atom migrates to the *ortho* position on the distant aromatic ring (Spence, Taylor & Buchardt, 1970). Some, but not all, are also photochromic in the solid state. In the mechanism originally proposed for this light-initiated

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transformation, nucleophilic attack by the azoxy oxygen occurs, followed by a subsequent hydrogen-abstraction reaction (Badger & Buttery, 1955). Solution studies on sterically crowded azoxybenzenes, however, have established that a number of side products are formed in lesser amounts implicating diazonium intermediates in the process; as a result, other mechanisms have also been proposed (Goon, Murray, Schoch & Bunce, 1973; Bunce, 1974). In our investigations of the photochemistry of azoxybenzenes, both in solution and in the solid state, we have succeeded in isolating a most unusual and previously unreported product (I) whose structure we now report.



Experimental. The title compound was obtained following irradiation of a 0.01 *M* solution of 4-methoxyazoxybenzene in THF for several days. Pale-yellow single well-formed crystals were obtained by crystallization from a CH₂Cl₂/petroleum ether solu-

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