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Three 2,4,6-trimethylpyridine–benzoic acid complexes at 150 K

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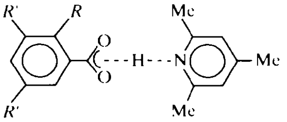
Abstract

The crystal structures of three 1:1 adducts of 2,4,6-trimethylpyridine with benzoic acid, $C_8H_{11}N\cdot C_7H_6O_2$, (I), 2-nitrobenzoic acid, $C_8H_{12}N^+\cdot C_7H_4NO_4^-$, (II), and 3,5-dinitrobenzoic acid, $C_8H_{12}N^+\cdot C_7H_3N_2O_6^-$, (III), determined at 150 K show that the carboxylic proton has been transferred to the pyridine-N atom only in the nitrobenzoic derivatives, (II) and (III). In all three structures, both moieties are hydrogen bonded to each other *via* their respective OH, (I), and N⁺H, (II) and (III), groups with N···O distances of 2.613 (4), 2.596 (3) and 2.597 (2) Å, respectively.

Comment

As part of our work on proton transfer in heterocyclic compounds, the structure determination of the title compounds (2,4,6-trimethylpyridine carboxylic acid derivatives) was undertaken to establish unambiguously whether the proton of the carboxylic acid is transferred to the 2,4,6-trimethylpyridine molecule. The Cambridge Structural Database (CSD, October 1998 release; Allen *et al.*, 1991) contains three organic 2,4,6-trimethylpyridinium salts, namely 2,4,6-trimethylpyridinium 2,6-dichloro-4-nitrophenolate (CSD refcode REPMUU; Majerz *et al.*, 1995), 2,4,6-trimethylpyridinium pentabromophenolate (GASHAJ; Majerz *et al.*, 1987) and pentachlorophenolate (PARNAX; Majerz *et al.*, 1992), but this is the first time that a neutral complex, (I), has been studied. Of 20 further complexes with other pyridine derivatives, only in bis(benzene-1,3,5-tricarboxylic acid)–tris(4,4′-pyridine) (RAPHAR; Sharme & Zaworotko, 1996) has the proton not been transferred from the carboxylic acid moiety. It is worthy of mention that only in the benzoic acid complex pentakis(4-dimethylaminopyridine)–tris(benzoic acid) decahydrate (ZAPNIN; Biradha *et al.*, 1995) have all three benzoic acid molecules transferred their protons to another three out of the five independent pyridine molecules. The ions, the neutral pyridines and the waters of crystallization are connected as follows: two pyridinium cations form dimers with two neutral pyridines while the remaining pyridinium is hydrogen bonded to a benzoate anion. The other two benzoates and the waters are involved in a complex hydrogen-bonded network.



(I) $R = R' = H$
(II) $R = NO_2$, $R' = H$
(III) $R = H$, $R' = NO_2$

The three title structures differ from each other in the following geometric features. The carboxylic group proton transfers to the pyridine moieties in (II) and (III) (Figs. 1, 2 and 3). This transfer was obvious from the difference Fourier synthesis and is also manifested in the C2—N1—C6 angle of the pyridine ring, in the C10—O17/O18 bonds and in the angles of the carboxylic group around C10 (Tables 1, 3 and 5). The C2—N1—C6 angle is much larger and the C10—O17/O18 bonds and C11—C10—O17/O18 angles are more alike in (II) and (III) than in (I). All these values compare fairly well with those retrieved from the CSD and mentioned above [122.2 (7)°, 1.259 (20), 1.248 (15) Å, 117 (1), 118 (2)° *versus* 117.8 (16)°, 1.307 (12), 1.213 (8) Å, 114 (1), 122 (1)°; the numbers in parentheses represent the standard deviation of the sample for the 17 and three fragments (16 and one structures) of each type found, respectively, among the 20 mentioned above].

The benzene rings are at angles of 47.4 (1), 7.7 (1) and 46.0 (1)° to the pyridine ring in (I), (II) and (III), respectively, and are almost coplanar with their carboxy groups [C12—C11—C10—O17 = −5.9 (5), −24.1 (4) and 10.1 (2)°, respectively]. The large angle in (II) could be due to the *ortho* nitro group attached to C16: it is twisted by −69.4 (3)° to avoid steric hindrance with the neighbouring carboxylate group. The bond angles within the benzene rings show significant differences from ideal values, being affected by the electronwithdrawing nitro and carboxylic groups (Tables 1, 3 and 5): their variations are in good agreement with the values reported for these groups (Domenicano & Murray-Rust, 1979).

In all three structures, the benzoic/benzoate and the 2,4,6-trimethylpyridine/2,4,6-trimethylpyridinium moieties are linked together by strong OH···N or $N^+H\cdots O^-$ hydrogen bonds reinforced by intramolecular C7—H···O18 bonds (Tables 2, 4 and 6 and Figs. 1, 2 and 3). The $N^+H\cdots O^-$ hydrogen bonds are stronger than those observed in the 2,4,6-trimethylpyridinium salts (2.616–2.619 Å in GASHAJ and PARNAX, respectively), in the benzoate salt (2.634 Å, ZAPNIN) or in other pyridine derivatives (2.621–2.923 Å). Compounds (II) and (III) present similar topological structures. The synthon (Desiraju, 1995) formed by the $N^+H\cdots O^-$ bond results in chains along the *b* and *a* axes (Figs. 4*b* and 4*c*) through CH···O=C/O=N contacts (Tables 4 and 6) with C···O distances within the range of analogous contacts reported recently [3.185 (5)–3.725 (5) Å;

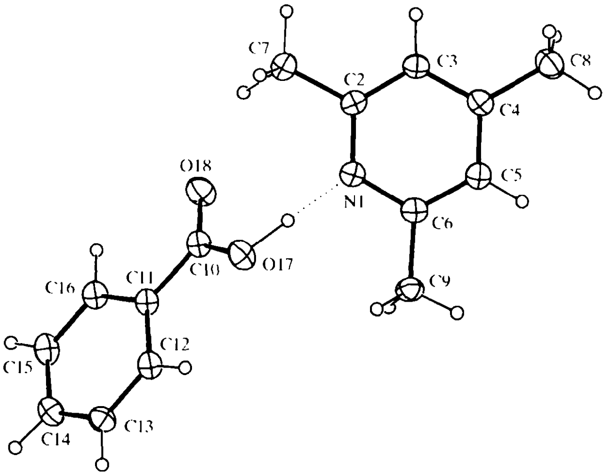


Fig. 1. View of the molecular structure of compound (I) showing the numbering scheme. Ellipsoids are drawn at the 30% probability level.

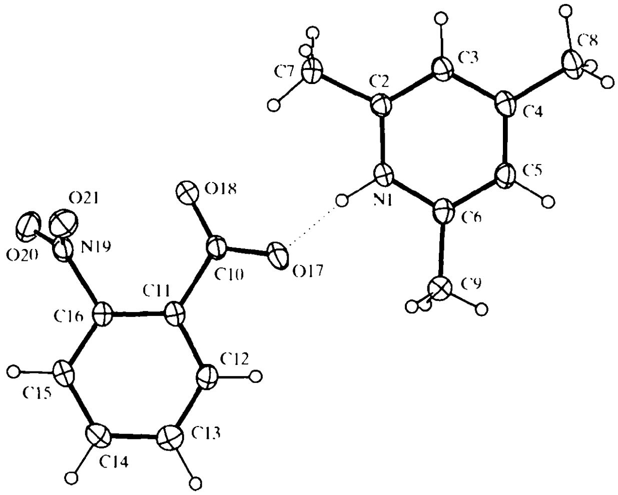


Fig. 2. View of the molecular structure of compound (II) showing the numbering scheme. Ellipsoids are drawn at the 30% probability level.

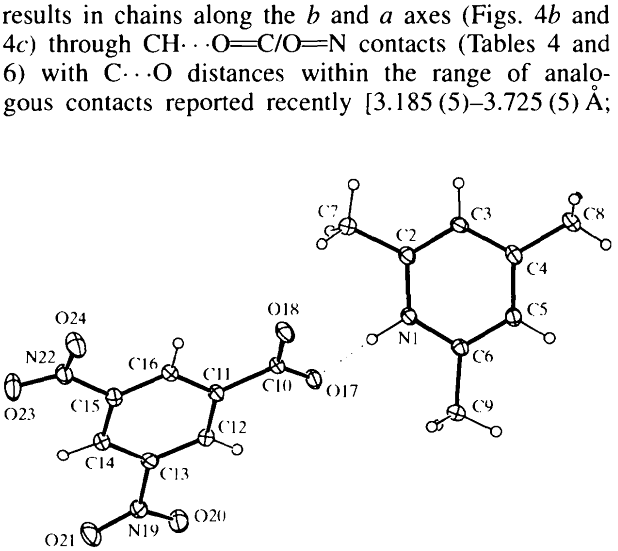


Fig. 3. View of the molecular structure of compound (III) showing the numbering scheme. Ellipsoids are drawn at the 30% probability level.

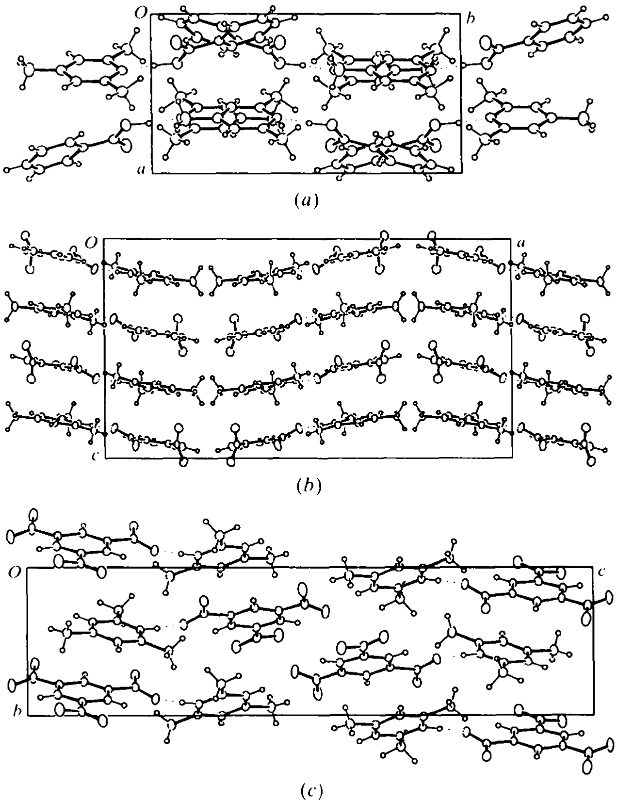


Fig. 4. Crystal packing of compounds (*a*) (I), (*b*) (II) and (*c*) (III) along the *c*, *b* and *a* axes, respectively, showing the similar stacking of the pairs of molecules in columns [(II) and (III)] and the differences in the packing of these columns.

Thalladi *et al.*, 1998]. Piles of stacked chains arranged in a head-to-tail fashion are linked by CH···O═N contacts in (II), whereas in (III) this type of contact does not connect molecules in the right-hand column with those in the left (Fig. 4*c*). The non-coplanarity of the pyridine and benzene rings in (III) seems to prevent the alignment of molecules in one column with respect to neighbouring ones as in (II). Moreover, the interchain separation in (II) ($c/4$ = 3.49 Å) is shorter than that observed in (III) ($b/2$ = 3.66 Å), where the interpenetration of columns starts to take place. The crystal structure of (I) can be considered as a modification of that of (III), where the interpenetration of adjacent columns is fully achieved (Fig. 4*a*).

On the basis of these structures, the results indicate that in 2,4,6-trimethylpyridine and benzoic acid derivative complexes, the nitro group is necessary for proton transfer to take place.

Examination of the structures (Cano & Martínez-Ripoll, 1992) using the contact radii of Vainshtein *et al.* (1982) showed that there were no solvent-accessible voids in the crystal lattices and that the closest packing is displayed by (III), the total packing coefficient values being 0.685, 0.692 and 0.713 for (I), (II) and (III), respectively.

Experimental

Collidine (2,4,6-trimethylpyridine) is a Merck reagent for chromatography. Benzoic acid, 2-nitrobenzoic acid and 3,5-dinitrobenzoic acid were obtained from the Aldrich Chemical Company.

The collidine–benzoic acid complex, (I), was prepared by adding collidine (0.135 ml, 1.02 mmol) to a solution of benzoic acid (0.12 g, 0.98 mmol) in dichloromethane. After removal of the solvent, the residue was washed twice with diethyl ether (2 ml) to remove the excess of collidine. Complex (I) was crystallized from diethyl ether at 253 K, m.p. 339 K. ^{1}H NMR ($CDCl_3$, 270 MHz), δ: 8.10, 7.57, 7.44, 3.76 p.p.m. (broad) (benzoic acid); 6.79, 2.50, 2.26 p.p.m. (collidine). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67 MHz), δ: 170.99 (CO), 133.10, 132.59, 130.5, 128.82 p.p.m. (benzoic acid); 157.16, 150.08, 122.81, 23.37, 21.60 p.p.m. (collidine). Analysis calculated for $C_{15}H_{17}NO_2$: C 74.1, H 7.0, N 5.8%; found: C 73.4, H 6.91, N 5.27%.

The collidine–2-nitrobenzoic acid complex, (II), was prepared using the same procedure as in (I), m.p. 361 K. ^{1}H NMR ($CDCl_3$, 270 MHz), δ: 10.3 (broad), 7.77, 7.55, 7.44 p.p.m. (nitrobenzoic acid); 7.08, 2.69, 2.38 p.p.m. (collidine). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67 MHz), δ: 169.80 (CO), 148.20, 133.39, 132.30, 129.66, 123.62 p.p.m. (nitrobenzoic acid); 154.74, 153.59, 123.15, 21.43, 20.64 p.p.m. (collidine). Analysis calculated for $C_{15}H_{16}N_2O_4$: C 62.5, H 5.56, N 9.72%; found: C 62.28, H 5.60, N 9.58%.

The collidine–3,5-dinitrobenzoic acid complex, (III), was also prepared using the same procedure as in (I), m.p. 423 K. ^{1}H NMR ($CDCl_3$, 270 MHz), δ: 10.0 (broad), 9.21, 9.09 p.p.m. (dinitrobenzoic acid); 7.10, 2.74, 2.45 p.p.m. (collidine). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67 MHz), δ: 167.53 (CO), 149.01, 131.79, 130.21, 124.78 p.p.m. (dinitrobenzoic acid); 158.02, 154.94, 121.05, 22.28, 20.98 p.p.m. (collidine). Analysis calculated for $C_{15}H_{15}N_3O_6$: C 54.05, H 5.05, N 12.62%; found: C 54.06, H 4.55, N 12.59%.

Compound (I)

Crystal data

$C_8H_{11}N\cdot C_7H_6O_2$
M_r = 243.31
Monoclinic
$P2_1/c$
a = 7.4875 (6) Å
b = 14.4756 (14) Å
c = 12.1879 (12) Å
β = 92.702 (7)°
V = 1319.5 (2) Å^3
Z = 4
D_x = 1.225 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 66 reflections
θ = 2–45°
μ = 0.6489 mm^{-1}
T = 150 K
Rectangular prism
0.46 × 0.43 × 0.37 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2482 measured reflections
2202 independent reflections
1723 reflections with $I > 2\sigma(I)$

R_{int} = 0.054
θ_{max} = 64.47°
$h = 0 \rightarrow 8$
$k = -16 \rightarrow 0$
$l = -14 \rightarrow 14$
2 standard reflections
frequency: 90 min
intensity decay: 9%

Refinement

Refinement on F
R = 0.068
wR = 0.091
S = 1.00
1723 reflections
168 parameters
H atoms not refined
$w = k\{(A + BF_o)^2[C + D(\sin\theta)/\lambda]\}^{-1}$
$(\Delta/\sigma)_{max}$ = 0.009

$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 204 (11)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

N1—C6	1.351 (4)	C10—O17	1.310 (4)
N1—C2	1.357 (4)	C10—C11	1.491 (5)
C10—O18	1.219 (5)		
C6—N1—C2	118.5 (3)	O17—C10—C11	113.8 (3)
O18—C10—O17	123.6 (3)	C16—C11—C12	118.9 (3)
O18—C10—C11	122.6 (3)		
O17—C10—C11—C12	5.9 (5)	O18—C10—C11—C12	173.7 (4)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
O17—H17···N1	1.09 (5)	1.53 (5)	2.613 (4)	174 (4)
C7—H72···O18	1.01	2.51	3.443 (5)	154
C13—H13···O18^i	0.99	2.53	3.478 (5)	161

Symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$C_8H_{12}N^+\cdot C_7H_4NO_4^-$
M_r = 288.30

Cu $K\alpha$ radiation
λ = 1.5418 Å

Orthorhombic
Pbca
$a = 25.732\ (3)$ Å
$b = 7.8359\ (4)$ Å
$c = 13.954\ (1)$ Å
$V = 2813.6\ (5)$ Å^3
$Z = 8$
$D_x = 1.361$ Mg m^{-3}
D_m not measured

Cell parameters from 85 reflections
$\theta = 2$–45°
$\mu = 0.8305$ mm^{-1}
$T = 150$ K
Rectangular prism
0.50 × 0.40 × 0.33 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2396 measured reflections
2396 independent reflections
1977 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 65.07°$
$h = 0 \rightarrow 30$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 16$
2 standard reflections
frequency: 90 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.059$
$wR = 0.07$
$S = 0.947$
1977 reflections
195 parameters
H atoms not refined
$w = k\{(A + BF_o)^2[C + D(\sin\theta)/\lambda]\}^{-1}$
$(\Delta/\sigma)_{\max} = 0.025$

$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $9.6\ (3) \times 10^2$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (II)*

N1—C2	1.346 (4)	C10—C11	1.512 (4)
N1—C6	1.352 (4)	C16—N19	1.475 (4)
C10—O18	1.238 (4)	N19—O21	1.223 (4)
C10—O17	1.256 (3)	N19—O20	1.224 (3)
C2—N1—C6	122.8 (2)	C15—C16—N19	116.3 (2)
O18—C10—O17	127.3 (3)	C11—C16—N19	120.4 (2)
O18—C10—C11	117.7 (2)	O21—N19—O20	123.9 (3)
O17—C10—C11	115.0 (3)	O21—N19—C16	118.4 (2)
C16—C11—C12	116.2 (2)	O20—N19—C16	117.6 (2)
C15—C16—C11	123.2 (3)		
O17—C10—C11—C12	−24.1 (4)	C11—C16—N19—O21	−71.9 (3)
O18—C10—C11—C12	155.2 (3)	C15—C16—N19—O20	−69.4 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O17	0.94 (4)	1.65 (4)	2.596 (3)	171 (3)
C7—H73···O18	1.01	2.44	3.453 (4)	176
C13—H13···O18$^{\text{i}}$	1.02	2.41	3.426 (4)	176
C7—H72···O17$^{\text{ii}}$	1.00	2.43	3.314 (4)	146
C8—H83···O20$^{\text{iii}}$	0.97	2.75	3.672 (4)	159
C9—H91···O21$^{\text{iv}}$	0.91	2.84	3.668 (4)	151
C8—H81···O21$^{\text{ii}}$	1.05	2.89	3.557 (4)	122

Symmetry codes: (i) $x, 1+y, z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Compound (III)

Crystal data

$C_8H_{12}N^+{\cdot}C_7H_3N_2O_6^-$
$M_r = 333.30$
Monoclinic
$P2_1/c$
$a = 7.5078\ (4)$ Å
$b = 7.3190\ (4)$ Å
$c = 27.632\ (8)$ Å
$\beta = 92.060\ (9)°$
$V = 1517.4\ (5)$ Å^3
$Z = 4$
$D_x = 1.459$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 68 reflections
$\theta = 2$–45°
$\mu = 0.9757$ mm^{-1}
$T = 150$ K
Rectangular prism
0.40 × 0.23 × 0.10 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2836 measured reflections
2560 independent reflections
2286 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
$\theta_{\max} = 64.9°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 32$
2 standard reflections
frequency: 90 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.052$
$S = 0.977$
2286 reflections
222 parameters
H atoms not refined
$w = k\{(A + BF_o)^2[C + D(\sin\theta)/\lambda]\}^{-1}$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 138 (5)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 5. *Selected geometric parameters (Å, °) for (III)*

N1—C6	1.345 (2)	C15—N22	1.468 (2)
N1—C2	1.353 (2)	N19—O20	1.217 (2)
C10—O18	1.233 (2)	N19—O21	1.225 (2)
C10—O17	1.268 (2)	N22—O23	1.222 (2)
C10—C11	1.522 (2)	N22—O24	1.225 (2)
C13—N19	1.476 (2)		
C6—N1—C2	122.6 (1)	O20—N19—O21	124.1 (2)
O18—C10—O17	127.2 (2)	O20—N19—C13	118.3 (1)
O18—C10—C11	117.9 (2)	O21—N19—C13	117.6 (2)
O17—C10—C11	114.8 (1)	O23—N22—O24	124.1 (2)
C12—C11—C16	119.9 (2)	O23—N22—C15	117.8 (2)
C14—C13—C12	123.3 (2)	O24—N22—C15	118.1 (1)
C14—C15—C16	123.2 (2)		
O17—C10—C11—C12	10.1 (2)	C14—C13—N19—O21	−9.3 (3)
O18—C10—C11—C12	−171.5 (2)	C14—C15—N22—O23	−14.1 (3)
C14—C13—N19—O20	171.0 (2)	C14—C15—N22—O24	165.5 (2)

Table 6. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O17	0.98 (3)	1.62 (3)	2.597 (2)	176 (3)
C7—H73···O18	0.96	2.52	3.401 (2)	153
C9—H93···O18$^{\text{i}}$	0.96	2.59	3.433 (2)	146
C9—H91···O17$^{\text{ii}}$	0.97	2.63	3.523 (2)	153
C7—H71···O18$^{\text{iii}}$	0.97	2.69	3.544 (2)	147
C7—H73···O20$^{\text{iv}}$	0.96	2.72	3.352 (3)	125
C9—H92···O20$^{\text{v}}$	1.00	2.91	3.451 (2)	115
C16—H16···O21$^{\text{iv}}$	0.97	2.95	3.461 (2)	114

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1+x, y, z$; (v) $-x, \frac{1}{2}+y, \frac{3}{2}-z$.

The crystals were sealed in Lindeman capillary tubes and the data were collected at 150 K using an Oxford Cryosystems

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1262). Services for accessing these data are described at the back of the journal.

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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