Cooler (Cosier & Glazer, 1986), the presence of which limited the maximum achievable θ angle to 65°. The structures were solved using direct methods (Altomare *et al.*, 1994). All the H atoms were located unambiguously in the corresponding difference Fourier maps and all, except those of type N—H and O—H, were kept fixed in the last cycles of refinement with $U_{\rm iso}$ values tied to $U_{\rm eq}$ of the carrier atoms. Empirical weighting schemes were computed so as to give no trends in $<w\Delta^2F>$ *versus* $<|F_o|>$ or $<\sin\theta/\lambda>$ (*PESOS*; Martínez-Ripoll & Cano, 1975). The parameters *A*, *B*, *C* and *D* were adjusted to flatten the initial trends.

For all compounds, data collection: *PW*1100 *Software* (Hornstra & Vossers, 1973); cell refinement: *LSUCRE* (Appleman, 1984); data reduction: *Xtal DIFDAT SORTRF ADDREF* (Hall *et al.*, 1997); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *Xtal CRYLSQ*; molecular graphics: *Xtal ORTEP*; software used to prepare material for publication: *Xtal BONDLA CIFIO*.

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5,6,7,8,9,10,11,12,18,19,21,22-Dodecahydro-8,9:18,19-dibenzo-1,4,7-trioxa-11,16-diaza-cyclononadeca-10,16-diene

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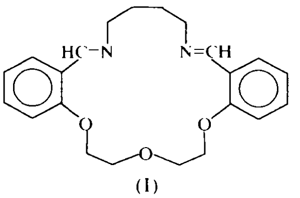
Abstract

The title compound, $C_{22}H_{26}N_2O_3$, is a 19-membered Schiff base crown ether ligand containing two imine-N and three etheral-O atoms. In the macrocyclic ring, the mean N···O distance is 6.248 (3) Å. The relative macrocyclic inner hole size, estimated as twice the mean distance of the donor atoms from their centroid is approximately 2.53 Å. The mean C=N imine bond length [1.256 (3) Å] and C—N=C imine bond angle [117.8 (2)°] are smaller than the corresponding values in salicylaldimine and naphthaldimine Schiff base ligands.

Comment

Macrocyclic multidentate N_2O_2 and N_2O_3 donor-type ligands have been examined extensively as potential transition-metal ion selective reagents (Lindoy *et al.*, 1993; Adam *et al.*, 1983). Alkaline, alkaline earth and transition-metal ion recognition with particular metal-ion binding applications are of fundamental importance to broad areas of inorganic and coordination chemistry and biochemistry (Lindoy, 1997). A large number of open-chain and macrocyclic multidentate Schiff base ligand complexes has been examined extensively in order to understand their synthetic, thermodynamic and/or structural properties of complex formation (Adam *et al.*, 1983, 1993, 1994). However, there are a few reports about the structures of the free macrocyclic multidentate N_2O_2 and N_2O_3 donor type ligands (Adam *et al.*, 1983; Chia *et al.*, 1991).

The structure determination was carried out in order to estimate the relative macrocyclic ring hole size and to understand the effects of the macrocyclic ring on the C=N imine bond lengths and C—N=C bond angles. The title compound, (I), may be a potential metal-ion selective reagent for transition, alkaline and alkaline earth metal ions. Fig. 1 shows compound (I) with the atomic numbering scheme. The macrocyclic ring consists of two imine-N and three etheral-O atoms. The ligand cavity plays an important role in metal-ion selectivity. The intramolecular C22···O2 [7.236 (3)], N2···O1



(I)

[6.760 (2)], N2···O2 [6.210 (2)], N1···O3 [6.185 (3)] and N1···O2 [5.835 (2) Å] distances may indicate the hole size of the macrocyclic ring. When only the N and O atoms are taken into account, the mean N···O distance is 6.248 (3) Å. A least-squares plane defined by atoms N1, N2, O1 and O3 has maximum deviations to either side of the plane of 0.126 (2) (O1) and 0.124 (2) Å (O3). The relative macrocyclic inner-hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately 2.53 Å, using the 'modified covalent radii' of the Nsp^2 (0.66 Å) and Osp^3 (0.76 Å) atoms as in the literature method (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Drummond *et al.*, 1982). The mean C═N imine bond length [1.256 (3) Å] and C—N═C imine bond angle [117.8 (2)°] are smaller than the corresponding values in 1,8-di[*N*-2-oxyphenylsalicylidene]-3,6-dioxaoctane [1.270 (3) Å and 123.5 (2)°; Yıldız *et al.*, 1998], *N*-*n*-propyl-2-oxo-1-naphthylidene methylamine [1.303 (2) Å and 125.3 (2)°; Kaitner & Pavlović, 1996], 1-[*N*-(4-methyl-2-pyridyl)aminomethylidene]-2(1*H*)-naphthalenone [1.322 (4) Å and 125.3 (2)°; Elerman *et al.*, 1998] and *N*-salicylidene-3-aminopyridine [1.277 (9) Å and 121.1 (6)°; Moustakali-Mavridis *et al.*, 1980].

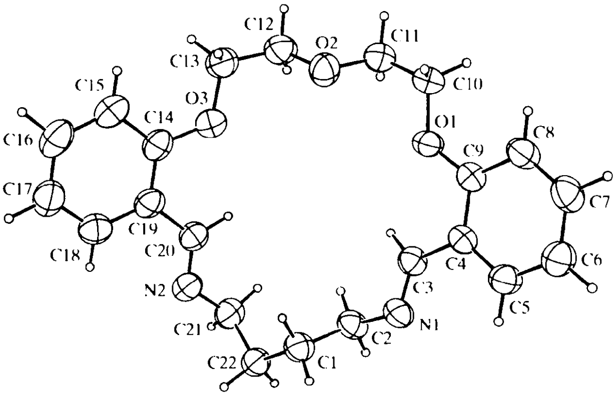


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Intramolecular hydrogen bonding and keto–amine, phenol–imine tautomerism are observed in naphthaldimine and salicylaldimine Schiff bases (Yıldız *et al.*, 1998; Costamagna *et al.*, 1992). These effects lead to lengthening of the C═N imine bond. C═N imine bond lengthening is also observed in the Schiff base complexes (Fernández-G. *et al.*, 1986; Calligaris *et al.*, 1972). Consequently, in the free naphthaldimine and salicylaldimine Schiff bases, tautomerism causes lengthening of the C═N imine bond as a result of the quinoidal effect (Gavranić *et al.*, 1996). In (I), the C═N imine bond has double-bond character, however, in the salicylaldimine and naphthaldimine Schiff bases, the double-bond character of the C═N imine bond is decreased, and the C—N═C imine bond angle is increased.

Experimental

Compound (I) was obtained from the reaction of 1,7-bis-(formylphenyl)-1,4,7-trioxaheptane (5.0 g, 1.56×10^{-2} mol) and 1,4-diaminobutane (1.6 ml, 1.57×10^{-2} mol) in dry tetrahydrofuran (500 ml) with argon passing over the reaction mixture for 6 h. The mixture was evaporated and then distilled water (400 ml) was added; it was kept at 273 K for 24 h. The crystals formed were filtered and recrystallized from a mixture of dichloromethane and *n*-hexane (1:1), yield 4.86 g (85%), m.p. 416 K.

Crystal data

$C_{22}H_{26}N_2O_3$
$M_r = 366.46$
Monoclinic
$P2_1/a$
$a = 8.001$ (1) Å
$b = 15.639$ (1) Å
$c = 16.405$ (1) Å
$\beta = 94.15$ (1)°
$V = 2047.3$ (3) Å^3
$Z = 4$
$D_x = 1.189$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–11°
$\mu = 0.0793$ mm^{-1}
$T = 298$ K
Block
0.30 × 0.25 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{\min} = 0.976$, $T_{\max} = 0.984$
4627 measured reflections
4142 independent reflections

3490 reflections with $F > 0$
$R_{\rm int} = 0.017$
$\theta_{\max} = 26.3°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -20 \rightarrow 20$
3 standard reflections frequency: 120 min intensity decay: 1%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.060$
$S = 1.06$
3490 reflections
348 parameters
H atoms: see text
$w = 1/[\sigma(F^2) + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C9	1.364 (3)	C1—C2	1.506 (3)
O1—C10	1.429 (3)	C1—C22	1.515 (3)
O2—C11	1.418 (3)	C3—C4	1.470 (3)
O2—C12	1.414 (3)	C4—C9	1.400 (3)
O3—C13	1.433 (3)	C19—C20	1.473 (3)
O3—C14	1.367 (3)	C10—C11	1.491 (4)
N1—C2	1.456 (3)	C12—C13	1.488 (3)
N1—C3	1.256 (3)	C14—C19	1.398 (3)
N2—C20	1.256 (3)	C21—C22	1.520 (3)
N2—C21	1.455 (3)		
C9—O1—C10	118.7 (2)	O3—C13—C12	108.9 (2)
C11—O2—C12	111.3 (2)	O3—C14—C15	123.5 (2)
C13—O3—C14	117.9 (2)	O3—C14—C19	116.3 (2)
C2—N1—C3	116.6 (2)	C1—C22—C21	115.0 (2)
C20—N2—C21	119.0 (2)	O1—C9—C4	115.4 (2)
C2—C1—C22	112.5 (2)	O1—C9—C8	124.5 (2)
N1—C2—C1	112.1 (2)	O1—C10—C11	107.9 (2)
N1—C3—C4	123.3 (2)	C14—C19—C20	121.8 (2)
C3—C4—C5	121.3 (2)	C18—C19—C20	120.1 (2)
C3—C4—C9	119.9 (2)	N2—C20—C19	121.7 (2)
O2—C11—C10	110.2 (2)	N2—C21—C22	110.7 (2)
O2—C12—C13	109.8 (2)		

The structure was solved by direct methods. The H-atom positions were located by difference synthesis and refined isotropically.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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1-Nitrobenzo[*c*]cinnoline

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Abstract

The title compound, $C_{12}H_7N_3O_2$, is a 1-nitro derivative of the ligand benzo[*c*]cinnoline. The rings in the benzo[*c*]cinnoline skeleton are close to planarity, while the skeleton itself is non-planar. The dihedral angles between the rings in the benzo[*c*]cinnoline skeleton are $\alpha^\wedge\beta$ 4.0 (5), $\alpha^\wedge\gamma$ 8.4 (2) and $\beta^\wedge\gamma$ 4.5 (4)°; in benzo[*c*]cinnoline the $\alpha^\wedge\gamma$ dihedral angle is 2.5°. The difference is caused by steric interactions between the nitro group and benzo[*c*]cinnoline skeleton.

Comment

Nitrobenzo[*c*]cinnolines are the starting materials for other benzo[*c*]cinnoline derivatives (Barton & Cocket, 1962; Kılıç & Tüzün, 1992). Benzo[*c*]cinnoline and some of its derivatives are known to have mutagenic (Leary *et al.*, 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958), herbicidal (Entwistle *et al.*, 1981) and carcinogenic (Ashby *et al.*, 1980) physiological activities. They have also been used as bleach catalysts in the processing of photographic silver-dye bleach materials (Jan, 1980). The structures of benzo[*c*]cinnoline (van der Meer, 1972) and octachlorobenzo[*c*]cinnoline (King *et al.*, 1983) have been described as complexes with bis(tricarbonyliron) (Doedens, 1970) and copper(I)-benzoato (Toth *et al.*, 1987). The structures of 1-morpholinobenzo[*c*]cinnoline (Hökelek *et al.*, 1990), 1- and 3-piperidinobenzo[*c*]cinnoline (Hökelek *et al.*,