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2,5,8-Trioxa-16,20-diazatricyclo[20.4.0.0^{9,14}]-hexacosa-9,11,13,15,20,22,24,26-octaene

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Abstract

The title molecule, $C_{21}H_{24}N_2O_3$, an N_2O_3-type crown compound, is a crystallographically centrosymmetric multidentate Schiff base ligand containing two imine N and three ether O atoms. It has a short C=N imine bond length [1.254 (4) Å] and a narrow C—N—C angle [117.9 (3)°] compared with salicylaldimine and naphthaldimine Schiff bases.

Comment

Macrocyclic Schiff base ligands, such as the 16-membered ring composed of the $-O_xN_y-$ donor type (where x = 2, 3 and y = 2, 3), have been investigated previously as potential metal-ion-selective reagents (Goodwin *et al.*, 1982; Lindoy *et al.*, 1993). A large number of these investigations has involved the synthetic, thermodynamic and/or structural properties of complex formation of a range of transition metal ions (Adam *et*

al., 1979, 1983; Fenton *et al.*, 1987). Some Schiff base complexes have also been used in catalytic reduction reactions (Tafesh & Weiguny, 1996). In 1983, Adam and co-workers synthesized compound (3), without isolating compound (2), from the reaction of (1) with 1,3-diaminopropane (see Scheme below). We have isolated compounds (2) and (3) separately. The structure determination of the title compound, (2), was undertaken in order to determine the effects of the macrocyclic ring on the C=N imine bond system and to compare the results obtained with those of acyclic salicylaldimine and naphthaldimine Schiff bases.
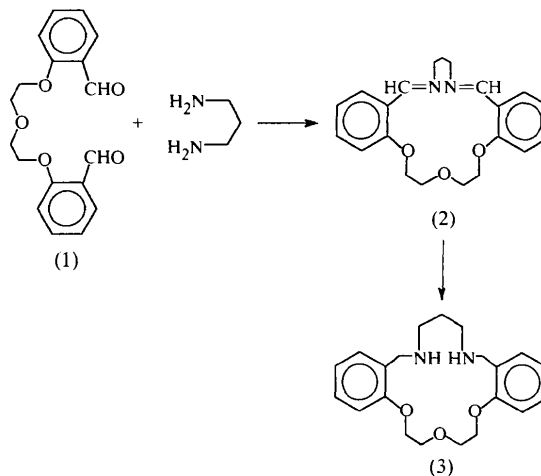
Since it has two N- and three O-donor atoms in the macrocyclic ring, compound (2) may be a potential metal-ion-selective reagent for transition, alkaline and alkaline earth metal ions. The molecule of (2) (Fig. 1) is crystallographically centrosymmetric and a half molecule occupies the asymmetric unit. The intramolecular distances C1···O2 6.690 (3), N1···O2 5.645 (2) and C3···O2 4.600 (3) Å reflect the size of the hole of the macrocyclic ring. The C1···O2 distance is larger than the N···N distance in the potassium complex of substituted diaza-18-crown-6 (6.253 Å; Gandour *et al.*, 1986). The N1=C3 imine bond is in the same plane as the benzene ring. The torsion angles O1—C10—C11—O2, C10—C11—O2—C11', N1—C2—C1—C2' and C3—N1—C2—C1 are −58.1 (7), −126.0 (4), −73.9 (2) and 127.3 (3)°, respectively [symmetry code: (') $1 − x$, y, $\frac{1}{2} − z$]. All of these correspond to a *gauche* conformation (Hilgenfeld & Saenger, 1982). The Csp^3—Csp^3 mean bond length is given in the literature as 1.524 (14) Å (Allen *et al.*, 1987) and in (2), the corresponding values are 1.387 (7) and 1.512 (4) Å. The C=N imine bond distance and the C—N—C angle are 1.254 (4) Å and 117.9 (3)°, respectively, which are small compared with values of 1.270 (3) Å and 123.6 (2)° found in 1,8-di(*N*-2-oxyphenylsalicylidene)-3,6-dioxaoctane (Yıldız *et al.*, 1998), 1.313 (8) Å and 122.5 (6)° found in 2-hydroxy-*N*-

n-propyl-1-naphthaldimine (Hökelek *et al.*, 1995), and 1.277 (9) Å and 121.1 (6)° found in *N*-salicylidene-3-aminopyridine (Moustakali-Mavridis *et al.*, 1980). In naphthaldimine and salicylaldimine Schiff bases, intramolecular hydrogen bonding and keto–amine/phenol–imine tautomerism are observed (Yıldız *et al.*, 1998), which causes a lengthening in the C=N imine bond as a result of the quinoidal effect. Consequently, the C=N imine bond has double-bond character in (2), but in the salicylaldimine and naphthaldimine Schiff bases, the double-bond character of the C=N imine bond is decreased. Unfortunately, along the macrocyclic ring, the O1—C10—C11—O2—C11′—C10′—O1′ chain is highly flexible which may explain the unusually large displacement parameters of the O2 and C11 atoms. As a result of this effect, the C10—C11 and C11—O2 bond lengths are unexpectedly shortened with respect to their conventional values.
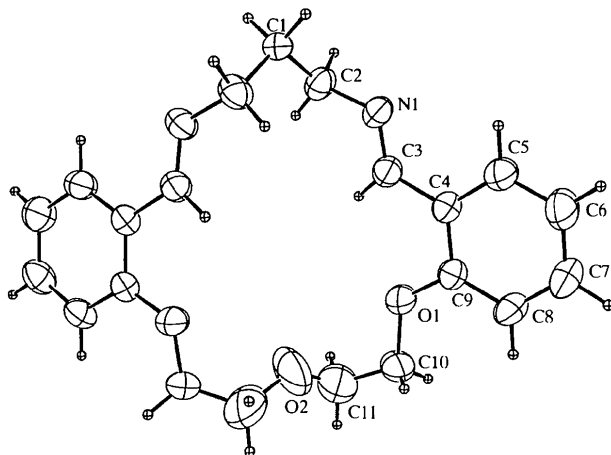

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Experimental

1,7-Bis(formylphenyl)-1,4,7-trioxaheptane, (1), was obtained by a modification of the literature method of Adam *et al.* (1983). The title compound, (2), was obtained from the reaction of 1,3-diaminopropane (0.71 g, 9.6 mmol) and (1) (3.01 g, 9.4 mmol) in THF (30 ml), with argon being passed over the reaction mixture {yield 68%; m.p. 471 K; MS (*m/e*): 352 (calculated), 352 (found); elemental analysis [calculated% (found%)]: C 71.57 (70.04), H 6.86 (6.62), N 7.95 (8.14); IR (KBr, cm⁻¹): 1635 (*s*, $\nu_{C=N}$)}. Compound (3) was obtained by the reduction of (2) with NaBH₄ in methanol [m.p. 357 K, literature m.p. 357 K (Adam *et al.*, 1983)].

Crystal data

C₂₁H₂₄N₂O₃
M_r = 352.43

Mo *Kα* radiation
λ = 0.71069 Å

Monoclinic
C2/c
a = 14.901 (2) Å
b = 15.785 (1) Å
c = 8.012 (2) Å
β = 98.67 (2)°
V = 1863.0 (6) Å³
Z = 8
D_x = 2.5131 Mg m⁻³
D_m not measured

Cell parameters from 25 reflections
θ = 9–18°
μ = 0.1688 mm⁻¹
T = 298 K
Block-like
0.30 × 0.25 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: empirical via ψ scan (*MolEN*; Fair, 1990)
T_min = 0.947, T_max = 0.964
2030 measured reflections
1882 independent reflections

1279 reflections with F > 1.5σ(F)
R_int = 0.039
θ_max = 26.3°
h = 0 → 18
k = 0 → 19
l = −9 → 9
3 standard reflections frequency: 120 min intensity decay: 1%

Refinement

Refinement on F
R = 0.069
wR = 0.075
S = 1.15
1279 reflections
126 parameters
H atoms: see below
w = 1/[σ(F)² + (0.02F)² + 1.0]

(Δ/σ)_max = 0.01
Δρ_max = 0.44 e Å⁻³
Δρ_min = −0.28 e Å⁻³
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_eq
O1	0.3375 (1)	0.9743 (1)	0.1492 (3)	0.0553 (5)
O2	1/2	1.0571 (4)	1/4	0.2409 (3)
N1	0.3647 (2)	0.7228 (2)	0.1844 (3)	0.0454 (5)
C1	1/2	0.6333 (3)	1/4	0.0448 (9)
C2	0.4407 (2)	0.6846 (2)	0.1175 (4)	0.0468 (6)
C3	0.3528 (2)	0.8011 (2)	0.1655 (4)	0.0413 (6)
C4	0.2768 (2)	0.8460 (2)	0.2251 (4)	0.0382 (6)
C5	0.2108 (2)	0.8019 (2)	0.2942 (4)	0.0488 (7)
C6	0.1400 (2)	0.8435 (2)	0.3522 (5)	0.0587 (8)
C7	0.1341 (2)	0.9302 (2)	0.3400 (4)	0.0560 (7)
C8	0.1982 (2)	0.9759 (2)	0.2730 (4)	0.0501 (7)
C9	0.2701 (2)	0.9345 (2)	0.2153 (4)	0.0413 (6)
C10	0.3462 (2)	1.0639 (2)	0.1689 (5)	0.0624 (8)
C11	0.4328 (3)	1.0901 (3)	0.149 (1)	0.1534 (2)

Table 2. *Selected geometric parameters (Å, °)*

C3—C4	1.476 (4)	N1—C2	1.455 (4)
C3—N1	1.254 (4)	C5—C6	1.382 (5)
C9—O1	1.359 (4)	C7—C6	1.374 (5)
C9—C4	1.402 (4)	C7—C8	1.371 (5)
C9—C8	1.392 (4)	C1—C2	1.512 (4)
O1—C10	1.427 (4)	C10—C11	1.387 (7)
C4—C5	1.388 (4)	O2—C11	1.299 (6)

C4—C3—N1	122.4 (3)	C3—N1—C2	117.9 (3)
O1—C9—C4	115.6 (3)	C4—C5—C6	121.3 (3)
O1—C9—C8	124.4 (3)	C6—C7—C8	120.8 (3)
C4—C9—C8	120.1 (3)	C5—C6—C7	119.5 (3)
C9—O1—C10	118.4 (3)	N1—C2—C1	111.6 (2)
C3—C4—C9	120.8 (3)	O1—C10—C11	110.8 (3)
C3—C4—C5	120.9 (3)	C10—C11—O2	116.9 (6)
C9—C4—C5	118.3 (3)	C9—C8—C7	120.0 (3)
N1—C3—C4—C9	174.3 (3)	C8—C9—O1—C10	12.7 (5)
N1—C3—C4—C5	−4.9 (5)	C9—O1—C10—C11	159.4 (5)
C4—C3—N1—C2	178.7 (3)	C3—N1—C2—C1	127.3 (3)
C4—C9—O1—C10	−166.5 (3)	O1—C10—C11—O2	−58.1 (7)

The space group could not be determined uniquely from the Laue class and extinctions; it may be *C2/c* or *Cc*. The structure was solved in the *C2/c* space group by direct methods. The positions of atoms H51, H101, H102, H111 and H112 were calculated geometrically, while the remaining H-atom positions were located in a difference synthesis and their displacement parameters refined isotropically. A riding model was used in the refinement of all H-atom positions.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Tetrabenzo-24-crown-8†

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Abstract

The structure of tetrabenzo-24-crown-8, $C_{32}H_{32}O_8$, does not exhibit a binding cavity for alkali metal ions, but is collapsed in on itself. The conformation may be a result of inter- and intramolecular hydrogen bonding. The molecule lies on an inversion center.

Comment

We recently reported that tetrabenzo-24-crown-8, (I), exhibits promise as a selective and efficient extractant for

(I)
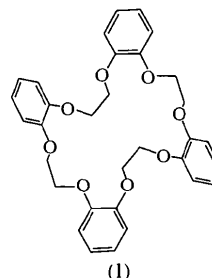
Cs⁺ from mixtures of alkali metal ions (Sachleben *et al.*, 1996; Sachleben, Deng & Moyer, 1997). Specifically, it was shown that tetrabenzo-24-crown-8 extracts Cs⁺ more strongly, and is more selective for Cs⁺ over Rb⁺, than a number of other benzo-substituted crown-8 and crown-7 extractants (Sachleben *et al.*, 1996). We undertook to investigate its structure to see if the four arene groups placed on the crown ring facilitate preorganization of this crown for Cs⁺ binding.

The structure of the title compound is depicted in Fig. 1, and clearly demonstrates that the crown cavity is not preorganized for Cs⁺ binding; rather, it is collapsed in on itself, the cavity being filled primarily by methylene groups, as is commonly observed for structures of large uncomplexed crown ether molecules (Sachleben, Bryan *et al.*, 1997). This may be due in part to

† Alternative name: 3,4,13,14,23,24,33,34-octahydro-2,5,12,15,22,25,-32,35-octaoxopentacyclo[34.4.0.0⁶,¹¹.0¹⁶,²¹.0²⁶,³¹]tetraconta-6(11),7,-9,16(21),17,19,26,28,30,36,38,40-dodecaene.